

## Fast On-line Solvent Extraction with the SISAK-3 Centrifuge System as a Test of Chemical Studies of the Elements 105 and 106

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### Abstract

The fast centrifuge system SISAK-3 has been applied to study in on-line experiments the chemical behavior of the homologs of Elements 105 and 106. Using 0.046 M trioctylamine dissolved in Shellsol T, the Group 5 homologs of Element 105 and the Group 6 homologs of Element 106 can be extracted from an unbuffered 1.0 M  $\alpha$ -hydroxyisobutyric acid solution with yields between 60% and 100%. Group 4 homologs of Element 104 and the lanthanides remain in the aqueous phase. Similar results were observed using lactic acid solutions.

### Introduction

According to the systematics of the Periodic Table, the Elements 105 and 106, hahnium and seaborgium, should be located in the Groups 5 and 6, with tantalum and tungsten presumed to be their closest relatives. Recent studies of the chemical behavior of Element 105 show, however, that this element behaves more like niobium, but is distinctly different from tantalum [1–5]. These results may be explained by relativistic effects [6, 7] which should have an influence on the structure of the electron shells and, hence, on the chemical behavior of the heaviest elements. No chemical studies of Element 106 have been reported thus far. The half-life of the known isotope  $^{263}\text{106}$  ( $T_{1/2} = 0.9$  s) is at the limit of what can be handled with present-day chemical techniques. Two recently discovered longer lived isotopes,  $^{265}\text{106}$  ( $T_{1/2} = 2\text{--}30$  s) and  $^{266}\text{106}$  ( $T_{1/2} = 10\text{--}30$  s) [8] may improve the situation but low production rates are still a problem.

For investigations of the chemistry of transactinide elements, fast separation systems are essential. The centrifuge system SISAK-3 permits on-line solvent extraction experiments with nuclides having half-lives down to about one second [9, 10]. It was the objective of the present investigation to explore the possibilities

of applying this system to study the chemistry of Elements 105 and 106. As a characteristic chemical property of the Group 5 and 6 elements, we chose the formation of their negatively charged complexes with  $\alpha$ -hydroxyisobutyric acid ( $\alpha$ -HIB), as well as lactic acid in weakly acid solutions. For selective separation, we used the solvent extraction of these complexes by the liquid anion exchanger trioctylamine (TOA) dissolved in an inert organic solvent. The formation of negatively charged complexes with  $\alpha$ -HIB has been applied previously in cation exchange experiments [5] to show that Element 105 accompanies pentavalent niobium, tantalum, and protactinium in the elution from a cation exchange column, while tetravalent zirconium and trivalent europium are retained on the column. The formation of negatively charged complexes of molybdenum and tungsten with lactic acid (L) and other hydroxy acids is well documented. The species  $[\text{Me}^{\text{VI}}\text{O}_2\text{L}_2]^{2-}$  is dominating in weakly acid solutions [11, 12]. The lanthanides, the trivalent actinides and the Group 4 elements are present as positively charged complexes in weakly acid solutions of  $\alpha$ -HIB and lactic acid and are not expected to be coextracted into TOA.

After an exploration of this approach by conventional batchwise solvent extraction, on-line studies were carried out with the SISAK-3 system using the homologs Zr-Nb-Mo-La produced by fission and Hf-Ta-W made by  $\alpha$ -particle induced reactions; La served as an analog element for the trivalent actinides. In these experiments, the subsequent steps of a radiochemical procedure were performed continuously: (i) production of the model elements by nuclear reactions, (ii) transport from the target area to the SISAK-3 set-up, (iii) chemical separation by solvent extraction, and (iv) inspection of the two final, organic and aqueous phases by  $\gamma$ -ray spectroscopy.

### Experimental

*Radioactive tracers.* For the batch experiments, the following tracer activities were produced by neutron capture reactions in respective metal salts irradiated

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in a neutron flux of  $7 \times 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$  in the Mainz TRIGA reactor: 17-h  $^{97}\text{Zr}$ , 40-h  $^{140}\text{La}$ , 42-d  $^{181}\text{Hf}$ , and 114-d  $^{182g}\text{Ta}$ . In addition, 58-s  $^{97m}\text{Nb}$  and 74-min  $^{97g}\text{Nb}$  were obtained carrier-free by  $\beta^-$ -decay of  $^{97}\text{Zr}$ . In the SISAK experiments carrier-free fission products of neutron-irradiated  $^{239}\text{Pu}$  were applied using the nuclides 7.1-s  $^{100}\text{Zr}$ , 15-s  $^{99g}\text{Nb}$ , 36-s  $^{105}\text{Mo}$ , and 41-s  $^{144}\text{La}$  as most characteristic tracers of the lighter homologs. In one experiment the fission products were mixed with carrier-free 27-d  $^{233}\text{Pa}$  produced by neutron capture in thorium and subsequent  $\beta^-$ -decay and with carrier-containing  $^{181}\text{Hf}$  and  $^{182g}\text{Ta}$ . Carrier-free tracers of the heavier homologs, 51-min  $^{177m2}\text{Hf}$ , 16-min  $^{182m}\text{Ta}$ , 2.2-h  $^{177}\text{W}$ , and 6.4-min  $^{179m}\text{W}$ , were obtained by irradiation of hafnium and tungsten targets with 49 MeV  $\alpha$ -particles (average particle beam intensity 0.5  $\mu\text{A}$ ) at the Philips cyclotron of PSI Villigen.

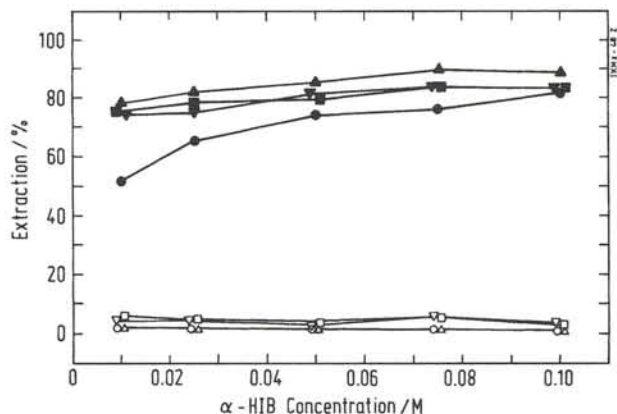
**Batch experiments.** Batch experiments were carried out by shaking in a separatory funnel for five seconds an aqueous solution spiked with tracers and an equal volume of the organic solution containing the extracting agent. The pH-value of the aqueous phase was adjusted with HCl or  $\text{NH}_4\text{OH}$ . After phase separation, the extraction yields were determined by measuring aliquots of each phase by  $\gamma$ -ray spectroscopy using Ge (HPGe) or Ge(Li) detectors (resolution 1.8 and 3.0 keV FWHM at 1333 keV, respectively).

**SISAK-3 experiments.** The fast centrifuge system SISAK-3 applied in the on-line extraction experiments is described elsewhere in detail [9, 13]. Two different construction materials were used, namely Ti passivated with Pd or polyetheretherketone (PEEK). Both materials are resistant to the solutions used in our experiments.

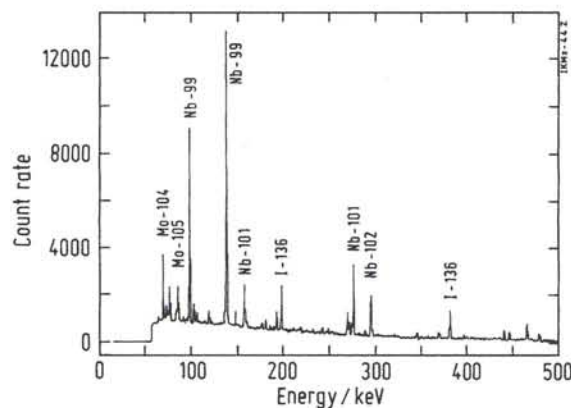
The reaction products were transported from the target chamber to the SISAK-3 system by means of a  $\text{N}_2/\text{KCl}$ -gas jet in Mainz or a  $\text{He}/\text{KCl}$ -gas jet at PSI. The nuclear reaction products attached to aerosols in the gas jet were dissolved by means of a stationary mixer in an aqueous phase heated to about 70 °C. The gaseous reaction products and the carrier gas were removed in a degasser with an inner volume of 0.1 ml. The aqueous phase was then contacted with an organic solution containing the extracting agent and the mixed phases were fed into the centrifuge, inner volume 0.3 ml, and separated in about 0.1 s. Flow rates were typically about 0.5  $\text{ml s}^{-1}$  for both phases. The extraction yields were determined from  $\gamma$ -ray measurements performed using HPGe and Ge(Li) detectors on the outgoing phases in teflon capillaries (2 mm i.d.) or in teflon cells of various volumes, depending on half-life and count rate of the nuclides. Counting times were typically 15 minutes.

## Results and discussion

The experiments covered the following range of parameters:



**Fig. 1.** Extraction yields of hafnium (open symbols) and tantalum (filled symbols) in batch experiments at various concentrations of  $\alpha$ -hydroxyisobutyric acid ( $\alpha$ -HIB) in the aqueous phase, with the following concentrations of trioctylamine (TOA) in the organic solvent Shellsol T:  $\circ$  0.023 M,  $\triangle$  0.058 M,  $\nabla$  0.115 M,  $\square$  0.172 M.



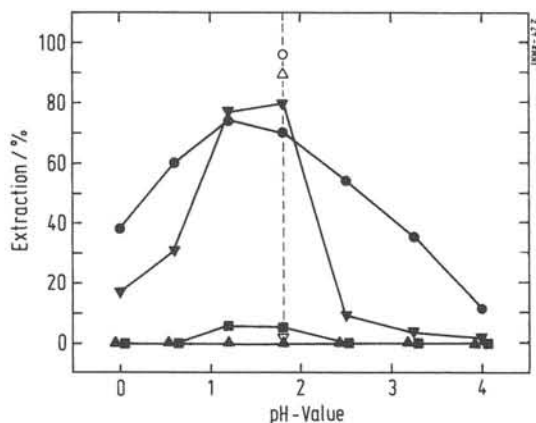
**Fig. 2.** Example of the  $\gamma$ -ray spectra measured on-line in SISAK experiments; organic phase after solvent extraction of a fission product mixture with 0.023 M TOA/Shellsol T from 1.0 M  $\alpha$ -HIB at pH 1.8.

- $\alpha$ -hydroxyisobutyric acid ( $\alpha$ -HIB) solutions at various pH-values (0 to 4) and concentrations (0.01 M to 5.0 M),
- 1.0 M lactic acid solutions at pH-values from 1 to 3.5,
- trioctylamine (TOA) dissolved in Shellsol T (0.011–0.17 M) as the organic solvent.

As an example for the batch experiments, Fig. 1 shows the extraction yields of Hf and Ta at various concentrations of  $\alpha$ -HIB and TOA. We note an increase of the yield for Ta up to 90% at the highest  $\alpha$ -HIB and TOA concentrations applied, whereas the yield for Hf remains below 5% at all concentrations. The same trend of high extraction yield is found for Nb, whereas Zr and also La are extracted very little or below the detection limit.

In a series of SISAK-3 experiments with the lighter homologs,  $\alpha$ -HIB-concentrations ranged from 0.1 M to 5.0 M and TOA-concentrations from 0.011 M to 0.114 M. The pH-value of the aqueous phases was



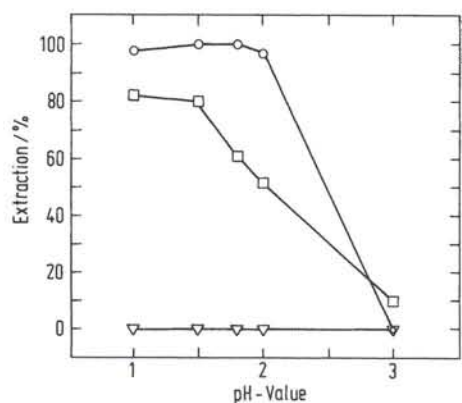


**Fig. 3.** Extraction yields of zirconium (■), niobium (●), molybdenum (▼), lanthanum (▲), hafnium (▽), tantalum (○), and protactinium (△) from 1.0 M  $\alpha$ -HIB at various pH-values with 0.046 M TOA/Shellsol T in SISAK on-line experiments. Dashed line: optimum pH-value (1.8).

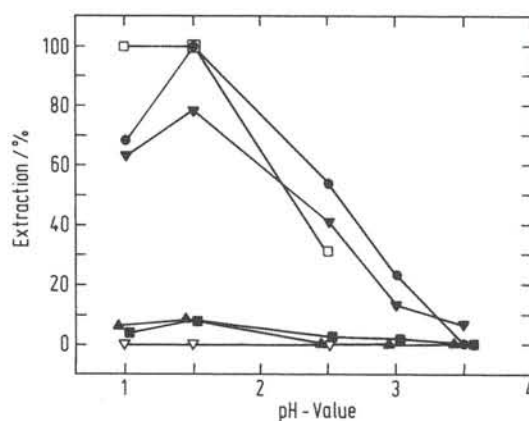
fixed at pH 1.0. With 0.023 M TOA, the highest extraction yields for Nb and Mo are obtained at an  $\alpha$ -HIB-concentration of 1.0 M. Under these conditions, Zr and La remain in the aqueous phase. Figure 2 shows an example of the  $\gamma$ -ray spectra observed in the organic phase during an on-line experiment. We note a clear enrichment of niobium (15-s  $^{99}\text{Nb}$ , 7.1-s  $^{101}\text{Nb}$ , 4.3-s  $^{102}\text{Nb}$ ) and Mo activities (60-s  $^{104}\text{Mo}$ , 36-s  $^{105}\text{Mo}$ ) from the complex fission product mixture, with 47-s  $^{136}\text{I}$  being the only strong contaminant, as is usually found in SISAK solvent extraction procedures.

In further experiments with the lighter homologs, the pH-value of the  $\alpha$ -HIB-solutions was varied from 0 to 4. The highest extraction yields are obtained for an unbuffered 1.0 M  $\alpha$ -HIB-solution which has a pH-value of 1.8 and with 0.046 M TOA (2 Vol. %) as the organic solution, as can be seen in Fig. 3. Mo is extracted to 80%, Nb to 70%, Zr to  $\leq 5\%$ , whereas La is found only in the aqueous phase. At these conditions carrier-free Pa and neutron-activated Ta and Hf were added to the aqueous phase. The extraction yields are 88% for Pa, 96% for Ta, and 2% for Hf. These experiments have been performed with Ti as well as with PEEK centrifuges and the results were the same. It is interesting to note that Pa follows Nb and Ta in their high extraction yields. As in many other chemical properties, Pa behaves like a Group 5 element where it would be located in an extrapolation of the Periodic Table beyond Ac, if the actinide concept would not be taken into account.

In another series of SISAK-3 experiments the heavier Group 4, 5 and 6 elements were used in carrier-free form. As Fig. 4 depicts, extraction from 1.0 M  $\alpha$ -HIB solutions showed nearly 100% yield for Ta at pH-values from 1.0 to 2.0 and almost 80% for W from pH-values 1.0 to 1.5. Hf is not extracted in the pH-range studied. The best results for Ta were again obtained with an unbuffered solution of 1.0 M  $\alpha$ -HIB as aqueous and 0.046 M TOA/Shellsol T as organic



**Fig. 4.** Extraction yields of carrier-free hafnium (▽), tantalum (○), and tungsten (□) from 1.0 M  $\alpha$ -HIB at various pH-values with 0.046 M TOA/Shellsol T in SISAK on-line experiments.



**Fig. 5.** Extraction yields of zirconium (■), niobium (●), molybdenum (▼), lanthanum (▲), hafnium (▽), and tungsten (□) from 1.0 M lactic acid at various pH-values with 0.046 M TOA/Shellsol T in SISAK on-line experiments.

phase, whereas for W a slightly lower pH-value is preferable.

With lactic acid instead of  $\alpha$ -HIB as the aqueous solution similar extraction yields, Fig. 5, are found. Again the highest yields result for an unbuffered solution of 1.0 M lactic acid (pH 1.5). Mo is extracted to 78%, Nb and W to 100%, Zr, La and Hf only to a small extent.

With the heavier homologs, several experiments were performed under slightly modified conditions. Addition of dodecanol to the aqueous phase improves the phase separation without any effect on extraction yields. The use of toluene as diluent for TOA (replacing Shellsol T) did not change the extraction yields of Ta and W but did increase slightly the extraction of Hf.

## Conclusions

According to our experiments, the homologs of the Elements 105 and 106 are efficiently extracted into TOA from unbuffered 1.0 M solutions of  $\alpha$ -HIB or lactic acid on time scales fast enough for application to

nuclides with half-lives of a few seconds. The fact that the Group 5 and Group 6 elements are extracted simultaneously is not considered to be a problem because Element 105 will not be formed in heavy-ion fusion reactions producing Element 106 and vice versa. Thus, the method presented here is one of the possible approaches to study the solution chemistry of Element 106 for the first time and to further investigate the chemical properties of Element 105.

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### References

- 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).
- Kratz, J. V., Zimmermann, H. P., Scherer, U. W., Schädel, M., Brüchle, 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., Nai-Qi, Y., Türlér, A., Lienert, C.: *Radiochim. Acta* **48**, 121 (1989).
- Gober, M. K., Kratz, J. V., Zimmermann, H. P., Schädel, M., Brüchle, 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).
- Schädel, M., Brüchle, W., Schimpf, E., Zimmermann, H. P., Gober, 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).
- Gäggeler, H. W., Jost, D. T., Kovacs, J., Scherer, U. W., Weber, A., Vermeulen, D., Türlér, A., Gregorich, K. E., Henderson, R. A., Czerwinski, K. R., Kadkhodayan, B., Lee, D. M., Nurmia, M. J., Hoffman, D. C., Kratz, J. V., Gober, M. K., Zimmermann, H. P., Schädel, M., Brüchle, W., Schimpf, E., Zvara, I.: *Radiochim. Acta* **57**, 93 (1992).
- Pershina, V., Fricke, B., Kratz, J. V., Ionova, G. V.: *Radiochim. Acta* **64**, 37 (1994).
- Kratz, J. V.: *J. Alloys Compounds* **213/214**, 20 (1994).
- Lazarev, Yu. A., Lobanov, Yu. V., Oganessian, Yu. Ts., Utyonkov, V. K., Abdullin, F. Sh., Buklanov, G. V., Gikal, B. N., Iliev, S., Mezentsev, A. N., Polyakov, A. N., Sedykh, I. M., Shirokovsky, I. V., Subbotin, V. G., Sukhov, A. M., Tsyganov, Yu. S., Zhuchko, V. E., Loughheed, R. W., Moody, K. J., Wild, J. F., Hulet, E. K., McQuaid, J. H.: *Phys. Rev. Lett.* **73**, 624 (1994).
- Persson, H., Skarnemark, G., Skålberg, M., Alstad, J., Liljenzin, J. O., Bauer, G., Haberberger, F., Kaffrell, N., Rogowski, J., Trautmann, N.: *Radiochim. Acta* **48**, 177 (1992).
- Altzitzoglou, T., Rogowski, J., Skålberg, M., Alstad, J., Herrmann, G., Kaffrell, N., Skarnemark, G., Talbert, W., Trautmann, N.: *Radiochim. Acta* **51**, 145 (1990).
- Caldeira, M. M., Ramos, M. L., Gil, V. M.: *Canad. J. Chem.* **65**, 827 (1987).
- Cruywagen, J. J., Krüger, L., Rohwer, E. A.: *J. Chem. Soc. Dalton Trans.* **1993**, 105.
- Alstad, J., Skarnemark, G., Haberberger, F., Herrmann, G., Nähler, A., Pense-Maskow, M., Trautmann, N.: *J. Radioanal. Nucl. Chem.* **189**, 133 (1995).