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# Development of an extraction system for the separation of dubnium from rutherfordium using MIBK and HCl/HF solutions

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**Abstract:** A chemical separation system was developed to separate group 4 and 5 elements using extraction from HCl/HF solution into methyl-isobutyl-ketone (MIBK). The system is proposed to be applied for a confident assignment of the spontaneous fissioning radionuclide produced as decay product of element 115 either as dubnium (Db,  $Z = 105$ ) or rutherfordium (Rf,  $Z = 104$ ). Moreover, extraction systems are proposed allowing the investigation of chemical properties of Db in comparison to the properties of its lighter homologs Nb and Ta.

**Keywords:** Superheavy elements, dubnium, liquid–liquid extraction, relativistic effects.

## 1 Introduction

The application of fusion reactions using a  $^{48}\text{Ca}$  beam on actinide targets at Joint Institute for Nuclear Research (Dubna, Russia), the so-called “hot fusion”, opened new dimensions in the field of synthesis and characterization of new superheavy elements (SHE) [1]. Unfortunately, most of the detected decay chains have ended in so far unknown spontaneous fissioning radionuclides, resulting in doubts on the findings within the International Union of Pure and Applied Chemistry at the time of their discovery.

In this respect, the discovery of the elements 115 and 113 in 2003 [2], followed by a confirmation experiment in 2004 [3, 4], was an important milestone regarding the acceptance of the Russian results. In [2], three chains assigned to the decay of  $^{288}115$  were found using the Dubna gas-filled recoil separator (DGFRS), which all were terminated by a long-lived spontaneous fissioning component

with a half-life of around 30 h. The confirmation experiment [3, 4] was based on a radiochemical separation of this terminating radionuclide supposed to be  $^{268}\text{Db}$  (or  $^{268}\text{Rf}$ , in the case that EC decay takes place prior to the terminating SF event) from all other contaminations, especially actinides. This experiment – although accepted as the first independent prove of the synthesis of superheavy elements in  $^{48}\text{Ca}$  induced nuclear reactions – had two weak points: (a)  $\alpha$ -spectra had not been shown, due to the high  $\beta$ -background rendering impossible the identification of a possible actinide contamination and (b) no differentiation between Db and Rf could be made because of their similar behavior in the selected chemical separation system, so that the assignment of the terminating isotope to a certain atomic number and, therewith, the end of the decay chain was eventually unclear [5]. The first problem had been solved by measuring the  $\alpha$ -spectra and SF events of a representative sample again 3 years after the experiment and demonstrating the absence of any possible actinide contamination [6].

For the second point, a final assignment decision is up to now lacking. The probability, that electron capture of  $^{268}\text{Db}$  to  $^{268}\text{Rf}$  takes place prior to the terminating SF event, has been discussed by several authors [1, 7]. Reliable theoretical predictions of the half-life of such an EC are not yet available. General trends in EC half-life systematics, as reviewed in [8] show no evidence for half-lives larger than 1000 s. In contradiction, the calculated half-lives for the  $^{268}\text{Rf}$   $\alpha$ -decay and/or SF do not exceed  $10^4$  s [9, 10], thus making the EC decay unlikely. In the here reported work we propose a chemical separation system which can distinguish between group 4 and 5 elements. Four possible outcomes of such an experiment have to be considered: (1) In the case that no EC decay takes place, all events will be found in the group 5 fraction. (2) This could also happen, if the EC decay is long-lived and the  $^{268}\text{Rf}$  SF half-life is short. (3) If the SF events are found in the group 4 fraction, then EC decay occurred shortly after the creation of  $^{268}\text{Db}$ , followed by a SF decay of  $^{268}\text{Rf}$  with a comparable long half-life. (4) The events could also be distributed more or less equally between the two fractions, which would mean that also the two half-lives are

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comparable. Only option one is not in contradiction with the theoretical estimations.

The chemical system applied in [3] allows for a safe, quick and complete isolation of the members of the groups 4 and 5 from actinides by dissolving the recoils collected on a copper catcher in HCl/HNO<sub>3</sub>, followed by several separation steps and ending up with 2 mL of 1 M HF solution, which quickly had been evaporated to dryness and transferred into the measurement device.

To separate group 4 and 5, a second chemical separation step has to be applied, fulfilling the following requirements: (1) mixing of the final 1 M HF solution containing the isotopes of interest with the applied medium should be possible to get the necessary starting concentration, (2) only one single and fast separation step should be applied (3) both fractions should easily be transferable into samples for  $\alpha$ - and SF spectrometry.

To meet these boundary conditions, we have selected liquid-liquid extraction from HF/HCl containing aqueous solutions into MIBK to be best suited to fulfill these requirements and tested the system with the lighter homologs Zr, Hf, Nb and Ta.

The first aim of the studies was to find experimental conditions where the members of group 4, Zr and Hf, remain in the aqueous solution, and Ta and Nb are completely extracted into the organic phase. The similar behavior of Nb and Ta is extremely important, since earlier experiments studying the chemical properties of Db using the short-lived isotopes <sup>262/263</sup>Db indicated a more Nb-like behavior of dubnium than similarities with its direct homologue Ta [11]. Therefore, the system should not be sensitive for changes in concentration over a relatively wide range. Only in this case, a clear assignment of the long-lived isotope either as Db or Rf can be guaranteed.

The second objective of this work is related to the already mentioned results of earlier experiments, where Db showed chemical properties more similar to the lighter homolog Nb than to Ta. At that time, the only known isotopes were <sup>262/263</sup>Db, having half-lives of ~ 30 s. It is not yet proved whether the observed unexpected chemical behavior of Db is caused by relativistic effects as proposed in [11] or kinetically founded. The discovery of the long-lived <sup>268</sup>Db ( $T_{1/2} = 26$  h) now opens possibilities for systematic investigations. For this task, chemical systems have to be applied where Nb and Ta behave clearly different.

## 2 Experimental

The isotopes <sup>181</sup>Hf ( $T_{1/2} = 42.39$  d), <sup>182</sup>Ta ( $T_{1/2} = 114.43$  d) and <sup>95</sup>Zr ( $T_{1/2} = 64.0$  d) were produced by neutron activation of the stable elements using the neutron activation facility at SINQ (PSI). <sup>95</sup>Nb ( $T_{1/2} = 34.97$  d) is produced as the decay product of <sup>95</sup>Zr. Stock solutions containing less than 10<sup>-6</sup> M of the stable elements were prepared in order to simulate low carrier conditions like in the real super-heavy element experiments.

All reagents were of p.a. grade. Concentration ranges from 0.5–20 M HF and 0–5 M HCl were studied by shaking 10 mL of the aqueous solution with up to 10 mL MIBK within 1 min.

The distribution of the radionuclides in both phases was determined by  $\gamma$ -spectrometry using a coaxial HPGe detector (ORTEC) with 18% relative efficiency using an acquisition interface module based measurement chain in combination with the GENIE2000 software from CANBERRA. All samples were measured in the same geometry and identical distance from the detector during 5 min. The uncertainties of the single measurements are then only dependent on the counting statistics and the uncertainties in the volume measurement.

## 3 Results

To obtain quantitative information on the studied extraction systems (given that all samples were measured in the same geometry), the distribution ratios of the radionuclides under study can be calculated using Equation (1):

$$D = \frac{A(\text{MIBK}) V(\text{H}_2\text{O})}{V(\text{MIBK}) A(\text{H}_2\text{O})} \quad (1)$$

where  $A(\text{MIBK})$ ,  $A(\text{H}_2\text{O})$  denotes the activity of the radio isotope in the MIBK phase and aqueous phase, respectively, and  $V(\text{MIBK})$ ,  $V(\text{H}_2\text{O})$  the volumes of the phases.

Since our primary goal was to find experimental conditions where radionuclides of one group are preferably completely separated from the others, we detected the activity in most of the cases in one of the phases only. The  $\gamma$ -spectra were evaluated according to the guidelines given in the international standard ISO 11929:2010 [12] as well as in the German DIN ISO national annex [13]. All spectra were treated as counting spectrometric measurements with a linear background in the vicinity of the  $\gamma$ -peaks of interest to overcome problems with the huge differences in the recorded count rates in the particular phases. Based on the deduced background count rate of the used regions of interest for the individual isotopes under investigation, the

detection limit and the quantification limit with a 5% probability error for type I and II, respectively, were calculated. The detection limit was used as an upper limit in the case that the obtained net count rate was lower as this value. In the case the net count rate was in between the detection limit and the quantification limit, the average of these limits was used as an estimate of the count-rate with an uncertainty covering the range between these limits. Otherwise, symmetrical confidence limits covering 95% were calculated. In Figure 1 the region of interest for  $^{95}\text{Nb}$  and  $^{95}\text{Zr}$  is plotted together with the result of a 24 h blank measurement (blue line). The data results from the measurement of the MIBK phase (red line) and the aqueous phase (green line) in the case of an extraction with 0.5 M HF and 5 M HCl. The regions used for the background determination of the individual peaks are marked as blue filled areas. It is obvious that all peaks in the aqueous phase are well above the detection- and quantification limit, whereas in the MIBK phase this is only true for the  $^{95}\text{Nb}$  peak. The first  $^{95}\text{Zr}$  peak is slightly above the detection limit but well below the quantification limit, but the second  $^{95}\text{Zr}$  exceeds the quantification limit only by a factor of two.

The following  $\gamma$ -lines were used:  $^{95}\text{Nb}$  765.8 keV;  $^{95}\text{Zr}$  724.2 keV and 756.7 keV;  $^{181}\text{Hf}$  133.0 keV, 345.9 keV and 482.2 keV;  $^{180}\text{Ta}$  100.1 keV, 222.1 keV, 1121.3 keV, 1189.0 keV, 1221.4 keV and 1231.0 keV. The distribution coefficients were calculated independently for each used  $\gamma$ -line and with exception of  $^{95}\text{Nb}$  afterwards averaged for the individual isotopes. The uncertainty of the given distribution values results from a propagation of the ob-

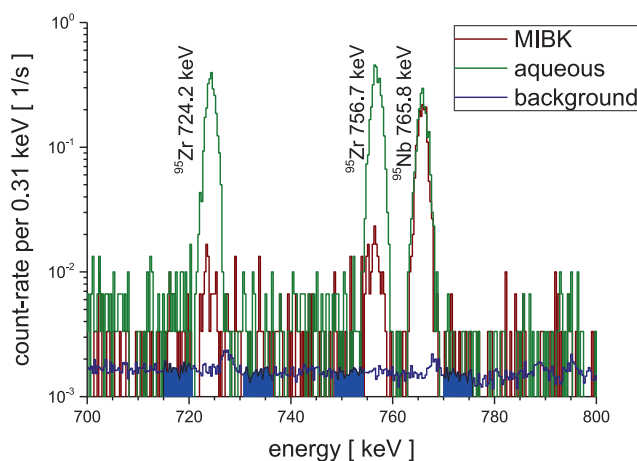
tained uncertainties of the count rates to the particular values and finally to the averaged value. They represent combined standard uncertainties extended to a coverage factor  $k = 1.96$ , corresponding to coverage of 95%.

It shall be noted that only for Zr, Hf and Nb distribution ratios could be calculated in all experiments. Due to the strong extraction of Ta into MIBK under the selected experimental conditions, the  $^{180}\text{Ta}$   $\gamma$ -peaks fall in most of the experiments below the detection limit in the aqueous phase. In these cases, the  $D$  value of a particular  $\gamma$ -line was calculated using the detection limit as an upper limit of the count rate, resulting in a lower limit for the  $D$  value. The minimum of all  $D$  values obtained in one measurement was finally used as conservative lower limit, keeping in mind that the real values can be much higher.

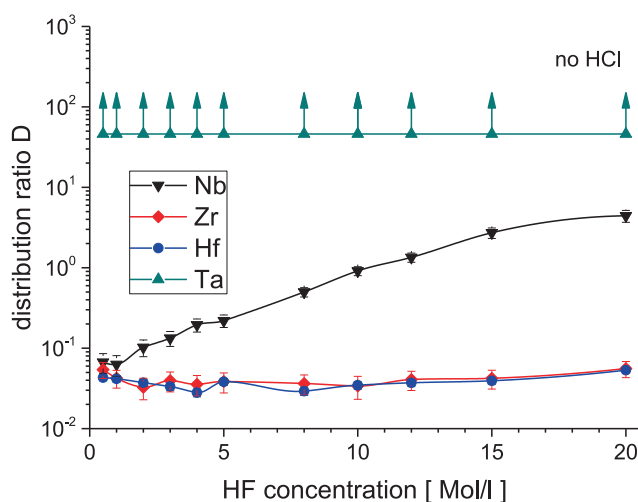
### 3.1 Dependence of the extraction efficiency on the HF concentration

1 M HF solution was first tested, because it would have been the ideal case to extract the group 5 members directly from the final solution of the first separation step.

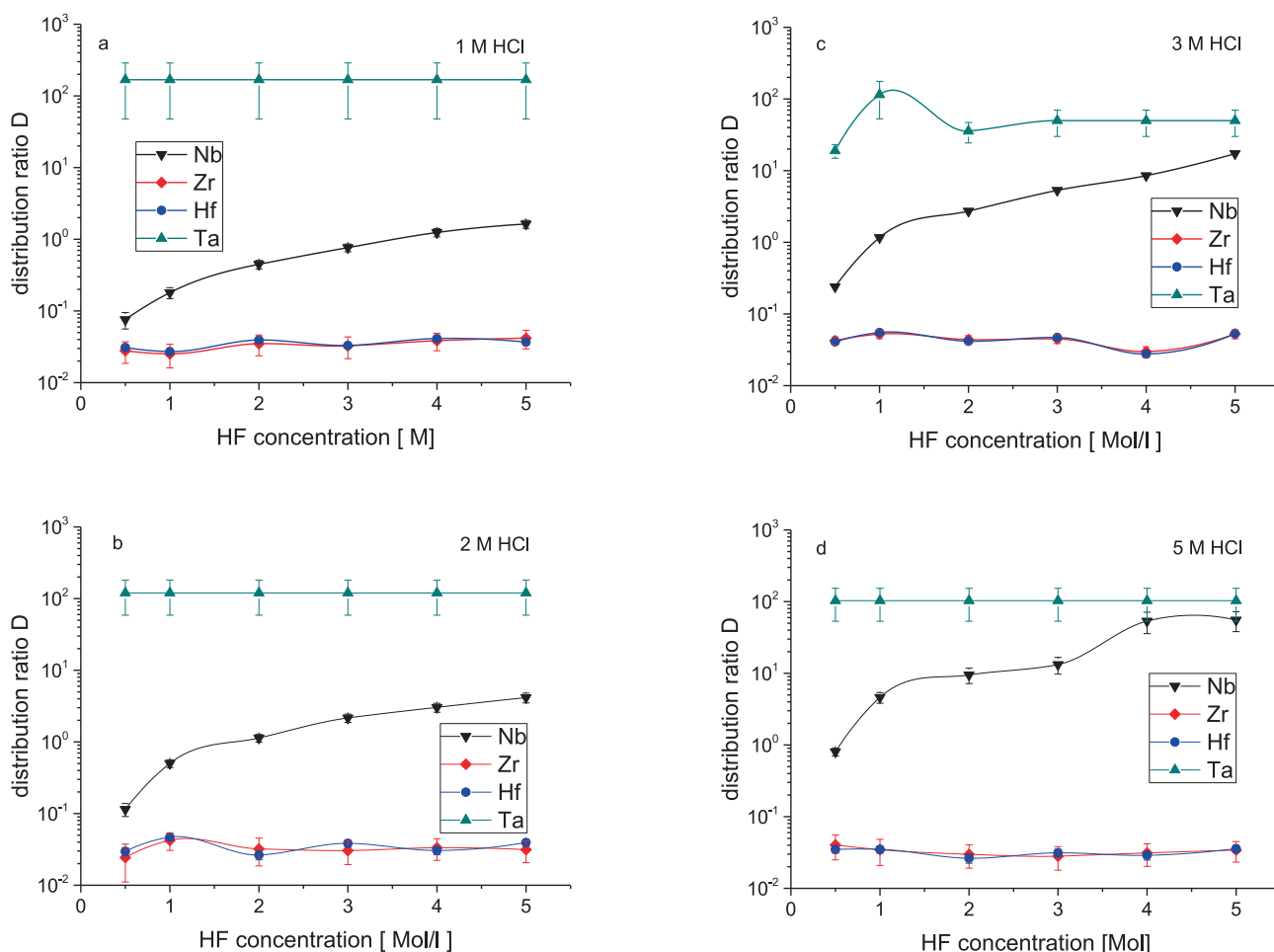
Figure 2 shows the distribution coefficients  $D$  obtained in these extraction experiments. As can be seen Ta is the only complete extractable element under these conditions, while Nb is not extracted. The signals of all  $^{180}\text{Ta}$   $\gamma$ -peaks fall below the detection limit. Therefore, only lower limits of the  $D$ -values were obtained. The displayed values represent the minimum of all these  $D$ -values.



**Fig. 1:** Selected part of  $\gamma$ -spectra taken from extraction experiments with 0.5 M HF and 5 M HCl. The count-rates of the MIBK phase (red) and aqueous phase (green) recorded within 5 min are compared with the count rate of a 24 h long term blank measurement. In addition the used regions to determine the background count rates are indicated in blue (for more details see text).



**Fig. 2:** Extraction of the group 4 and 5 elements Zr, Hf, Nb and Ta into MIBK in dependence on the HF concentration. 10 mL of aqueous and MIBK phase were used, respectively. The lines are Akima interpolations [14] for a better guide for the eyes.



**Fig. 3:** (a–d) Extraction of the group 4 and 5 elements Zr, Hf, Nb and Ta into MIBK in dependence on the HF concentration at various HCl concentrations. 10 mL of aqueous and MIBK phase were used, respectively. The lines are Akima interpolations [14] for a better guide for the eyes.

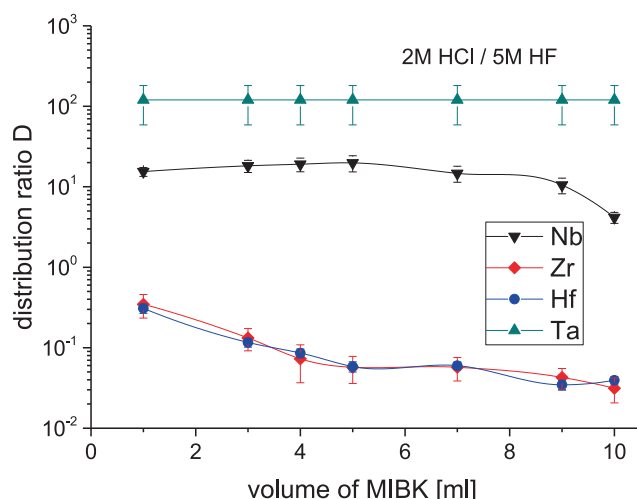
Increasing the HF concentration results in a better extraction performance for Nb, but only at comparable high HF concentrations above 15 M acceptable amounts are removed from the aqueous phase. This high acid concentration is not suitable for the further processing of the fractions for sample preparation. HF concentrations above 5 M should not be used due to environmental problems with evaporation during the final sample preparation step.

For distinguishing between group 4 and 5, this system is not suitable, but extraction from 1 M HF solution into MIBK directly after the first separation is excellently suited for the studies of the chemical properties of Db concerning its similarity either with Nb or with Ta.

### 3.2 Dependence of the extraction efficiency on the HF and HCl concentration in mixed solutions

Figure 3a–d shows the extraction behavior of the four elements in dependence on the HF concentration in the presence of different HCl concentrations.

From the depicted graphs it is clearly visible, that with increasing HCl concentration the extraction ability of Nb is much improving with increasing HF content. In 5 M HCl, already 1 M HF is enough to reach a sufficiently high  $D$  value for Nb. Ta is completely extracted in all cases. Group 4 elements do not extract over the entire studied concentration ranges. Mixtures of at least 5 M HCl/1 M HF or 5 M HF/2 M HCl and above are applicable for a separation of group 4 from group 5 elements. These concentrations can easily be reached by mixing the 2 mL of the final 1 M



**Fig. 4:** Extraction efficiency of Zr, Hf, Nb and Ta, in dependence of the MIBK volume using 2 M HCl/5 M HF. 10 mL of aqueous phase were used. The lines are Akima [14] interpolations for a better guide for the eyes.

HF solution from the first separation with the required amounts of concentrated acid and water.

### 3.3 Dependence of the extraction efficiency on the MIBK volume

In order to minimize the volumes, which have to be evaporated for preparing the measurement samples, we finally studied the influence of the volume ratio of the aqueous and organic phase. In Figure 4, the dependence of the extraction performance of all four elements on the volume of MIBK with 10 mL aqueous phase is shown for a selected HCl/HF mixture. Ratios of 1 : 2 (MIBK : aqueous phase) or higher are suitable for a sufficient extraction of group 5 elements.

## 4 Discussion

The extraction behavior of Nb and Ta into organic solvents from HF-containing acid solutions is well-known from mineral processing and extractive metallurgy [15–17]. Usually, MIBK is used as extractant together with acids like  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$  or HCl containing various contents of HF for an industrial-scale production and purification of niobium. The separation efficiency from tantalum is based on the different chemical properties of Ta and Nb. This means: Ta is being extracted as  $\text{H}_2\text{TaF}_7$  over a broad concentration range, whereas Nb is hydrolyzed under similar conditions to  $\text{H}_2\text{NbOF}_5$ , which is not extractable [18]. The ex-

tractability of both elements is dependent on the HF and the acid concentration, but to a much more extent for Nb than for Ta. However, despite of the well-developed metallurgical technology, these systems cannot be fully applied to our special task without further checking, because they use macro amounts of metal (in [17] around 20 g/L were applied), and we have to operate in the range of non-carrier added (n.c.a.) amounts of metal, in the case of Db/Rf even one-atom-at-a-time-chemistry has to be applied. Therefore, a careful and extended investigation of the extraction behavior of all involved elements was necessary under our special conditions.

The HCl/HF extraction system had been studied in [17] very systematically. In principal, we reproduce the general trend – higher concentrations of acid suppress the hydrolysis of Nb and lead to a better extraction efficiency – as well as the increase of the HF concentration does. However, for the extractability of Ta in pure HF solutions, we found 100% in all cases whereas the authors in [17] report a maximum for Ta of ~ 60% over the entire range of concentration (1–16 M). This is caused by the high fluoride excess in the case of n.c.a. radionuclides and a probable formation of inert fluoride complexes. Group 4 elements are not extracted in all studied concentration ranges.

The question, whether relativistic effects change the chemical properties of transactinides in comparison to their lighter homologs or not, has been a hot topic in the SHE community already for many years [19–21]. Dubnium was the first SHE element, where such effects had been discussed. The first studies on the chemistry of Db have been performed in 1988 investigating its extraction into MIBK with a mixture of 3.8 M  $\text{HNO}_3$  + 1.1 M HF [22]. As a – at that time – very surprising result, Db did not extract into MIBK under these conditions like tantalum, but remained, similar to Nb, in the acid solution. This non Ta-like behavior was confirmed later on in a second experiment using extraction of halide complexes with TiOA from an aqueous medium of 12 M HCl + 0.03 M HF [23]. On the other hand, an ARCA-II (Automated Rapid Chemistry Apparatus [24, 25]) experiment using cation exchangers and  $\alpha$ -hydroxy isobutyric acid ( $\alpha$ -HIB) as the eluent showed that Db, together with Nb and Ta are eluted promptly from the column while tri- and tetravalent ions are sorbed [26]. In this experiment, Db was clearly identified as a member of group 5.

Chemical experiments with SHE are generally challenging not only due to the low production rates, resulting in “one-atom-at-a-time-chemistry”, but also due to the short half-lives, requiring simple and fast separation systems. Therefore, in systems where kinetic effects have to be expected, experiments using short-lived isotopes could

give contradictory results, if the reaction time is much longer than the half-life. With the discovery of the long-lived isotope  $^{268}\text{Db}$ , unique possibilities have opened for systematic investigations of the chemical and physico-chemical properties of this superheavy element.

One first attempt in this direction was started in 2005 in Dubna using the same nuclear reaction as in [2–4] and two different modified wet chemistry procedures allowing for the isolation of three fractions: group 4 fraction, Ta-fraction and Nb-fraction [27]. The authors used lanthanum as carrier and HF to precipitate  $\text{LaF}_3$  carrying the actinides and group 4 elements, while group 5 elements stay as fluoride complexes in solution. Afterwards ion exchange or extraction into MIBK was used for further fractionation. Unfortunately; no  $\alpha$ -spectra are shown, no total kinetic energies and neutron multiplicities are given, and there is no description how the group 4 fraction – containing all actinides after precipitation with HF – was chemically processed to get an actinide-free sample. Nevertheless, the authors claim to observe 5 SF events from total 8 irradiations in the Ta-fraction, and no one in the other two, which would be in direct contradiction to the earlier findings in [22]. In a second paper [28], the authors studied the proposed chemical system using MIBK extraction in detail, but without any improvement of the drawbacks given above. Although the system was on-line tested with the  $^{243}\text{Am} + ^{48}\text{Ca}$  reaction, there are no information on actinide separation and possible contamination. It is doubtful if this system is generally suitable to fulfill the requirements of a complete actinide separation. Moreover, since it is well-known that rutherfordium forms stable anionic fluoride complexes [27–31] already at low HF concentrations, a differentiation between Rf and Db using precipitation of  $\text{LaF}_3$  in HF containing solution is clearly not possible using this system.

## 5 Conclusions

Since the pioneering experiments in 2004 the production of  $^{268}\text{Db}$  as decay product of  $^{288}115$  was reproduced several times at the DGFERS [34, 35] and was confirmed in an independent experiment at the TransActinide Separator and Chemistry Apparatus (TASCA) (GSI) [36–38]. In addition, in the reaction  $^{249}\text{Bk} + ^{48}\text{Ca}$  a second long lived dubnium isotope  $^{270}\text{Db}$  was discovered at the DGFERS [39, 40] (for reviews of these results see [41, 42]).

However, the assignment to the atomic number of the members of the registered decay chains remains puzzling. In a very ambitious nuclear spectroscopy experiment using the multicoincidence spectroscopy TASISpec

(TASCA in Small Image mode Spectroscopy) detector setup (GSI) [43] it was searched for characteristic x-ray fingerprints of the members in the  $^{288}115$  decay chain. Unfortunately, only in one out of 23 decay chains a pair of  $\gamma$ -rays was observed which are consistent with the K-x-rays of element meitnerium (Mt,  $Z = 109$ ) [44–46]. However, this assignment is rather weak and the authors discuss the possibility of randomly caught scattered photons in [44]. Nevertheless, this experiment shows that nuclear spectroscopy has the potential to directly determine the atomic number in region of superheavy elements. In addition it was discussed in [44] that for  $^{289}115$  and  $^{285}113$  experimental evidence for an electron capture decay branch was found. This supports new theoretical results of a “narrow pathway” of possible  $\text{EC}/\beta^+$  decaying isotopes towards the middle of the island of stability [47]. With these results the definitive assignment to an atomic number of the members in the observed superheavy element decay chains becomes disputable. Nuclear chemistry experiments could be able to support such assignments in the case of the longer lived isotopes.

To assign the long-lived SF activity terminating the decay chain of 115 [2] either to group 4 or 5, one should use for the first separation step the chemical system which was applied successfully in the first chemistry experiment [3, 4].

No evidence for contamination with actinides was found in a long-term post examination of the sample with the highest observed SF-event rate [6] proving that the selected separation system worked proper and reliable.

We propose for the additional extraction step a mixture of 5 M HCl/2 M HF – a system providing a clear distinction between group 4 and 5 within one min contact time.

For studies of the chemical behavior of Db in comparison to its lighter homologs – assuming that there is no short-lived EC-branch of  $^{268}\text{Db}$  – pure 1 M HF solution or a mixture of 1 M HCl/1 M HF is suitable. To get a more complete picture, the extraction behavior of the pseudo homologue Pa shall be included as well in further investigations. Moreover, the kinetic aspects have to be addressed in more detail. While for the proposed system, one minute contact time was obviously sufficient to reach equilibrium, this has not necessarily to be the case for every system. In particular, when ARCA-II was used, equilibrium conditions cannot be supposed due to the short contact time of only some seconds. Therefore, extended time-dependent studies, both considering shorter contact times and longer ones will be necessary to investigate the influence of kinetic effects.

For the future,  $^{268}\text{Db}$  may be used for extended and systematic studies of the chemical properties of dubnium, complementary to those started already several years ago very successful in Japan (see for example [32, 33]).

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