

SISAK Liquid-Liquid Extraction Experiments with Preprepared ^{257}Rf

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The SISAK liquid-liquid extraction system was used to extract 4.0-s ^{257}Rf . The ^{257}Rf was produced in the reaction $^{208}\text{Pb}(^{50}\text{Ti}, 1n)^{257}\text{Rf}$ with 237-MeV beam energy on target, separated in the Berkeley Gas-filled Separator (BGS) and transferred to a gas jet using the Recoil Transfer Chamber (RTC). The activity delivered by the gas jet was dissolved in 6-M HNO_3 and Rf was extracted into 0.25-M dibutyl-phosphoric acid in toluene. This was the first time a transactinide, i.e., an element with $Z \geq 104$, was extracted and unequivocally identified by the SISAK system. Thus, this pilot experiment demonstrates that the fast liquid-liquid extraction system SISAK, in combination with liquid-scintillation detectors, can be used for investigating the chemical properties of the transactinides. The extraction result is in accordance with the behaviour shown by the Rf group IV homologues Zr and Hf.

1. Introduction

SISAK¹ is a fast chemical-separation system for liquid-liquid extraction. It was developed to investigate short-lived nuclei recoiling out of an irradiated target and transported in a gas jet. The system is based on small centrifuges with a continuous feed and output.^{2–4}

During recent years, work has been undertaken to deploy SISAK in studies of the chemical properties of the transactinide elements ($Z \geq 104$).^{2,5,6} The only suitable detection method found was liquid-scintillation (LS) detection.⁷ This was mainly because of the rather high flow rates (0.5–2.0 mL/s) encountered in the SISAK system. Other detection methods usually require either thin, dry samples or very thin liquid films. No suitable method was found to prepare such samples without an unacceptable time delay between separation and detection.

LS counting has high efficiency, but suffers from relatively poor energy resolution (about 300-keV FWHM at 7-MeV α energy) and is sensitive to β particles and γ rays. This puts very stringent demands on the separation system, because most of the β - and γ -emitting contaminants are produced with orders of magnitude higher yield than the transactinide under study. A huge effort was made to develop methods for LS detection of very low levels of α activity under these conditions. The most important techniques implemented are:

- Pulse-shape discrimination is used to reduce the β background in the α spectra by a factor >1000 . Without this technique the β - and γ -induced background from the surroundings and from nuclides produced in the target will interfere with the α spectrum to such an extent that it becomes useless.⁸
- Real-time scintillation-yield monitoring by continuous measurement of the Compton edge of 662-keV ^{137}Cs γ rays. The position of the Compton edge is used to automatically adjust the energy calibration. Based on this adjustment the event gates used for switching the detection cells between mother and daughter mode (open or closed valve, respectively) will always be set on the correct energy range.⁹

- Adding the scintillator chemicals after the final extraction step and flushing the mixture with an inert gas (He or Ar) to remove O_2 . Oxygen quenches the scintillation process, in particular the time resolution necessary for the pulse-shape discrimination is severely affected. This procedure also improves the phase separation and extraction yield.^{2,10}
- Improving the light transfer between the detection cell and the photomultiplier tube by improved light-guide design.¹⁰

In November 2000 a successful test experiment with the SISAK LS detectors was performed at the Lawrence Berkeley National Laboratory (LBNL). ^{257}Rf was produced in the reaction $^{208}\text{Pb}(^{50}\text{Ti}, 1n)^{257}\text{Rf}$ and separated in the Berkeley Gas-filled Separator (BGS). By using such a pre-separation technique, the background is reduced by more than three orders of magnitude. This gives the experimenter two significant advantages:

- The chemistry apparatus is liberated from the need to reject unwanted activities produced in huge quantities by various unwanted reactions between the beam and target. Thus, the chemistry can be optimized for studying the chemical properties of the given transactinide without at the same time functioning as an extremely efficient separation system. This gives more freedom in designing the chemical system used to investigate the transactinide.
- The amount of unwanted activity is so low that the transactinide under study can be detected directly, without any chemical separation. This gives the experimenter the opportunity to observe the transactinide in the detector system without using the chemical separation system. Furthermore, using pre-separated activity enables direct measurement of the amount entering the chemistry apparatus. Because the activity in the raffinate (the aqueous phase) is not measured, this is an important number in order to calculate extraction yields with good accuracy. The activity in the raffinate cannot be measured directly because water and acids destroy the energy resolution that is necessary for precise LS α -spectroscopy.

An overview of a typical SISAK experimental setup, with pre-separation, is given in Figure 1.

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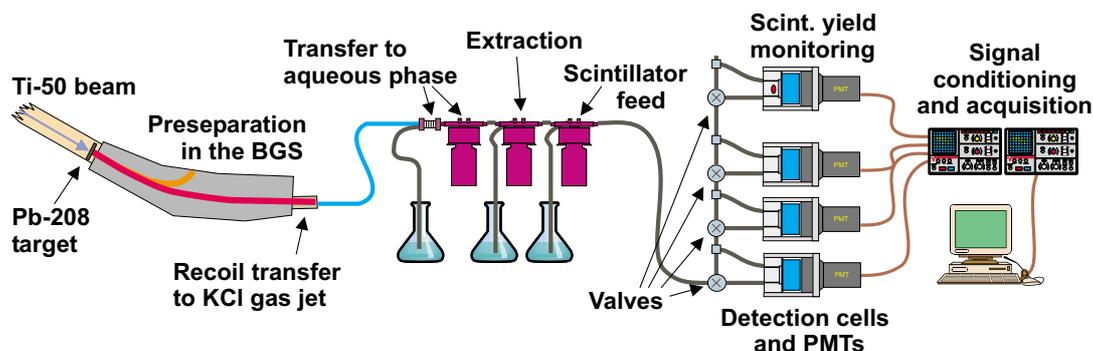


Figure 1. Overview of the SISAK-BGS setup.

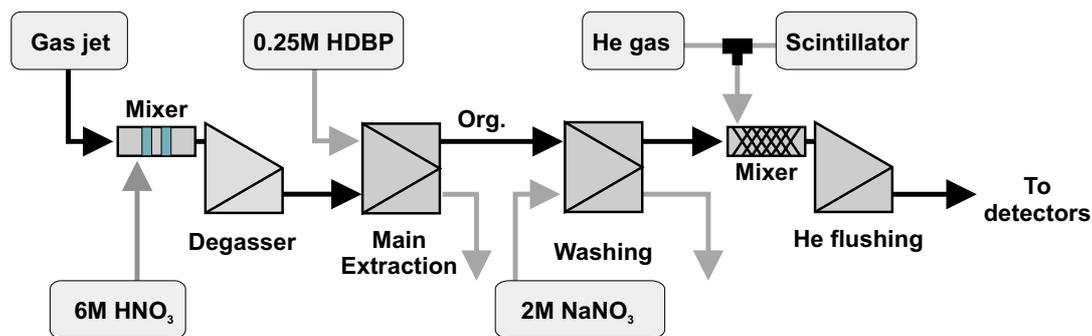


Figure 2. Schematic diagram of the SISAK liquid-liquid extraction system.

2. Experimental

An experiment in which the BGS was used as a preseparator was performed. ^{257}Rf was produced in the reaction $^{208}\text{Pb}(^{50}\text{Ti}, 1n)^{257}\text{Rf}$, which has a cross section of about 10 nb. ^{257}Rf has a metastable state with half-life = 4.0 s and a ground state with half-life 3.5 s. About 63% of the decay is from the metastable state.¹¹

The 237-MeV $^{50}\text{Ti}^{12+}$ beam was delivered by the LBNL 88-Inch Cyclotron with about 200–300 pA intensity. The ^{208}Pb targets was mounted on the standard BGS rotating target-wheel. At the exit of the BGS the separated ^{257}Rf -ions were transferred to a He/KCl gas jet by the recently constructed Recoil Transfer Chamber (RTC).¹²

The amount of ^{257}Rf entering the RTC was measured with an array of Si-strip detectors. Six to seven ^{257}Rf – ^{253}No $\alpha\alpha$ -correlations per hour were detected. This corresponds to about 25 ^{257}Rf nuclides entering the RTC per hour.¹³

The mean transport time from the RTC to the SISAK-LS detector cells was measured using Hf activity produced in the reaction $^{120}\text{Sn}(^{50}\text{Ti}, xn)^{170-x}\text{Hf}$. The main activity detected in an HPGe detector facing the detection cell was from 164 – ^{166}Hf nuclides and their daughters. The half-lives of these nuclides are larger than one minute, thus their decay should not influence the shape of the transport-time distribution to any significant degree. A transport time of about 6 s for break-through and about 11 s for the main part of the reaction products was observed.¹³

A test with the SISAK LS-detectors was then performed. Any α -event with an energy between 8.3 and 10.5 MeV forced the cell to close, i.e., switch to daughter mode. The cell remained in daughter mode for more than five daughter (^{253}No) half-lives. The measured correlation matrix clearly shows that the SISAK LS-detection system is able to detect nuclides at a rate of less than one atom per hour. Experimental details can be found in Reference 13.

Thus having proven that the LS detection system worked, pilot liquid-liquid extraction experiments were performed: Rf was extracted from a 6-M HNO_3 solution into 0.25-M dibutyl-phosphoric acid (HDBP) in toluene as a nitrate-dibutyl-phosphate complex. Figure 2 shows a schematic diagram of the experimental setup. In the first section, the mixer/degasser,

the gas-jet transported activity (1.3 ± 0.1 L/min He with KCl aerosol particles) is dissolved in the 6-M HNO_3 solution (0.50 ± 0.05 mL/s flow rate at 60°C) and the gas is removed. In the next centrifuge the main extraction is performed. Here the Rf-nitrate complexes in the aqueous phase are thoroughly contacted (~ 50 – 100 ms) with the 0.25-M HDBP solution (0.42 ± 0.05 mL/s flow rate) and extracted as a nitrate-dibutyl-phosphate complex into the organic toluene solution. Then the organic phase is washed with 2.0-M NaNO_3 (0.42 ± 0.05 mL/s flow rate) to remove dissolved HNO_3 , which severely quenches and oxidizes the scintillator ingredients otherwise. After the washing step the scintillator ingredients, methyl-naphthalene, dimethyl-POPOP, and trioctyl-amine (TOA), are mixed with the organic phase in a 1 : 1 ratio. The scintillator cocktail (i.e., the mixture of the organic phase and the scintillator ingredients) fed to the detectors consisted of: 1.5-g/L dimethyl-POPOP, 25-vol% methyl-naphthalene, 3-mL/L TOA, 0.125-M HDBP, and toluene as solvent. The TOA prevents any HNO_3 traces left after the washing step from interfering with the scintillator performance. Together with the scintillator ingredients, He gas is also forced into the second mixer to remove O_2 , which quenches the scintillation process. In the final centrifuge the He is removed and the organic phase/scintillator mixture is pumped to the detectors at a flow rate of 0.84 ± 0.07 mL/s.

3. Results

The HDBP extraction experiment collected data for a total of 17.8 hours. The beam integral was 8.34×10^{16} $^{50}\text{Ti}^{12+}$ particles, corresponding to an average beam intensity of 208 pA. During this period five ^{257}Rf – ^{253}No $\alpha\alpha$ correlations were observed in detector 1 and none in detector 2. Detector 3 was not used. In Figure 3 the correlation matrix is shown for detector 1. The analysis method is thoroughly described in Reference 13.

During an experiment in which the activity introduced into the system was detected directly, 37 correlations were observed in the same energy region in a 31.3 hour experiment with a beam integral of 1.86×10^{17} (Ref. 13). In this experiment the activity was dissolved directly in the scintillator and led straight to the detectors with a flow rate of 0.84 ± 0.06 mL/s. As three of the four centrifuges in Figure 2 were not used in this experiment,

the transport time was much faster. Therefore, the number of correlations in the two experiments cannot be compared directly, since corrections for decay losses must be taken into account.

It is important to be able to calculate the decay correction factor between the extraction experiment reported in this paper and the measurement of the activity entering the SISAK system reported in Reference 13. The reason for this is that the distribution ratio D (or extraction yield) is calculated from the number of correlations observed in these experiments:

$$D \equiv \frac{[Rf]_{org.}}{[Rf]_{aq.}} = \frac{R_{org.}/V_{org.}}{R_{aq.}/V_{aq.}} = \frac{R_{org.}}{R_{tot.} - R_{org.}} \cdot \frac{V_{aq.}}{V_{org.}}, \quad (1)$$

where $R_{org.}$ and $R_{aq.}$ are the number of correlations (activity) observed in the respective phases, $R_{tot.} = R_{org.} + R_{aq.}$, $V_{org.}$ and $V_{aq.}$ are the volumes of the two phases, which for a system with continuous mixing and separation like SISAK are equivalent to the flow rates of the respective phases.

The transport through the RTC, the SISAK system, the detector cells, and the interconnecting capillaries will result in a time distribution with a definite break-through time and peaked shape. Generally, if the volume of the entire system increases, the distribution will become broader and more tailed and the main part of the activity will arrive later. Thus, the correction necessary for calculating $R_{aq.}$ from $R_{tot.}$ and $R_{org.}$ has to take these two distributions for the different setups into account. One way to do this is to perform Monte Carlo simulations, where the modelled distributions are based on empirical data. A computer program, called SimSISAK, has been developed for such calculations.¹⁴

By using SimSISAK to calculate the amount of decay losses, the activities can be normalised to a chosen mean transport-time. The SimSISAK calculations gave 91.0% decay loss for the HDBP experiment and 73.8% for the experiment where the activity was dissolved directly in the scintillator (referred to as the "scintillator experiment" in the following).

The additional loss for the HDBP experiment corresponds to an average delay of 6.2 s, which is what is expected. (²⁵⁷Rf has a half-life of 4.0 s, experience suggests about 2 s average delay per added centrifuge at the flow rates used.)

The amount of activity in the "scintillator experiment" would have been only 12.7 $\alpha\alpha$ -correlations if the decay loss had been

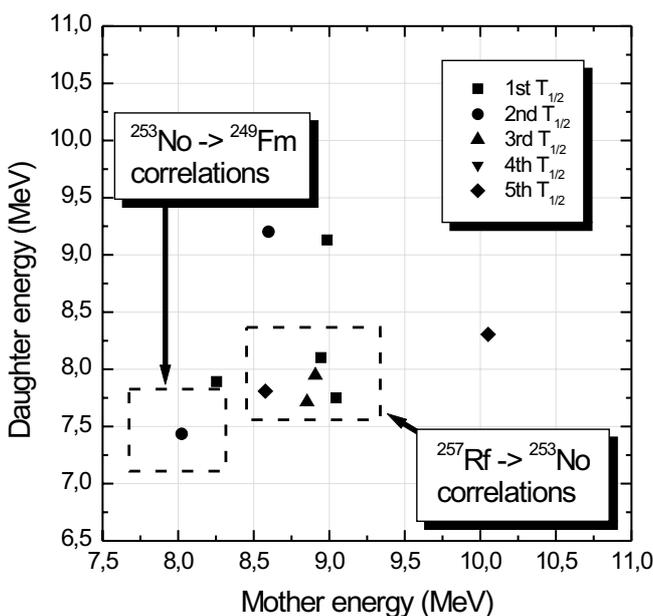


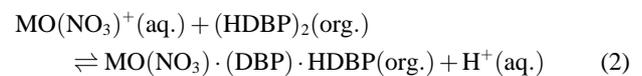
Figure 3. Correlation matrix showing the expected energy ranges for ²⁵⁷Rf-²⁵³No and ²⁵³No-²⁴⁹Fm $\alpha\alpha$ correlations. The data are from the first detector cell. The energy gates used in the SISAK extraction experiment correspond to the plot, i.e., an α with energy between 7.5 and 11 MeV switched the detector cell from mother to daughter mode (from open to closed). There are no correlations hidden behind the text boxes.

91.0% (as in the HDBP experiment). Taking into account the beam integrals, this number is reduced to 5.7. This last number can be directly compared to the five counts measured in the HDBP experiment.

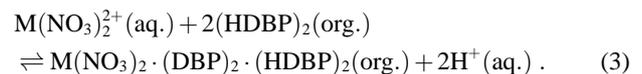
The transport time through the detector cells was equal for both experiments. Thus, no corrections need to be done on behalf of correlation-detection efficiency.

Assuming $R_{tot.} = 5.7$ then $R_{aq.} = 5.7 - 5.0 = 0.7$. From eq 1 the distribution ratio can then be calculated to be $8.5^{+10}_{-7.5}$. The huge uncertainty is mainly due to the small number of counts in the organic phase. The extraction yield is $90^{+10}_{-30}\%$, i.e., the extraction of Rf is above 50% in this system. Thus, Rf behaves similar to its lighter homologues Hf and Zr. The ¹⁶⁵Hf data are from SISAK experiments at the Oslo Cyclotron Laboratory and the ¹⁰⁰Zr data from SISAK experiments performed at the Mainz TRIGA reactor. The Hf and Zr experiments were performed by Dyve and coworkers.¹⁵

In toluene HDBP will mainly be present as the dimer (HDBP)₂.¹⁶ The Group IV metal ion will most likely be present as $M(NO_3)_2^{2+}$ or $MO(NO_3)^+$. Then the extraction reactions might be:



and



In the first case one would expect an extraction curve slope (on a log-log plot) equal to one, in the second case it should be two. In Figure 4 we observe a slope of around 1.5 for both Zr ($0.008 \text{ M} \leq [HDBP] \leq 0.03 \text{ M}$) and Hf ($0.1 \text{ M} \leq [HDBP] \leq 0.5 \text{ M}$). This indicates that the metal is present in about equal amounts as $M(NO_3)_2^{2+}$ and $MO(NO_3)^+$. It should be noted that extraction in the SISAK centrifuges is too fast to achieve equilibrium, thus the data in Figure 4 cannot be directly compared to data from, e.g., batch experiments under equilibrium conditions.

As Rf seems to behave similarly to Hf and Zr, it is reasonable to expect Rf to also be extracted in this manner. However, more detailed studies must be undertaken before such a conclusion can be made.

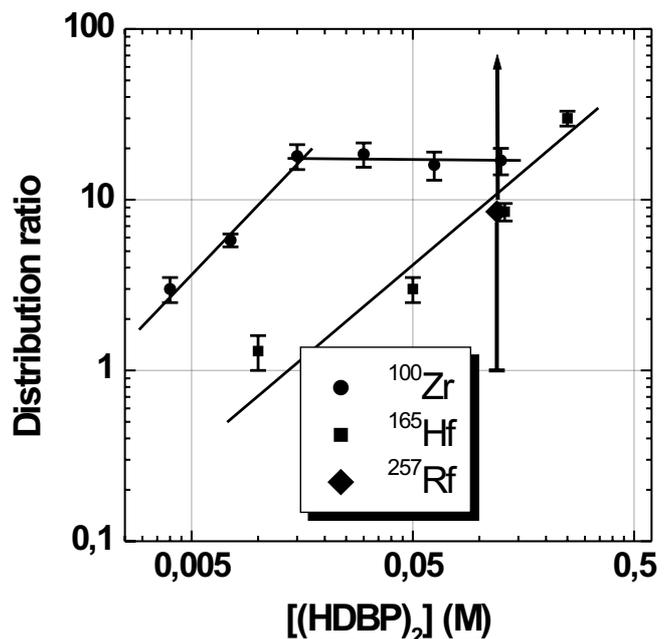


Figure 4. On-line SISAK liquid-liquid extraction of Zr, Hf, and Rf with HDBP into toluene from 6-M HNO₃. The lines are drawn to guide the eye.

4. Conclusion and Future Work

The work reported here was the first to use preseparation in a transactinide chemistry experiment. As can be seen from Figure 3 and thoroughly discussed in Reference 13, this eliminates most of the background activity. The correlations outside the indicated ^{257}Rf - ^{253}No correlation box, which are not daughter-granddaughter correlations, are most likely also ^{257}Rf - ^{253}No correlations, but with shifted α energies due to α -electron coincidence summing. Such events are currently under investigation, but until their nature is clearly understood they are not included in the calculations. Regardless of the nature of these events, it's clear that preseparation offers great improvement in the noise-to-background ratio and permits greater freedom in designing the experiment.

For SISAK type of experiments, and any experiment in which the activity only can be measured in one of the phases, the ability to precisely determine the amount of activity entering the chemistry apparatus, using the same detector system as in the chemistry experiment, is a great advantage. Estimating the amount of activity by more indirect methods inevitably leads to larger uncertainties. Therefore, as has been demonstrated in this experiment, using preseparation not only makes the data analysis easier and less uncertain, but enables more accurate measurements of extraction yield, distribution values, etc.

It is also clear from our results and the SimSISAK decay loss calculation of 91.0%, that using such short-lived activity as ^{257}Rf demands as rapid as possible transport. In this respect, the rather low flow rates used in this experiment can be significantly increased. From this alone a yield increase by a factor of two should be easily achievable. This has already been demonstrated in another LBNL SISAK Rf-experiment where trioctyl-amine was used to extract Rf from oxalic acid (work in progress). Furthermore, improvements to the RTC and gas-jet transport are expected to give another factor of two yield increase. With these improvements, more detailed SISAK experiments for studying the aqueous chemistry of Rf are possible and are in preparation.

It should be noted that the current experiment was designed to give maximum extraction yield of Rf. Therefore, conditions under which both Hf and Zr are extracted with high yield were selected. This is generally not an advantage for deducing chemical differences from such liquid-liquid extraction experiments. Usually one would like to be able to distinguish between a Hf- and a Zr-like behaviour of Rf. This is possible at HDBP concentrations below 0.1 M. The results from this pilot experiment will be used to design experiments, using preseparated activity, for detailed studies of the chemistry of Rf where these considerations are taken into account.

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