

## Chemical Properties of Element 105 in Aqueous Solution: Back Extraction from Triisooctyl Amine into 0.5 M HCl

By H. P. Zimmermann, M. K. Gober, J. V. Kratz

Institut für Kernchemie, Universität Mainz, D-6500 Mainz, Germany

M. Schädel, W. Brühle, E. Schimpf

Gesellschaft für Schwerionenforschung mbH, D-6100 Darmstadt, Germany

K. E. Gregorich, A. Türlér, K. R. Czerwinski, N. J. Hannink, B. Kadkhodayan, D. M. Lee, M. J. Nurmia,  
D. C. Hoffman

Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720, USA

H. Gäggeler, D. Jost, J. Kovacs, U. W. Scherer and A. Weber

Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland

(Received April 3, 1992)

*Element 105 / Chemical properties /  
Anion exchange chromatography*

### Abstract

Previous studies of the halide complex formation of element 105 and its anion exchange with triisooctyl amine (TIOA) were continued. The experiments were performed on a one-minute time scale with the computer-controlled liquid chromatography system ARCA II on a mixture of 34-s  $^{262}\text{Ha}$  and 27-s  $^{263}\text{Ha}$  produced in the  $^{249}\text{Bk}(^{18}\text{O},5n)$  and  $^{249}\text{Bk}(^{18}\text{O},4n)$  reactions at a beam energy of 99 MeV. The Ha isotopes were detected by measuring the spontaneous fission and  $\alpha$ -activities associated with their decay, and the  $\alpha$ -decays of their daughters, 4-s  $^{258}\text{Lr}$ , and 6-s  $^{259}\text{Lr}$ . Time-correlated pairs of parent and daughter  $\alpha$ -particles were also registered.  $^{262,263}\text{Ha}$  was absorbed on the TIOA columns from either 12 M HCl/0.01 M HF or 10 M HCl, and was subsequently eluted in 0.5 M HCl/0.01 M HF like its homolog niobium, and the pseudohomolog protactinium, and unlike the closest homolog, tantalum, which remains in the amine phase under these conditions. The effluent was divided into an early Pa fraction and a subsequent Nb fraction. By varying the cut between the Pa fraction and the Nb fraction in rough steps, it was shown that the elution of element 105 occurs closer to the Pa elution position, i.e., earlier than the elution of Nb. These results confirm the non-tantalum like behavior of element 105 in 0.5 M HCl/0.01 M HF, and corroborate previously suggested structural differences between the halide complexes of element 105, niobium, and protactinium, on the one hand, and those of tantalum on the other hand.

### 1. Introduction

Studies of the aqueous chemistry of element 105 have provided expected results as well as surprises [1–3]. The sorption of 34-s  $^{262}\text{Ha}$  on glass surfaces after fuming with nitric acid was compared with tracers of the group 4 elements Zr and Hf and the group 5 elements Nb and Ta produced under similar conditions [1]. Even after washing with 1.5 M  $\text{HNO}_3$ , Ha

was found to adhere to the glass, a property characteristic of the group 5 elements. Experiments to investigate whether Ha is extracted into methylisobutyl ketone (MIBK) under conditions in which the lighter homolog Ta extracts but the next lighter homolog Nb does not, were also conducted [1]. It was expected that Ha would behave more like Ta than Nb but, surprisingly, Ha did not extract from mixed nitric acid/hydrofluoric acid solutions although Ta did. The formation of polynegative anions is a possible explanation.

Later, a large number of anion exchange chromatographic separations using triisooctyl amine (TIOA) on an inert support was performed in order to compare in detail the halide complexation of element 105 with the lighter group 5 elements Nb and Ta, and with the pseudo-group 5 element Pa [2]. Complete extraction-elution cycles were performed on a one-minute time scale with Ha, Nb, Ta, and Pa, produced under similar conditions. It was found [2] that Ha sorbs on the columns from either 12 M HCl/0.02 M HF or 10 M HCl like its homologs Nb, Ta, and Pa. In elutions with 4 M HCl/0.02 M HF (Pa-Nb fraction), and with 6 M  $\text{HNO}_3$ /0.015 M HF (Ta fraction), the Ha activity was found in the Pa-Nb fraction showing that the anionic halide complexes of Ha are different from those of Ta, and are more like those of Nb and Pa, indicating a reversal in the trend in going from Nb via Ta to Ha. In another series of experiments, after the extraction into TIOA from 10 M HCl, elutions were performed with 10 M HCl/0.025 M HF (Pa fraction) and 6 M  $\text{HNO}_3$ /0.015 M HF (Nb strip). The Ha activity was divided almost equally between these two fractions, showing again a behavior very different from Ta, and close to Nb and Pa [2]. It was suggested [2] that the non-tantalum like halide complexation of Ha is indicative of the formation of oxyhalide or hydroxyhalide

complexes like  $[\text{NbOCl}_4]^-$  and  $[\text{PaOCl}_4]^-$  or  $[\text{Pa}(\text{OH})_2\text{Cl}_4]^-$ , in contrast to the pure halide complexes of Ta, such as  $[\text{TaCl}_6]^-$ .

Stimulated by the similarity of the aqueous-phase chemistry of element 105 to that of Nb and Pa, further automated extraction chromatography experiments [3] were conducted in the system HBr/HCl-diisobutylcarbinol (DIBC). The extraction, from concentrated HBr, was followed by the elution of a Nb fraction in 6 M HCl/0.0002 M HF, and a Pa fraction in 0.5 M HCl. Some Ha activity was observed in the Nb fraction but with an apparent cross section which indicated that less than 45% of the Ha was extracted into the DIBC from concentrated HBr. It was concluded that, under these conditions, the bromide complexing of Ha is closer to that of Nb than to that of Pa, indicating a greater tendency to form non-extractable polynegative anions in the sequence  $\text{Pa} < \text{Nb} < \text{Ha}$ .

In the present work, we have returned to the HCl/HF – TIOA system in order to see whether the close similarity in the aqueous-phase chemistry of Ha to Nb and Pa persists also at much lower HCl concentrations than in our previous studies [2]. After extraction into TIOA from 12 M HCl/0.01 M HF or 10 M HCl, the back extraction of Ha into 0.5 M HCl/0.01 M HF was investigated. Under these conditions, Ta remains in the organic phase while Pa is eluted in a narrow peak followed by a rather broad elution peak for Nb. Thus, the chromatographic separations were suitable to differentiate once more between a Ta-, Nb-, or Pa-like behavior of Ha.

## 2. TIOA separations

Based on the measured distribution ratios for tracer activities of Nb, Ta, and Pa in the system HCl/0.03 M HF – TIOA [2], 0.5 M HCl/HF was selected for the present chromatographic separations for the following reasons: i) the extraction of Ta is still quantitative (it decreases below 0.1 M HCl), ii) the extraction yields for Nb (82%) and Pa (50%) are sufficiently different to make possible a separate elution of a Pa fraction and a Nb fraction.

These conditions were tested in manually performed high performance liquid chromatography (HPLC) separations using  $1.7 \times 25$  mm Teflon columns filled with TIOA-coated Voltalef® (weight ratio 1:5, particle size 32–63  $\mu\text{m}$ ). Carrier free radioactive tracers were chemically separated from fission products ( $^{95}\text{Zr}$ ,  $^{95}\text{Nb}$ ) and from neutron irradiated  $^{232}\text{Th}$  ( $^{233}\text{Pa}$ ). The irradiations were performed at the Mainz TRIGA reactor. Commercially available  $^{152}\text{Eu}$  was used to simulate the behavior of the heavy actinides. The tracers were fed onto the columns in 12 M HCl/0.02 M HF through a sample loop. While Nb and Pa were sorbed on the columns Zr and Eu were eluted with the feed solution, as previously observed [2]. Then, Pa and Nb were eluted in 0.5 M HCl/0.02 M

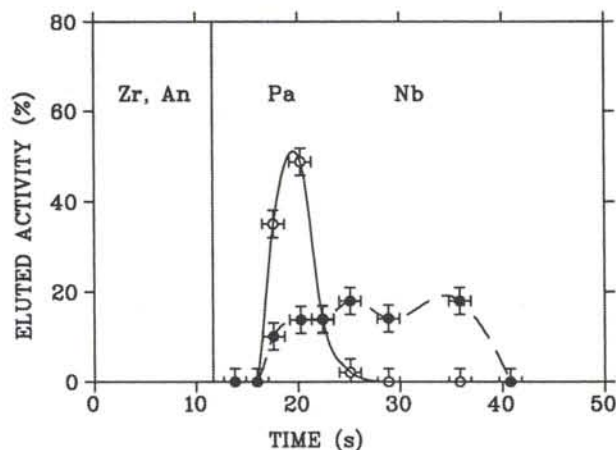


Fig. 1. Elution of Pa and Nb with 0.5 M HCl/0.01 HF from a  $1.6 \times 23$  mm TIOA/Voltalef® column in ARCA II at a flow rate of 0.5 ml/min. In this example, feeding of the activities and the elution of Zr and the actinides (An) occurred in 12 M HCl/0.01 M HF. Upon feeding of the activities in 10 M HCl, the Pa elution peak is shifted to the right by 1 s.

HF. During the elution of the Pa fraction, part of the Nb activity ( $\approx 25\%$ ) eluted with the remaining Nb activity eluting in a relatively broad peak. The breakthrough of some Nb activity into the Pa fraction was a (tolerable) problem that was not solved during this work. It is easily understood; upon changing the aqueous effluent from 12 M HCl to 0.5 M HCl one creates a transition stage in which a narrow band of intermediate HCl concentration passes through the column. Unfortunately, the distribution ratios for both Nb and Pa exhibit a minimum at 4 M HCl [2] so that the band of intermediate HCl concentrations tends to move Nb and Pa down the column and jeopardizes their separation.

When these separations were performed with the Automated Rapid Chemistry Apparatus ARCA II [4], using the usual  $1.6 \times 8$  mm columns contained in movable magazines, the losses of Nb into the Pa fraction became intolerable, and it was decided to replace the columns by the  $1.6 \times 23$  mm columns that had already been used in the DIBC extraction studies [3]. Another improvement resulted from reduction of the effluent flow rate from 1.0 ml/min to 0.5 ml/min, and from adjusting the HF content of the HCl solutions to 0.01 M. Fig. 1 shows the results of such a separation. The horizontal error bars result from the uncertainty associated with the transformation of a number of drops into volumes and times due to fluctuations in the drop size. Depending on the choice of the cut between the Pa and the Nb fraction, somewhat more or less than 35% of the Nb was lost to the Pa fraction. In order to speed up the elution of the Nb fraction, there is the possibility, after the elution of the Pa fraction in 0.5 M HCl/0.01 M HF, to switch to 4 M HCl/0.02 M HF in which a rapid elution of Nb (and Ha) had previously been demonstrated [2].

ARCA II [4] consisted of three chemically inert HPLC pumps, each pumping one eluent, e.g., one

12 M HCl/0.01 M HF, the other 0.5 M HCl/0.01 M HF, and the third 4 M HCl/0.02 M HF, through Teflon tubing of 0.3 mm i.d. to the central Teflon unit containing various Kel-F sliders and two movable magazines containing twenty chromatographic columns (1.6 × 23 mm) each. The column material was TIOA/Voltaf® (32–63 μm), weight ratio 1:5, as in the test experiments. A He/KCl-gas jet deposited the transported reaction products onto one of two alternating polyethylene frits of 35 μm pore size. After a ≈ 50-s collection (for details see Section 4), the first frit was moved on top of one of the TIOA columns, washed with 12 M HCl/0.01 M HF (1 ml/min), whereby the reaction products were dissolved, complexed, and extracted into the amine (in the case of Nb, Ta, and Pa), while the non-extractable species ran through into the waste (≈ 11 s). The column was then washed with 0.5 M HCl/0.01 M HF (0.5 ml/min) for selected times ranging from 13.8 s down to 6.4 s, see Section 4, and the effluent (Pa fraction) was collected on a Ta disk and quickly evaporated to dryness by intense infra-red light and hot He gas. Next, the Nb fraction was eluted either in 4 M HCl/0.02 M HF or in 0.5 M HCl/0.01 M HF, collected on a Ta disk, and evaporated to dryness. The Ta disks were flamed, cooled to room temperature and inserted into the counting chambers about 35 through 57 s after the end of collection, see Section 4. After about 50 s, the next collection of activity on the twin frit was complete. That frit was moved on top of another TIOA column contained in the opposite magazine, and the next separation cycle was carried out. After each separation, the magazines were moved by one step, thus introducing a new column into the elution position. After 40 continuous collection and separation cycles the program was stopped, the used magazines were removed, two new magazines were inserted, and another 40 cycles were started.

### 3. Production, transport and detection of $^{262,263}\text{Ha}$

#### 3.1. Production and transport

The nuclides 34-s  $^{262}\text{Ha}$  and 27-s  $^{263}\text{Ha}$  were produced at the LBL 88-inch Cyclotron by the  $^{249}\text{Bk}(^{18}\text{O},5n)$  and the  $^{249}\text{Bk}(^{18}\text{O},4n)$  reactions, respectively. A 118-MeV  $^{18}\text{O}^{5+}$  beam was passed through a 1.8 mg/cm<sup>2</sup> Havar window, 0.38 mg/cm<sup>2</sup> N<sub>2</sub> cooling gas, and the 2.49 mg/cm<sup>2</sup> Be target backing before passing through the  $^{249}\text{Bk}$  target material. The beam energy in the target was 99 MeV. The target originally consisted of 0.54 mg/cm<sup>2</sup> of freshly purified  $^{249}\text{Bk}$  deposited on the Be backing by molecular plating and converted to the oxide. During these experiments, the target composition varied between 0.53 mg/cm<sup>2</sup> and 0.51 mg/cm<sup>2</sup> of 330-d  $^{249}\text{Bk}$  due to its decay, with the remainder of the total thickness being its  $^{249}\text{Cf}$  daughter. The beam current was about 0.5 particle microamperes.

The reaction products recoiling out of the target were stopped in He gas (1.2 bar) which had been loaded with KCl aerosols produced by sublimation from the surface of KCl powder at 670°C. The activity, attached to the aerosols, was swept out of the recoil chamber with the He gas (2 l/min) into a polyvinylchloride capillary (1.34 mm i.d.) and transported 5 m to the collection site in ARCA II. There, the He gas was pumped through a polyethylene frit by a mechanical pump. The activity-bearing aerosols were collected on that frit and, after the end of the collection time, the frit was shuttled into position for chemical processing of the activity, as described in Section 2.

The He/KCl-jet transport efficiency was measured frequently during the experiments. This was done by dissolving the activity in 12 M HCl/0.01 M HF and eluting it through an empty column directly onto a Ta disk. After evaporation to dryness and flaming, the production rate of the  $^{252-255}\text{Fm}$  transfer products was determined by  $\alpha$  pulse-height analysis. For normalization, separate bombardments of the Bk target were performed in which all of the products recoiling from the target were caught in a gold catcher foil located directly behind the target. After one hour of irradiation, the foil was dissolved in aqua regia to which an aliquot of  $^{241}\text{Am}$  had been added to trace the yield of actinides. The gold was removed on an anion exchange column. The actinide fraction which passed through the column was collected and dried on a Pt disk for  $\alpha$ -particle spectroscopy. By comparing the apparent production rates measured after transport through the He/KCl-jet with the absolute production rates from the gold catcher experiments, the He-transport efficiency was determined. In these experiments, the transport efficiency was 50% on the average but varied between 21 and 79%. These gas-transport yields are usually based on the measurement of 50–100 counts, so they are only accurate to 10 or 20%.

#### 3.2. Detection of alpha and SF activities

Alpha-particle and spontaneous fission (SF) fragment pulse-height analyses were performed on each sample for 450 s using a system of ten 300 mm<sup>2</sup> passivated ion-implanted planar silicon (PIPS) detectors. The energy of each event was stored in list mode on magnetic tape along with the time after start of counting and the detector identification. The energy resolution for  $\alpha$ -particle energies between 5 and 10 MeV was about 50 to 60 keV.

The detector efficiency for  $\alpha$  particles was 35%, implying 70% efficiency for the detection of fragments from SF decay.  $^{262}\text{Ha}$  decays predominantly by  $\alpha$ -particle emission [5, 6],  $I_{\alpha} = 67\%$ ,  $I_{\text{SF}} = 33\%$ . In the decay of  $^{263}\text{Ha}$ , spontaneous fission predominates [5, 6],  $I_{\alpha} = 43\%$ ,  $I_{\text{SF}} = 57\%$ . The  $\alpha$  decay of 34-s  $^{262}\text{Ha}$  ( $E_{\alpha} = 8.45\text{--}8.67$  MeV) is followed by the  $\alpha$  decay of its daughter, 3.9-s  $^{258}\text{Lr}$  ( $E_{\alpha} = 8.57\text{--}8.65$  MeV), [7]. The  $\alpha$  decay of  $^{263}\text{Ha}$  ( $E_{\alpha} = 8.36$  MeV) [5] will be followed



**Table 1.** Parameters of the extraction-elution experiments for the system TIOA–0.5 M HCl/0.01 M HF

Run	F		G		H		I	
Number of expts.	126		179		71		225	
Collection time [s]	49.9		52.3		51.7		52.1	
Fraction*	“Pa”	“Nb”	“Pa”	“Nb”	“Pa”	“Nb”	“Pa”	“Nb”
Start counting [s]	47.3	57.6	41.5	48.1	35.3	42.3	36.9	43.0
Elution time [s]	8.3/13.8	10.5	11.0	9.4	8.9	7.4	6.4	7.4
Ha decays								
$\alpha$	3**	—	8	—	1	—	4**	4
SF	2	—	1	1	—	—	4	9

\* See Fig. 1 for quality of separation.

\*\* Includes a correlated pair of mother-daughter  $\alpha$  particles.

by the decay of its daughter, 6.4-s  $^{259}\text{Lr}$  ( $E_{\alpha} = 8.45$  MeV,  $I_{\text{SF}} = 23\%$ ), [5, 7]. The efficiency for detecting the parent (35%) and missing the daughter (65%) is  $0.35 \times 0.65 = 0.23$ . Likewise, for missing the parent and detecting the daughter it is  $0.65 \times 0.35 = 0.23$ . The efficiency for detecting both  $\alpha$  particles is  $0.35 \times 0.35 = 0.12$ . If the detection of both parent and daughter is treated as the decay of two atoms, the overall efficiency for detecting any  $\alpha$  decay from  $^{262}\text{Ha}$  and  $^{263}\text{Ha}$  or their daughters is  $2 \times 0.23 + 2 \times 0.12 = 0.70$ .

#### 4. Results

601 collection and elution cycles with time sequences as outlined below were run to get an estimate of the elution position of Ha from the TIOA columns in 0.5 M HCl/0.01 M HF relative to the rather well-defined elution peak of Pa. To this end, the cut between the Pa fraction and the Nb fraction was varied in four series of experiments. Their parameters and the associated results are summarized in Table 1.

The somewhat different collection times are the result of changes in the computer program necessary to vary the elution times for both the Pa and Nb fractions. We have not attempted to compensate for this effect. In run F, feeding of the activities onto the columns was done in 12 M HCl/0.01 M HF, in runs G–I this was done in 10 M HCl. In run F, the elution time for the Pa fraction was increased after about half of the number of experiments. The Nb fraction in run F was eluted with 4 M HCl/0.02 M HF. In the later runs, elutions were only conducted with 0.5 M HCl/0.01 M HF.

Run F indicated that the elution position of Ha is relatively early as no events were detected in the Nb fraction. In order to obtain a more precise estimate for the elution position of Ha, the cut between the fractions was moved successively forward until, in run I, the cut was such that only about 25% of the Pa activity was found in the “early” Pa fraction and the remainder in the “late” Pa/Nb fraction.

While the results of runs F, G, and H, indicate consistently that element 105 is eluted earlier than the bulk of the Nb activity, the distribution of the Ha decays in run I among the “early” Pa fraction and the

“late” Pa/Nb fraction allows for a more quantitative conclusion about the elution position of Ha. In the “early” Pa fraction, in which only about 25% of the total Pa activity was detected, 8 Ha (and/or Lr) decays were registered, corresponding to 38% of the total Ha activity in run I. This information can be used to estimate the peak position of the Ha elution curve under the assumption that the shapes of the elution curves for Ha and Pa are identical. Then, the net retention time,  $t'_R$ , corresponding to the peak position defines the distribution coefficient,  $K_D$ :

$$t'_R = t_0 \cdot K_D \cdot V_{\text{org stat}} / V_{\text{aq mob}},$$

where  $t_0$  is the dead time of the column,  $V_{\text{org stat}}$  is the volume of the stationary organic phase, and  $V_{\text{aq mob}}$  is the net retention volume of the mobile aqueous phase. The distribution coefficient, in turn, is connected to the fractional extraction, %p, in a batch extraction experiment as

$$K_D = [(100/\%p) - 1]^{-1} \cdot V_{\text{aq}} / V_{\text{org}}.$$

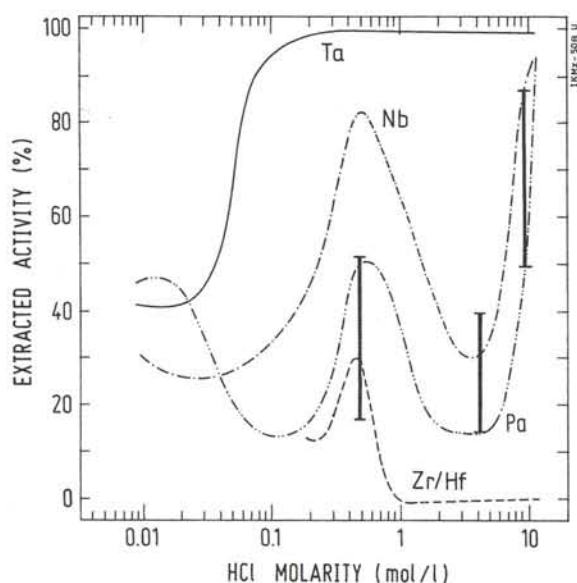
Fractional extractions into TIOA for carrier-free activities of Nb, Ta, Pa, Zr, and Hf, as a function of HCl concentration for pure HCl or HCl/0.03 M HF were determined in batch extractions in Ref. [2]. Therefore, it is of interest to deduce from the earlier Ha elutions [2], and from the estimated elution position in the present work, the corresponding fractional extractions, %p. These are given in Table 2.

The large uncertainties in the fractional extractions %p in Table 2 are mainly due to statistical uncertainties in the number of Ha decays, to uncertainties in the dead and retention volumes which are often on the same order of magnitude. Also, the volume of the organic phase is not constant because of uptake of acid or water molecules. This varies the ratio of the volumes of the stationary and the mobile phases. This can be taken into account in the conversion of elution data into fractional extractions by normalizations derived from the existing extraction data for Nb and Pa. However, these data themselves have experimental uncertainties.

Fig. 2 shows the fractional extraction as a function of HCl molarity in the system TIOA–HCl/0.03 M HF as determined in Ref. [2] for Ta, Nb, Pa, and Zr/Hf. The bold bars encompass the upper and lower

**Table 2.** Fractional extraction of Ha into TIOA from various HCl and mixed HCl/HF solutions

Separation step	Aqueous phase		Ref.	Fractional extraction [%]		
	HCl (mol/l)	HF (mol/l)		%p	upper limit	lower limit
Feed	12	0.02	[2]	> 90	100	90
Feed	10		[2]	> 90	100	90
Nb/Pa el.	4	0.02	[2]	27	39	15
Ta el.	6*	0.015	[2]	< 5	10	0
Pa-Nb sep.	10	0.025	[2]	68	86	50
Pa-Nb sep.	0.5	0.01	this work	32	52	17

\* HNO<sub>3</sub>.

**Fig. 2.** Fractional extraction, %p, of Ta, Nb, Pa, and Zr/Hf vs. HCl molarity in the system TIOA–HCl/0.03 M HF [2]. The bold bars encompass the upper and lower limits of %p deduced from the Ha elution positions. The bar for the extraction of Ha from 12 M HCl/0.02 M HF is not included in the figure for clarity. The figure suggests that the element with the unusual behavior is Ta.

limits for the fractional extraction values of Ha from Table 2 for those cases in which HCl/HF mixtures were used. The comparison of the Ha data with those for Ta, Nb, Pa, and Zr/Hf in Fig. 2 is strictly not correct because the HF molarities were somewhat different in the column separations from the 0.03 M HF solutions used in the batch extraction experiments. However, a comparison of the extraction curves for pure HCl [2] with those for HCl/0.03 M HF in Fig. 2 shows that the curves are qualitatively similar, i.e., show the same trends. In particular, the maximum in the extraction of Nb from 0.5 M HCl, the minimum for 4 M HCl, and the quantitative extraction from 12 M HCl, are common features for both sets of data. Therefore, the use of intermediate HF concentrations in the extraction chromatography experiments is not expected to have a significant effect on the outcome of the comparison of the Ha data with the Ta, Nb, Pa, and Zr/Hf data that is shown in Fig. 2. The result is

consistent with the following view: In 12 M HCl/HF complete extraction of Ha is achieved as for Nb, Ta, and Pa, and the results of the DIBC experiments [3] may be taken as an indication that Ha forms, at least in part, polynegative halide complexes in concentrated halide solutions. In 10 M HCl/HF, Ha behaves intermediate between Nb and Pa, and the same may be true in 4 M HCl/HF. In the latter case, however, no attempt was made [2] to find out whether the properties of Ha were closer to Nb or to Pa. Oxygen containing structures such as  $[\text{NbOCl}_4]^-$ ,  $[\text{PaOCl}_4]^-$  or  $[\text{Pa}(\text{OH})_2\text{Cl}_4]^-$  are likely to exist also for Ha, and explain an anion exchange behaviour very different from that of Ta for which pure halide complexes such as  $[\text{TaCl}_6]^-$  are predominant [8]. The present work shows that in 0.5 M HCl/HF, the properties of Ha are definitely closer to Pa than to Nb, and again very different from Ta. This may indicate that the tendency of Ha to form (partially) hydrolyzed structures in dilute HCl/HF is similar to that of Pa for which structures of the type  $[\text{Pa}(\text{OH})_3]^{2+}$ ,  $[\text{Pa}(\text{OH})_4]^+$ ,  $[\text{Pa}(\text{OH})_3\text{X}]^+$ , or  $[\text{Pa}(\text{OH})_4\text{X}]$  where  $\text{X} = \text{F}^-$  or  $\text{Cl}^-$  have been proposed [9, 10].

## 5. Conclusions

We have further investigated by automated reversed-phase anion exchange chromatography with TIOA the halide complexing of element 105 in comparison to its homologs Nb and Ta, and to the pseudo-group 5 element Pa. As in our previous studies [2], we have extracted 34-s  $^{262}\text{Ha}$  and 27-s  $^{263}\text{Ha}$  into the amine from either 12 M HCl/0.01 M HF or from 10 M HCl. Elutions in 0.5 M HCl/0.01 M HF of a Pa fraction and a subsequent Nb fraction show that Ha closely follows the Pa activity. By fractionation of the effluent, the elution position of Ha was estimated to be identical to the Pa position or before the Pa peak. From the elution position of Ha in 0.5 M HCl/0.01 M HF, and from the previously determined [2] elution positions in 4 M HCl/0.02 M HF and 10 M HCl/0.025 M HF, the fractional extractions of Ha at these acid molarities were deduced and compared to those of Nb, Ta, and Pa. It is found that Ha behaves differently from Ta at all these acid molarities. In detail, Ha behaves in a

manner intermediate between Nb and Pa in 10 M HCl/0.025 M HF, and very similarly to Pa in 0.5 M HCl/0.01 M HF. This reflects structural similarities to both the Nb complexes and the Pa complexes in 10 M HCl such as  $[\text{NbOCl}_5]^{2-}$ ,  $[\text{NbOCl}_4]^-$ ,  $[\text{PaOCl}_4]^-$ , or  $[\text{Pa}(\text{OH})_2\text{Cl}_4]^-$ . In 0.5 M HCl/0.01 M HF, the close similarity of the Ha behavior to that of Pa suggests a similar tendency in Ha to form partially hydrolyzed species such as  $[\text{Pa}(\text{OH})_3]^{2+}$ ,  $[\text{Pa}(\text{OH})_4]^+$ ,  $[\text{Pa}(\text{OH})_3\text{X}]^+$ , and  $[\text{Pa}(\text{OH})_4\text{X}]$  where  $\text{X} = \text{F}^-$  or  $\text{Cl}^-$ .

### Acknowledgements

The authors are indebted to the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, for making the  $^{249}\text{Bk}$  target material available through the transplutonium element production facilities at the Oak Ridge National Laboratory.

We wish to thank the staff and crew of the LBL 88-inch Cyclotron for providing the  $^{18}\text{O}$  beam and for technical support.

The German and Swiss groups have enjoyed the hospitality of the Lawrence Berkeley Laboratory Nuclear Science Division.

This work was supported by the German Federal Minister for Research and Technology (BMFT) under Contract No. 03-HE2MAI, by the Swiss National Science Foundation under Contract No. 2.204-0.86, and by the Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC030-76SF00098.

### References

1. Gregorich, K. E., Henderson, R. A., Lee, D. M., Nurmia, M. J., Chasteler, R. M., Hall, H. L., Bennett, D. A., Gannett, C. M., Chadwick, R. B., Leyba, J. D., Hoffman, D. C., Herrmann, G.: *Radiochim. Acta* **43**, 223 (1988).
2. Kratz, J. V., Zimmermann, H. P., Scherer, U. W., Schädel, M., Bröchle, W., Gregorich, K. E., Gannett, C. M., Hall, H. L., Henderson, R. A., Lee, D. M., Leyba, J. D., Nurmia, M. J., Hoffman, D. C., Gäggeler, H., Jost, D., Baltensperger, U., Ya Nai-Qi, Türlér, A., Lienert, Ch.: *Radiochim. Acta* **48**, 121 (1989).
3. Goyer, M. K., Kratz, J. V., Zimmermann, H. P., Schädel, M., Bröchle, W., Schimpf, E., Gregorich, K. E., Türlér, A., Hannink, N. J., Czerwinski, K. R., Kadkhodayan, B., Lee, D. M., Nurmia, M. J., Hoffman, D. C., Gäggeler, H., Jost, D., Kovacs, J., Scherer, U. W., Weber, A.: *Radiochim. Acta* **57**, 77 (1992).
4. Schädel, M., Bröchle, W., Jäger, E., Schimpf, E., Kratz, J. V., Scherer, U. W., Zimmermann, H. P.: *Radiochim. Acta* **48**, 171 (1989).
5. Kratz, J. V., Goyer, M. K., Zimmermann, H. P., Schädel, M., Bröchle, W., Schimpf, E., Gregorich, K. E., Türlér, A., Hannink, N. J., Czerwinski, K. R., Kadkhodayan, B., Lee, D. M., Nurmia, M. J., Hoffman, D. C., Gäggeler, H., Jost, D., Kovacs, J., Scherer, U. W., Weber, A.: *Phys. Rev.* **C45**, 1064 (1992).
6. Schädel, M., Bröchle, W., Schimpf, E., Zimmermann, H. P., Goyer, M. K., Kratz, J. V., Trautmann, N., Gäggeler, H., Jost, D., Kovacs, J., Scherer, U. W., Weber, A., Gregorich, K. E., Türlér, A., Czerwinski, K. R., Hannink, N. J., Kadkhodayan, B., Lee, D. M., Nurmia, M. J., Hoffman, D. C.: *Radiochim. Acta* **57**, 85 (1992).
7. Gregorich, K. E., Hall, H. L., Henderson, R. A., Leyba, J. D., Czerwinski, K. R., Kreek, S. A., Kadkhodayan, B., Nurmia, M. J., Lee, D. M., Hoffman, D. C.: *Phys. Rev.* **C45**, 1058 (1992).
8. *Comprehensive Coordination Chemistry*, ed. Wilkinson, G., Vol. 3, p. 591, Pergamon (1987).
9. Scherff, H.-L., Herrmann, G.: *Radiochim. Acta* **6**, 53 (1966).
10. Guillaumont, R., Bouissières, G., Muxart, R., *Actinides Rev.* **1**, 135 (1968).