

Dissertation for the degree of Doctor Scientiarum

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**Liquid Chemistry of Hassium Tetroxide
using Osmium
in Model Experiments with SISAK**



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November 2010

Preface

During the last several decades the number of man-made elements has been continually increasing. New elements are produced artificially and placed in the Periodic Table of elements according to their chemistry, following the rules of the Periodic Table. The last of these artificial elements are Transactinides or superheavy elements (with $Z \geq 104$) which are produced by bombardment of suitable target materials with heavy ion beams from accelerators in a few laboratories in the world. The production rate of transactinides is very low and most of them last only for a few seconds or less; in such a case we have only one atom of these elements at any time. Chemical investigation of transactinides has become of great interest during the recent decades. The reason behind such difficult, time consuming and expensive studies is perhaps human curiosity: The elements are fundamental for our understanding of matter around us. Exploring properties of unknown elements is important in this perspective and receive worldwide attention. It is predicted that the relativistic effects in the heaviest elements can alter the classical rules of periodicity in the elements. Chemical investigations of these elements are the only means which can verify these predictions. Thus these studies lead to our better understanding of the universe.

The aim of this work is to develop and test a system for chemical study of hassium, one of the transactinide elements, which has not been much chemically investigated. Chemical study of an element, with a production rate of one atom per day and a half-life of about 10 seconds, is challenging and demands for special equipments. SISAK system is one of appropriate setups to be used for chemical investigation of transactinides. This system which is a continuous solvent extraction apparatus has been developed during 70s for the study of short-lived isotopes. This work is to develop a SISAK extraction system for chemical study of Hs. In order to achieve this aim a suitable chemistry has to be selected according to the properties of the anticipated homologues of Hs and the system has to be tested before adoption for an Hs experiment. This work was carried out as a part of SISAK-project at the SAFE Center and Department of Chemistry, University of Oslo and the experiments were partly performed at GSI with the financial support from the Norwegian Research council.

I am grateful for being a tiny part of the international "transactinide community" and I owe this opportunity to my supervisor, Professor Jon Petter Omtvedt, for having me as his student. Thanks for helping me throughout my study and supporting me in every respect whenever I needed.

My co-supervisor Professor Tor Bjørnstad is gratefully acknowledged for the helpful discussions and giving me basic knowledge about the solvent extraction method. Thanks for all your encouragements.

A special thank to Professor Emeritus Jorolf Alstad who always was ready to listen to my different ideas and answering my various questions. I am greatly indebted to you for your generous help and attentions both in study and life.

I am really grateful of the helps I got from Dr. Liv Stavsetra both in English corrections of the text and sharing of her valuable scientific ideas for this thesis.

The operators of the Oslo Cyclotron, Eivind A. Olsen, Andrey Semchenkov and Jon C. Wikne who provided me stable beam for my experiments are gratefully acknowledged.

The trainees and fellow students who helped me with my experiments are much appreciated. The experiments in Oslo were performed with assistance of Marita Clause, Joachim Halgren and Fredrik Lunde and the experiments at GSI, Germany, with assistance of Johannes Nilssen, Heidi Ottesen, Saleha Qureshi, Christine Roth and Frøydís Schulz. The performance of the experiments was not possible without your assistance.

Professor Matthias Schädel and other staff and crew at GSI who always welcomed me to participate in different experiments are gratefully appreciated. Attending in these experiments was a very valuable experience for me.

Professor Jens Kratz and his group who kindly shared their beam-time with us to perform our experiment at GSI are acknowledged.

The operators of UNILAK, the linear accelerator at GSI, who provided me beam for my experiments are appreciated.

The former students and postdocs who contributed in developing of the SISAK system are acknowledged.

My fellow students and colleagues who I enjoyed working with are gratefully appreciated.

Many thanks go to my friends in Norway who made my stay in Norway pleasant.

The Bahá'í community of Norway who received me warmly and aided me a lot during my stay in Norway in such a way that I felt really at home among them are gratefully appreciated.

A special thank to my friends, Neda and Mahsa, for being with me. You have been as members of family for me and I am grateful for having you.

Last but not least I am gratefully thankful of my parents and family who encouraged and supported me a lot all throughout my study. Mehran and Kian who were the source of inspiration and love at the last stages of my work are gratefully thanked.

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Abstract

A SISAK extraction system for chemical study of Hs was developed and then tested in a pilot experiment using its lighter homologue Os as a model. Applying this system the reaction of HsO_4 with NaOH in the solution can be studied. In order to develop the system γ -emitting isotopes of osmium were used. In this stage the distribution of OsO_4 between toluene and NaOH solution was studied and a distribution curve for various NaOH solutions was obtained. The trend in the distribution curve was interpreted based on formation of hydroxyl complexes of OsO_4 . By fitting the results with this model the equilibrium constants for the formation of $[\text{OsO}_4(\text{OH})]^-$ and $[\text{OsO}_4(\text{OH})_2]^{2-}$ were obtained. The proper detection system for a transactinide SISAK experiment is the liquid scintillation method. However, this method cannot be directly used for measurement of the aqueous phase due to quenching effects. Thus a second extraction stage was developed to extract the remaining Os from the aqueous phase into a second appropriate organic phase. The latter is then measured using scintillation detection. This procedure was achieved by acidification of the raffinate from the first extraction stage to break down the hydroxyl complexes and retrieve OsO_4 , which is highly soluble in toluene. The yield of extraction for the second stage was as high as $(90 \pm 3) \%$.

A pilot experiment with α -emitting Os isotopes was performed at GSI Helmholtzzentrum für Schwerionenforschung GmbH (GSI), Darmstadt, Germany using the whole setup with two array detection cells as an Hs experiment is planned. In these experiments the gas-filled preseparator TASCA (TransActinide Separator and Chemistry Apparatus) was used to separate Os nuclides from projectile and other unwanted nuclear reaction by-products. During these experiment the results from Oslo could be reproduced and the transport time of the Os nuclides from production site to the Chemistry apparatus (SISAK setup) and the transport yield were measured. It can be said that the development of the SISAK extraction system for chemical study of Hs is now completed and ready for a real experiment in principle.

List of Papers

- I) Omtvedt, J. P., Alstad, J., Bjørnstad, T., Düllmann, Ch.E., Gregorich, K. E., Hoffman, D. C., Nitsche, H., Opel, K., Polakova, D., Samadani, F., Schulz, F., Skarnemark, G., Stavsetra, L., Sudowe, R., Zheng, L.: *Chemical properties of the transactinide elements studied in liquid phase with SISAK*. European Physical Journal D: Atomic, Molecular, Optical and Plasma Physics. 2007, **45**(1), p. 91-97.
- II) Samadani, F., Alstad, J., Bjørnstad, T., Omtvedt, J.: *Development of a SISAK Extraction System for Chemical Studies of Element 108, Hassium*, Accepted for publication in Radiochimica Acta.
- III) Samadani, F., Alstad J., Bjørnstad T., Düllmann, Ch.E., Eberhardt, K., Even, J., Gates, J.M., Hild, D., Jäger, Khuyagbaatar, E. J., Kratz, J.V., J. Krier, Nilssen, J., Ottesen, H.B. Qureshi, S. Roth, Ch., Schädel, M., Schausten B., Schulz, F., Türlér, A., Wiehl, N., Yakushev A., Omtvedt, J.P.: *Test of SISAK Extraction System for Hs with α -emitting Os*, To be submitted to Radiochimica Acta.

List of Reports and Workshop contributions

- I) M. Schädel, D. Ackermann, L.-L. Andersson, J. Ballof, M. Block, R.A. Buda, W. Bröchle, I. Dragojevi, Ch.E. Düllmann, J. Dvorak, K. Eberhardt, J. Even, J.M. Gates, J. Gerl, A. Gorshkov, P. Golubev, R. Graeger, K.E. Gregorich, E. Gromm, W. Hartmann, F.P. Heßberger, D. Hild, R. Hoischen, A. Hübner, E. Jäger, J. Khuyagbaatar, B. Kindler, I. Kojouharov, J.V. Kratz, J. Krier, N. Kurz, S. Lahiri, D. Liebe, B. Lommel, M. Maiti, M. Mendel, E. Merchán, H. Nitsche, D. Nayak, J. Nilssen, J.P. Omtvedt, K. Opel, P. Reichert, D. Rudolph, A. Sabelnikov, F. Samadani, H. Schaffner, B. Schausten, R. Schuber, E. Schimpf, A. Semchenkov, L. Stavsetra, J. Steiner, J. Szerypo, P. Thörle-Pospiech, A. Toyoshima, A. Türlér, J. Uusitalo, N. Wiehl, H.-J. Wollersheim, T. Wunderlich, and A. Yakushev: *TASCA Commissioning Completed*, GSI Scientific Report 2008, NUSTAR-SHE-08 (2009).
- II) A. Gorshkov, R. Graeger, A. Türlér, A. Yakushev, D. Ackermann, W. Bröchle, Ch. E. Düllmann, E. Jäger, F. Heßberger, J. Khuyagbaatar, J. Krier, M. Schädel, B. Schausten, E. Schimpf, L.-L. Andersson, D. Rudolph, K. Eberhardt, J. Even, J.V. Kratz, D. Liebe, P. Thörle, N. Wiehl, I. Dragojevi, J.M. Gates, L. Stavsetra, J.P. Omtvedt, A. Sabelnikov, F. Samadani, J. Uusitalo: *Measurements of $^{260-262}\text{Rf}$ produced in $^{22}\text{Ne} + ^{244}\text{Pu}$ fusion reaction at TASCA*, GSI Scientific Report 2008, NUSTAR-SHE-09 (2009).

- III) R. Graeger, A. Gorshkov, A. Türler, A. Yakushev, D. Ackermann, Ch. E. Düllmann, E. Jäger, F. P. Heßberger, J. Khuyagbaatar, J. Krier, D. Rudolph, M. Schädel, B. Schausten, J. Dvorak, M. Chelnokov, V. Chepigin, A. Kuznetsov, O. Petrushkin, J. Even, D. Hild, J. V. Kratz, J. P. Omtvedt, F. Samadani, K. Nishio and Q. Zhi: *Observation of ^{270}Hs in the complete fusion reaction $^{36}\text{S}+^{238}\text{U}$* , GSI Scientific Report 2008, NUSTAR-SHE-02 (2009).
- IV) M. Schädel, D. Ackermann, L.-L. Andersson, J. Ballof, M. Block, R.A. Buda, W. Bröchle, I. Dragojević, Ch.E. Düllmann, J. Dvorak, K. Eberhardt, J. Even, J.M. Gates, J. Gerl, A. Gorshkov, P. Golubev, R. Graeger, K.E. Gregorich, E. Gromm, W. Hartmann, F.P. Heßberger, D. Hild, R. Hoischen, A. Hübner, E. Jäger, J. Khuyagbaatar, B. Kindler, I. Kojouharov, J.V. Kratz, J. Krier, N. Kurz, S. Lahiri, D. Liebe, B. Lommel, M. Maiti, M. Mendel, E. Merchán, H. Nitsche, D. Nayak, J. Nilssen, J.P. Omtvedt, K. Opel, P. Reichert, D. Rudolph, A. Sabelnikov, F. Samadani, H. Schaffner, B. Schausten, R. Schuber, E. Schimpf, A. Semchenkov, L. Stavsetra, J. Steiner, J. Szerypo, P. Thörle-Pospiech, A. Toyoshima, A. Türler, J. Uusitalo, N. Wiehl, H.-J. Wollersheim, T. Wunderlich, and A. Yakushev: *TASCA – A New Tool in the Quest for Superheavy Element Studies*, presented at 7th Workshop on the Chemistry of the Heaviest Elements, Johannes Gutenberg University, Mainz, October 2009.

Objective

The chemical study of transactinides, elements with $Z \geq 104$, has been of special interest during the last several decades [1]. It is predicted that relativistic effects [2] have their highest influence on the chemistry of elements at this heavy-mass region of the Periodic Table. By chemical investigation of the heaviest elements these theoretical predictions can be examined. The high influence of relativistic effects might alter the classical trends in the Periodic Table. Thus these kinds of chemical experiments also aid the placement of the newly discovered elements in the appropriate position in the Periodic Table. Transactinides do not exist in the nature and are produced artificially in nuclear fusion reactions. Because of their low production rates and short half-lives, a synthesized atom most likely decays before the next is produced. For that reason the chemistry of the transactinides is often referred to as “one-atom-at-a-time chemistry”. Thus, special equipments as well as some fast reactions are required to investigate their chemical behaviors [3]. The SISAK (Short-lived Isotopes Studied by the AKUFVE¹ technique) system, equipped with liquid scintillation detection arrangement is one of the appropriate setups for chemical studies of transactinides in the liquid phase [4]. This setup was successfully applied for chemical study of transactinide element 104, rutherfordium (Rf) [5-7]. During these experiments the ability of the scintillation detection system to detect α -decays with the rates in the range of one atom per 4 hours and even lower was confirmed and performing of SISAK experiments with heavier transactinids was anticipated.

This work was to develop a SISAK extraction system for chemical study of element 108, hassium, and to examine the possibility of an Hs SISAK experiment.

¹ AKUFVE is a Swedish acronym for an arrangement for continuous investigation of distribution ratios in liquid-liquid extraction.

1 Introduction

“When I want to understand what is happening today or try to decide what will happen tomorrow, I look back.”

Omar Khayyam 1048-1131

1.1 Transactinides

Transactinides are located after the actinides [8] series in the Periodic Table. They are produced in heavy-ion fusion reactions through bombardment of a suitable target by heavy ions from an accelerator. Various combinations of projectiles and targets are in principle possible for the synthesis of transactinides:

- Actinide targets irradiated by light projectiles of elements in the range from neon to calcium. These reactions are called *hot fusion* reaction due to high excitation energy of the compound nucleus ($E^* \sim 30\text{-}50$ MeV)
- Targets of lead and bismuth irradiated by projectiles from calcium to krypton. These reactions are called *cold fusion* reaction due to lower excitation energy of the compound nucleus ($E^* \sim 10\text{-}20$ MeV),
- Recently, doubly magic ^{48}Ca beam on actinide targets are called *warm fusion* reaction due to intermediate excitation energy of the compound nucleus.

Hot and warm fusion reactions lead to more neutron-rich and longer-lived isotopes of transactinides than cold fusion reactions. A continuous decrease of the cross sections was measured from microbarns for the synthesis of nobelium down to picobarns for the synthesis of element 112. The increasing Coulomb repulsion starts to severely affect the

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fusion cross-section for production elements beyond fermium. The decrease of the cross sections has the same slope for both cold and hot fusion, but surprisingly the cross sections of reactions with ^{48}Ca projectiles are behaving differently and the cross sections remain stable at a level of a few picobarns for all reactions with actinide targets. The experimental cross sections gained in cold, hot and warm fusion reactions are presented in Fig. 1-1.

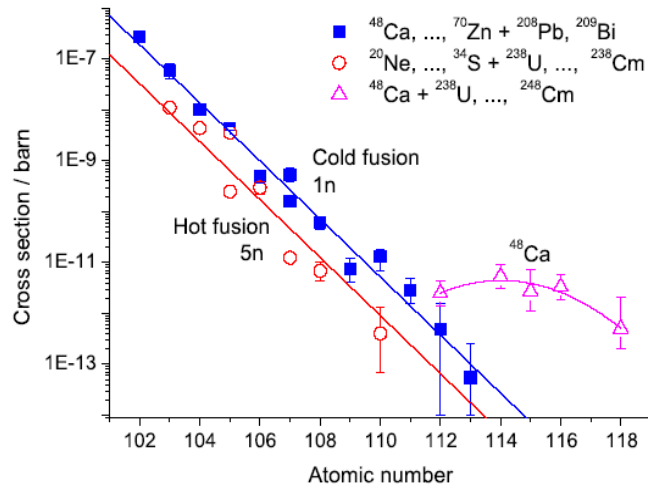


Fig. 1-1 Experimental cross sections for the formation of nuclei with $Z \geq 102$ in (■) the 1n evaporation channel of cold fusion reactions, (○) the 5n channel of hot fusion reactions, and (Δ) the fusion reaction with the ^{48}Ca + actinide targets. (Figure courtesy by J. Dvorak)

1.1.1 Superheavy Elements

All the elements heavier than U ($Z=92$) (the transuraniums) do not exist on earth at least in easily detectable quantities. Transuranium elements which might have existed previously have decayed because their half-lives are much shorter than the age of the earth. As the nuclei become heavier they become increasingly unstable with respect to spontaneous fission and α -decay. Spontaneous fission was explained by the liquid drop model (LDM) assuming that the nuclear matter is a structureless body like a drop of electrically charged liquid [9]. However, this model could not explain all the properties of the nucleus. For example at the “magic” numbers of protons and neutrons the observed nuclear binding energy is higher than the theoretical values based on LDM. Applying quantum mechanics for the description of the nucleus brings forth local variation of the energy levels occupied by the different nucleons. In analogy with electron levels in an atom, there are so-called magic numbers in the nucleus, which are referred to closed shells. The magic numbers are: 2, 8, 20, 28, 50 and 82 for both protons and neutrons. In addition 126 is also a closed shell for neutrons. In such cases that both protons and

neutrons have magic numbers, the nucleus is spherical and has a substantial stability with respect to spontaneous fission.

A combination of the liquid-drop model (macroscopic part) with shell corrections (microscopic part) has been used to calculate the next proton and neutron shell closure. Consequently a region far beyond the upper end of the then known chart of nuclides was predicted and would only exist due to the shell effects [10]. This region was called the region of SuperHeavy Elements (SHEs).

The heaviest stable nuclide with both closed proton and neutron shells is ^{208}Pb ($Z=82$, $N=126$). In recent calculations the next proton and neutron number for the shell closures are expected to be in the region of $Z=114-126$ and $N=172$ or $N=184$, respectively, depending on the model used (see e.g. [11-15]).

Despite the widely accepted opinion that shell effects vanish with increasing deformation of nucleus, it was found that in highly deformed nuclei a redistribution of the nucleons take place which makes the nucleus more stable. In 1989, Patyk et al. calculated nuclear masses in a high deformation state, and they predicted the nuclei around $Z=108$ and $N=162$ to be rather stable [16, 17], and ^{270}Hs was predicted to be a deformed doubly-magic nuclide with a relatively high nuclear binding energy and α -emission as the main decay mode and a half-life of about 0.1 s. Latest calculations pointed to even longer half-lives. In recent experiments, a half-life of about 23 s was estimated [18] from measured α -energy using a phenomenological formula [19]. This rather long half-life confirmed that ^{270}Hs is a deformed doubly magic nucleus. Thus, the classical spherical "superheavies" are no longer thought to be separated by a sea of instability from the region around uranium, but to be connected via deformed nuclei around ^{270}Hs .

Since the transactinide elements owe their existence to the shell effects they are often by definition entitled as superheavy elements as well.

1.1.2 Chemical Investigation of Transactinides

The full relevance of relativistic effects in heavy element chemistry was not discovered until the 1970s. The theory of relativity suggests that the mass of the electron increases when its velocity increases to values comparable to the velocity of light according to this equation:

$$m = \frac{m_0}{\sqrt{1 - \left(\frac{v}{c}\right)^2}} \quad \text{Eq. 1-1}$$

where m_0 is the rest mass of electron, v is the velocity of the electron and c is the speed of light. As the nuclear charge increases the velocity and subsequently also the mass of the inner electrons increases. This leads to several relativistic effects: the relativistic radial contraction and energetic stabilization of the s and $p_{1/2}$ shells, spin-orbit splitting and the radial expansion and energetic destabilization of the $p_{3/2}$ and (outer) d and all f shells. All the effects are of the same order and grow roughly like Z^2 [2].

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In the year 1869, Mendeleev [20] formulated the periodic law of elements. The Periodic Table still provides a basic tool for prediction of general chemical behaviors of elements. Fig. 1-2 shows the modern Periodic Table of elements including elements 113 and 115-118, the discovery of which still remains to be verified. The discovery of element 112 is now officially recognized by IUPAC and is named as copernicium (Cn). The discovery of element 114 reported by Yu. Ts. Oganessian et al. [21] is now confirmed by two other teams [22, 23], but still is not officially recognized by the IUPAC. The synthesis of

1 He																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	* 57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	** 89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo

Lantanides *	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinides **	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Fig. 1-2 The periodic table of the elements. Reported elements (element 113 and 115-118) which are not confirmed yet, are also included.

element 117 is recently reported by Yu. Ts. Oganessian et al. [24].

The chemical properties of the elements depend strongly on the outer electronic structure which is in its turn affected by relativistic effects. Thus, relativistic effects which show their largest influence on the heaviest elements may alter the classical rule of periodicity within the elements. Chemical investigation of heaviest elements and especially transactinide elements offers an exceptional opportunity to validate the theoretical predictions on the relativistic effect influencing the chemical behavior of elements and to observe the trends in the Periodic Table.

1.1.3 Synthesis, Separation and Identification of Transactinides

Chemical experiments on transactinides require longer-lived isotopes of these elements which are located in the neutron-rich region of the chart of nuclides and are produced in hot and warm fusion reactions. Due to the low production cross-sections in the order of nanobarn or even picobarn, high beam intensities and target densities in the order of mg/cm^2 have to be applied. This is challenging since several actinide nuclids like ^{244}Pu

and ^{248}Cm are available only in very limited amounts, thus special techniques have to be implemented to produce suitable targets [25].

The produced transactinide nuclides have to be separated from all other unwanted by-products as well as from the beam particles. Physical separation of short-lived nuclides produced in heavy-ion-induced fusion reactions is a powerful and well-known method and often applied in investigations of the transactinides. Spatial separation from the projectile and other reaction products is achieved by combined electric and magnetic fields. In this approach, the transactinide element of interest is isolated in a physical recoil separator and then extracted from this machine. By extracting these nuclides from a recoil separator, they can be made available for transport to setups located outside the irradiation area such as chemistry setups. Physical pre-separation overcomes many limitations currently facing in the chemical investigation of transactinides [26]. Two types of recoil separator have been developed:

- Gas-filled separators use the different magnetic rigidities of the recoils and projectiles travelling through a low pressure (about 1 mbar) gas-filled volume in a magnetic dipole field [27]. A mean charge state of the ions is achieved by frequent collisions with the atoms of the gas, examples of such separators are: Berkeley Gas-filled Separator (BGS) [28] in Berkeley, California, Transactinide Separator and Chemistry Apparatus (TASCA) in Darmstadt, Germany [29]
- Wien-filter or energy separators use the specific kinematic properties of the fusion products. The latter are created with velocities and energies different from the projectiles and other reaction products which is achieved by additional magnetic fields or symmetric arrangements of electric fields. An example of such a separator is the velocity filter SHIP in Darmstadt, Germany [30].

Whereas the first transuranium elements were identified by chemical means, the discovery of new elements has shifted to the field of nuclear physics due to the very short half-lives of the nuclei at the end of the nuclear chart. The produced transactinide nuclides are identified by time-correlated mother–daughter decay chains leading to known nuclides. The detector type to be selected depends on the particle rate, energy, decay mode, and half-life. Experimental as well as theoretical data on the stability of heavy nuclei show that they decay by α -particle emission, electron capture or fission, with half-lives ranging from microseconds to days.

At the interface between the separator and chemistry apparatus there is a Recoil product Transfer Chamber (RTC). The RTC is filled with an appropriate gas, usually at 1–2 bar, in which the nuclear reaction products are stopped. The gas-filled separator is operated at low pressure, typically 0.5–1 mbar. A thin Mylar foil is used to separate the low-pressure region in the separator from the RTC, often this foil is referred to as the RTC window. The transport from the RTC to the chemistry apparatus can be performed, e.g., by using a gas-jet (either with or without aerosol particles). The chemical investigation of transactinides is expected to dramatically advance using new pre-separators and RTCs designed for the chemical experiments with transactinides.

1.2 Chemical Experiments with Transactinides

Chemical experiments with transactinides are challenging, due to the specific feature of one-atom-at-a-time chemistry. In the classical macro-amount chemistry, the equilibrium constant is defined in terms of the chemical activities of the components which can undergo reversible transformation. As a single atom cannot exist in different chemical forms simultaneously, the classical law of mass action is not valid anymore. Therefore, the concept of chemical equilibrium needs to be substituted by an equivalent expression in which the chemical activities are replaced by probabilities of finding the atom in a given state. Through dynamic partition experiments, this probability, which is proportional to the time the atom or molecule spends in that state, can be determined. In these kinds of experiments, the separation step is repeated many times. Consequently, one expects a single atom to behave statistically just like macro-amounts of the same substance. Examples of such methods are chromatography, solvent extraction, and ion-exchange which have been used successfully for chemical studies of transactinides [3].

Transactinide chemical experiments are expensive and time-consuming and the conclusions usually have to be made on observation of a few events. Therefore it is not feasible to perform these experiments by a trial and error approach. To design transactinide experiments their predicted homologues are utilized as models to develop suitable systems. Theoretical methods (relativistic vs. non-relativistic) are usually used to predict the behavior of the transactinide element in a given system. By applying these systems for the transactinides, their chemical behaviors can be compared to their homologues and the theoretical predictions. In such a way, the deviations from known trends in the Periodic Table due to relativistic effects can be recognized.

1.3 Element 108, Hassium

The transactinide element targeted for chemical investigation in this work, is hassium (Hs) with atomic number of 108. The discovery of Hs was reported in 1984 [31] with identification of the nuclide ^{265}Hs with a half-life of $T_{1/2} = 1.5$ ms. Different isotopes of Hs are discovered since then in different nuclear reactions [18, 32-39]. Table 1-1 gives a list of discovered isotopes, the year of discovery and the related nuclear reaction in which the Hs isotopes were produced, either directly or observed in the decay chains.

Table 1-1 The discovered Hs isotopes, the year of discovery and the nuclear reaction used

Isotope	Year of discovery	Nuclear reaction used	Type of fusion reaction	Half-life
^{263}Hs	2008	$^{208}\text{Pb}(^{56}\text{Fe},n)$ [33]	Cold	0.74 ms
^{264}Hs	1986	$^{207}\text{Pb}(^{58}\text{Fe},n)$ [34]	Cold	0.85 ms
^{265}Hs	1984	$^{208}\text{Pb}(^{58}\text{Fe},n)$ [32]	Cold	0.9 ms
^{266}Hs	2000	$^{207}\text{Pb}(^{64}\text{Ni},n)$ [35]	Cold	2.3 ms
^{267}Hs	1995	$^{238}\text{U}(^{34}\text{S},5n)$ [36]	Hot	26 ms
^{269}Hs	1996	$^{208}\text{Pb}(^{70}\text{Zn},n)$ [37]	Cold	10 s
^{270}Hs	2004	$^{248}\text{Cm}(^{26}\text{Mg},4n)$ [18]	Hot	23 s
^{271}Hs	2004	$^{248}\text{Cm}(^{26}\text{Mg},3n)$ [38]	Hot	4 s
^{275}Hs	2003	$^{242}\text{Pu}(^{48}\text{Ca},3n)$ [39]	Warm	0.15 s
^{277}Hs	1999	$^{244}\text{Pu}(^{48}\text{Ca},3n)$ [35]	Warm	16.5 min

In 1996, ^{269}Hs , with a half-life of about 10 seconds, was observed in the α -decay chain of $^{277}\text{112}$ [36]. As mentioned earlier, $Z=108$ is calculated to be a deformed proton magic number. Besides, $N=162$ has been calculated as a deformed neutron magic number and hence the nucleus ^{270}Hs is a deformed doubly-magic nucleus. In recent experiments a half-life of about 23 s and a cross-section of about 3 pb were observed for the reaction $^{248}\text{Cm}(^{26}\text{Mg},4n)^{270}\text{Hs}$ at a beam energy of 136 MeV. For the reaction $^{248}\text{Cm}(^{26}\text{Mg},5n)^{269}\text{Hs}$, a half-life of 10 s and cross-section of about 7 pb were found at 145 MeV beam energy [18]. Synthesis of ^{269}Hs and ^{270}Hs support the assignment of $N=162$ as a magic closed shell. The production of Hs using ^{248}Cm target and ^{26}Mg as the projectile was utilized in several chemical investigations [40, 41]. It is evident that the reactions with higher cross-sections for production of longer-lived isotopes of Hs are favorable in chemical experiments. The reactions $^{36}\text{S} + ^{238}\text{U}$ and $^{48}\text{Ca} + ^{226}\text{Ra}$ are predicted to result in higher cross-sections for production of ^{270}Hs [42] (see Fig. 1-3). The cross section for the reaction $^{48}\text{Ca} + ^{226}\text{Ra}$ was predicted to be almost 3 times higher than for the reaction $^{26}\text{Mg} + ^{248}\text{Cm}$. However, the validity of these calculations had to be confirmed experimentally. The $^{36}\text{S} + ^{238}\text{U}$ reaction at 4n channel was tested at GSI recently [43], however, the observed cross section was much less than predicted and about $0.8^{+2.5}_{-0.7}$ pb. The nuclear reaction $^{48}\text{Ca} + ^{226}\text{Ra}$ at 4n channel was recently checked in experiments at the Dubna Gas-Filled Recoil Separator (DGFRS) at the Flerov Laboratory of Nuclear Reactions (FLNR) Dubna by Oganessian et al. The result from this experiment is not published yet.

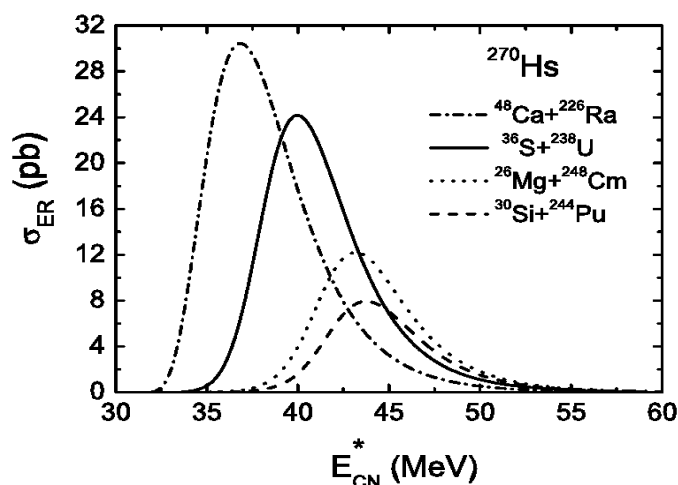


Fig. 1-3 Calculated Evaporation Residue cross sections (σ_{ER}) for the 4n channel of the fusion reactions $^{26}\text{Mg} + ^{248}\text{Cm}$, $^{30}\text{Si} + ^{244}\text{Pu}$, $^{36}\text{S} + ^{238}\text{U}$, and $^{48}\text{Ca} + ^{226}\text{Ra}$. Adopted from [42]

1.3.1 Hassium in the Periodic Table

The 5f electron series ends with element 103, lawrencium (Lr), which is the last actinide. Subsequently a new 6d electron transition series is predicted to begin with element 104, rutherfordium (Rf). Elements 104 through 112, are placed in the Periodic Table under their predicted lighter homologues in the 5d electron series, from Hf to Hg. Thus, by extrapolating from the trends in the Periodic Table they are expected to follow the general properties of transition metals.

According to the text above Hs is tentatively placed in the group-8 elements under Os. Group-8 elements are found in various number of oxidation states: Fe is known in the oxidation states from -2 through +6, Ru in the states -2 through +8 (with the exception of +1 that has not been observed) and Os in all states from -2 through +8. These metals form the maximum valence within their periods. Ru and Os are the only elements which form an oxidation state as high as 8+ with the exception of Xe, which is known to form tetrahedral XeO_4 . Due to the lanthanide contraction, the atomic radius of Os (133.8 pm) is very similar to that of Ru (132.5 pm), whereas that of Fe (124.1 pm) is significantly smaller. Consequently, chemical behaviors of Ru and Os in most cases are similar while Fe behaves differently. Extrapolations from trends within group-8 are then preferentially made only from Ru via Os to Hs. Relativistic effects have been calculated to change the electron levels in the heavier elements. Figure 1-4 shows the theoretical calculation of energy levels for Ru, Os and Hs by non-relativistic assumptions and the relativistic assumptions [44, 45] for comparison.

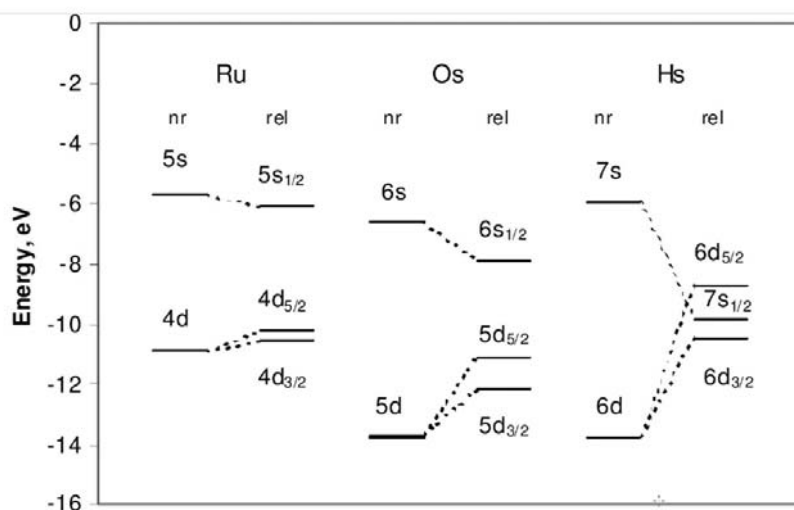


Fig. 1-4 Hartree-Fock (non-relativistic) and Dirac-Fock (relativistic) energy-levels for group-VIII elements Ru, Os and Hs [44, 45]. (Figure courtesy by V. Pershina).

1.3.2 Hs Chemical Experiments

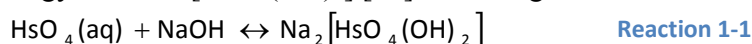
Group-8 elements Ru and Os form highly volatile tetroxides, while FeO_4 does not exist. The boiling point for OsO_4 is as low as 130 °C and in experiments using carrier-free amounts it is volatile even at room temperature. RuO_4 is behaving in the same way, however it decomposes to $\text{RuO}_2 + \text{O}_2$ at 108 °C and its boiling point has been calculated to be (133 ± 5) °C by extrapolation [46]. From gas-phase experiments, it has been shown that Hs forms a volatile tetroxide as well [40]. This observation provided strong evidence that hassium is a real member of group-8 of the Periodic Table. Using gas phase adsorption thermochromatography [47], the temperature at which HsO_4 deposits, with a chromatographic column along which a stationary negative temperature gradient is maintained was measured. The chromatographic column, the Cryo OnLine Detector (COLD), also served as detection system for the identification of decaying atoms of $^{269,270}\text{Hs}$. The adsorption enthalpy (ΔH_{ads}) of the compound on the stationary phase was estimated from the measured deposition distribution by using Monte Carlo simulations of the trajectories of single molecules as they move along the column under real experimental conditions. The high volatility of group-8 tetroxides allows excellent separation from heavy actinides and lighter transactinides and other nuclear reaction byproducts. The calculated properties were used to determine the adsorption energy of HsO_4 on inert surfaces using a physisorption model. The latest theoretical calculations indicate a reversal of the trend in the volatility of MO_4 (as desorption from the surface) in group-8, $\text{RuO}_4 < \text{OsO}_4 > \text{HsO}_4$, a trend that is also observed experimentally. Although inclusion of relativistic effects is crucial for obtaining precise energetics, the general trends in the properties (e.g., volatility) of the MO_4 compounds are already reproduced within a nonrelativistic treatment [48].

Another interesting chemical property of Hs is the acidic behavior of its tetroxide analogous to OsO_4 . It is generally accepted that OsO_4 is the anhydride of osmium (VIII)

10 Introduction

acid. However different dissociation constants of the acid are suggested by various researchers [49-54]. According to Sidgwick acid formation of osmium tetroxide occurs by coordination of two water molecules to the central atom [55]. Compounds of OsO_4 of the type $\text{M}_x[\text{OsO}_4(\text{OH})_2]$, in which M is an alkaline or alkaline earth metal have been prepared [56], and these can be considered the salts of the Os(VIII) acid. According to Nevskii et al. and Ivanov-Emin et al. the deep red salts which are formed in the reaction of OsO_4 with hydroxides of Li^+ [57], Na^+ [58], Sr^{2+} and Ba^{2+} [59] contain $\text{cis-}[\text{OsO}_4(\text{OH})_2]^{2-}$ ions. The cis arrangement of hydroxide ligands allows the maximum number of orbitals to be available for π bonding from hydroxo groups since Os VIII is $5d^0$. Preparation of corresponding ruthenium salts is precluded by their very readily reduction to ruthenate in the presence of alkalis.

In recent experiments with volatile tetroxides, it was shown that HsO_4 reacts with moisturized NaOH and most probably forms sodium hassate (VIII), $\text{Na}_2[\text{HsO}_4(\text{OH})_2]$, by analogy with $\text{Na}_2[\text{OsO}_4(\text{OH})_2]$ [41] according to the reaction:



Theoretical calculations of electronic structures of $[\text{MO}_4(\text{OH})_2]^{2-}$ and $\text{Na}_2[\text{MO}_4(\text{OH})_2]$, where M = Ru, Os and Hs, and of the relative values of the free energy change of reactions of their formation from the volatile tetroxide have shown that the hassate(VIII) should be almost as stable as osmate. The hassate should be more covalent than the osmate, as in the case for MO_4 (M=group-8 element). HsO_4 should however have a slightly weaker reaction with NaOH (by less than 52 kJ/mol) than OsO_4 . ΔG° for the formation of $[\text{RuO}_4(\text{OH})_2]^{2-}$ from RuO_4 was found to be ~ 300 kJ/mol more positive than ΔG° for analogous reactions of Os and Hs, which explains why the Ru(VIII) complex is not known. The predicted trend for the formation of $[\text{MO}_4(\text{OH})_2]^{2-}$ in group-8 is: $\text{Os} > \text{Hs} \gg \text{Ru}$ [60].

From the result of the latter experiment, it was concluded, that for the first time, an acid-base reaction was performed with the tetroxide of hassium leading to the formation of a hassate (VIII). However, the predicted slightly lower reactivity of HsO_4 as compared to that of OsO_4 has so far not clearly been revealed experimentally and remains an open question.

2 Methods and Instruments

“Every contrivance of man, every tool, every instrument, every utensil, every article designed for use, of each and every kind, evolved from a very simple beginning.”

Robert Collier 1885-1950

2.1 Solvent Extraction

Solvent extraction involves the distribution of a solute or of solutes between two immiscible liquid phases in contact. A solute A, which initially is dissolved in only one of the two liquids, eventually distributes between them. In many cases, an extraction reagent might be used as well. There exist several kinds of extraction reagents, e.g. chelating reagents and ion exchange reagents. When the distribution reaches equilibrium, the solute is at concentration $[A]_{\text{aq}}$ in the aqueous phase and at concentration $[A]_{\text{org}}$ in the organic phase. The distribution ratio of the solute or the D-value is defined as the total analytical concentration of the substance in the organic phase to its total analytical concentration in the aqueous phase, usually measured at equilibrium:

$$D = [A]_{\text{org}} / [A]_{\text{aq}} \quad \text{Eq. 2-1}$$

By also using the fact that the concentration of a radioactive element is proportional to its radioactivity concentration for a radioactive element A^* :

$$D = [A^*]_{\text{org}} / [A^*]_{\text{aq}} = \frac{\text{Radioactivity concentration of the organic phase (Bq/mL)}}{\text{Radioactivity concentration of the aqueous phase (Bq/mL)}}$$

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The distribution ratio, D , is dependent on, among other things, the concentration of the chemical reagents involved in the extraction mechanism e.g. the ligands. It is possible to obtain stability constants by observing the changes in the distribution ratio as a function of these species [61]. The extraction mechanism varies for each type of reagent and the knowledge of mechanism is essential for such investigations. On the other hand the study of changes of distribution ratio as a function of concentration of different reagents helps our understanding of the mechanism of the reactions. Accordingly, the solvent extraction technique has a great potential value in the development of methods for chemical investigations. Since it is possible to find and develop fast solvent extraction systems, it is especially suitable for study of short-lived radionuclides such as transactinides.

2.2 The SISAK System

The SISAK system is an automatic, on-line solvent extraction system. It was developed during the 1970s for rapid, continuous (radio) chemical separations [62].

The SISAK apparatus includes static mixers and centrifugal separators which are connected together by perfluoro-alkoxyalkane (PFA) tubing. During the last two decades, it was decided to utilize SISAK and its method of fast continuous solvent extraction to investigate transactinide chemistry. Applied on transactinides, the measurement method has to be based on α -spectroscopy techniques. To achieve this purpose, the fast centrifuge arrangement of the SISAK system, was equipped with liquid scintillation counters, enabling on-line detection of α -particles. The liquid scintillation detection [63] method is uniquely able to handle the rather high liquid flow rates needed in the SISAK system and offers almost a 4π detection efficiency. In order to detect very low α -activity from the transactinide elements under the presence of β and γ -background the method of Pulse-Shape Discrimination (PSD) has been adapted to selectively differentiate α -particles from electrons and β -particles.

This system has been successfully applied in a continuous manner with the SISAK setup. Test experiments demonstrated that the counting method can be used to identify short-lived α -decay radionuclides on a one-atom-at-a-time basis [64]. Since then several extraction systems have been developed applying the SISAK system to model the chemistry of the transactinide elements, using their homologues (for example see references [65, 66]).

The first successful transactinide experiment with the SISAK system was performed with ^{257}Rf [67]. This experiment successfully demonstrated that liquid scintillation provides a very useful and highly efficient detection method for transactinides.

2.2.1 SISAK Apparatus

In a typical SISAK setup the produced compound nuclei is de-excited by evaporation of some nucleons (normally called evaporation residues abbreviated as EVRs) and the produced nuclides are transferred to the SISAK apparatus, attached to the aerosols in a carrier gas. Thereupon, they are dissolved into the liquid phase by a static mixer. The liquid and the gas are separated by centrifugal force in a SISAK degassing unit. The

liquid is pumped to another static mixer to be contacted with an immiscible organic phase while the gas is fed into the exhaust system of the laboratory. A drawing of the HG-0.1 degasser centrifuge unit [68] is shown in Fig. 2-1. The internal volume of the degasser is only about 0.1 mL, which allows a fast separation of gas and liquid.

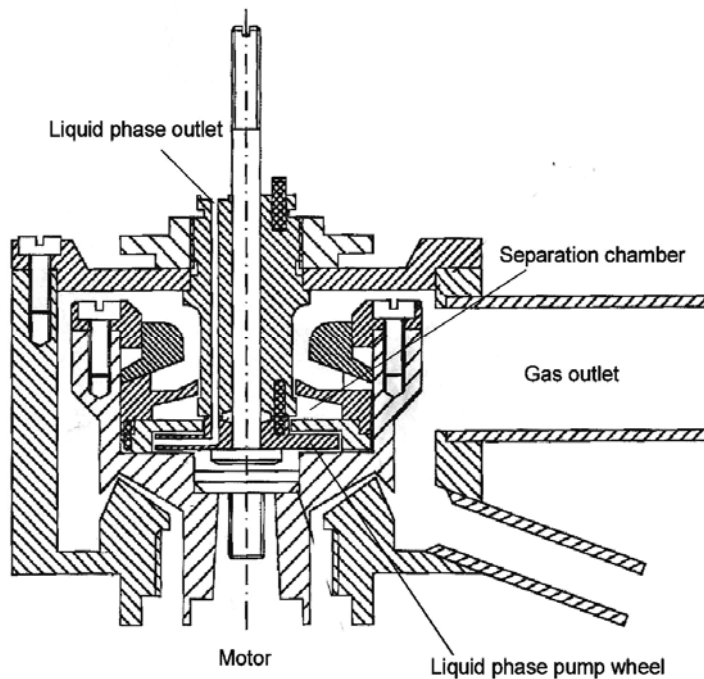


Fig. 2-1 Cut-away drawing of the HG-0.1 degasser centrifuge. The inlet is not shown in the drawing.

Static mixers are connected to the inlet of the centrifuges. Two main types of static mixers are used at the present time:

- the *zigzag* mixer shown in Fig. 2-2a is a PEEK (polyetheretherketone) rod with milled tracks, inserted in a quartz or PEEK tube
- the *PEEK wool packed* mixer shown in Fig. 2-2b is a PEEK tube which is packed with shavings of PEEK

PEEK is a material that withstands organic solvents and all common acids except concentrated sulfuric acid.

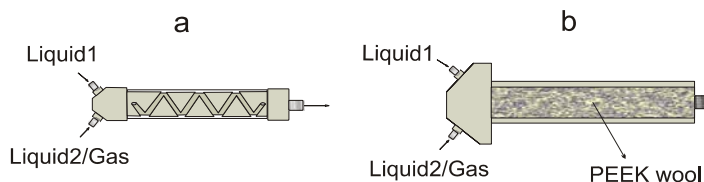


Fig. 2-2 The SISAK mixers

Inside the static mixers small droplets of immiscible phases are formed to provide a high surface to volume ratio, which ensures efficient mixing and phase boundary

transfer. By adjustment of the mixer length, it is possible to reach extraction equilibrium for suitable and rather fast systems. In the case of PEEK wool packed mixers, the effectiveness of the mixer depends on the compactness of PEEK wool used and diameter of the PEEK fibers.

The emulsion of two liquids from the static mixers is separated by a centrifuge unit and the separated liquids are pumped out of the centrifuge through throttle valves. A drawing of the H-0.3 centrifuge unit is shown in Fig. 2-3.

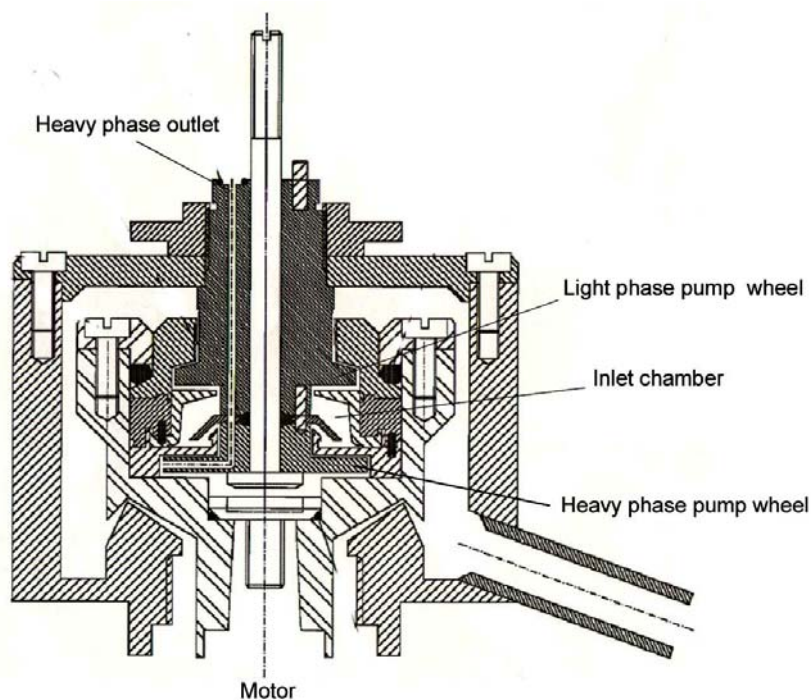


Fig. 2-3 Cut-away drawing of the H-0.3 centrifuge. The inlet is not shown in the figure.

The purity of the phases leaving the centrifuges is monitored by measuring the optical transmittance through the liquid. In a phase containing entrainment of the opposite phase, the light will be refracted at the boundaries between the two phases. The measuring devices, which consist of a small light emitting diode (LED) and a photo transistor, are connected to a computer. On the screen, the phase purity and its fluctuations with time can be easily displayed. The phase purity is adjusted manually by throttle valves affecting the counter-pressure on the phases leaving the centrifuge. These valves make it possible to adjust the liquids outlet flow until both phases are free from entrainment of the other phase. The SISAK centrifuges are presently made of PEEK. Centrifuges head and mixers connected together by PFA tubing plus the phase purity meters are shown in Fig. 2-4. Chemically inert cog-wheel pumps are used in the SISAK equipments as feed pumps. The flow capacity of these pumps can be continuously varied up to about 3 mL/s. The flow-rates of the pumps are measured with mass flow meters and variation from the desired amount is controlled and adjusted automatically by a computer. The control software which allows full automatization of the system is written in LabView™.

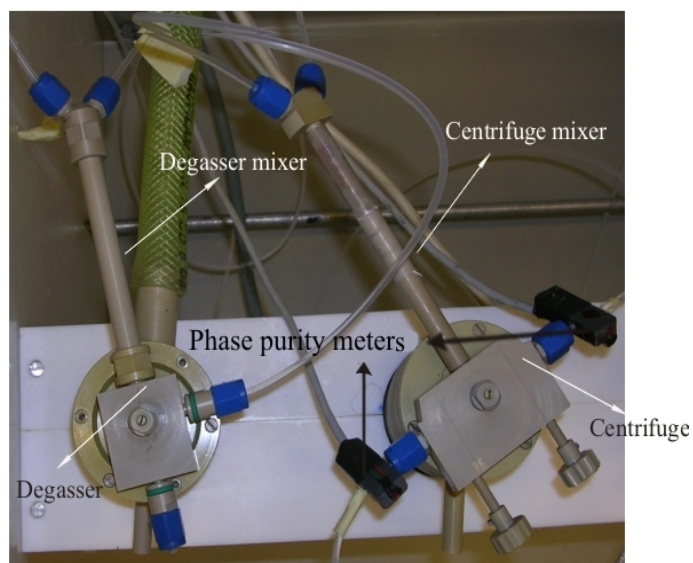


Fig. 2-4 SISAK centrifuges and mixers from above

Model studies of transactinides using radioactive isotopes of their homologues are often based on γ -ray detection of these nuclides. However, as mentioned earlier in a transactinide SISAK experiments, the detection of α -particles is based on the liquid scintillation method [69, 70]. The scintillation cocktail normally consists of three components: (I) toluene as the solvent, (II) 1-methyl naphthalene as primary scintillator and (III) dimethyl-POPOP as secondary scintillator. Fig. 2-5 is a detailed drawing of the detection cell made of Teflon with a meander-shaped track [71]. The diameter is 65 mm and the volume 5.5 mL. A thin disk of Kel-F covers the track and protects the plexi-glass light-guide from organic solvent. The window of the photo-multiplier tube is matching the detection cell. The light-guide spreads the scintillation light uniformly over the photo cathode. A photo of SISAK centrifuges and its detection cell can be found in Appendix II. The current status of the SISAK system in connection with chemical investigation of transactinides is explained in paper (I).

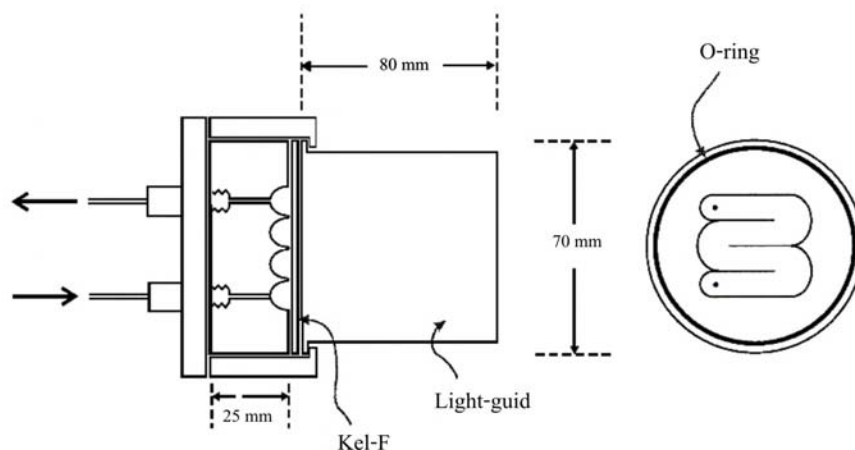


Fig. 2-5 Detection cell, used for continuous liquid scintillation detection of α -particles in the SISAK system. (Figure courtesy by L. Stavsetra)

2.3 The Proposed SISAK Extraction System for an Hs experiment

In this work an extraction experiment using SISAK equipment was proposed based on the known chemical properties of Hs:

- The transport from the production site to the chemistry apparatus is based on formation of the volatile tetroxide of Hs
- The intended chemistry is the reaction of HsO_4 with $\text{NaOH}_{(\text{aq})}$ in solution

Since the results from the previously described gas phase experiment [41] on the reaction between HsO_4 and NaOH were not unambiguously in agreement with the theoretical calculations (see section 1.3.2), the present work has been designed to provide an enhanced assessment of this reaction. The schematic set-up of the proposed extraction system for an Hs SISAK experiment is illustrated in Fig. 2-6.

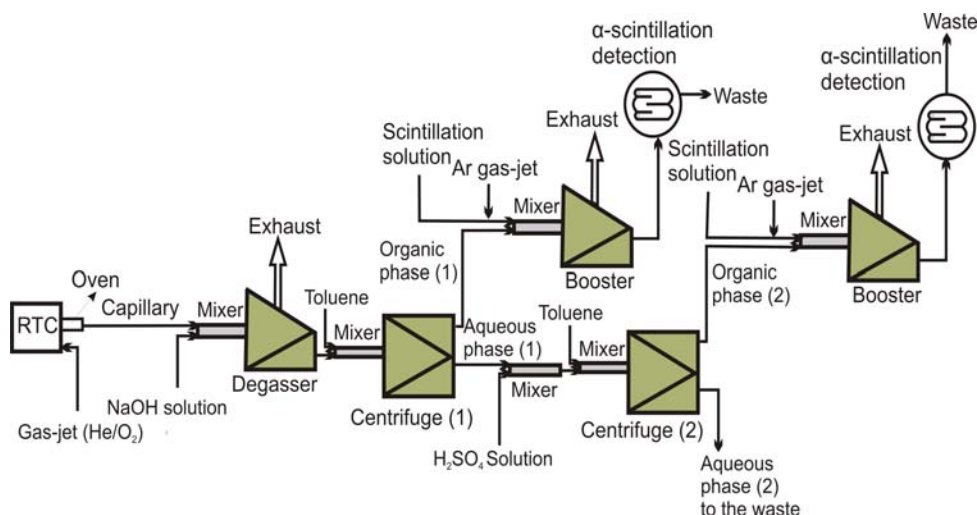


Fig. 2-6 Schematic drawing of the proposed SISAK setup for chemical study of Hs

The produced Hs nuclides form volatile tetroxide in a He/O₂ gas and are transported by the carrier gas through capillary tubing to the SISAK apparatus. Thereafter Hs tetroxide is dissolved in NaOH solution and the carrier gas is exhausted by the degasser unit. The liquid effluent of the degasser is contacted with an organic phase in a static mixer and the two phases are then separated in a SISAK centrifuge. It is important that solvents and reagents in a SISAK transactinide experiment should not quench the scintillation process. Aromatic solvents like benzene and toluene are suitable as an organic phase. However, the aqueous phase destroys the scintillation signals by its strong quenching effect. This problem can be resolved by adding a second extraction step which enables to transfer of the desired component from the aqueous phase into a second organic phase for detection as it is explained in paper (I).

The α -events from Hs in the two organic phases are measured online using liquid scintillation method. The organic output from the centrifuge is mixed with scintillation solution previously purged with argon gas to remove any dissolved O₂ which is a quencher, interfering with the Pulse-Shape Discrimination (PSD). The argon gas is then separated using another SISAK degasser which is also functioning as a booster. The output of the booster then flows into the detection cell and the amount of radioactivity is measured. The aqueous phase activity is obtained from measuring of the organic effluent from the second extraction stage. The second organic phase is then treated like the first organic phase for the α -measurement. In this work the proposed system was developed and tested using radioactive isotopes of Os which is a lighter homologue of Hs.

2.3.1 Reactions

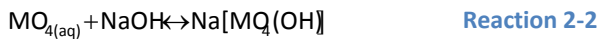
The assumed chemical reactions at each stage are explained in the following (where M= Os or Hs):

- First extraction stage

MO_4 is dissolved in the aqueous phase:



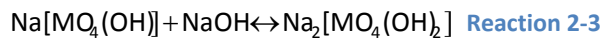
It reacts with NaOH in the aqueous solution:



The equilibrium constant is:

$$K_1 = \frac{[\text{Na}[\text{MO}_4(\text{OH})]]}{[\text{MO}_4][\text{NaOH}]} \quad \text{Eq. 2-2}$$

Further reaction with NaOH may also take place:



The 2nd stepwise equilibrium constant is:

$$K_2 = \frac{[\text{Na}_2[\text{MO}_4(\text{OH})_2]]}{[\text{Na}[\text{MO}_4(\text{OH})]][\text{NaOH}]} \quad \text{Eq. 2-3}$$

At the first mixer-centrifuge unit, MO_4 is distributed between NaOH solution and toluene. Hs and Os are assumed to be extracted into the organic phase only in the form of their tetroxides:



K_D , the distribution constant for distribution of MO_4 between aqueous solution and toluene, is defined as:

$$K_D = \frac{[\text{MO}_4]_{(\text{org})}}{[\text{MO}_4]_{(\text{aq})}} \quad \text{Eq. 2-4}$$

The apparent D-value then is:

$$D = \frac{[\text{MO}_4]_{(\text{org})}}{[\text{MO}_4]_{(\text{aq})} + [\text{Na}[\text{MO}_4(\text{OH})]] + [\text{Na}_2[\text{MO}_4(\text{OH})_2]]} \quad \text{Eq. 2-5}$$

Using Eq. 2-2, Eq. 2-3 and Eq 2-4 the above equation can be written in the terms of the equilibrium constants:

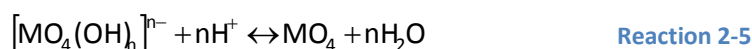
$$D = \frac{K_D}{1 + K_1[\text{NaOH}] + K_1K_2[\text{NaOH}]^2} \quad \text{Eq. 2-6}$$

As Eq. 2-6 shows, the D-value is a function of the NaOH concentration. By measuring the D-value in different NaOH concentrations an extraction curve is obtained. By slope analysis of the extraction curve the value of K_1 and K_2 can be calculated. Considering the low production cross-section of Hs, these kinds of experiments with Hs are practically

impossible. Therefore, the system has to be tested using Os as a model for Hs. In this work the complex formation constants for the equivalent compounds for Os were obtained. γ -emitting isotopes of Os produced at the Oslo Cyclotron Laboratory (OCL) were used to perform these experiments. For a Hs experiment a suitable NaOH concentration has to be chosen to result in most elucidating data. Hs is supposed to behave like Os. Performing a real Hs experiment can reveal any difference in behaviour of these two elements. Theoretical predictions on the chemical behaviour of Hs can be utilized as a guide to choose appropriate conditions for performing an Hs experiment.

- Second extraction stage

The efficiency of extraction in this step is achieved by acidification of the alkaline aqueous phase from the first stage. That retrieves MO_4 which is highly extractable into toluene:



Hence after acidification, the aqueous phase is mixed with toluene in another static mixer and the two phases are separated using a second SISAK centrifuge. To test the efficiency of this method, γ -emitting isotopes of Os were used. Other alternatives like extracting with tri-n-octylamine (TOA) or Aliquat-336 were also tested. Paper (II) presents the experiment at OCL with γ -emitting Os isotopes.

3 Experiments and Results

“If we knew what we were doing, it wouldn’t be called research, would it?”

Albert Einstein 1879-1955

The initial stages of development of the proposed SISAK extraction system for chemical investigation of Hs were completed at OCL using γ -emitting Os as a model for Hs. Both batch and on-line SISAK experiments for measuring distribution of the tetroxide of Os between NaOH solution and toluene were performed.

On-line Ru experiments were not feasible. The explanation is given in the following sections, however, some batch Ru experiments were performed to compare the distribution of Ru with Os.

To test the full SISAK setup with double α -detector arrays, in the same way as an Hs experiment, α -emitting Os isotopes were employed. These nuclides were produced at GSI’s linear accelerator UNILAC (UNIversal Linear ACcelerator).

3.1 Os OCL Experiments

3.1.1 Target and Beam

The radioactive isotopes of Os were produced via bombardment of nat-W target in the form of 0.025 mm thick metal foil with a 45 MeV $^3\text{He}^{2+}$ -beam from the MC35 Scanditronix cyclotron at OCL. The available beams at OCL are listed in Table 3-1.

22 Experiments and Results

Table 3-1 The beams available at the Oslo Cyclotron Laboratory (OCL)

Particle type	Energy (MeV)	Beam intensity (μA)
Proton	2-35	100
Deuteron	4-18	100
$^3\text{He}^{2+}$	6-47	50
$^4\text{He}^{2+}$	8-35	50

The relevant nuclear reactions by the bombardment of the target were:



The recoiling EVRs stopped in a gas mixture of He and O₂ with the ratio of 10 to 1 respectively. This medium provides in-situ oxidation of Os nuclides into their volatile tetroxides which were carried with the gas through PFA tubing to the SISAK apparatus. The total gas flow rate was 0.5 L/min. The radioactive isotopes of ruthenium were also produced via bombardment of natural molybdenum metal foil target with a 45-MeV $^3\text{He}^{2+}$ -beam at OCL:



However, Ru unlike Os could not be transported to the chemistry laboratory after in-situ oxidation to its volatile tetroxide. This might be due to instability of RuO₄ which results in decomposition to some nonvolatile compounds. Thus the OCL experiments were limited to Os; and for Ru, only off-line experiments were performed.

3.1.2 On-line SISAK experiments

The 145 keV γ -line in the decay of 2.7 min $^{181\text{m}}\text{Os}$ was used for calculation of D-values in on-line experiments. The measured half-life of the 145 keV peak, was 2.70 ± 0.01 min (Fig. 3-1) which agrees with the half-life of $^{181\text{m}}\text{Os}$ in the literature [72].

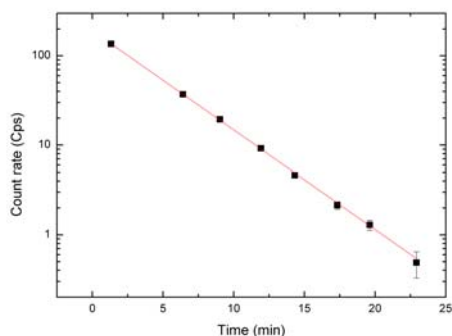


Fig. 3-1 The decay curve for 145 keV γ -peak in the spectrum collected from SISAK degasser effluent. The Os isotopes were produced in bombardment of nat-W target with ^3He and carried to the SISAK apparatus in a He/O_2 gas jet. The half-life was measured to be 2.70 ± 0.01 min which agrees with the half-life of $^{181\text{m}}\text{Os}$.

The distribution of OsO_4 between NaOH solution and toluene was studied in on-line SISAK experiments. In these experiments OsO_4 was dissolved into various dilute NaOH solutions through a mixer-degasser unit. Subsequently, the effluent from the degasser was mixed with toluene and OsO_4 was distributed between the aqueous phase and toluene using a second static mixer. The application of the mixer provides sufficiently long contact time in order to obtain the equilibrium state. The phases were then separated from each other with a SISAK centrifuge and the effluent phases were pumped through tube coils placed in front of two HPGe detectors. To avoid the calibration of the detection system, two subsequent runs were performed in which only the two phases were interchanged as it is explained in paper (II). Here the measurement of both phases using γ -detectors is possible, but in a real transactinide experiment where liquid scintillation method is applied for observation of α -events from transactinides, the direct measurement of the aqueous phase is not possible. Thus, as it is explained in paper (I), a second extraction stage is needed to extract aqueous-phase Hs; preferentially with a high yield, so that the amount of activity in the aqueous phase is determined by measurement of the extract. In order to check a “complete” extraction of osmium, as a model for Hs, from the aqueous phase, the solution from the degasser was acidified directly after degassing. This was followed by one-step extraction into toluene. The schematic set-ups for the first and the second extraction stages are shown in Fig. 3-2 and Fig. 3-3 respectively.

24 Experiments and Results

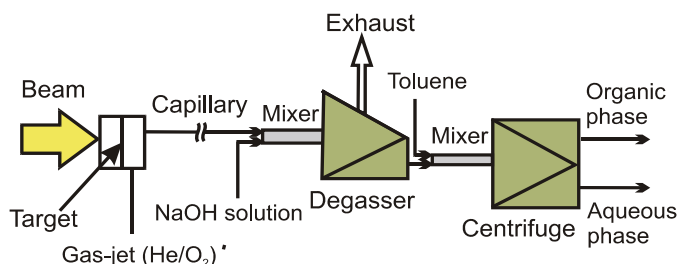


Fig. 3-2. The SISAK on-line setup used to study the distribution of OsO_4 between various dilute NaOH solutions and toluene.

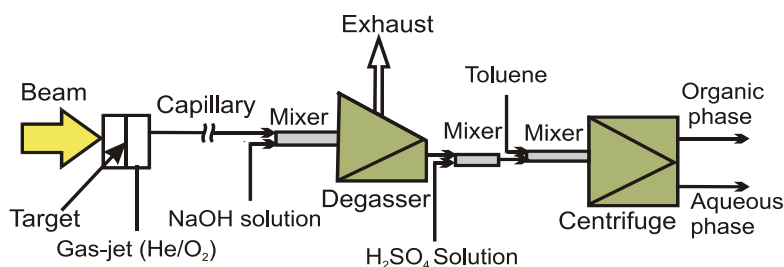


Fig. 3-3. The SISAK on-line setup used to study the extraction of osmium from the aqueous phase into toluene when OsO_4 is first dissolved in NaOH solution and then acidified by H_2SO_4 .

For the first stage the ionic strength of the aqueous phase was primarily kept at 1 molar using NaCl which is considered an inert salt as explained in paper (I). However, since the NaOH solutions used were quite dilute, it seemed unnecessary to add salt to keep the ionic strength constant. Thus, the experiments were later performed without addition of any salt. Fig. 3-4 shows the results of experiments with and without adding NaCl to the aqueous phase for comparison. It was expected that the salting-out effect increases the D -values when adding salt to the aqueous phase. However, it was observed that adding salt to the solutions is not changing the D -values noticeably and the salting-out effect is not very high.

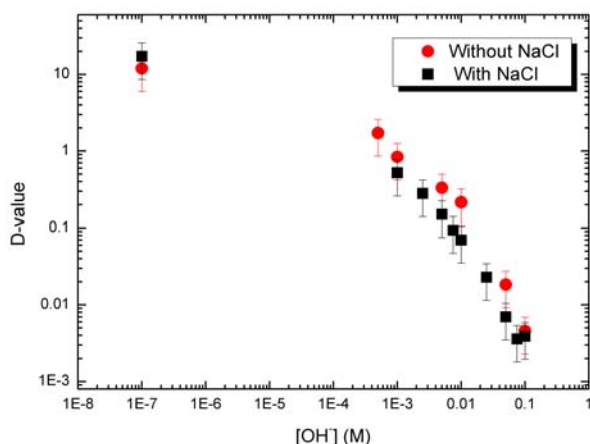
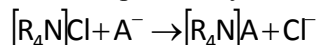


Fig. 3-4 A comparison of D-value vs. $[\text{OH}^-]$ in extraction of OsO_4 from NaOH solution into toluene when NaCl is added to the aqueous phase to keep the ionic strength constant at 1 M and when there is no NaCl added into the aqueous phase

For the second stage, extractions using Aliquat-336 and TOA were also tested. Aliquat-336 is a quaternary amine and extracts negatively charged ions:



The $[\text{R}_4\text{N}]\text{A}$ has a lipophilic property and is extracted into the organic phase. For this experiment the alkaline liquid phase from the degasser was mixed with a solution of Aliquat 336 in toluene and the two phases were separated using a SISAK centrifuge. The phase purity was poor but the extraction efficiency was close to 100%.

For extraction with TOA the alkaline effluent from the degasser was acidified and then mixed with a solution of TOA in toluene. This experiment was to check if there is any negative-charged species present in the solution in addition to OsO_4 after acidification of the raffinate from the first stage. Extraction of negatively-charged species from acidic solutions with TOA is shown by this reaction:



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The concentration of NaOH solution was 0.001 M and different concentrations of H₂SO₄ was used to acidify the alkaline solution. TOA concentration was 0.01 M. The results are shown in Fig. 3-5. An experiment was performed without TOA for comparison. The results show that the D-value increases with the H₂SO₄ concentration in extractions with

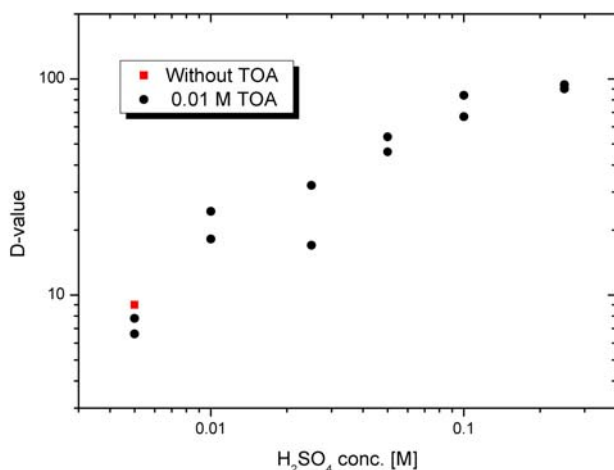


Fig. 3-5 The D-value of extraction of Os from acidified alkaline solution into toluene with and without TOA vs. acid concentration. The original concentration of NaOH was 0.001 M. Two parallel experiments were performed at each acid concentration.

TOA. This can be explained by the formation of some negatively-charged species with increasing H₂SO₄ concentration. This kind of reactions needs a further investigation and is not in the scope of this thesis.

3.1.3 Os batch experiment using tracer produced at OCL

The aim of the batch experiments was to provide a different way to test and confirm the results from the on-line experiments and also to check how close to extraction equilibrium these on-line results were. In the batch experiment the phases can be in contact for sufficiently long time to ensure extraction equilibrium has been obtained. Longer-lived nuclides are therefore needed for batch experiments.

For Os batch experiments, the same procedure as explained in section 3.1.1 was used to produce and transport Os isotopes to the SISAK apparatus. 13-h ¹⁸³Os produced in the nuclear reaction: Nat-W (³He, xn) ¹⁸⁰⁻¹⁸³Os is appropriate for batch experiments. However, to have a sufficient amount of the nuclide, 100 mL of de-ionized water circulated in a closed loop through a static mixer and degasser to collect OsO₄ from the carrier gas, as shown schematically in Fig. 3-6. Activity was collected for about 30 minutes, and then an appropriate amount of strong NaOH solution was added to obtain

the desired OH^- concentration. For example 1 mL of 1 M NaOH was added to 100 mL of the mentioned stock solution of Os nuclides to obtain 0.01 M NaOH and so on for other NaOH concentrations. 100 mL toluene was promptly added and the mixture was stirred for 15 minutes. After phase separation, samples of 80 mL were withdrawn and the 382 keV γ -line from ^{183}Os was counted with an HPGe detector.

The results from Os on-line and batch experiments at OCL are reported in paper (II).

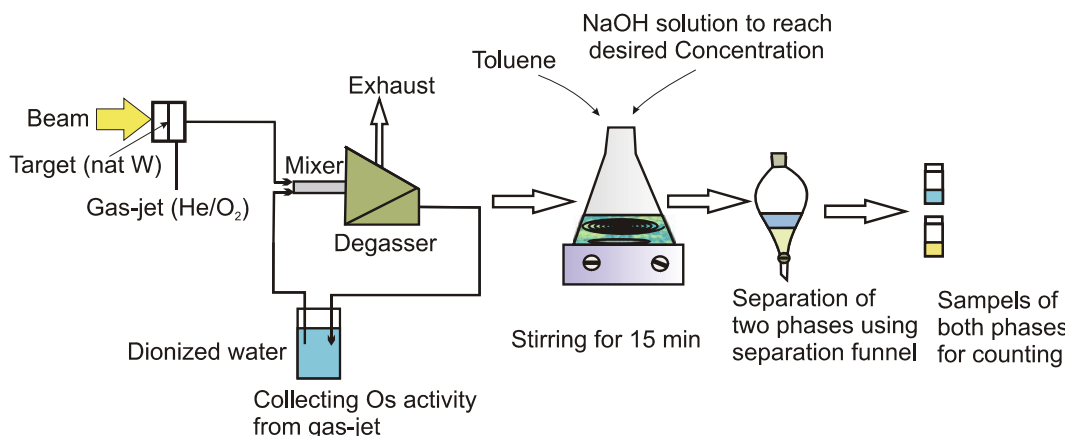


Fig. 3-6 Schematic setup and procedure for the batch experiments.

3.1.4 Transport Yield Measurements

The transfer yield of Os nuclides from the target chamber to the liquid phase using SISAK mixer-degasser unit was measured. The measurement was performed by means of an Al foil attached to the back of the target foil to collect all the recoiling EVRs from the target foil. The γ -activity of ^{183}Os in the Al foil normalized by the beam integral was determined by measurement of the 382-keV γ -peak and was considered as the reference value. Consecutively the EVRs were transported in a He-O₂ gas mixture through capillary tubes to the SISAK degasser. Liquid samples from the degasser effluent were then collected and measured in the same manner as the Al foil and compared to the reference value to obtain the yield. Different liquids were used as the solvent and compared for the yield. The transport yield of the gas-jet of pure He containing KCl clusters was also compared with the cluster-free carrier gas composed of 10% O₂ and 90% He. In this experiment the KCl clusters were collected in a direct catch setup on a filter. The results are given in Table 3-2. The results show that the transport yield of Os using pure He seeded with clusters (which is the usual way for transportation of EVRs) is much lower than the yield using He-O₂ gas mixture.

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Table 3-2 The transport yield of recoiled ^{183}Os from the target chamber to the degasser solvent, using gas jet composed of He and O_2 . With a He gas jet containing KCl clusters the activity was collected on a filter and measured for comparison

O_2 /He ratio	Gas flow rate (L/min)	Liquid phase	Yield %
0	0.5	Toluene	0
1/10	0.5	Toluene	73 ± 5
1/10	0.5	Water	57 ± 5
1/10	0.5	NaOH 0.001 M	72 ± 5
1/10	0.5	NaOH 0.01 M	62 ± 5
Pure He/KCl cluster using direct catch on a filter			12 ± 7

3.2 Os and Ru Experiments Using Tracer Made by Neutron-Activation

As OCL on-line Ru experiment was hindered because it appeared not feasible to transport Ru by in-situ oxidation, the following experiment was performed to compare the behavior of OsO_4 to that of RuO_4 in distribution between NaOH solution and toluene.

The tracers for this experiment were produced at the nuclear research reactor JEEP-II at Kjeller, Norway by neutron activation of 3 mg of $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ for Ru tracer and 3 mg of $(\text{NH}_4)_2\text{OsCl}_6$ for Os tracer. Relevant radio-nuclides used for detection in these experiments were 39.35-d ^{103}Ru and 4-s $^{191\text{m}}\text{Ir}$ which is the daughter of 15.4-d ^{191}Os . As the half-life of $^{191\text{m}}\text{Ir}$ is short compared to ^{191}Os , it is in secular equilibrium with the mother nuclide and their decay rates are equal.

To perform the experiments on distribution of tetroxides of Ru and Os between NaOH solution and toluene, the first step was to produce their tetroxides. Acidic solution of $\text{Ce}(\text{SO}_4)_2$ has proven to be a suitable oxidizing agent for this reaction [73]. The experiments were performed both in test tubes and using the SISAK apparatus. For the experiments in test tubes, tracer amounts of neutron activated Os and Ru were added to 50 mL of 0.03 M $\text{Ce}(\text{SO}_4)_2$ 0.2 M H_2SO_4 solution. The solution was heated in a water bath to 85 °C. 5 mL of this solution was shaken with 5 ml toluene in a test tube. After separation of the two phases using a centrifuge, 4 mL of each phase were withdrawn and Os and Ru activities were measured using an HPGe detector. Os and Ru are expected to

be oxidized to their tetroxides in acidic solution of $\text{Ce}(\text{SO}_4)_2$. The tetroxide can then be extracted into toluene. Os and Ru showed different behaviors in this experiment. The D-value for extraction of Os was: 0.27 ± 0.05 and D-value for Ru was 14 ± 3 which is significantly higher than that of Os. It is likely that Os is not oxidized as Ru by acidic solution of $\text{Ce}(\text{SO}_4)_2$.

In a following step the organic phase was shaken with NaOH solution. A 3 mL aliquot of each phase was then measured using the HPGe detector. During this experiment a white precipitate was observed which made the aqueous phase look gray. A large amount of the Ru and Os activities were located on the surface of the test tubes, and the very small amounts of activity remaining in the solutions resulted in irreproducible and unreliable data.

A similar chemical experiment as described above was carried out using the SISAK equipment and was named as “off-line SISAK experiment”. Tracer amounts of neutron-activated Os and Ru were added to and well mixed with 100 mL of 0.03 M $\text{Ce}(\text{SO}_4)_2$, 0.2 M H_2SO_4 solution. This liquid was heated to 85 °C and contacted with toluene in the first mixer-centrifuge unit. The organic effluent of this first centrifuge was then mixed with NaOH solutions. Samples from organic and aqueous effluents of the second centrifuge were collected and counted. The applied SISAK setup is shown in Fig. 3-7.

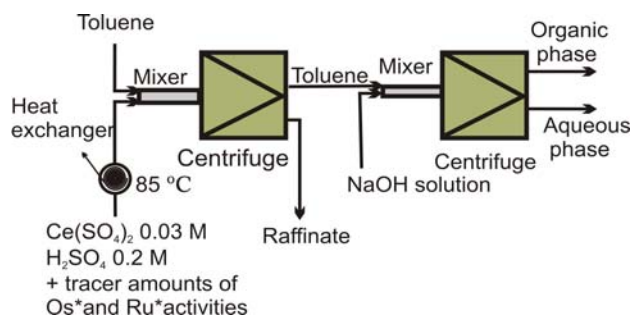


Fig. 3-7 The schematic setup for off-line SISAK experiment preparing the phases for distribution ratio measurements of OsO_4 between toluene and NaOH solutions.

During this experiment centrifuges were often clogged by a yellow deposit of CeO_2 and had to be flushed with a H_2SO_4 solution or in the worst case they were dismantled and cleaned before continuing. A large amount of activity was deposited inside the static mixers and on the centrifuge heads. Fig. 3-8 shows the results from the off-line SISAK experiments.

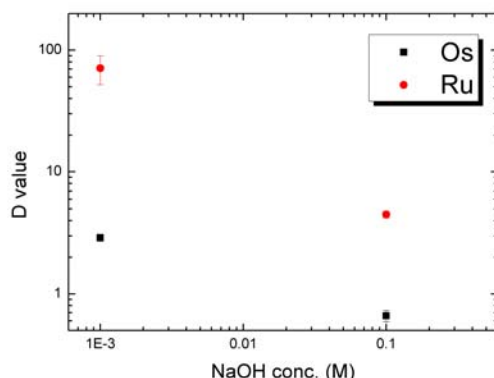


Fig. 3-8 Results of measured distribution ratios for Os and Ru between toluene and NaOH solutions using the off-line SISAK setup. The NaOH concentration on the abscissa axis is the input solution concentration that might have changed after mixing with the organic effluent from the first centrifuge.

The above mentioned problems made these experiments cumbersome; however, the conclusion is that RuO_4 is extracted to a higher degree than OsO_4 which is in accordance with the theoretical predictions and literature values as it will be discussed in chapter 4. Nevertheless these results are preliminary and there is a need for a more thorough study. For example here the attainment of the equilibrium conditions was not checked and the reason for deposition of Os and Ru activities on the surfaces was not fully understood.

3.3 Experiments with α -emitting Osmium at GSI, Germany

An experiment with α -emitting isotopes of Os was performed at GSI, Darmstadt. $^{172-175}\text{Os}$ nuclides were produced using a 6.0 MeV/u $^{40}\text{Ar}^{11+}$ beam of intensity about 200 particle nA from UNILAC on a rotating target wheel with three arc-shaped target sections (Artesia) [74] containing nat-Ce. The gas-filled separator TASCA (TransActinide Separator and Chemistry Apparatus) [75] was used to separate osmium isotopes from other nuclear reaction by-products and beam particles. TASCA has two operational modes which vary in the sequence of horizontal and vertical focusing of the quadrupole doublet:

- The High Transmission Mode (HTM) in which the dipole magnet (D) is followed by a horizontally (Q_h) and a vertically (Q_v) focusing quadrupole (DQ_hQ_v)
- The Small Image-size Mode (SIM), with a configuration of DQ_vQ_h

The EVR transmission is lower in SIM. However, its very small momentum dispersion at the end has a substantial advantage for a fast transport of short-lived nuclide to any chemistry device [76].

For the experiments in this work the HTM operational mode was employed. The dipole magnet current of TASCA was adjusted to get the optimum yield of desired Os isotopes. The schematic of the setup for this measurement is shown in Fig. 3-9.

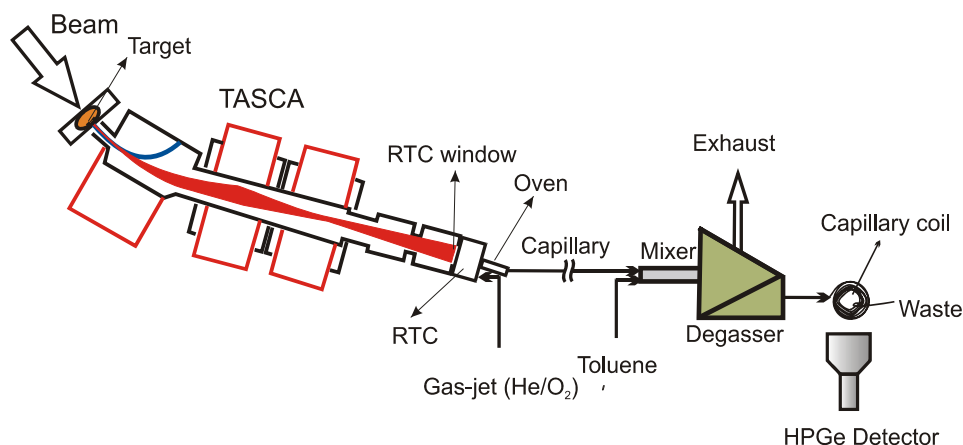


Fig. 3-9 Schematic of the setup used for adjustment of TASCA magnet setting to gain maximum yield for desired isotopes.

Chamber (RTC) [26] was mounted. For each operational mode of TASCA a special RTC is designed in such a way that the RTC window covers the image at the focal plane, thus there are two types of RTC: SIM type and HTM type [77]. Here, of course, the HTM type of RTC was applied to match the TASCA's operational mode. The RTC window which is a supported Mylar foil divides TASCA's low pressure region (≤ 1 mbar He) from the RTC chamber. The EVRs were thermalized in the RTC at 1.8 bar pressure and made available for transport to the SISAK setup. The RTC was flushed out with an O₂/He gas mixture flowing directly into an oven which is a quartz tube with a quartz wool-plug heated to 600 °C, to ensure fast and complete oxidation of Os. The volatile tetroxide was then transported by the gas-jet in a 20 meter long Teflon capillary of 2 mm i. d. to the SISAK apparatus. To optimize the TASCA magnet setting for the highest yield of the desired isotopes the activities of daughters and granddaughters of the Os isotopes were monitored at various magnet settings by γ -spectroscopy. The results are presented in Table 3-3.

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Table 3-3 The results from the experiments performed for adjustment of the TASCA magnet settings.

Exp no.	Magnet setting			Beam integral	^{174}Re	^{172}Re	^{173}W	^{173}Re	Live time (s)
	I_D	A	I_Q		A	$B\rho$	Tm	(243.4 keV)	
1	380	340	1.47	28007	1102±56	153±30	473±37	548±46	893.7
2	390	390	1.54	29368	1543±66	183±34	466±38	861±56	891.4
3	400	360	1.54	31914	1583±67	152±36	470±39	892±57	891.2
4	410	370	1.57	30899	1193±59	149±32	269±32	670±49	893.0
5	430	340	1.64	34580	884±51	66±25	289±31	485±41	894.9
6	440	400	1.67	34090	465±38	55±19	139±22	241±33	896.6

Fig. 3-10 shows the count rates normalized by the beam integral vs. dipole magnet current. The magnet setting of $I_D^* = 390$ A, $I_Q^\dagger = 355$ A, $B\rho^\ddagger = 1.54$ Tm resulted in the highest yield for the desired Os isotopes. The results show that the amounts of all three Os isotopes varied similarly with increasing the dipole magnet current.

* Dipole magnet current

† Quadrupole magnet current

‡ Magnetic rigidity

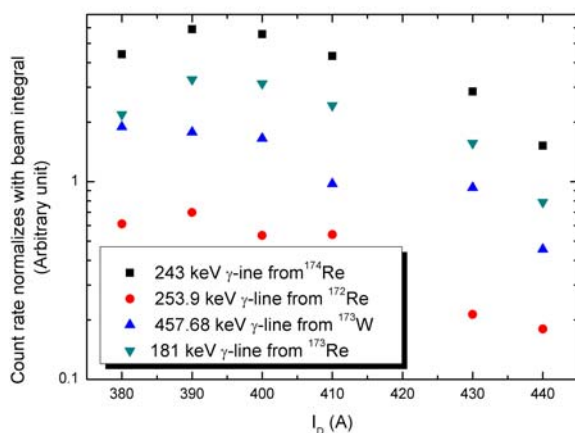


Fig. 3-10 The variation of the count rate normalized by the beam integral vs. TASCA dipole magnet current. These measurements were performed to optimize the transmission yield.

An overview of the applied SISAK set-up for the experiments for the measurement of distribution ratios at GSI is shown in Fig. 3-11.

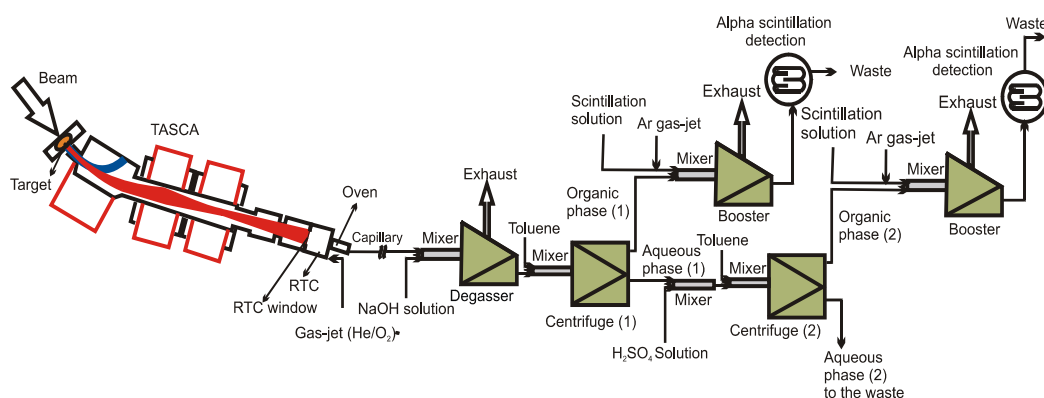


Fig. 3-11 Schematic set-up of the SISAK apparatus used for determination of distribution ratio of $^{172-174}\text{OsO}_4$ between NaOH solutions and toluene in a pilot model experiment for hassium.

OsO_4 was dissolved in NaOH solution from the carrier gas through a static mixer and the gas was separated from liquid phase using the SISAK degasser unit. The effluent of the degasser was contacted with pure toluene in a second static mixer and two phases were separated from each other by a SISAK centrifuge unit. The amount of OsO_4 in the organic phase could be directly measured using liquid scintillation. The organic output from the centrifuge was mixed with the scintillation solution previously purged by argon gas to remove interfering dissolved O_2 . The argon gas was then separated using a SISAK

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degasser which was also acting as a booster, pumping (or injecting) the solution through the flow cell for detection. The output of the booster then pumped into the detection cell and the amount of α -activity was measured. The aqueous output from the centrifuge was acidified and mixed with toluene in a second extraction stage by which the aqueous Os was transferred to a second organic phase for α -activity detection.

The liquid scintillation detection method for α -particles is sensitive to β and γ -radiation. The pulse shape discrimination method as described in [5] was used to distinguish the α -particles from other events. Fig. 3-12 shows a typical matrix of Pulse-Shape discrimination vs. energy accumulated during one of the measurements. The β particles, having an energy continuum, cover the whole energy range. In this figure α -particles from $^{172-174}\text{Os}$ isotopes can be seen but mixed with pile up events due to chance coincidence of β events. These events cannot be distinguished from α -particles by PSD. So there is a background of pile up events in α -events window.

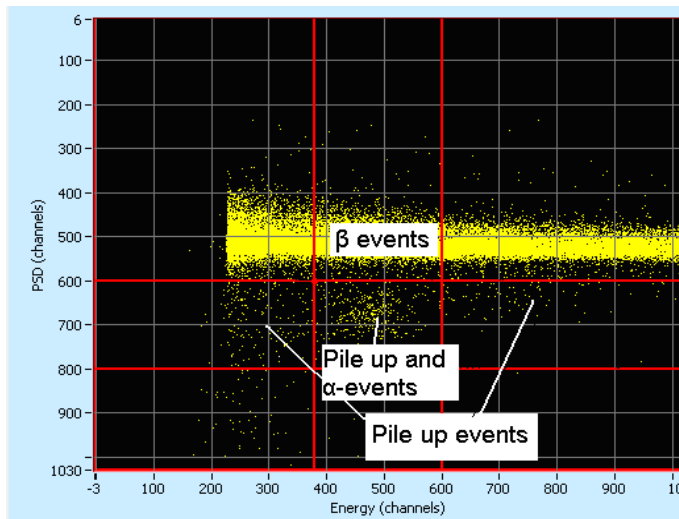


Fig. 3-12 A typical matrix of Pulse-Shape Discrimination vs. Energy, accumulated from one of the SISAK extraction experiments, by liquid scintillation detection method.

In a given energy window the rate of pile up events is proportional to the rate of β particles. Thus the background can be obtained by setting the ratio of the number of β -particles in the same energy window as the α -events to the number of β -particles in another energy window outside the α -events region equal to the ratio of pile up events in the same mentioned windows in the Energy-PSD matrix. In this way the background in the α -events window can be calculated. The procedure for calculation of background is shown in Fig. 3-13. In this procedure the number of events in four windows of the matrix was measured by introducing gates. Window (I) is gated on β -events which have the same energy as measured α -event. In the Window (II) which is outside of the α -events energy window, the number of β -events is measured. In window (IV) which has the same energy range as Window (II) the number of pile up events is measured. In Window (III)

which is the α -events window, the total number of α -events and pile up events is measured. The pile up events in the Window (III) can be then calculated:

$$\text{Number of pile up events in Window (III) [background]} = \frac{\text{Number of } \beta \text{ events in Window (I)} \times \text{Number of pile up events in Window (IV)}}{\text{Number of } \beta \text{ events in Window (II)}} \quad \text{Eq. 3-3}$$

Thus the number of α -events is obtained by subtracting of calculated pile up events in Window (III) from the total number of events in this window.

The transport time and the efficiency of the gas transport were measured here also. The transport efficiency was measured using the 113-keV and 234-keV γ -lines from ^{174}Re . To make sure that these γ -peaks belong to 2.4-min ^{174}Re a half-life measurement was performed. The measured half-lives are $t_{1/2} = 2.26 \pm 0.14$ min for 243 keV and $t_{1/2} = 2.1 \pm 0.2$ min for 113 keV. The measured half-lives are in agreement with the literature value [78] for half-life of ^{174}Re within the uncertainty. The decay curves are shown in Fig. 3-14. These decay curves are obtained by collecting a γ -spectrum every minute from

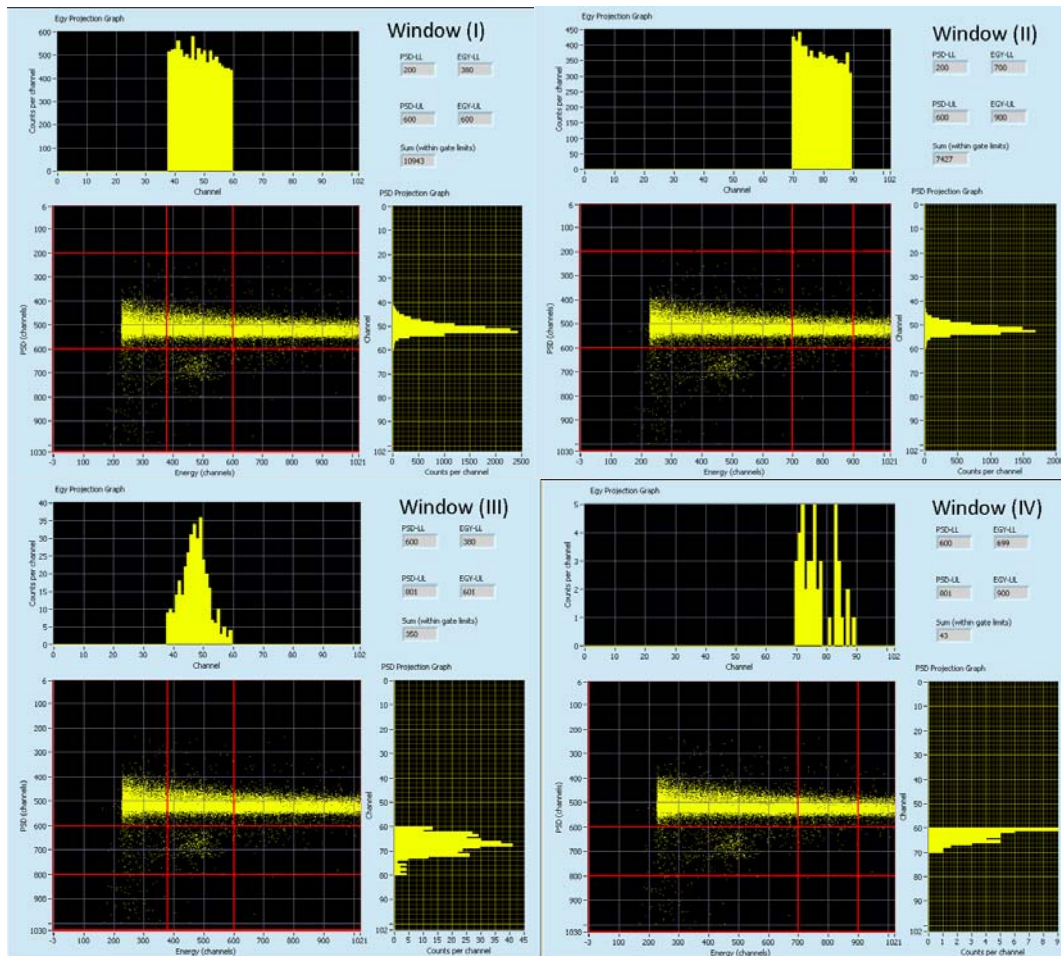


Fig. 3-13 The selected windows for obtaining of the background (number of pile up events) in the α -events window. The windows can be selected by setting an upper and lower limit for energy and PSD and the background is obtained by Eq. 3-3.

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the Al foil catching the EVRs at the RTC window. The details of the procedures and the results from the experiment performed at GSI are presented in paper (III).

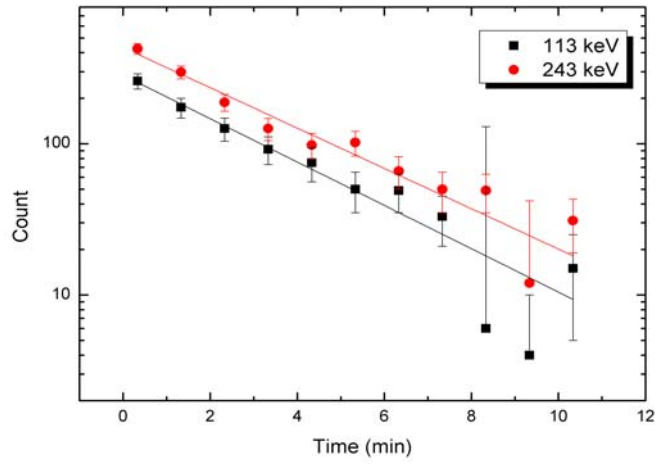


Fig. 3-14 The decay curves of the 113 and 243 keV γ -peaks from the activity from Al foil at the RTC window. The foil collected EVRs produced in bombardment of nat-Ce with an $^{40}\text{Ar}^{11+}$ beam of 6.0 MeV/u.

4 Discussion

“As far as the laws of mathematics refer to reality, they are not certain, and as far as they are certain, they do not refer to reality.”

Albert Einstein 1879-1955

4.1 Theoretical Predictions

The behaviour of Hs in the proposed system can be predicted using theoretical calculations. These predictions will make the performance of the Hs experiment more instructive, and the experimental results will be a tool for evaluation of the theoretical models. In the following sections the behaviour of HsO₄, distributing between NaOH solution and toluene, is discussed.

As mentioned the D-value can be related to the distribution constant, K_D , and the complex formation constants K_1 and K_2 according to the expression:

$$D = \frac{K_D}{1 + K_1[\text{OH}^-] + K_1K_2[\text{OH}^-]^2} \quad \text{Eq. 4-1}$$

To calculate the D-value for HsO₄, K_D , K_1 and K_2 for Hs have to be estimated.

K_D can be approximated to the D-value when the concentration of NaOH is zero i.e. the distribution of HsO₄ between toluene and pure water.

A general expression for the distribution of nonelectrolytes between water and organic solvents takes into account all the differences in the solute interaction with the solvents i.e. the aqueous phase and the organic phase. In such cases the energetics of relevant interactions consists of the work required for the creation of a cavity to accommodate the solute and the Gibbs energy for the dispersion force interactions and for donation and acceptance of hydrogen bonds. For a given solute:

$$\log D = A_v V_{\text{solute}} \Delta \delta^2 + A_\pi \pi_{\text{solute}}^* \Delta \pi^* + A_\alpha \alpha_{\text{solute}} \Delta \beta + A_\beta \beta_{\text{solute}} \Delta \alpha \quad \text{Eq. 4-2}$$

Where V_{solute} is the molar volume of the solute and the difference factors are:

$\Delta\delta^2 = \delta_{solvent}^2 - \delta_{water}^2$, $\Delta\pi^* = \pi_{solvent}^* - \pi_{water}^*$, $\Delta\alpha = \alpha_{solvent} - \alpha_{water}$ and $\Delta\beta = \beta_{solvent} - \beta_{water}$ i.e. the difference between the relevant properties of the organic solvent and those of water. δ^2 is the cohesive energy density, π^* is the polarity and polarizability parameter α is the hydrogen bond donation acidity parameter and β is the hydrogen bond donation basicity parameter.

It is established that the coefficients A_v , A_π , A_α and A_β are independent of the solutes and solvents employed provided that the organic solvent at equilibrium is dry, that is its water content is approximately $x_w < 0.13$ [79].

So, to compare the distribution ratio of HsO_4 between toluene and water to those of OsO_4 and RuO_4 the knowledge of properties of these molecules is needed. The calculated values based on relativistic and nonrelativistic and experimental values of some properties of RuO_4 , OsO_4 and HsO_4 are given in [48].

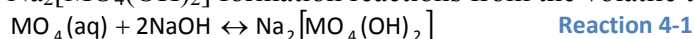
The experimental value for distribution ratio of OsO_4 between toluene and water from this work is $D = 11 \pm 5$ at $t = 30 \pm 5$ °C. Experiments with RuO_4 were not performed here but the distribution ratio between water and CCl_4 from [80] is $D = 59 \pm 1$ at $t = 20$ °C. The distribution of OsO_4 between water and CCl_4 from [49] is $D = 12.5$ and from [50] is $D = 12.8$. As Eq. 3-2 suggests the size of the molecule and the strength of the bonds between water and the molecules are main factors in determination of the D-value of nonelectrolyte molecules. As the size of OsO_4 and RuO_4 (calculated value: 1.719 Å and 1.712 Å respectively [48] and experimental value: 1.711 Å and 1.706 Å respectively [81]) is about the same, they must have almost the same D-value provided the cavity formation is the only factor here. However, RuO_4 has a higher D-value which indicates another factor is involved as well. The lower D-value for OsO_4 might be due to the formation of chemical bonds between OsO_4 and water producing the un-ionized form of Os (VIII) acid: $\text{OsO}_4(\text{OH}_2)_2$ in water which stays in the aqueous phase while Ru might not have such a feature.

To calculate the complex formation constants for formation of $[\text{OsO}_4(\text{OH})]^-$ and $[\text{OsO}_4(\text{OH})_2]^{2-}$ the free energy change, ΔG^f for formation of the complexes is needed. The complex formation constants can be obtained using this formula:

$$\Delta G_f = -RT \ln K \quad \text{Eq. 4-3}$$

where R is the ideal gas constant and T the temperature.

The calculations of the free energy change, ΔG^f , of the $[\text{MO}_4(\text{OH})_2]^{2-}$ and $\text{Na}_2[\text{MO}_4(\text{OH})_2]$ formation reactions from the volatile tetroxides and NaOH:



have shown that HsO_4 should be slightly less reactive than OsO_4 , with the difference in ΔG^f being less than 52 kJ/mol. In the experimental study of the deposition of OsO_4 and HsO_4 on the surface of NaOH in the presence of water [41], such a difference in reactivity has not yet been clearly revealed.

ΔG^f for the formation of $[\text{RuO}_4(\text{OH})_2]^{2-}$ from RuO_4 was found to be ~300 kJ/mol more positive than ΔG^f for analogous reactions of Os and Hs which implies that, the anionic complex of Ru(VIII) is much less stable than those of Os and Hs. That explains why the Ru(VIII) complex is not known [60]. Accordingly, predicted trend for the formation of $\text{Na}_2[\text{MO}_4(\text{OH})_2]$ in the reaction 3-1 in group-8 is:

Os > Hs >> Ru

By dissolving of the tetroxides in NaOH solution the hydroxo complexes form. Since during extraction into toluene the hydroxo complexes tend to remain in the aqueous phase while the tetroxides are more soluble in toluene and immigrate into the organic phase, progression of reaction 4-1 towards right decrease the D-value. Thus, the D-values sequence according to the trend for $\text{Na}_2[\text{MO}_4(\text{OH})_2]$ formation can be predicted to be:

Ru >> Hs > Os

The above discussion considers only formation of $[\text{MO}_4(\text{OH})_2]^{2-}$, however, as mentioned earlier in an aqueous alkaline solution the reaction goes first through the formation of $[\text{MO}_4(\text{OH})]^-$ and the calculation of the difference in the free energy of formation of this species for Os and Hs would enable us to estimate the first complex formation constant for Hs using the experimental value of the complex formation constant for Os obtained here.

In the present work from the off-line SISAK experiments (section 3.1.3); it was observed that the distribution ratio for RuO_4 between dilute NaOH solutions and toluene is higher than that of OsO_4 which agrees with the predictions above.

4.2 Comparison of the Results with the Literature Values

Examples of studies on the distribution of OsO_4 between organic liquids (normally CCl_4) and NaOH solution are found in the literature. The researchers agree on the acidic behaviour of OsO_4 . Fig. 4-1 shows the results obtained in the present work with some of literature results.

In Yost et al. work [49] CCl_4 is used as the organic phase to extract OsO_4 from NaOH solutions and the experiment is performed at 25 °C. Chemical methods, including

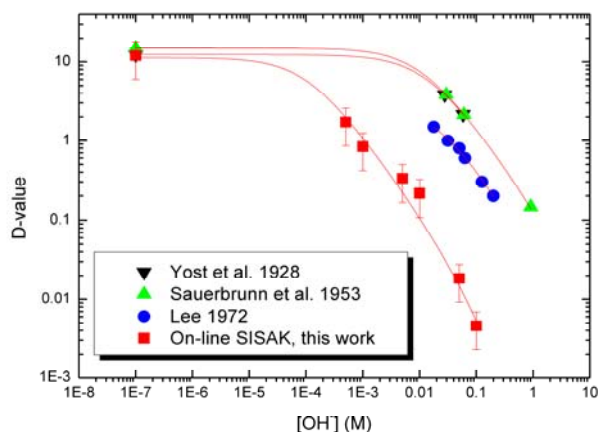


Fig. 4-1 The D-value vs. $[\text{OH}^-]$ in distribution of OsO_4 between alkaline solutions and an organic phase; from Yost et al. [49], Sauerbrunn et al. [50] and Lee [52] and the results obtained in this work. The solid lines show the fitting of results with Eq. 2-6.

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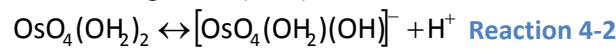
titration, were used for determination of the amount of Os in the phases.

In the Sauerbrunn et al. work [50] the original concentration of OsO_4 was either 0.00081 or 0.0016. The ionic strength of the aqueous phase was kept 1 M using sodium perchlorate and the organic phase used to extract OsO_4 from NaOH solutions was CCl_4 . The experiment was performed at 25 °C. Osmium was determined using a photometrically method.

In Lee's work [52] OsO_4 was extracted from aqueous solution of either NaOH or KOH by CCl_4 and the D-value was determined. This experiment performed at room temperature $[(24 \pm 1) \text{ }^\circ\text{C}]$ and ^{191}Os was used as tracer.

In the previous works the equilibrium constants are reported as acidic constants for the osmium (VIII) acid. It is possible to convert the complex formation constants K_1 and K_2 (in equations 2-2 and 2-3) to acidic constants by the following assumptions:

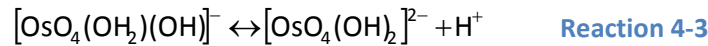
Considering $\text{OsO}_4(\text{OH}_2)_2$ as the un-ionized form of acid, it can be written:



The primary acidic constant is:

$$K_{a1} = \frac{[\text{OsO}_4(\text{OH}_2)(\text{OH})]^- [\text{H}^+]}{[\text{OsO}_4(\text{OH}_2)_2]} \quad \text{Eq. 4-4}$$

And the second ionization of the acid:



The second acidic constant is given by:

$$K_{a2} = \frac{[\text{OsO}_4(\text{OH})_2]^{2-} [\text{H}^+]}{[\text{OsO}_4(\text{OH}_2)(\text{OH})]^-} \quad \text{Eq. 4-5}$$

It can be assumed $\text{OsO}_4(\text{OH}_2)_2$ is the same species as $\text{OsO}_{4(\text{aq})}$ and $[\text{OsO}_4(\text{OH}_2)(\text{OH})]^-$ is the same as $[\text{OsO}_4(\text{OH})]^-$ in equations 2-2 and 2-3.

The ionization constant of water is:

$$K_w = [\text{OH}][\text{H}^+] = 10^{-14} \quad \text{Eq. 4-6}$$

The combination of Eq. 2-2 and 2-3 with Eq. 4-6 gives:

$$K_{a1} = K_1 K_w \quad \text{Eq. 4-7}$$

$$K_{a2} = K_2 K_w \quad \text{Eq. 4-8}$$

Table 4-1 gives the value of the K_1 and K_2 obtained by fitting of the results from different works with equation 2-6 and K_{a2} and K_{a1} calculated using Eq. 4-7 and 4-8.

Table 4-1 The Complex formation constant for formation of $[\text{OsO}_4(\text{OH})_n]^{n-}$ obtained by fitting of results from different research works with Eq.2-6 and acidic constants for ionization of Os (VIII) acid, $\text{OsO}_4(\text{OH})_2$, obtained using Eq. 4-7 and Eq. 4-8.

K_1	K_2	K_{a1}	K_{a2}	Reference
80	–	8×10^{-13}	–	Yost et al.[49]
97 ± 1	0.22 ± 0.16	$(9.7 \pm 0.1) \times 10^{-13}$	$(2.2 \pm 1.6) \times 10^{-15}$	Sauerbrunn et al [50].
61 ± 23	–	$(6.1 \pm 23) \times 10^{-13}$	–	Lee [52]
$(1 \pm 0.5) \times 10^4$	12 ± 8	$(1 \pm 0.5) \times 10^{-10}$	$(1.2 \pm 0.8) \times 10^{-13}$	This work

In this work, the experiments were performed at room temperature but as the centrifuges moving parts produce some heat and the temperature of the solutions elevated to $(30 \pm 5) ^\circ\text{C}$. As it can be seen the acidic constant obtained here is higher than the values in previous works. The reason could be that equilibrium is not attained in the on-line experiments in this work. As it is described in paper (I) an experiment was performed to find the appropriate length of the static mixer to reach equilibrium. However this was performed using pure water as the aqueous phase and as it can be seen in Fig. 4-1 the D-value for the extraction from water agrees with the results from other works, but how about the extraction from NaOH solutions? Are they performed at a non-equilibrium condition and therefore the D-values are lower than the previous works' values? To answer these questions some batch experiments were performed. The procedure of the batch experiments is described in paper (II). Fig. 4-2 shows the results of on-line and batch experiments. The results from batch experiments are in a good agreement with on-line experiments, which strongly verifies that the on-line experiment have been at equilibrium conditions.

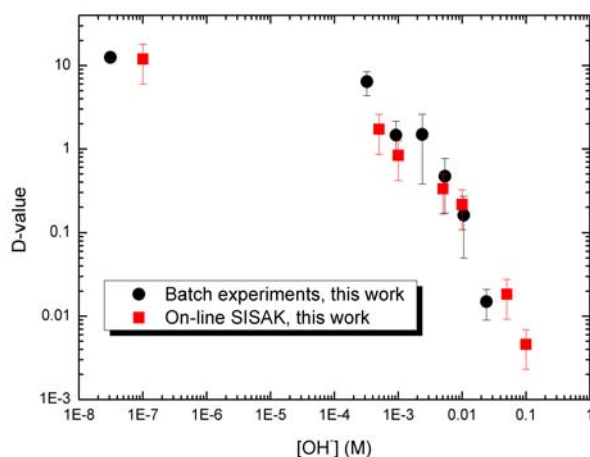


Fig. 4-2 D-value vs. $[\text{OH}^-]$. The results from both batch and on-line SISAK experiment performed in this work for extraction of OsO_4 from NaOH into toluene are shown.

A study of the distribution of RuO_4 between CCl_4 and NaOH solution in different concentrations has been reported in [80]. From that experiment it was concluded that RuO_4 forms a weak acid in alkaline solutions and the K_a was measured to be $(6.8 \pm 0.1) \times 10^{-12}$. In the same work, it was also found that for hydroxide concentrations below ~ 0.01 results were reproducible, but in more alkaline solutions reduction to ruthenate slowly occurred and as the hydroxide concentration approached normality reduction became very rapid. Fig. 4-3 shows the results of Ru and Os off-line SISAK experiment and the results of Os on-line SISAK experiments obtained in this work with the Ru results from [80].

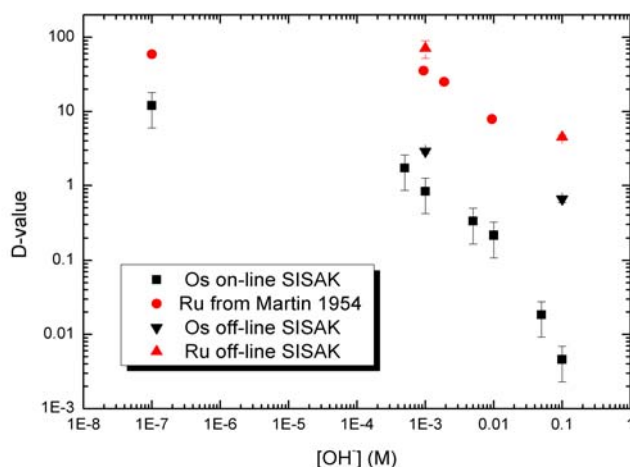


Fig. 4-3 Distribution of OsO_4 between toluene and NaOH solutions at $t = 30 \pm 5^\circ\text{C}$ from this work and distribution of RuO_4 between CCl_4 and water at $t = 20^\circ\text{C}$ taken from Martin work [80]. The result from off-line SISAK experiment for RuO_4 and OsO_4 in this work is illustrated as well for comparison.

As explained earlier in section 3.2, the OH^- concentration for the off-line SISAK experiment is the input solution concentration but it might be less when contacted with the organic phase from the first centrifuge. That is why the D-values for Os off-line SISAK experiments seem higher than Os on-line experiments. Nevertheless, the off-line experiments results clearly show the difference between the behaviour of Os and Ru in this system and the results are in fair agreement with [80].

4.3 Required Beam-time and Chemicals for an Hs SISAK Experiment

As the production cross-section for transactinides are low and the beam-time available for a transactinide experiment is limited, it follows that conclusions from chemical investigations have to be based on a small number of radioactive decay events. In liquid-liquid extraction the ratio of two small numbers yields a distribution coefficient or D-value to be compared with data obtained for the homologues. An important question is, however, the statistical significance of the data obtained and the minimum data required for conclusions rather than assumptions. The problem of how many atoms are needed to determine a specific D-value with a given accuracy has been considered in [82]. Table 4-2 gives the needed number of counts for a specified uncertainty at a given D-value. As it can be seen from Table 4-2 the D-values of around 1 are associated with lower uncertainty with a given number of observed events.

Since the uncertainty of the Hs data is expected to be large, to reveal any distinction in D-values of Os and Hs, it is important to choose the experimental conditions in which these two elements are anticipated to have a significant different behaviour. The difference has to be almost one order of magnitude, thus it is important to theoretically derive D-value of HsO_4 for an appropriate experimental condition.

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Table 4-2 Number of detected atoms needed to achieve a given uncertainty for a D value taken from [82]

D value	10% uncertainty	20% uncertainty	50% uncertainty
0.1	1187	303	48
0.2	709	180	29
0.5	444	113	18
0.8	402	102	16
1	397	100	16
1.2	400	101	16
1.5	413	104	17
2	444	113	18
4	620	157	25
6	815	205	33
8	1004	254	41
10	1187	303	48

It is also important to remember not all atoms made will be detected. If we consider the overall efficiency to be about 50% the beam-time can be estimated in the following way:

As Table 4-2 shows, at D-values around 1 with a standard deviation of 50% about 16 detected atoms are needed. Accordingly, in an Hs experiment with a production rate in the range of 1 atom per day and overall efficiency of 50% the duration of the experiment will be around 4 weeks. This long period required for a SISAK experiment would need amounts of chemicals and man power. For a flow rate of 0.2 mL/s, which is a normal flow rate for a SISAK experiment, the consumption for each stream would be about 5.2×10^3 L during the 4-week experiment. Although it is possible to reuse the organic phase by distillation, it will require a crew for the recycling if not an on-line process is implemented. High consumption of chemicals in running the SISAK system is a serious

limitation for transactinide elements with so low production rate. Thus it is important to develop an appropriate system for recycling of the organic phase.

4.4 Chemical separation vs. preseparators for Hs SISAK experiment

Hs has an exceptional feature of forming volatile tetroxide which provides its excellent separation from other nuclear reaction by-products. The efficiency of the transport in this method is estimated to be as high as 80% [83] and in the work presented here, a transport yield of about 70% was measured for transportation of Os from the target chamber to the liquid phase using SISAK degasser unit (see section 3.1.4).

The transmission of different gas-filled separators for the reaction: $^{48}\text{Ca} + ^{238}\text{U} \rightarrow ^{244}\text{Pu} \rightarrow 112/114$ are given in Table 4-3 [see Appendix III (E)].

Table 4-3 Measured, estimated or calculated transmissions for $^{48}\text{Ca} + ^{238}\text{U} \rightarrow ^{244}\text{Pu} \rightarrow 112/114$ using different gas-filled separators

Separator	DGFRS	GARIS	BGS	TASCA (High Transmission Mode)	TASCA (Small Image Mode)
Transmission %	35	40	49-59	60	35

As the numbers in Table 4-3 suggest the transmission of EVRs through the gas-filled preseparators at the highest yield is lower than the chemical transport yield for group-8 elements.

In the gas phase experiment for group-8 elements using a hot quartz wool filter a separation factor $> 10^6$ was reached for the separation of formed volatile molecules from non-volatile species [83]. That makes sure that only volatile species can be transferred to the chemistry apparatus. In the Hs experiments, the only volatile by-products besides HsO_4 in these conditions are noble gases and halogens and OsO_4 which can be transported to the SISAK system. Considering the proposed system outlined here (section 3.1.4) the interference of these by-products to the detection of Hs can be eliminated as follows: (I). Noble gases will be removed with the He gas in the degasser. (II) Halogens which will react with alkaline solutions forming A^- and AO_3^- species, are soluble in such solutions. However the negative-charged ions are not extracted in the organic phase and since only the organic phases are measured for radioactivity the interference of these species will be eliminated. (III) The only other interfering by-product is OsO_4 . The α -energy of Os isotopes is in the range of 5-7 MeV which is much lower than α -energy of Hs isotopes in the range of 9-10 MeV. The energy resolution of α -scintillation detection is about 300 keV and thus Hs can be easily distinguished from Os. Thus all the

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interferences are eliminated and as the transport yield of Hs is also high in the chemical separation method, this technique is the recommended procedure for such Hs experiments.

5 Conclusion and Future Perspective

“To be suspicious is not a fault. To be suspicious all the time without coming to conclusion is the defect.”

Lu Xun 1881-1936

The proposed SISAK extraction system in this work is based on the known chemical behaviours of Hs: transportation based on formation of volatile tetroxide and solvent extraction based on formation of hydroxocomplexes in the reaction of tetroxid with sodium hydroxide. Here, the behaviour of Os was studied as a model for Hs. In the initial stages γ -emitting nuclides of Os were applied and their properties were found to be in accordance with some known reactions. The results were reproducible within the system's intrinsic error.

A pilot experiment, applying α -emitting Os isotopes was performed at GSI which cleared many aspects of a real Hs experiment. The transport time and yield were measured. The entire SISAK setup with double α -detector arrays could be tested and it was the first SISAK experiment in connection with TASCA. The results were in good agreement with the work performed in Oslo with the γ -emitting Os isotopes. It was concluded that such experiment for Hs is feasible in principle, though practically it is still challenging with respect to the low production rate of Hs. The estimated beam-time to get sufficient events for D-values around unity with 50% uncertainty is about one month. The conventional SISAK system consumption of chemicals is high and produces volumes of waste to be handled during this long period. Although SISAK system has been modified in several generations to reduce the inner volumes of the centrifuges [84, 85] its high consumption of chemicals and waste production still remain a limitation for its application. It is possible to distill the organic effluent and reuse it to lower the amount of waste and this method has been employed in previous SISAK transactinide experiments and this work on Os at GSI.

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To overcome the problem of high chemical consumption using the SISAK system, another arrangement called MicroSISAK [86] is under development. MicroSISAK is a miniaturized apparatus for performing fast and continuous liquid-liquid separations at flow rates of mL/min. Its main components are: (i) an inlet with interdigital channels for intense mixing of the phases and (ii) a filter unit with a Teflon membrane for phase separation. MicroSISAK system is currently being tested for lighter homologues of different transctinides [see Appendix III (D)]. The proposed extraction system outlined in the present work should be an option for an Hs microSISAK experiment.

6 Some Relevant Experiments at GSI

Participation in some of the TASCA commissioning program was relevant for future SISAK transactinide experiments. The successful coupling of SISAK to BGS [87], gives the anticipation that chemical study of transactinides by coupling of SISAK with TASCA will be promising as well (see Report I and VI). TASCA is a new, highly efficient gas-filled preseparator which has been designed and built at GSI with the aim of studying chemical and physical properties of superheavy elements [29]. Extensive studies have been performed to obtain optimized parameter sets for different parts of TASCA such as the target thickness and stability, the gas pressure and the gas filling (He, H₂ and mixtures), the dipole settings (Bp) and quadrupole focusing, RTCs window (material and thickness, support structures), and size and shape of the RTC chamber, gas-jet transport of pre-separated products, and the coupling and performance of devices like Rotating wheel On-line Multidetector Analyzer (ROMA) and the Automated Rapid Chemistry Apparatus (ARCA) [see Report VI]. University of Oslo was heavily involved in construction of SIM-RTC to be used for chemical experiments online with TASCA. A picture of the constructed SIM-RTC is shown in Appendix II. The yield of gas-jet transport from SIM-RTC in different gas-jet flow rates, RTC pressure and depth of the RTC was measured using 3.5-min ¹⁹²Pb, 5.8-min ^{193m}Pb and 12-min ¹⁹⁴Pb activity produced in the ^{nat}Gd(⁴⁰Ar¹⁰⁺, xn) reaction. The test experiments with SIM-RTC will be published in a separate paper, but this publication was not written at time of publication of this thesis.

Production and decay of ²⁶⁰Rf, ^{261a,b}Rf and ²⁶²Rf [88-90], produced in the nuclear fusion reaction ²⁴⁴Pu(²²Ne,xn) was studied in the final experiments of the commissioning phase of TASCA (See Report II). Separated reaction products were implanted into a Focal Plane Detector (FPD). In other experiments, EVRs were guided to an RTC, where they passed a Mylar window and were thermalized in 1.2 bar He in the RTC and transported to the ROMA by a He/KCl jet through a polyethylene capillary. It was the first transactinide experiment using TASCA as a preseparator. In this experiment a new Rf isotope, ^{261b}Rf, was also observed for the first time.

Another relevant experiment at GSI which I participated in was testing of a new nuclear fusion reaction for production of Hs. For an Hs chemistry experiment it is critical

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to apply a nuclear reaction with as high as possible production rate. The reaction, $^{238}\text{U}(^{36}\text{S},4\text{n})^{270}\text{Hs}$, is predicted to have a higher cross-section for production of ^{270}Hs than the previously employed reaction: $^{248}\text{Cm}(^{26}\text{Mg},4,5\text{n})^{269,270}\text{Hs}$. This prediction was tested experimentally at GSI. For the experiment, the separation and detection system COMPACT (Cryo On-line Multidetector for Physics and Chemistry of Transactinides) [18] which was connected to a recoil chamber installed behind the ARTESIA target wheel was applied. A beam of $^{36}\text{S}^{5+}$ ions was accelerated by the UNILAC up to 7.13 MeV/u and impinged on a rotating ^{238}U target wheel. The separation of the Hs nuclei from other reaction products was achieved with the COMPACT system, which is an improved highly-efficient rapid chemical separation and on-line detection apparatus based on the cryo thermo chromatography method [40, 91, 92]. EVRs leaving the target were thermalized in a dried He/O₂ (10% O₂) gas in the recoil chamber, which was heated to 350-400°C. Volatile HsO₄ and OsO₄ were formed and flushed out of the recoil chamber passing through a quartz wool filter heated up to 650°C. The volatile species then were transported to the detection system of COMPACT. This experiment was the first measurement of the complete nuclear fusion reaction $^{36}\text{S} + ^{238}\text{U}$ and a cross section of $0.8^{+26}_{-0.7}$ pb for production of ^{270}Hs at 51 MeV excitation energy was observed [43] [see also Report III].

7 References

1. Schädel, M., *Superheavy element chemistry-achievements and perspectives*. Journal of Nuclear and Radiochemical Sciences, 2007. **8**(2): p. 47-53.
2. Pyykkö, P. and J.P. Desclaux, *Relativity and the periodic system of elements*. Acc. Chem. Res., 1979. **12**(8): p. 276-281.
3. Schädel, M., *The Chemistry of Superheavy Elements*. 2003, Dordrecht, The Netherlands: Kluwer Academic Publishers. pp.318.
4. Omtvedt, J.P., et al., *Review of the SISAK system in transactinide research recent developments and future prospects*. Journal of Alloys and Compounds, 1998. **271-273**: p. 303-306.
5. Stavsetra, L., et al., *Liquid-scintillation detection of pre-separated ^{257}Rf with the SISAK-system*. Nuclear Instruments & Methods in Physics Research, Section A: Accelerators, Spectrometers, Detectors, and Associated Equipment, 2005. **543**(2-3): p. 509-516.
6. Omtvedt, J.P. and D. Polakova, *Study of Liquid-Liquid Extraction of Element 104, Rutherfordium-Sulphate Complexes by the SISAK System*. To be published.
7. Omtvedt, J.P., et al., *SISAK Liquid-Liquid Extraction Experiments with Pre-separated ^{257}Rf* . Journal of Nuclear and Radiochemical Sciences, 2002. **3**(1): p. 121-124.
8. Seaborg, G.T., *Actinides*. Kirk-Othmer Encycl. Chem. Technol., 2nd Ed. , 1963. **1**: p. 351-71.
9. Bohr, N. and J.A. Wheeler, *The mechanism of nuclear fission*. Physical Review, 1939. **56**: p. 426-450.
10. Myers, W.D. and W.J. Swiatecki, *Nuclear properties according to the Thomas-Fermi model*. Nuclear Physics A, 1996. **A601**(2): p. 141-167.
11. Möller, P. and J.R. Nix, *Stability of heavy and superheavy elements*. Journal of Physics G: Nuclear and Particle Physics, 1994. **20**(11): p. 1681-1747.
12. Cwiok, S., et al., *Shell structure of the superheavy elements*. Nuclear Physics A, 1996. **A611**(2,3): p. 211-246.

52 References

13. Gupta, R.K., S.K. Patra, and W. Greiner, *Structure of $^{294,302}_{120}$ nuclei using the relativistic mean-field method*. Modern Physics Letters A, 1997. **12**(23): p. 1727-1736.
14. Rutz, K., et al., *Superheavy nuclei in self-consistent nuclear calculations*. Physical Review C: Nuclear Physics, 1997. **56**(1): p. 238-243.
15. Kruppa, A.T., et al., *Shell corrections of superheavy nuclei in self-consistent calculations*. Physical Review C: Nuclear Physics, 2000. **61**(3): p. 034313/1-034313/13.
16. Patyk, Z., et al., *Potential energy and spontaneous-fission half-lives for heavy and superheavy nuclei*. Nuclear Physics A, 1989. **A502**: p. 591c-600c.
17. Patyk, Z. and A. Sobiczewski, *Main deformed shells of heavy nuclei studied in a multidimensional deformation space*. Physics Letters B, 1991. **256**(3-4): p. 307-310.
18. Dvorak, J., et al., *Doubly Magic Nucleus $^{270108}\text{Hs}^{162}$* . Physical Review Letters, 2006. **97**(24): 242501/1-242501/4.
19. Sobiczewski, A. and A. Parkhomenko, *Description of alpha -decay half-lives of heaviest nuclei*. Physics of Atomic Nuclei, 2006. **69**(7): p. 1155-1157.
20. Mendeleyev, D.I., *Ueber die Beziehungen der Eigenschaften Zu den Atomgewichten der Elements*. Zeitschrift für Chemie 1869(12): p. 405-406.
21. Oganessian, Yu.Ts., et al., *Synthesis of nuclei of the superheavy element 114 in reactions induced by ^{48}Ca* . Nature, 1999. **400**(15 July): p. 242-245.
22. Stavsetra, L., et al., *Independent Verification of Element 114 Production in the $\text{Ca}48+\text{Pu}242$ Reaction*. Physical Review Letters, 2009. **103**(13): p. 132502.
23. Düllmann, Ch.E., et al., *Production and Decay of Element 114: High Cross Sections and the New Nucleus ^{277}Hs* . Physical Review Letters, 2010. **104**(25): p. 252701.
24. Oganessian, Yu.Ts., et al., *Synthesis of a New Element with Atomic Number $Z=117$* . Physical Review Letters, 2010. **104**(14): p. 142502.
25. Eberhardt, K., et al., *Preparation of targets for the gas-filled recoil separator TASCA by electrochemical deposition and design of the TASCA target wheel assembly*. Nuclear Instruments & Methods in Physics Research, Section A: Accelerators, Spectrometers, Detectors, and Associated Equipment, 2008. **590**(1-3): p. 134-140.
26. Düllmann, Ch.E., *Physical preseparation: A powerful new method for transactinide chemists*. European Physical Journal D: Atomic, Molecular, Optical and Plasma Physics, 2007. **45**(1): p. 75-80.
27. Leino, M., *Gas-filled separators - An overview*. Nuclear Instruments & Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms, 2003. **204**: p. 129-137.
28. Ninov, V., K.E. Gregorich, and C.A. McGrath, *The Berkeley gas-filled separator*. AIP Conference Proceedings, 1998. **455**(ENAM 98): p. 704-707.
29. Semchenkov, A., et al., *The TransActinide Separator and Chemistry Apparatus (TASCA) at GSI - Optimization of ion-optical structures and magnet designs*. Nuclear Instruments & Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms, 2008. **266**(19-20): p. 4153-4161.

30. Münzenberg, G., et al., *The velocity filter SHIP, a separator of unslowed heavy ion fusion products*. Nuclear Instruments & Methods, 1979. **161**(1): p. 65-82.
31. Münzenberg, G., et al., *The identification of element 108*. Zeitschrift für Physik A: Atoms and Nuclei (1975), 1984. **317**(2): p. 235-236.
32. Dragojevic, I., et al., *New isotope ^{263}Hs* . Physical Review C: Nuclear Physics, 2009. **79**(1): p. 011602/1-011602/4.
33. Münzenberg, G., et al., *Evidence for $^{264}108$, the heaviest known even-even isotope*. Zeitschrift für Physik A Atomic Nuclei, 1986. **324**(4): p. 489-490.
34. Hofmann, S., et al., *The new isotope $^{270}110$ and its decay products ^{266}Hs and ^{262}Sg* . European Physical Journal A: Hadrons and Nuclei, 2001. **10**(1): p. 5-10.
35. Lazarev, Y.A., et al., *New Nuclide $^{267}108$ Produced by the $^{238}\text{U} + ^{34}\text{S}$ Reaction*. Physical Review Letters, 1995. **75**(10): p. 1903.
36. Hofmann, S., et al., *The new element 112*. Zeitschrift fuer Physik A: Hadrons and Nuclei, 1996. **354**(3): p. 229-30.
37. Dvorak, J., et al., *Observation of the 3n evaporation channel in the complete hot-fusion reaction $^{26}\text{Mg}+^{248}\text{Cm}$ leading to the new superheavy nuclide ^{271}Hs* . Physical Review Letters, 2008. **100**(13): p. 132503/1-132503/4.
38. Oganessian, Yu.Ts., et al., *Measurements of cross sections and decay properties of the isotopes of elements 112, 114, and 116 produced in the fusion reactions $^{233,238}\text{U}$, ^{242}Pu , and $^{248}\text{Cm} + ^{48}\text{Ca}$* . Physical Review C: Nuclear Physics, 2004. **70**(6): p. 064609/1-064609/14.
39. Oganessian, Yu.Ts., et al., *Synthesis of superheavy nuclei in the $^{48}\text{Ca} + ^{244}\text{Pu}$ reaction*. Physical Review Letters, 1999. **83**(16): p. 3154-3157.
40. Düllmann, Ch.E., et al., *Chemical investigation of hassium (element 108)*. Nature (London, United Kingdom), 2002. **418**(6900): p. 859-862.
41. von Zweidorf, A., et al., *Evidence for the formation of sodium hassate(VIII)*. Radiochimica Acta, 2004. **92**(12): p. 855-861.
42. Liu, Z.H. and J.-D. Bao, *Q-value effects on the production of superheavy nuclei*. Physical Review C: Nuclear Physics, 2006. **74**(5): p. 057602/1-057602/4.
43. Graeger, R., et al., *Cross section limits for the $^{238}\text{U}(^{36}\text{S}, xn)^{274-x}\text{Hs}$ reactions*. To be published.
44. Desclaux, J.P., *Relativistic Dirac-Fock expectation values for atoms with atomic numbers $Z = 1-120$* . Atomic Data and Nuclear Data Tables, 1973. **12**(4): p. 311-406.
45. Schwerdtfeger, P. and M. Seth, *Relativistic effects of the superheavy elements*, in *Encyclopedia of computational chemistry*. 1998, Wiley: New York. p. 2480-2499.
46. Rard, J.A., *Chemistry and thermodynamics of ruthenium and some of its inorganic compounds and aqueous species*. Chemical Reviews (Washington, DC, United States), 1985. **85**(1): p. 1-39.
47. Zvara, I., *Thermochromatographic Method of Separation of Chemical Elements in Nuclear and Radiochemistry* Isotopes in Environmental and Health Studies, 1990. **26**(6): p. 251-258.
48. Pershina, V., J. Anton, and T. Jacob, *Fully relativistic density-functional-theory calculations of the electronic structures of MO_4 ($M = \text{Ru}$, Os , and element 108, Hs) and prediction of physisorption*. Physical Review A: Atomic, Molecular, and Optical Physics, 2008. **78**(3): p. 032518.

54 References

49. Yost, D.M. and R.J. White, *The acid-forming properties of osmium tetroxide*. Journal of the American Chemical Society, 1928. **50**: p. 81-84.
50. Sauerbrunn, R.D. and E.B. Sandell, *Ionization constants of osmic(VIII) acid*. Journal of the American Chemical Society, 1953. **75**: p. 4170-4172.
51. Bavay, J.C., G. Nowogrocki, and G. Tridot, *Acidity of aqueous solutions of osmium tetroxide, OsO₄. Determination of the constants of various acid-base couples*. Bulletin de la Societe Chimique de France, 1967(6): p. 2026-2030.
52. Lee, D.A., *Extraction of osmium tetroxide and evidence for anionic osmium(VIII) species*. Journal of Inorganic and Nuclear Chemistry, 1972. **34**(1): p. 375-378.
53. Leipoldt, J.G., et al., *A kinetic study of the osmium(VIII) catalyzed oxidation of tellurium(IV) by octacyanomolybdate(V) and octacyanotungstate(V) ions in an alkaline medium*. Inorganica Chimica Acta, 1979. **34**(2): p. 237-240.
54. Galbács, Z.M., A. Zsednai, and L.J. Csanyi, *The acidic behavior of osmium(VIII) and osmium(VI)*. Transition Metal Chemistry (Dordrecht, Netherlands), 1983. **8**(6): p. 328-32.
55. Sidgwick, N.V., *The Chemical Elements and Their Compounds. Vols. I and II*. 1950. 1703 pp.
56. Krauss, F. and D. Wilken, *Osmium tetroxide. II. Compounds of osmium tetroxide*. Zeitschrift fuer Anorganische und Allgemeine Chemie, 1925. **145**: p. 151-167.
57. Nevskii, N.N., et al., *Crystal structure of a new lithium hydroxoosmate(VIII) (Li₂[OsO₄(OH)₂])*. Doklady Akademii Nauk SSSR, 1982. **266**(3): p. 628-630 [Crystallogr].
58. Nevskii, N.N., et al., *Crystal structure of sodium tetraoxodihydroxoosmate (VIII) (Na₂[OsO₄(OH)₂].2H₂O)*. Doklady Akademii Nauk SSSR, 1982. **266**(5): p. 1138-1141 [Crystallogr].
59. Ivanov-Emin, B.N., et al., *Synthesis and study of alkaline earth metal tetraoxodihydroxoosmates(VIII)*. Zhurnal Neorganicheskoi Khimii, 1984. **29**(5): p. 1241-1244.
60. Pershina, V., *Theoretical investigations of the reactivity of MO₄ and the electronic structure of Na₂[MO₄(OH)₂], where M = Ru, Os, and Hs (element 108)*. Radiochimica Acta, 2005. **93**(7): p. 373-376.
61. Rydberg, J., et al., *Principles and Practices of Solvent Extraction*. 1992, New York, USA: Marcel Dekker. 584 pp.
62. Aronsson, P.O., et al., *SISAK [Short-lived Isotopes Studied by the AKufve technique]. New technique for rapid, continuous radiochemical separations*. Journal of Inorganic and Nuclear Chemistry 1974. **36**(11): p. 2397-2403.
63. McDowell, W.J. and B.L. McDowell, *Liquid scintillation alpha spectrometry*. 1994. 192.
64. Wierczinski, B., et al., *First chemical on-line separation and detection of a subsecond α -decaying nuclide, ²²⁴Pa*. Journal of Radioanalytical and Nuclear Chemistry, 2001. **247**(1): p. 57-60.
65. Fure, K., *SISAK ekstraksjonskjemi for grunnstoff 107, bohrium*, in *Department of Chemistry*. 1998, University of Oslo: Oslo.
66. Johansson, M., *Radiochemical separation systems adopted for studying transactinide chemistry with SISAK*, in *Department of Chemistry*. 2000, University of Oslo: Oslo.

67. Stavsetra, L., et al., *Liquid - scintillation detection of preprepared ^{257}Rf with the SISAK system*. Nuclear Instruments & Methods in Physics Research, Section A: Accelerators, Spectrometers, Detectors, and Associated Equipment, 2005. **543**(2-3): p. 509-516.
68. Persson, H., et al., *SISAK 3 - an improved system for rapid radiochemical separations by solvent extraction*. Radiochimica Acta, 1989. **48**(3-4): p. 177-180.
69. Wierczinski, B., et al., *A liquid scintillation detector for online alpha -particle and spontaneous fission measurements*. 1994, Inst. Kernchem., Univ. Mainz, Germany. p. 240.
70. Stavsetra, L., *Achievements using the countinuous SISAK α -liquid scintillation technique, and its application in detection of ^{257}Rf atoms*, in *Department of Chemistry*. 2005, University of Oslo: Oslo.
71. Wiehl, N., et al., *Weiterentwicklung des Detektionssystems zur on-line Flüssigszintillations-Spektroskopie*. Jahresbericht, Universität Mainz, 1996.
72. Firestone, R.B., *Nuclear data sheets update for $A = 181$* . Nucl. Data Sheets, 1991. **62**(1): p. 101-57.
73. Skarnemark, G., et al., *Rapid continuous separation procedures for arsenic and ruthenium from complex reaction product mixtures*. Radiochim. Acta 1983. **33**(2-3): p. 97-100.
74. Schädel, M., *Chemistry of superheavy elements*. Angewandte Chemie, International Edition, 2006. **45**(3): p. 368-401.
75. Schädel, M., *Superheavy element chemistry at GSI - status and perspectives*. European Physical Journal D: Atomic, Molecular, Optical and Plasma Physics, 2007. **45**(1): p. 67-74.
76. Semchenkov, A., et al., *The TransActinide Separator and Chemistry Apparatus (TASCA) at GSI - Optimization of ion-optical structures and magnet designs*. Nuclear Instruments & Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms, 2008. **266**(19-20): p. 4153-4161.
77. Even, J., et al., *The Recoil Transfer Chamber - A new interface to connect the physical preseparator TASCA with chemistry setups*. To be published.
78. Kibedi, T., et al., *New features in the systematics of low-spin states in $^{170-178}\text{W}$* . Acta Physica Hungarica New Series: Heavy Ion Physics, 1998. **7**(1): p. 87-96.
79. *Solvent extraction principles and practice (2nd edition) edited by J. Rydberg, M. Cox, C. Musikas and G. Choppin*. Chemistry & Industry (London, United Kingdom). 2005.
80. Martin, F.S., *Distribution of RuO_4 between carbon tetrachloride and aqueous alkali, acid, and neutral salt solutions*. Journal of the Chemical Society, 1954: p. 2564-2570.
81. Krebs, B. and K.D. Hasse, *Refinements of the crystal structures of potassium pertechnetate, potassium perrhenate, and osmium tetroxide. The bond lengths in tetrahedral oxo-anions and oxides of d0 transition metals*. Acta Crystallographica, Section B: Structural Crystallography and Crystal Chemistry, 1976. **B32**(5): p. 1334-1337.
82. Ekberg, C. and G. Skarnemark, *Uncertainty evaluation for one-atom-at-a-time studies of transactinides*. Journal of Radioanalytical and Nuclear Chemistry, 2005. **263**(1): p. 71-74.

56 References

83. Dvorak, J., *Decay properties of nuclei close to $Z=108$ and $N=162$* . Thesis: Technische Universität München, 2007.
84. Skarnemark, G., et al., *An improved system for fast, continuous chemical separations ("SISAK 2") in nuclear spectroscopic studies*. Nuclear Instruments & Methods, 1980. **171**(2): p. 323-328.
85. Persson, H., et al., *SISAK 3 - an improved system for rapid radiochemical separations by solvent extraction*. Radiochimica Acta, 1989. **48**(3-4): p. 177-80.
86. Eberhardt, K., et al., *MicroSISAK: A device for fast and continuous liquid-liquid-extractions on a micro l-scale*. Abstracts of Papers, 233rd ACS National Meeting, Chicago, IL, United States, March 25-29, 2007, 2007: p. NUCL-130.
87. Omtvedt, J.P., et al., *SISAK Liquid-Liquid Extraction Experiments with Preseparated ^{257}Rf* . Journal of Nuclear and Radiochemical Sciences, 2002. **3**(1): p. 121-124.
88. Somerville, L.P., et al., *Spontaneous fission of rutherfordium isotopes*. Physical Review C: Nuclear Physics, 1985. **31**(5): p. 1801-1815.
89. Lane, M.R., et al., *Spontaneous fission properties of ^{262}Rf* . Physical Review C: Nuclear Physics, 1996. **53**(6): p. 2893-2899.
90. Düllmann, Ch.E. and A. Türler, *$^{248}\text{Cm}(^{22}\text{Ne}, xn)^{270-x}\text{Sg}$ reaction and the decay properties of ^{265}Sg reexamined*. Physical Review C: Nuclear Physics, 2008. **77**(6): p. 064320/1-064320/10.
91. Kirbach, U.W., et al., *The Cryo-Thermochromatographic Separator (CTS): A new rapid separation and alpha -detection system for on-line chemical studies of highly volatile osmium and hassium ($Z=108$) tetroxides*. Nuclear Instruments & Methods in Physics Research, Section A: Accelerators, Spectrometers, Detectors, and Associated Equipment, 2002. **484**(1-3): p. 587-594.
92. Düllmann, Ch.E., et al., *IVO, a device for In situ Volatilization and On-line detection of products from heavy ion reactions*. Nuclear Instruments & Methods in Physics Research, Section A: Accelerators, Spectrometers, Detectors, and Associated Equipment, 2002. **479**(2-3): p. 631-639.

Appendix I: List of abbreviations

AKUFVE: (Swedish acronym) “Anordning för Kontinuerlig Undersökning av Fördelingsjämvikter vid Vätske Extraktion” meaning: “arrangement for continuous investigation of distribution ratios in liquid-liquid extraction”

ARCA: Automated Rapid Chemistry Apparatus

ARTESIA: A Rotating Target wheel for Experiments with Superheavy-element Isotopes at GSI using Actinides as target material

BGS: Berkeley Gas-filled Separator

COMPACT: Cryo On-line Multidetector for Physics And Chemistry of Transactinides

Dimethyl-POPOP: 1,4-Di-2-(4-methyl-5-phenyloxazolyl)-benzene, C₂₆H₂₀N₂O₂

DGFRS: Dubna Gas-Filled Recoil Separator

EVR: Evaporation Residues

FLNR: Flerov Laboratory of Nuclear Reactions

GSI: GSI Helmholtzzentrum für Schwerionenforschung GmbH

HPGe detector: High Purity Germanium detector

IUPAC: International Union of Pure and Appplied Chemistry

LED: Light Emitting Diode

LDM: Liquid Drop Model

OCL: Oslo Cyclotron Laboratory

PEEK: PolyEtherEtherketone

PFA: PerFluoro-Alkoxyalkane

PSD: Pulse-Shape Discrimination

ROMA: Rotating wheel On-line Multidetector Analyzer

RTC: Recoil-product Transfer Chamber

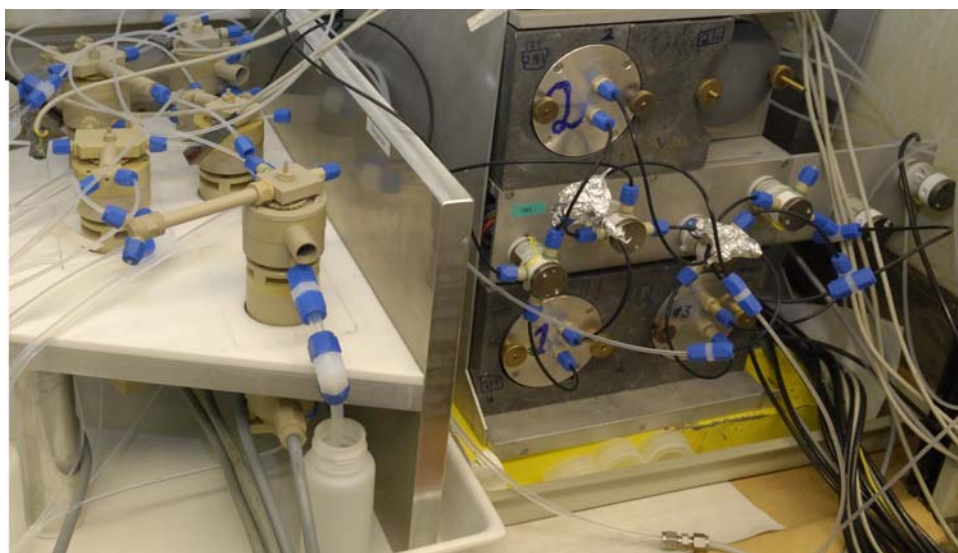
SHE: SuperHeavy Element

SISAK: Short-lived Isotope Studied by the AKufve technique

TASCA: TransActinide Separator and Chemistry Apparatus

TOA: Tri-n-octylamine, (C₈H₁₇)₃N

Appendix II: Picture of instruments



SISAK centrifuges and detection cells.



SIM RTC constructed at the University of Oslo

Chemical properties of the transactinide elements studied in liquid phase with SISAK

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Received 25 September 2006 / Received in final form 5 April 2007

Published online 27 June 2007 – © EDP Sciences, Società Italiana di Fisica, Springer-Verlag 2007

Abstract. This article starts with a review of the current SISAK liquid-liquid extraction system, as used after the physical preseparator BGS at LBNL for chemical studies of transactinide elements. Emphasis will be on new additions and developments. Then the possibilities offered by the new TASCA separator at GSI and the use of actinide targets at both GSI and LBNL are discussed with respect to future SISAK transactinide experiments. Finally, current and future liquid-liquid extraction systems for studying elements Rf up to Hs are discussed.

PACS. 23.60.+e Alpha decay – 27.90.+b $220 \leq A < 294$.0 Mc Scintillation detectors

1 Introduction

The on-line liquid-liquid extraction system SISAK¹ has been adapted for studies of the chemical properties of the transactinide elements. SISAK [1,2] 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 and is one of the fastest systems available for liquid-phase studies of transactinide elements. For transactinide experiments, liquid scintillation (LS) [3,4] is used to detect their nuclear decay. The LS detectors have high detection efficiency, but limited energy resolution. Therefore, transactinide

experiments with SISAK are performed with a physical preseparator between the target and SISAK to suppress unwanted reaction products. Until now, the Berkeley Gas-filled Separator (BGS) at Lawrence Berkeley National Laboratory (LBNL) has been used, see Stavsetra et al. [5, 6]. Recently, a new separator, named TransActinide Separator and Chemistry Apparatus (TASCA) [7], at the Gesellschaft für Schwerionenforschung (GSI) in Darmstadt, entered the commissioning phase. Thus it will soon be possible to also perform SISAK experiments at this facility.

2 Status of the SISAK system

2.1 Double detector setup

To achieve a sufficient energy resolution in the LS detectors, only the LS occurring in the organic phase can be measured. The aqueous phase cannot be measured due to severe quenching of the LS process. For the same reason, only carefully selected organic solvents and solutes can be used [3,6]. Liquid-liquid distribution ratios of the element under study between the two phases could therefore only be determined indirectly. The amount in the aqueous phase had to be deduced from the measured activity that

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¹ SISAK = Short-lived Isotopes Studied by the AKUFVE-technique, where AKUFVE is a Swedish acronym for an arrangement for continuous investigations of distribution ratios in liquid-liquid extraction.

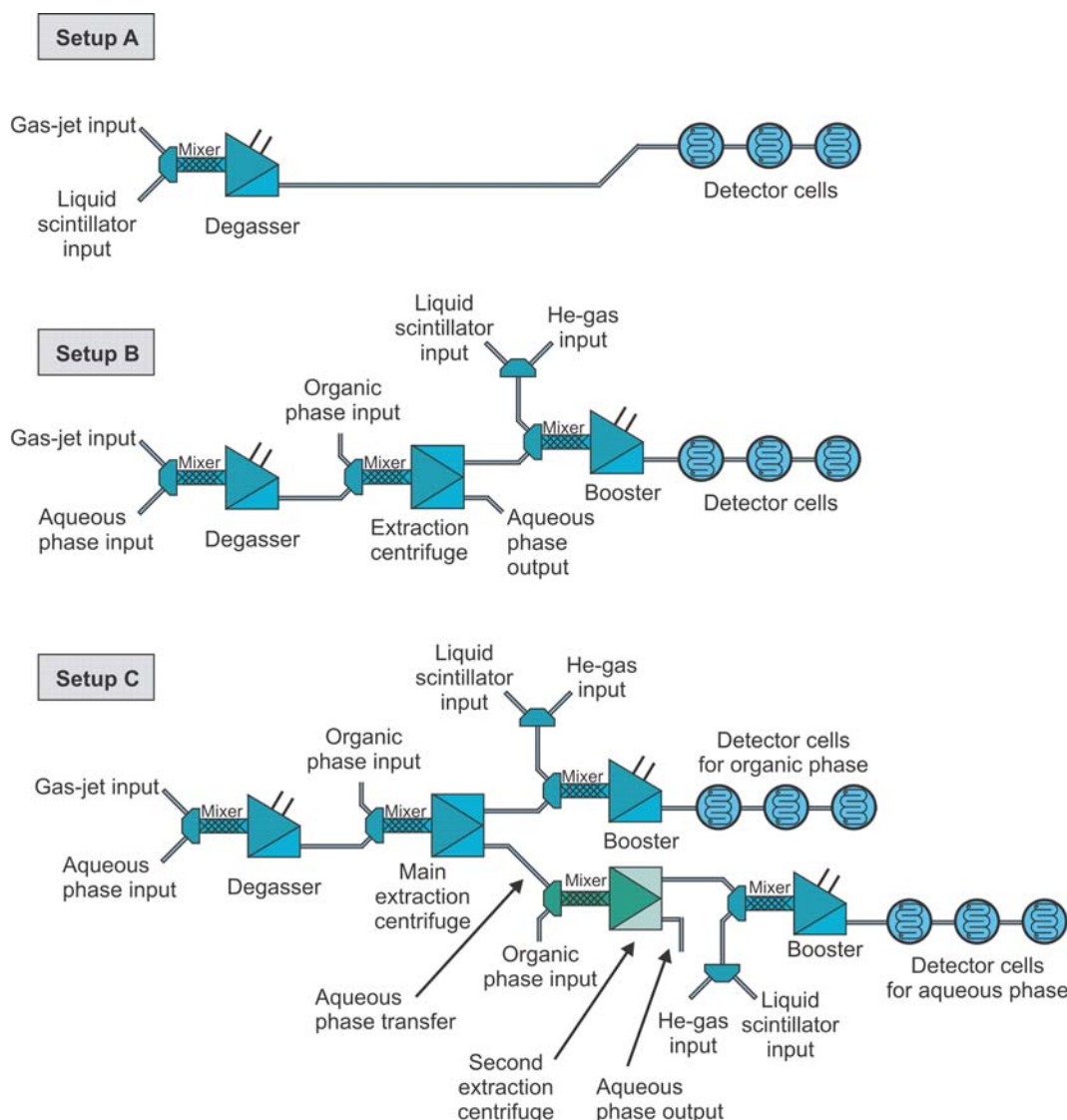


Fig. 1. (Color online) Schematic drawings of SISAK setups used in investigations of transactinide elements. Setup A is used to measure the amount of activity entering the system. The gas-jet carried activity is dissolved directly in a liquid scintillator cocktail and measured. No chemical separation is performed. Setup B is used to measure the amount of activity in the organic phase after liquid-liquid extraction. The amount of activity in the aqueous phase is not measured but must be deduced from a separate experiment with setup A. Setup C enables the measurement of activity in both phases using a second extraction step and a second array of liquid-scintillator detectors.

entered the extraction centrifuge and the amount in the organic output phase. Since these two measurements cannot be done simultaneously, the experiment takes twice as much time and is susceptible to variations in the gas-jet transfer yield between the two measurements. In order to overcome this disadvantage, the SISAK system was recently extended to include a second extraction step in which part or all of the activity remaining in the aqueous phase after the first extraction stage is transferred to a second organic phase [8]. This way the amount of radionuclides in the two phases exiting the first extraction stage can be measured simultaneously, allowing direct determination of the distribution ratio. See Figure 1 for a schematic drawing of the different setups which have been used for investigations of transactinide elements with

SISAK. The relationship between the distribution ratio in the first extraction stage and the amount of activity in the first and second organic phase is explained in [8].

The new system with a second extraction stage to transfer the activity in the aqueous phase from the first stage into a second organic phase, was used for the first time in an rutherfordium experiment at LBNL in April 2005 [9]. See Section 3.1 for further discussion of this experiment.

2.2 Preseparator limitations

So far, only heavy-ion induced cold-fusion reactions with targets of ^{208}Pb and ^{209}Bi have been possible at LBNL if the BGS is used as a preseparator for chemistry

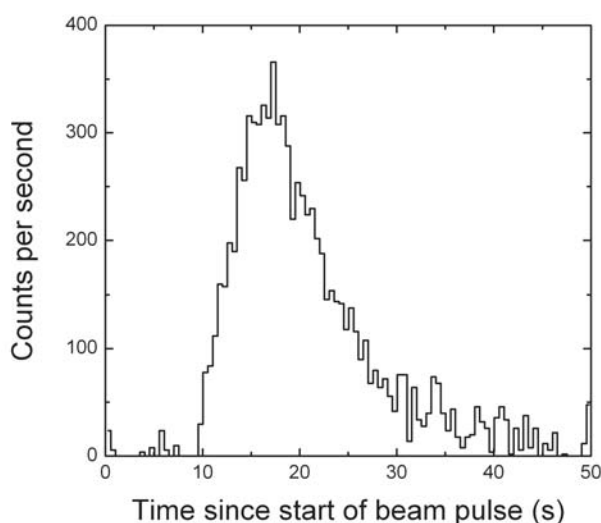


Fig. 2. Measured transport time from target to the first detector through a SISAK setup with one extraction stage. The flow rate was 0.8 mL/s. The average hold-up time is about 18.5 s.

experiments. This is mainly due to the required momentum of the evaporation residues (EVR), as explained below. The only transactinide elements available for liquid-phase chemistry studies after physical pre separation were Rf and Db by using 4.7-s ^{257}Rf and 4.4-s ^{258}Db . Other transactinide nuclei available from cold fusion reactions do not have long enough half lives for chemistry studies with SISAK. The ^{257}Rf and ^{258}Db nuclei have much shorter half lives compared to the more commonly used 78-s ^{261}Rf and 34-s and 27-s $^{262,263}\text{Db}$ nuclei produced in hot-fusion reactions. Hot fusion reaction products cannot be used in the current pre separation setups due to the low momentum of the evaporation residues (EVR) produced in the asymmetric reactions with beams of e.g. ^{18}O or ^{22}Ne . This is because the EVRs will not be able to pass through the vacuum window separating the low-pressure (~ 1 mBar) environment of the separator and into the high-pressure (1.5–2.2 Bar) gas-jet recoil transfer chamber (RTC). Alternative reactions suitable for pre separators are being sought, see Section 3 below.

The restrictions to 4–5 s nuclei impose very stringent limits on the transport time that the EVRs need to travel from the RTC to the detectors. Figure 2 shows a transport-time measurement made in an experiment with a setup equal to setup B in Figure 1 [10]. The transport time was measured by using $^{164-166}\text{Hf}$ activity produced in a $^{120}\text{Sn}(^{50}\text{Ti}, xn)^{170-x}\text{Hf}$ reaction with a pulsed beam (3 s on and 87 s off). The $^{164-166}\text{Hf}$ nuclei have half lives equal to 114 s, 76 s, and 6.8 m, respectively. The Hf activity carried with the gas-jet was dissolved in a liquid scintillation solution in the degasser stage and pumped through the remaining apparatus and detection cells. The scintillation solution was pumped in a closed loop at 0.8 mL/s and changed when needed. Using the data shown in Figure 2 and a Monte-Carlo simulation, the number of ^{257}Rf atoms surviving long enough to be detected in cell 1 was

estimated. For this estimation a 50% gas-jet, 67% gas to liquid transfer, and 80% extraction yield were used. This simulation showed that only 7 out 1000 ^{257}Rf nuclei reached the detector [11].

One bottleneck is the liquid transport through the chemistry apparatus (SISAK). Thus, a method was developed to enable rapid and precise measurements of the transport time through the SISAK system without the use of pulsed beams or radioactive tracers. In this way flow-through time measurements can be done easily and quickly in connection with tests and developments to reduce the transit time. This system uses coloured solutions and light transmittance transducers (LTT) to detect the presence of the coloured solution [10]. A schematic drawing of the setup for measuring the transport time through the degasser is shown in Figure 3. An example of the use of such measurements is given in Figure 4. Here, the hold-up time of different lengths of mixers for flow rates of 0.4 mL/s and 0.8 mL/s is shown. The results clearly show the difference in flow-through time for the two flow rates measured. Further measurements show that the average transport-time for a centrifuge with an attached mixer at the inlet is 2.5 ± 0.2 s at typical flow-rates for transactinide experiments (0.4–0.5 mL/s of each liquid phase). The same transport time was measured for a degasser unit, including the gas/liquid phase mixer. This implies that each stage in a SISAK setup adds about 2.5 s to the overall hold-up time. Taking into account the tubing and connectors coupling the whole system together, it can be estimated that the average hold-up time for setup B and the first extraction stage in setup C in Figure 1 is about 10 s. From Figure 2 it can then be deduced that about 55% of the hold-up time is due to the SISAK apparatus and about 45% due to the RTC and gas-jet transfer.

3 Target and RTC development

Work to develop thinner vacuum windows between the separator and the gas-jet transfer chamber is currently in progress both at LBNL and GSI [12]. This, in combination with the use of actinide targets like U or Pu, will allow the production of a broader range of nuclei since the recoil energy of these hot fusion reaction products will be high enough to pass through such an improved window. Therefore, in the future it will be possible to perform SISAK experiments with elements heavier than rutherfordium.

3.1 New possibilities with Pu targets

Work is in progress at the BGS at LBNL and at TASCA at GSI to enable the use of Pu targets with the separators. This has previously not been possible at the BGS due to concerns regarding safety and maintaining a low-level detection environment. At GSI, the TASCA separator is being designed from the start with such targets in mind. Thus, a wider range of reactions will soon become

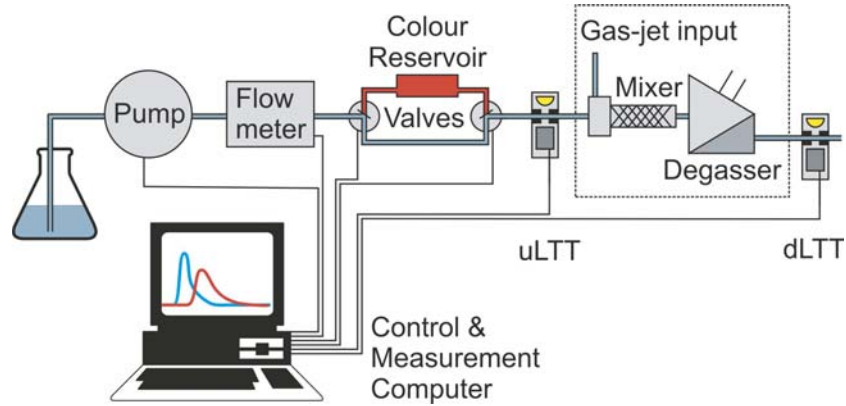


Fig. 3. (Color online) Setup for measuring the flow-through time using a coloured solution and detection by light transmittance transducers (LTT). The flow-through time is measured for the equipment placed within the dashed square. Different parts or sections of the SISAK setup can be selected for flow-through time measurement. uLTT and dLTT indicate upstream and downstream LTT, respectively.

Table 1. Likely reactions with ^{244}Pu targets for producing suitable isotopes for SISAK experiments on the transactinide elements Rf to Hs. The EVR recoil energy and the corresponding range in the mylar RTC window is shown for each reaction. For comparison, the reaction between ^{50}Ti and ^{208}Pb to produce ^{257}Rf is included. The decay loss is calculated on the assumption that the average transport time is 18.5 s, as the measurement shown in Figure 2 indicates. The relative yields in the last column are based on the decay loss column.

Reaction	Product $T_{1/2}$ (s)	EVR recoil energy (MeV)	Range in mylar (μm)	Decay loss in SISAK	Relative yield
$^{244}\text{Pu}(^{22}\text{Ne}, 5n)^{261}\text{Rf}$	78	9.5	1.7	15%	12
$^{244}\text{Pu}(^{23}\text{Na}, 5n)^{262}\text{Db}$	33	10.8	1.9	32%	9.7
$^{244}\text{Pu}(^{26}\text{Mg}, 5n)^{265}\text{Sg}$	7	13.5	2.4	84%	2.3
$^{244}\text{Pu}(^{27}\text{Al}, 4n)^{267}\text{Bh}$	15	14.4	2.6	57%	6.1
$^{244}\text{Pu}(^{30}\text{Si}, 5n)^{269}\text{Hs}$	14	18.1	2.9	60%	7.7
$^{208}\text{Pb}(^{50}\text{Ti}, 1n)^{257}\text{Rf}$	4.7	45.5	6	93%	1

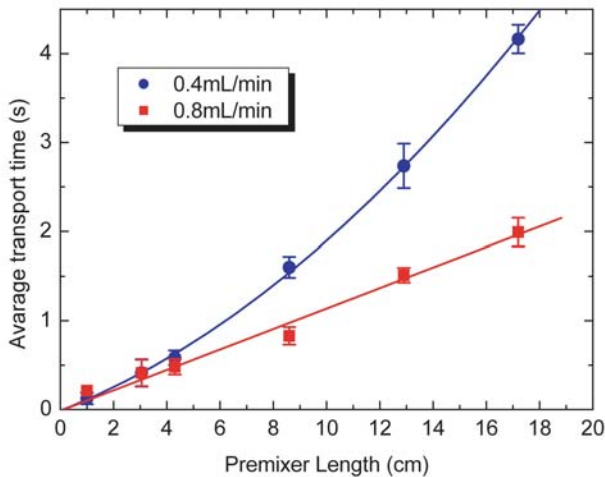


Fig. 4. (Color online) Hold-up time in mixers of different lengths for flow rates 0.4 mL/s and 0.8 mL/s measured by using coloured solutions and light transmittance transducers as explained in the text.

available for chemistry experiments behind physical separators. Some of the most relevant reactions for producing the elements from Rf through Hs are listed in Table 1.

It can be clearly seen from the table that the EVR recoil energy and corresponding range in the mylar foil used for the RTC window is much smaller than for the ^{50}Ti on ^{208}Pb reaction used so far. However, if thin enough windows can be constructed (see Sect. 3.2 below), much longer-lived isotopes become available. Considering the large decay-loss during the transport encountered in ^{257}Rf experiments, the smaller cross-sections for the indicated reactions will to a certain extent be compensated by the reduced transport-time loss, as indicated in the column for relative yield in the table. The gains will be particularly important for elements Rf and Db, which also are produced with the largest cross sections.

3.2 Small-volume RTC

The measurement of the average transport time encountered in SISAK experiments at LBNL indicate that the transport time from the RTC to SISAK is about 8–9 s. A 20-m long capillary with 1.56 mm i.d. is used to transport the EVRs attached to KCl aerosol particles with He gas flowing at 1.2 L/min. Most of the delay is due to the large volume of the BGS RTC chamber, which is necessary due to the large image size in the BGS focal

plane (140 mm $\times$ 57 mm). The RTC depth is 40 mm, thus the chamber volume is 320 mL. Necessarily, it takes more time to flush the EVRs out of such a large chamber than it would take to flush out a small chamber. With this in mind, the TASCA separator can be operated in two modes, small-image and high-transmission mode [13]. The high-transmission mode has, as the name implies, maximum transmission through the separator. The penalty is a relatively large focal-plane image of 140 mm $\times$ 40 mm. The small-image mode focuses the EVRs into a much smaller focal plane image of only 30 mm $\times$ 40 mm. Simulations [14, 15] done for ^{261}Rf EVRs produced in the ^{22}Ne on ^{244}Pu reaction indicate that the transmission in the small-image mode is 40% less than the high-transmission mode. Thus, for short-lived nuclei, the advantage of a shorter average transport-time out of a small-volume RTC will most likely out-weigh the disadvantage of the transmission loss in the separator. Furthermore, it seems reasonable to assume that the yield of a small RTC will be higher than for a large RTC, since the EVRs will spend less time in the chamber and thus be less likely to be adsorbed on the walls, etc. Two RTCs, one for each operating mode of TASCA, are being constructed and tests to investigate yields and transport times will be performed in the near future.

A new RTC-window design is being developed for TASCA [12] which will make it possible to use much thinner windows than what have been used at the BGS so far. A similar window construction should also be possible for the BGS. Thus, chemistry studies with EVRs from Pu-targets should be possible at both separators.

4 Transactinide elements available for SISAK

In Oslo, at the Centre for Accelerator Based Research and Energy Physics (SAFE), work has been undertaken to develop suitable extraction systems for the study of dubnium, seaborgium and hassium. This work is in preparation for the new possibilities emerging from the addition of using Pu targets with the BGS at LBNL and TASCA at GSI, as outlined above in Section 3.1. A brief description of the systems developed or being developed is given below.

4.1 Rutherfordium

A system to distinguish between Zr- and Hf-like behaviour was developed by Polakova et al. [16]. The group-4 elements are extracted with tri-octylamine from sulphuric acid solution into toluene. Two Rf experiments have been performed at LBNL with this system, one in 2003 and one in 2005. It was shown that Rf extracts to a lesser extent than Zr, and probably also slightly less than Hf. Preliminary extraction curves are shown in Figure 5. Full results and details can be found in [8, 9, 16]. The results are in accordance with recent theoretical calculations, which predict the extraction sequence $\text{Zr} > \text{Hf} > \text{Rf}$ [17] under the given conditions.

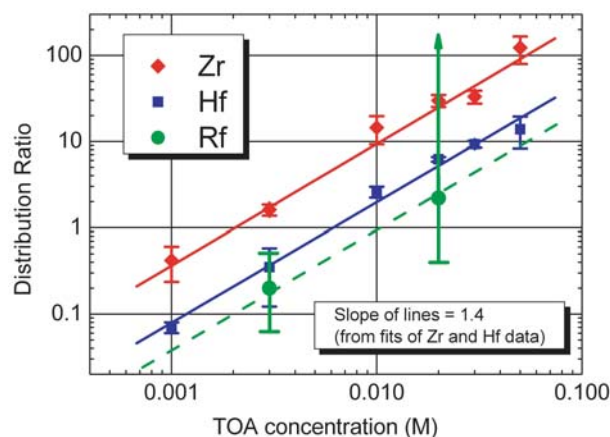


Fig. 5. (Color online) Extraction of group-4 elements from sulphuric acid using tri-octylamine in toluene with SISAK.

4.2 Dubnium

After Rf, Db is the transactinide element which can be made with the highest production rates. If Pu-targets can be used with the pre-separators, then the comparatively long half-life of ^{262}Db also enhances the experimental conditions for such experiments. Zheng et al. are working on developing an extraction system which clearly distinguishes between Nb and Ta behaviour. The system is based upon extraction from sulphate solutions, in a similar way as Rf is extracted. A suitable system is expected to be ready in 2008 [18].

4.3 Seaborgium

Early work on adopting SISAK for the study of transactinide chemistry included the development of several separation systems for Sg [19–22]. These systems were not designed with pre-separated reaction products in mind, as currently being used by the SISAK system, but focused on very high selectivity for group-6 elements with respect to all other elements. Today, when the input contains very little by-products, the focus is shifted toward constructing a system which yields as much chemical information as possible. One approach is to seek a liquid-liquid separation system which clearly distinguishes between the extraction, and thus e.g. complexation or redox properties, of the studied element's homologues. This approach is currently being followed by the SISAK Oslo group in a research project performed by Schultz and Opel. The aim is to develop a new separation system for the study of seaborgium, based on the experience gained in from the previous Sg separation systems and from the Rf experiments mentioned in Section 4.1. A suitable separation system is expected to be ready when pre-separated Sg will become available from the TASCA and BGS separators (within 2–3 years).

4.4 Bohrium

As for the case of Sg, several separation systems were developed for Bh [23,24]. None of these systems were ever tried in Bh experiments, but extensive test with homologues were carried out. Currently, no work to develop a system that takes advantage of pre-separated activity is performed. No such project is planned until results from experiments with Db and Sg are available.

4.5 Hassium

Due to the high volatility of the Hs tetroxide, it appears possible to perform experiments with Hs with low enough background without using pre-separated isotopes. This has been demonstrated in several gas-phase Hs-experiments, pioneered by Düllmann et al. [25]. In such experiments an aerosol-free gas-jet is used. Hence, only volatile compounds are transported to the chemistry apparatus and a high suppression of all non-volatile elements and/or compounds is achieved. Samadani [26] has developed a SISAK system which explores the properties of HsO_4 and can be used to study the formation of $[\text{HsO}_4(\text{OH})]^-$ and $[\text{HsO}_4(\text{OH})_2]^{2-}$ in aqueous solutions at pH in the range 11–13 (0.001 M to 0.1 M NaOH solutions). Model experiments using on-line Os-activity and 10% O_2 addition to the He gas-jet, fit well to the relationship between the distribution ratio D and the equilibrium constants K' and K'' defined in Figure 6. The relationship, as explained in [26] is:

$$D = \frac{K_D}{1 + K'[\text{OH}^-] + K'K''[\text{OH}^-]^2}$$

where K_D is the distribution constant for OsO_4 (not to be confused with D , the distribution ratio D of *all* Os species). The experimental data is shown in Figure 7. If Hs behaves similarly to Os in this system, it should be possible to prove this by measuring distribution values in the range between 0.1–10.

5 Conclusions

The SISAK collaboration has performed a number of successful Rf experiments through the last years. At the same time the collaboration has pioneered the use of pre-separators for transactinide chemistry experiments and enhanced the SISAK liquid-liquid extraction system and liquid-scintillation α -detectors. The experience gained during these experiments, the new TASCA separator, the use of Pu targets, and thinner RTC windows indicate that heavier elements than Rf are within reach of the SISAK system in the near future.

Financial support from the Norwegian Research Council (Project Nr. 148994/V30 and 166744/V30/ntm) is gratefully acknowledged. We thank the LBNL 88-Inch Cyclotron and ion-source operators for providing stable and high-intensity beams,

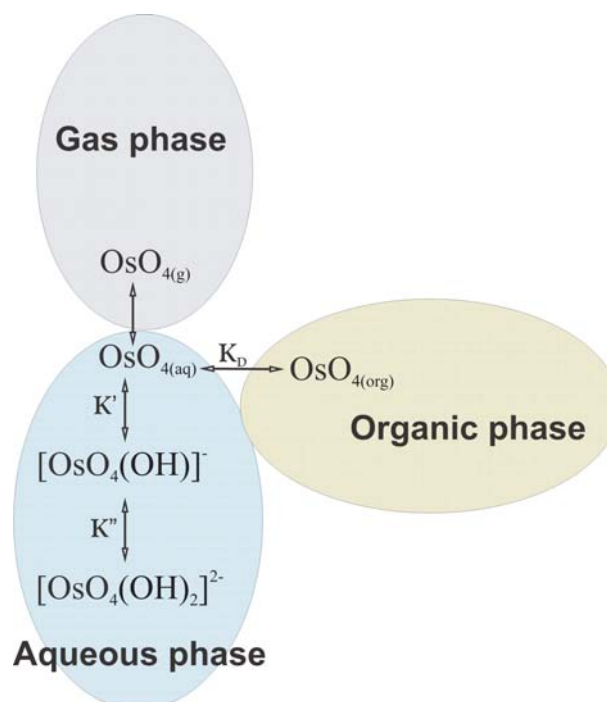


Fig. 6. A schematic drawing of the reactions that take place in the SISAK system during liquid-liquid extraction of OsO_4 .

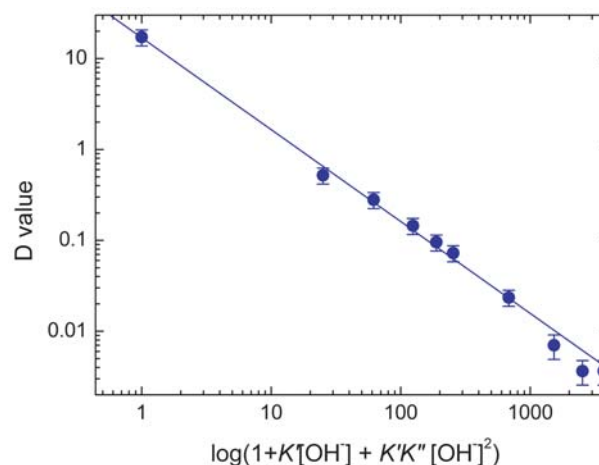


Fig. 7. Distribution ratio, D , vs. $1 + K'[\text{OH}^-] + K'K''[\text{OH}^-]^2$ measured for on-line SISAK extraction of OsO_4 into toluene from NaOH solutions up to 0.1 M in concentration. The ionic strength was kept approximately constant by keeping all solutions 1 M in NaCl.

Eivind A. Olsen at the OCL for operating the Oslo cyclotron and all help, and we thank technicians Suthajini Yagarajah, Fredrik B. Lunde and Joachim Hallgren for excellent help in the chemistry labs. Alexander Yakushev and Andrey Semchenkov communicated advances and results prior to publication.

References

1. J.P. Omtvedt et al., J. Alloy Comp. **271**, 303 (1998)
2. H. Persson et al., Radiochim Acta **48**, 177 (1989)

3. L. Stavsetra, J.P. Omtvedt, *Detection of Transactinides with Alpha-Liquid Scintillation*, in proceedings from *International Conference on Advances in Liquid Scintillation Spectrometry*, edited by J.N.S. Möbius, F. Schönhofer, *Radiocarbon* (University of Arizona, Tucson, Arizona, USA, 2001), p. 25
4. B. Wierczinski et al., *Nucl. Instrum. Meth. A* **370**, 532 (1996)
5. K.E. Gregorich et al., *Phys. Rev. C* **72** (2005)
6. L. Stavsetra et al., *Nucl. Instrum. Meth. A* **543**, 509 (2005)
7. M. Schädel, Homepage of the International Cooperation on Recoil Separators for Transactinide Chemistry and Physics, [http: www.gsi.de/tasca](http://www.gsi.de/tasca)
8. J.P. Omtvedt et al., *SISAK Liquid-Liquid Extraction Studies of Rutherfordium and Future Plans to Study Heavier Transactinides*, in proceedings from *The Eighth Actinide Conference (Actinides 2005)*, University of Manchester, UK, edited by I. May, R. Alvares, N. Bryan, The Royal Society of Chemistry, 2006
9. J.P. Omtvedt et al., *Study of Liquid-Liquid Extraction of Rutherfordium-Sulphate Complexes by the SISAK System*, Department of Chemistry, University of Oslo, 2006, in preparation
10. D. Poláková et al., *Measurement of Transport Times through the Continuous Liquid-Liquid Extraction System SISAK*, University of Oslo, 2006, in preparation
11. L. Stavsetra, Ph.D. thesis: *Achievements using the continuous SISAK alpha-liquid scintillation technique, and its application in detection of ^{257}Rf atoms*, Faculty of Mathematics and Natural Sciences, University of Oslo, 2005
12. A. Yakushev, *Development of new RTC windows for TASCA*, 2006, contribution to this conference
13. A. Semchenkov (2006), private communication
14. K.E. Gregorich et al., *Eur. Phys. J. A* **18**, 633 (2003)
15. A. Semchenkov (2006), private communication
16. D. Poláková et al., *Extraction by tri-octyl-amine of Zr and Hf from sulphuric acid as model for Rf experiments with SISAK*, Department of Chemistry, University of Oslo, 2006, in preparation
17. V. Pershina et al., *Radiochim. Acta* **94**, 407 (2006)
18. L. Zheng et al., *Radiochim. Acta* (to be published)
19. M. Johansson, Ph.D. thesis: *Radiochemical Separation Systems adapted for Studying Transactinide Chemistry with SISAK*, Faculty of Mathematics and Natural Sciences, University of Oslo, 2000
20. M. Johansson et al., *Radiochim. Acta* **91**, 351 (2003)
21. M. Johansson et al., *Radiochim. Acta* **89**, 619 (2001)
22. B. Wierczinski et al., *Radiochim. Acta* **69**, 77 (1995)
23. K. Fure, Masters degree thesis: *SISAK ekstraksjonskjemi for grunnstoff 107, bohrium*, Department of Chemistry, Faculty of Mathematics and Natural Sciences, University of Oslo, 1998
24. R. Malmbeck et al., *J. Radioanal. Nucl. Chem.* **246**, 349 (2000)
25. C.E. Dullmann et al., *Nature* **418**, 859 (2002)
26. F. Samadani, Master thesis: *Developing a SISAK Extraction System for Chemical Studies of Element 108, Hassium*, Department of Chemistry, Faculty of Mathematics and Natural Sciences, University of Oslo, 2006

Paper II

Development of a SISAK extraction system for chemical studies of element 108, hassium

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Received; accepted

Key words: transactinides, element 108, liquid-liquid extraction, super heavy elements, SISAK, one-atom-at-a-time chemistry, hassate (VIII).

Summary. A liquid-liquid extraction system suitable for studies of chemical properties of Hs (element 108), in the form of HsO_4 , was developed using γ -emitting isotopes of its homologue Os. The system is targeted for the fast on-line extraction system SISAK, which operates in a continuous manner and is suitable for liquid-phase studies of transactinide elements. The distribution of OsO_4 between various dilute NaOH solutions and toluene was studied. Both batch and SISAK on-line experiments were performed to develop an appropriate system. From analysis of the extraction curves equilibrium constants for the formation of the presumed complexes, $\text{Na}[\text{OsO}_4(\text{OH})]$ and $\text{Na}_2[\text{OsO}_4(\text{OH})_2]$, were obtained: $K_1 = (1 \pm 0.5) \times 10^4$ and $K_2 = 12 \pm 8$, respectively. The SISAK system includes a liquid-scintillation detection system for α measurements. Due to quenching effects it is not possible to perform direct measurement of the aqueous phase α 's. Therefore, a two-stage extraction method that provides an indirect measurement of the activity in the aqueous phase was developed as part of the proposed system for Hs: Acidification of the raffinate from the first stage result in recovery of OsO_4 , which is highly extractable into toluene. The yield of extraction in the second step, from 0.01 M NaOH solution after acidification with H_2SO_4 solution, was $(90 \pm 3) \%$.

1. Introduction

During the last several decades, chemical studies of transactinides, the man-made elements with $Z \geq 104$, has been of special interest [1]. They provide a good testing ground to highlight the influence of strong relativistic effects [2] on the chemical properties of elements in this heavy-mass region of the Periodic Table and provide important input for refinement and development of current state-of-the-art theoretical calculations [3] on chemical properties. Such

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investigations also provide the possibility for studying the chemical trends of elements in the high-Z part of the Periodic Table and suggesting the appropriate placement of new elements.

Transactinides are characterized by their short half-lives and therefore are not found in nature. They must be artificially produced using heavy-ion nuclear fusion reactions [4] but have very low reaction cross sections. This results in correspondingly low production rates. Even with the most intense particle beams available today combined with appropriate targets, the production versus disintegration rate is so low that their chemical properties can only be studied with "a single atom-at-a-time" approach; hence this subject is often referred to as "one-atom-at-a-time chemistry". In this case the classical rules of macro-amount chemistry and the definition of chemical equilibrium are not valid any more. Under special conditions and requirements, the equilibrium constants can be deduced from measurements of observation probabilities. Thus, special procedures and equipment are required to investigate the chemical behaviour of transactinide elements [5]. Liquid-liquid extraction (LLE) is one method which is suitable for such studies, provided the kinetics of the chemical reactions is fast enough. The SISAK (Short-lived Isotopes Studied by the AKufve†-technique) system [6, 7], equipped with a liquid-scintillation detection system, enabling on-line detection of α -particles, was adopted for performing such liquid-liquid extraction studies of transactinides [8, 9]. The liquid scintillation detection method is uniquely able to handle the rather high liquid flow-rates needed in the SISAK system and offers almost a 4π detection efficiency. The method was developed to be able to detect very low α -activity under the presence of β - and γ -background using Pulse-Shape Discrimination (PSD) to selectively differentiate α -particles from electrons and β - particles. It was subsequently successfully applied for chemical studies of the transactinide element 104, rutherfordium (Rf) with a detection rate of 1 atom per four hours [10, 11] which indicated that the SISAK system and its liquid scintillation detectors is sensitive enough to detect α -particles at very low rates.

The work presented here has developed a system to study chemical properties of element 108, hassium (Hs), using the SISAK system. Hs is placed in group 8 in the Periodic Table, below Os, on the basis of classical rules, its electronic configuration and later confirmation by the results from gas-phase chemistry experiments [12, 13]. The discovery of Hs was reported in 1984 with the identification of 1.5 ms ^{265}Hs [14]. In 1996, during the discovery of element 112 a more neutron rich isotope, ^{269}Hs with a half-life of $t_{1/2} \sim 10$ s, was observed as a member of the α -decay chain of the nuclide ^{277}Cn (element 112) [15]. Such a comparatively long half-life is sufficient for chemistry experiments. Therefore, this Hs isotope was used in gas-phase chemistry

† AKUFVE is a Swedish acronym for an arrangement for continuous investigations of distribution ratios in liquid-liquid extraction.

experiments, in which it was produced directly in the hot fusion reaction $^{248}\text{Cm}(^{26}\text{Mg},5\text{n})$ [12]. From these experiments it was proven that Hs form a volatile tetroxide in a He/O₂ gas mixture, analogous to its lighter homologues in group 8. This strongly supports its positioning as a group 8 element. The formation of the volatile tetroxide also enables its capillary transportation in a cluster-free carrier gas. This provides a very good chemical separation of Hs from almost all unwanted nuclear reaction by-products, made at much higher production rates. Since such by-products are non-volatile they will not be transported to the chemistry apparatus, thereby greatly enhancing the Hs to background ratio in the detectors.

The next chemical property of Hs studied experimentally, also in the gas phase, was the reaction of HsO₄ with moisturized NaOH [13]: An acid-base reaction with the tetroxide of hassium leading to the formation of a hassate (VIII), $[\text{HsO}_4(\text{OH})_2]^{2-}$, was performed. Theoretical calculations on ΔG° of formation of $[\text{MO}_4(\text{OH})_2]^{2-}$ from NaOH and MO₄ (where M means Os or Hs) have shown that HsO₄ should have a weaker reaction with NaOH (by less than 52 kJ/mol) than OsO₄ [16]. However, from the results of the gas-phase experiment, it was not possible to clearly distinguish differences between OsO₄ and HsO₄. Hence, whether HsO₄ has lower affinity to moisturized NaOH than OsO₄ remains an open question.

Later on ^{270}Hs was identified with an estimated half-life of about 23 s and a cross sections of about 3 pb for the reaction: $^{248}\text{Cm}(^{26}\text{Mg},4\text{n})^{270}\text{Hs}$ at a beam energy of 136 MeV. In the same experiment a cross section of 7 pb for the reaction: $^{248}\text{Cm}(^{26}\text{Mg},5\text{n})^{269}\text{Hs}$ at 145 MeV beam energy was obtained [17].

Performing chemistry experiments with radionuclides from reactions with such low cross-sections is extremely challenging and the Hs event-rate cannot be expected above one per day or even less. This implies that experiments must be run continuously for a week or more, demanding stable chemistry set-ups with preferentially a minimum of user interaction. Gas-phase chemistry is more suitable with respect to this demand in most cases, but not everything can be studied in the gas-phase. It is therefore desirable to perform liquid phase experiment with Hs.

The successful Rf SISAK experiment with the 4-s ^{257}Rf isotope [10] instead of the more usual ^{261}Rf indicate that it will be possible to perform a SISAK experiment even with Hs at some point. Additionally, the longer-lived ^{269}Hs and ^{270}Hs have the advantage that their activity are less reduced than that of 4-s ^{257}Rf due to decay during transport.

As previously indicated, the predicted slightly lower affinity of HsO₄ to react with NaOH as compared to that of OsO₄ [16] has so far not clearly been confirmed experimentally [13]. In the present work a SISAK extraction system was designed to provide an enhanced assessment on the reaction between HsO₄ and NaOH. Such a system was

developed utilizing Os in the form of OsO_4 as a model for Hs. The distribution of OsO_4 between dilute solutions of NaOH and toluene was studied using the SISAK apparatus. From slope analysis of the extraction curves the relevant equilibrium constants were obtained. The reaction between OsO_4 and NaOH had earlier been studied in different research works [18-22]. In these works, it is generally accepted that OsO_4 is the anhydride of osmium (VIII) acid. However, different compositions as well as different values for dissociation constants of the acid have been stated in various studies. The relevant suggested reactions and compositions are used here to explain the observed results.

2. Experimental Procedure

2.1 Production of radioactive isotopes of Os

Radioactive isotopes of Os were produced at the Oslo Cyclotron Laboratory at the University of Oslo by bombardment of a 0.025 mm thick, self-supporting target foil of natural tungsten. The beam used was 45-MeV $^3\text{He}^{2+}$ -ions, with an intensity of 400-500 nA (electrical), which resulted in the following nuclear reactions:



Reaction products recoiling out of the target foil are stopped in a gas-filled chamber behind the target. The gas used for this experiment was composed of 90% He and 10% O_2 . The gas mixture continuously sweeps any volatile products out of the chamber. In this case, the volatile product of interest is OsO_4 , which is transferred to the chemistry apparatus, located in a separate laboratory, through a 22 m long perfluoro-alkoxyalkane (PFA) capillary with an inner diameter of 1.6 mm (1/16"). A schematic diagram of the target arrangement is shown in Fig. 1.

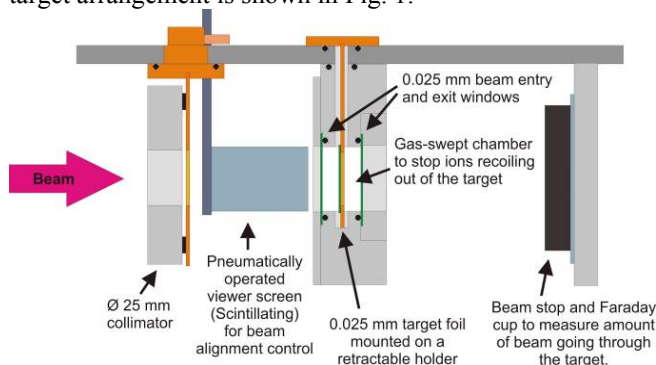


Fig. 1. Oslo Cyclotron Laboratory target-chamber arrangement for gas-jet transfer of products into the chemistry laboratory. The carrier gas flows across the down-stream side of the target foil in a laminar way (gas inlet and outlet not shown on drawing). The whole setup is mounted inside a vacuum chamber.

The beam current through the target is measured by a Faraday cup about 40 cm downstream of the target chamber connected to a current integrator. The integrated current is used to scale individual measurements in order to enable comparisons and yield monitoring.

145 keV γ -rays from decay of 2.7-min $^{181\text{m}}\text{Os}$ [23] were dominant in the spectrum and were therefore used to determine the extraction distribution ratios. For off-line (batch) measurements, 382 keV γ -rays from decay of 13-h ^{183}Os were used. The on-line measurements were performed by measuring the output stream from the centrifuge during continuous flow in a capillary coil placed in front of the detector until satisfactory counting statistics were obtained (usually 5-10 min). A typical spectrum can be seen in Panel A in Fig. 2. In off-line batch measurements, the activity was collected (as described in chapter 2.3 below) for about 30 min, then 15 min were used for performing the manual operation. The samples were then measured for 10 min. Panel B in Fig. 2 shows a typical spectrum.

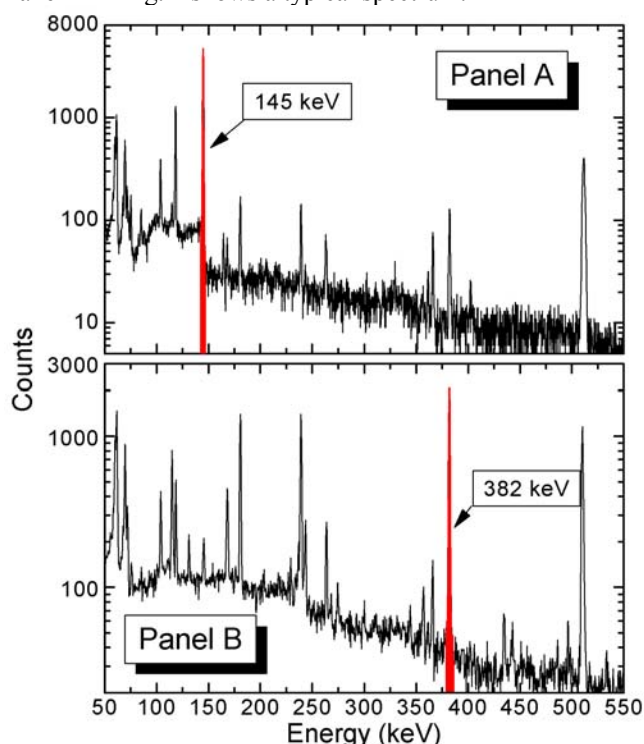


Fig. 2. Typical γ spectra of the organic phases. Panel A is from on-line measurements, Panel B is from batch experiments. In both cases the spectra were measured for 10 min.

Fast and complete oxidation of Os into its tetroxide needs an elevated temperature [24]. In the present work, the applied set-up was not equipped with an oven to achieve this. However, the oven did not seem to be necessary for our setup and Os count-rates high enough for our measurements were routinely achieved. It is not known if the same applies to Hs, so in a hassium experiment an oven should be added as close as possible to the chamber in which the ions are stopped.

2.2 Online SISAK experiment

OsO_4 was dissolved into various dilute NaOH solutions through a mixer-degasser unit. Subsequently, OsO_4 was extracted from the aqueous phase into toluene using a mix-

er-centrifuge unit. A schematic diagram of the on-line setup is shown in Fig. 3.

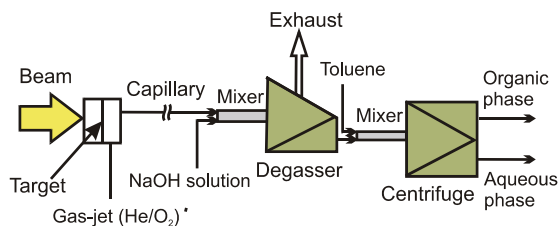


Fig. 3. The SISAK on-line setup used to study the distribution of OsO_4 between various dilute NaOH solutions and toluene.

The gas-liquid and liquid-liquid mixing efficiency is very important; it should ensure high yield for the gas to liquid transfer and for the liquid-liquid extraction. Furthermore, the transport time through the mixers must be as short as possible to minimize decay losses. This requires small mixer volumes. For SISAK, the best mixers were found to be short tubes made of PEEK (Poly EtherEtherKeton) stuffed with PEEK wool. The wool ensures that the phases are divided into small droplets and therefore have a high surface to volume ratio, which ensures efficient mixing and phase boundary transfer. After mixing the two phases are separated from each other using SISAK centrifuges. There are two centrifuge versions [6]: One is specially developed for gas-liquid separation and normally referred to as "degasser". The other one is for liquid-liquid separation, and referred to just as "centrifuge".

The effluents from the centrifuge are directed through tube coils mounted in front of two HPGe detectors.

The distribution ratio, D , of Os is obtained by γ -counting of the two phases, however, the two detectors, d1 and d2 as well as the two coils are not identical concerning detection efficiency and geometry. Consequently, a calibration of the detection system was needed. To evade the calibration of the system the determination of the distribution ratio was based on two subsequent runs, I and II, in which only the two phases were interchanged. In run I the selected γ -peak has $N_{\text{Org},d1}$ counts with an overall efficiency ε_1 and a counting live-time $t_{\text{Org},1}$ for the organic phase. The corresponding aqueous phase counts are $N_{\text{Aq},d2}$, overall efficiency ε_2 and counting live-time $t_{\text{Aq},2}$. The inner volumes of the coils are V_1 and V_2 for organic and aqueous phase respectively. The distribution ratio, D is:

$$D = \frac{C_{\text{Org}}}{C_{\text{Aq}}} = \frac{A_{\text{Org}}/V_{\text{Org}}}{A_{\text{Aq}}/V_{\text{Aq}}} \quad (1)$$

where C is the concentration of osmium in the phases, indicated by subscript Org and Aq, respectively. A and V are the activity and volume of the each phase respectively and are indexed in the same way as C . The activity, A , is equal to $N/\varepsilon t$, then equation (1) for run I can be written as:

$$D (\text{run I}) = \frac{C_{\text{Org}}}{C_{\text{Aq}}} = \frac{N_{\text{Org},d1}/\varepsilon_1 V_1 t_{\text{Org},1}}{N_{\text{Aq},d2}/\varepsilon_2 V_2 t_{\text{Aq},2}} \quad (2)$$

In the subsequent run II the corresponding values would be: $N_{Org,d2}$, ε_2 , $t_{Org,2}$ and $N_{Aq,d1}$, ε_1 , $t_{Aq,1}$. As the organic and aqueous phases are interchanged, V_1 and V_2 are now the volume of the coil for the aqueous phase and the organic phase respectively. The distribution ratio then is:

$$D(run II) = \frac{C_{Org}}{C_{Aq}} = \frac{N_{Org,d2} / \varepsilon_2 V_2 t_{Org,2}}{N_{Aq,d1} / \varepsilon_1 V_1 t_{Aq,1}} \quad (3)$$

The final value of the distribution ratio has the relationship:

$$D = \sqrt{D(run I) \times D(run II)} = \sqrt{\frac{N_{Org,d1} t_{Aq,2}}{N_{Aq,d2} t_{Org,1}} \times \frac{N_{Org,d2} t_{Aq,1}}{N_{Aq,d1} t_{Org,2}}} \quad (4)$$

All distribution ratios obtained in on-line experiments reported here are calculated in this way.

In a SISAK transactinide experiment, the quenching effects of the aqueous phase prevent the direct measurement of α -activity using the online liquid scintillation detectors. Instead a second extraction stage is included to extract the remaining activity in the aqueous phase after the first extraction. In this way it is possible to measure the α -activity in the aqueous phase *indirectly*. The principle behind this method is described in [9]. Normally, a second extraction step that will extract the desired component from the aqueous phase with 100% yield is sought. In most cases this is not achievable, and a correction for a partial extraction must be applied. This procedure must be used with great care for a transactinide experiment, as the extraction yield usually is unknown. In such cases, the unknown extraction yield must either be carefully estimated, e.g. from comparisons with the lighter homologues, or deduced from additional experiments, e.g. measurement of the difference between the amount of activity before the extraction stage and in the organic phase. As more experiments are performed, the validity of the initial estimate can be checked by evaluating the consistency of the extraction curve.

A second extraction stage suitable for transferring any Os (and probably Hs) species remaining in the aqueous phase after the first extraction stage was developed in order to check the complete extraction of osmium from the raffinate. The development work was done with only a single extraction stage (targeted to become the second extraction stage in a full-scale hassium experiment): the solution from the degasser was acidified directly after degassing. This was followed by one-step extraction into toluene. The schematic set-up used is shown in Fig. 4.

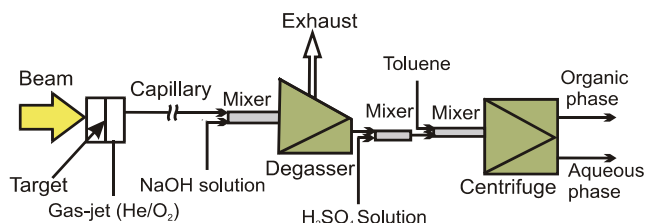


Fig. 4 The SISAK setup used to study the extraction of the osmium from the aqueous phase into toluene when OsO_4 is first dissolved in NaOH solution and then acidified by H_2SO_4 .

2.3 Batch experiment

The same procedure as explained in 2.1 was used to produce and transport Os isotopes to the SISAK apparatus. 100 mL of de-ionized water circulated in a closed loop with a static mixer and degasser to transfer OsO_4 from the carrier gas to the water, as shown schematically in Fig. 5.

Pure, de-ionized water was selected as solvent, to ensure that the contact time with NaOH (in the following step) was equal for all experiments. Changes in e.g. OsO_4 yield when using de-ionized water as solvent was not a problem since only the distribution ratio was measured and not the absolute yield.

Activity was collected for about 30 minutes, and then an appropriate amount of strong NaOH solution was added to obtain a desired concentration. For example 1 mL of 1 M NaOH added to obtain 0.01 M NaOH and so on for other NaOH concentrations. 100 mL toluene was promptly added and the mixture was stirred for 15 minutes. Then transferred to a separation funnel, from which samples of 80 mL were withdrawn and the 382 keV γ -line from ^{183}Os was counted with an HPGe detector.

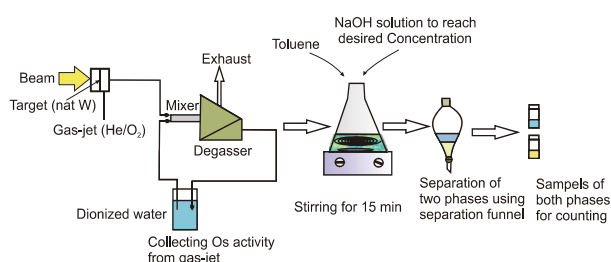


Fig. 5. Schematic setup and procedure for the batch experiments.

2.4 Chemicals

De-ionized water was used to prepare all the solutions. Sodium hydroxide pellets GR for analysis PA > 99.98% and sulphuric acid with a purity of 95%-97% from MERCK were utilized. Toluene with a purity between 99-99.5 % from BDH Prolabo or Univar was applied.

3. Results and Discussion

The development of the proposed system for studying liquid phase chemistry of hassium can be divided into three parts: 1) Ensuring that SISAK is set up in such a way that chemical equilibrium is obtained in a liquid-liquid extraction (LLE) stage. 2) Selecting and optimizing the LLE system. 3) Developing a high-yield second extraction stage to enable liquid-scintillation detection of hassium α -activity in the aqueous phase. The results from the development work are described below.

3.1 Attaining extraction equilibrium

In SISAK, the contact time between the two phases is governed by the length of the mixer upstream of the centrifuge and the liquid flow rates. The current SISAK setup is optimized for flow rates of 0.3-0.4 mL/s, which provides an acceptable compromise between consumption of chemicals, transport time and waste generation. Higher flow rates are technically possible, but lead to high back pressure and frequent leaks and breakdowns. Flow rates lower than 0.3 mL/s lead to very long transport times and therefore high decay losses. For the proposed setup for hassium chemistry, a flow rate of 0.4 mL/s was selected, which should give a mean transport-time of less than 20 s.

For a given flow rate and mixer type the contact time between the phases, and therefore the available time to reach equilibrium, is solely governed by the length of the mixer.

It is important that experiments are performed at equilibrium conditions for two reasons: (I) The interpretation of the results is only possible if the experiments are performed under equilibrium conditions. (II) Reproduction of the result is only possible under equilibrium conditions. If the system is not at equilibrium conditions small changes in e.g. liquid flow rates or performance of the mixer (due to clogging or changed flow pattern) will change the distribution ratio. Obtaining extraction curves and comparison between different curves will then be very uncertain and thus impractical.

To find the necessary mixer length to obtain equilibrium, distribution ratios were measured for different mixer lengths. Before equilibrium condition is reached, less than the equilibrium amount of activity is transferred to the organic phase and the distribution ratios will be too low (assuming the activity originally was dissolved in the aqueous phase). When no significant change occurs as a function of mixer length, equilibrium has been reached.

Determination of the required mixer length was performed using de-ionized water and 0.0005 M NaOH solution as aqueous phase. Pure toluene was used as organic phase. Mixers filled with PEEK-wool, as described previously, were used. The inner diameter was 4 mm. Fig. 6 shows the results, the curve is a Boltzmann fit to the data primarily for guiding the eye. The transport time for the 43 mm premixer, which is the one normally used in transactinide experiments, is less than 0.5 s for a 0.8 mL/s flow (0.4 mL/s per phase) [25]. From the kinetic curve the necessary mixer length can be selected by identifying the horizontal part. In this part of the curve the distribution ratio does not change, thus it is assumed that the system is at equilibrium. Notice that a mixer length of 0 means that no mixer was inserted. However, the phases are still mixed in the Y-piece at the entrance to the centrifuge. Based on the measured relationship between distribution ratios and mixer length, a length of 150 mm was selected, which corresponds to about 1.7 s mean residence-time in the mixer. This is on the borderline

of the horizontal plateau, and is the shortest residence-time under equilibrium conditions.

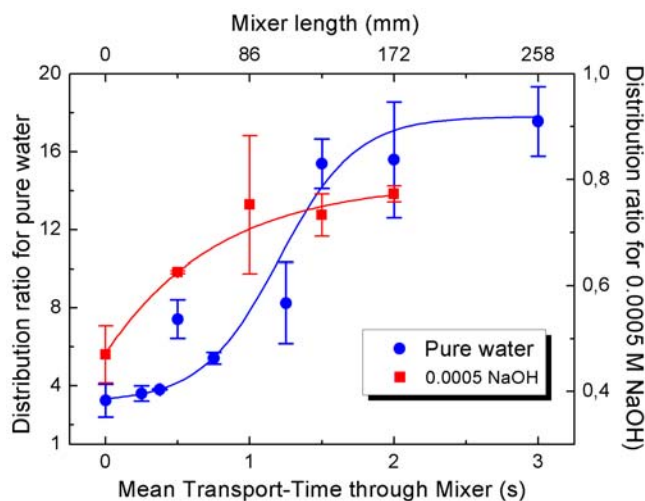


Fig. 6. Distribution ratio of OsO_4 between de-ionized water or 0.0005 M NaOH and toluene as a function of mixer length, measured for 0.4 mL/s flow rate for both phases. The curves are from fitting a Boltzmann function to the data to guide the eye.

3.2. The first extraction stage

OsO_4 is dissolved in the aqueous phase from the carrier gas using a mixer-degasser unit (as described earlier):



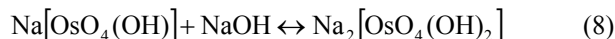
In the NaOH solution, the following reaction is assumed to take place:



The equilibrium constant will then be:

$$K_1 = \frac{[\text{NaOsO}_4(\text{OH})]}{[\text{NaOH}][\text{OsO}_{4(\text{aq})}]} \quad (7)$$

The reaction with NaOH may proceed to form $\text{Na}_2[\text{OsO}_4(\text{OH})_2]$ through the following reaction:



With the equilibrium constant:

$$K_2 = \frac{[\text{Na}_2\text{OsO}_4(\text{OH})_2]}{[\text{NaOH}][\text{NaOsO}_4(\text{OH})]} \quad (9)$$

When the Os-containing NaOH solution from the degasser is contacted with toluene in the liquid-liquid mixing stage, OsO_4 will be distributed between the two phases:



The distribution constant for OsO_4 then is:

$$K_D = \frac{[\text{OsO}_4]_{\text{org}}}{[\text{OsO}_4]_{\text{aq}}} \quad (11)$$

According to reference [26] OsO_4 forms a π complex with toluene and no red-ox reaction occurs between OsO_4 and toluene.

The distribution ratio for Os is defined as:

$$D = \frac{[\text{OsO}_4]_{\text{org}}}{[\text{OsO}_4]_{\text{aq}} + [\text{OsO}_4(\text{OH})^-] + [\text{OsO}_4(\text{OH})_2]^{2-}} \quad (12)$$

This distribution ratio can be written in terms of the equilibrium constants:

$$D = \frac{K_D}{1 + K_1[\text{OH}^-] + K_1K_2[\text{OH}^-]^2} \quad (13)$$

Fig. 7 shows the measured distribution ratios from both batch and on-line SISAK experiments. As can be seen, the on-line data is nicely fitted by eq. (13). The equilibrium constants obtained from the least square fitting of eq. (13) are: $K_D = 11 \pm 5$, $K_1 = (1 \pm 0.5) \times 10^4$, $K_2 = 12 \pm 8$.

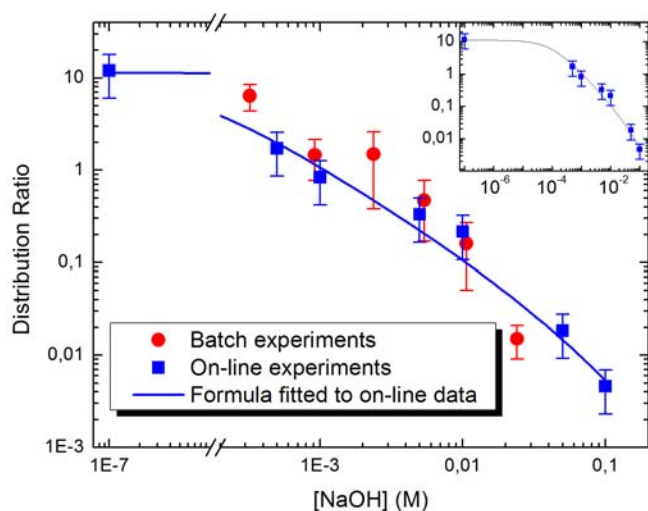


Fig. 7. Measured distribution ratio as function of $[\text{OH}^-]$ from both batch and on-line experiments. The solid line is a fit of eq. (13) to the on-line data. The 10^{-6} to 10^{-4} M concentration range was omitted in the main plot to show the data more clearly. In the inserted figure which shows the overall shape of the fitted curve and on-line measurement points can be seen.

3.3. The second extraction stage

As explained in the Experimental Procedure section, the activity remaining in the aqueous phase after extraction must be transferred to a second organic phase to be detected in the SISAK liquid scintillation detection system. I.e. a second extraction step must be added with a highly efficient extraction of Os from the basic aqueous phase into toluene. This was accomplished by acidification of the dilute NaOH solutions with sulphuric acid, then OsO_4 is retrieved by breaking up the hydroxide compounds:



In this case, it is not necessary to be exactly at the neutral point, and actually it is more reliable if the end point is in

the acidic region. However, further acidification to lower pH has no significant influence on the extraction of Os.

OsO₄ is then extracted with high yield into toluene. From a NaOH solution of 0.01 M, acidified with H₂SO₄ solution the extraction yield was measured to be $(90 \pm 3) \%$.

3.4. Prediction of Hs behavior in the proposed system

A schematic set-up of the proposed SISAK extraction system for a Hs chemistry is illustrated in Fig. 8. Hs isotopes will be produced via a fusion reaction and recoil to the (heated) target chamber and form a volatile tetroxide in the He/O₂ gas-jet. In the case of using a preseparator, the hassium nuclides will be separated from other products and the beam [27], then enter the Recoil Transfer Chamber (RTC) where they are stopped in a O₂-He gas mixture. Hs, probably in the form of HsO₄, can be flushed out of the RTC with the gas. At the RTC outlet the gas mixture will enter an oven heated to 600 °C to ensure complete and rapid formation of the volatile tetroxide. The oven will be constructed of a quartz tube with a quartz wool plug in the middle, heated to the required temperature. The tetroxide will be carried from the oven to the mixer in front of the SISAK degasser through a capillary tube. In the mixer the tetroxide will be dissolved into NaOH solution. The carrier gas should be removed by the degasser and the NaOH solution will be mixed with toluene in a second mixer (in front of the first liquid-liquid separation centrifuge). In the first liquid-liquid extraction stage, the chemical properties of Hs can be studied. The organic phase will be mixed with scintillator and fed to the first detector array. The aqueous phase will be fed into the second extraction stage for a “complete” extraction after acidification with H₂SO₄. The second organic phase will then, in a similar way to the first organic phase, be mixed with liquid scintillator and fed to a second liquid scintillation detector array. The aqueous effluent from the second centrifuge is discarded.

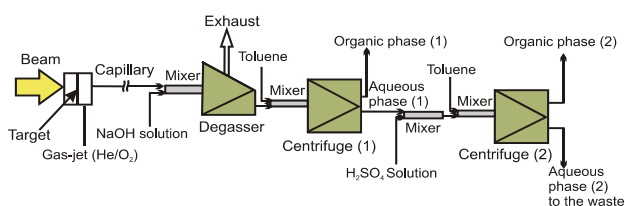


Fig. 8. A sketch for the proposed SISAK extraction system for chemical studies of Hs. The organic phase (1) and (2) then flow to the scintillation-detection system.

An important question however, is the statistical significance of the data obtained and the minimum data required for conclusions instead of assumptions. The problem of how many atoms are needed to determine a specific distribution-ratio with a given accuracy was considered in [28]. Accordingly, at distribution ratios around 1 with a standard

deviation of 50% about 16 detected atoms are needed. Accordingly in an Hs experiment with a production rate in the range of 1 atom per day and overall efficiency of 50% the duration of the experiment would be around 4 weeks.

Based on the achieved detection rates in gas-phase Hs experiments [12, 13] of about 1 event per day, the high efficiency achieved in today's preseparator [27] and results from previous SISAK transactinide experiments [9-11], a SISAK hassium experiment is estimated to be on the borderline of what can be achieved. However, target technology is steadily progressing, enabling higher beam intensities and thus higher production rates. Work is also in progress to simplify the SISAK system in order to reduce transport/residence time and enhance reliability/ease of operation. Thus, a SISAK hassium experiment should be reasonably realistic in 2-3 years, but will require a major investment in manpower and resources.

4. Conclusion

The study of the reaction between HsO_4 with OH^- in dilute NaOH solutions can be performed in liquid-liquid extraction experiments using the SISAK system. In this work the details of a model experiment were developed and tested using Os activity produced on-line at the Oslo Cyclotron Laboratory. The results fit well with the model based on formation of hydroxyl complexes of $[\text{OsO}_4(\text{OH})]^-$ and $[\text{OsO}_4(\text{OH})_2]^{2-}$ at low concentrations of NaOH in accordance with the proposed chemical reactions. The equilibrium constants for Os in these reactions were obtained from measured distribution ratios. For an Hs experiment a NaOH concentration resulting in distribution ratios around 1 is desirable because it is associated with the lowest uncertainty in distribution ratio with a given number of events [28]. From the results of Os experiments this NaOH concentration for OsO_4 would be around of 5×10^{-4} M. The distribution ratio for HsO_4 in the same system can be estimated using theoretical methods. Such an estimate will aid in choosing the most suitable conditions for an Hs SISAK experiment and should be undertaken before an actual experiment.

A full-scale test, using α -emitting Os isotopes, in order to test the full SISAK setup described here with double α -detector arrays in the same way as an Hs experiment has been performed at GSI Helmholtzzentrum für Schwerionenforschung GmbH in Darmstadt, Germany and will be reported separately [29].

Acknowledgements. We thank the Oslo Cyclotron Laboratory operators, Eivind. A. Olsen, Andrey Semchenkov and Jon C. Wikne, the mechanical workshop staff at the Department of Chemistry, University of Oslo, Marita Clausen, Joachim Halgren and Fredrik Lunde for their assistance during the experiments and the Norwegian Research Council for the financing of this project (No 177538).

References

- Schädel, M.: Superheavy Element Chemistry - Achievements and Perspectives. *J. Nucl. Radiochem. Sci.* **8**, 47 (2007).
- Pyykkö, P. and Desclaux, J.P.: *Accounts Chem. Res.* **12**, 276 (1979).
- Pershina, V.: The chemistry of superheavy elements and relativistic effects. In: *Relativistic electronic structure theory, Part 2: Applications* (P. Schwerdtfeger, ed.) Elsevier, Amsterdam, 2004.
- Münzenberg, G.: Production and Identification of Transactinide Elements. In: *Handbook of Nuclear Chemistry*, vol. 2 (A. Vértes, S. Nagy and Z. Klencsár ed.) Kluwer Academic Publishers, Dordrecht, 2003.
- Trubert, D. and Le Naour, C.: Fundamental Aspects of Single Atom Chemistry. In: *The Chemistry of Superheavy Elements* (M. Schädel ed.), Kluwer Academic Publishers, Dordrecht, 2003.
- Persson, H., Skarnemark, G., Skälberg, M., Alstad, J., Liljenzin, J.O., Bauer, G., Haberberger, F., Kaffrell, N., Rogowski, J., and Trautmann, N.: SISAK 3 - an improved system for rapid radiochemical separations by solvent extraction. *Radiochim. Acta* **48**, 177 (1989).
- Omtvedt, J.P., Alstad, J., Eberhardt, K., Fure, K., Malmbeck, R., Mendel, M., Nahler, A., Skarnemark, G., Trautmann, N., Wiehl, N., and Wierczinski, B.: Review of the SISAK system in transactinide research recent developments and future prospects. *J. Alloys Compd.* **271-273**, 303 (1998).
- Skarnemark, G.: Application of SISAK for fast continuous solvent extraction processes to study exotic nuclides. In: *Proc. Int. Solv. Extr. Conf. ISEC2002* (Sole, K.C., Cole, P.M., Preston, J.S. and Robinson, D.J. ed.), Chris Van Rensburg Pub. Ltd., Melville, Johannesburg, 2002.
- Omtvedt, J.P., Alstad, J., Bjørnstad, T., Düllmann, Ch. E., Gregorich, K.E., Hoffman, D.C., Nitsche, H., Opel, K., Polakova, D., Samadani, F., Schulz, F., Skarnemark, G., Stavsetra, L., Sudowe, R., and Zheng, L.: Chemical properties of the transactinide elements studied in liquid phase with SISAK. *Eur. Phys. J. D* **45**, 91 (2007).
- Stavsetra, L., Gregorich, K.E., Alstad, J., Breivik, H., Eberhardt, K., Folden III, C.M., Ginter, T.N., Johansson, M., Kirbach, U.W., Lee, D.M., Mendel, M., Omtvedt, L.A., Patin, J.B., Skarnemark, G., Sudowe, R., Wilk, P.A., Zielinski, P.M., Nitsche, H., Hoffman, D.C., and Omtvedt, J.P.: Liquid-scintillation detection of pre-separated ^{257}Rf with the SISAK-system. *Nucl. Instrum. Methods Phys. Res., Sect. A* **543**, 509 (2005).
- Omtvedt, J.P., Polakova, D., Alstad, J., Bjørnstad, T., Düllmann, Ch. E., Folden III, C.M., Garcia, M.A., Gates, J., Gregorich, K.E., Hoffman, D.C., Nelson, S.L., Nitsche, H., Omtvedt, L.A., Pershina, V., Samadani, F., Skarnemark, G., Stavsetra, L., Sudowe, R., Wilson, R.E., Zheng, L., and Zielinski, P.M.: SISAK Liquid-Liquid Extraction Study of Element 104: Rutherfordium Sulphate Complexes. (To be published).
- Düllmann, Ch. E., Bruchle, W., Dressler, R., Eberhardt, K., Eichler, B., Eichler, R., Gäggeler, H.W., Ginter, T.N., Glaus, F., Gregorich, K.E., Hoffman, D.C., Jäger, E., Jost, D.T., Kirbach, U.W., Lee, D.M., Nitsche, H., Patin, J.B., Pershina, V., Piguet, D., Qin, Z., Schädel, M., Schausten, B., Schimpf, E., Schott, H.J., Sovarna, S., Sudowe, R., Thorle, P., Timokhin, S. N., Trautmann, N., Türlér, A., Vahle, A., Wirth, G., Yakushev, A.B., and Zielinski, P.M.: Chemical investigation of hassium (element 108). *Nature* **418**, 859 (2002).

13. von Zweidorf, A., Angert, R., Bröchle, W., Bürger, S., Eberhardt, K., Eichler, R., Hummrich, H., Jäger, E., Kling, H.O., Kratz, J.V., Kuczewski, B., Langrock, G., Mendel, M., Rieth, U., Schädel, M., Schausten, B., Schimpf, E., Thörle, P., Trautmann, N., Tsukada, K., Wiehl, N., and Wirth, G.: Evidence for the formation of sodium hassate(VIII). *Radiochim. Acta* **92**, 855 (2004).
14. Münzenberg, G., Armbruster, P., Folger, H., Hessberger, F.P., Hofmann, S., Keller, J., Poppensieker, K., Reisdorf, W., Schmidt, K.H., Schott, H.J., Leino, M. E., and Hingmann, R.: The identification of element 108. *Z. Phys. A* **317**, 235 (1984).
15. Hofmann, S., Ninov, V., Hessberger, F.P., Armbruster, P., Folger, H., Münzenberg, G., Schott, H.J., Popeko, A.G., Yeremin, A.V., Saro, S., Janik, R., and Leino, M.: The new element 112. *Z. Phys. A* **354**, 229 (1996).
16. Pershina, V.: Theoretical investigations of the reactivity of MO_4 and the electronic structure of $\text{Na}_2[\text{MO}_4(\text{OH})_2]$, where $\text{M} = \text{Ru}, \text{Os}, \text{and Hs (element 108)}$. *Radiochim. Acta* **93**, 373 (2005).
17. Dvorak, J., Bröchle, W., Chelnokov, M., Dressler, R., Düllmann, Ch. E., Eberhardt, K., Gorshkov, V., Jäger, E., Krucken, R., Kuznetsov, A., Nagame, Y., Nebel, F., Novackova, Z., Qin, Z., Schädel, M., Schausten, B., Schimpf, E., Semchenkov, A., Thörle, P., Türlér, A., Wegrzecki, M., Wierczinski, B., Yakushev, A., and Yeremin, A.: Doubly magic nucleus $^{270}_{108}\text{Hs}^{162}$. *Phys. Rev. Lett.* **97**, 242501/1 (2006).
18. Yost, D.M. and White, R.J.: The acid-forming properties of osmium tetroxide. *J. Am. Chem. Soc.* **50**, 81 (1928).
19. Sauerbrunn and R.D.Sandell, E.B.: constants of osmic(VIII) acid. *J. Am. Chem. Soc.* **75**, 4170 (1953).
20. Bavay, J. C., Nowogroc, G., and Tridot, G.: Acidity of aqueous solutions of osmium tetroxide, OsO_4 . Determination of the constants of various acid-base couples. *Bull. Soc. Chim. Fr.* **2026** (1967).
21. Lee, D.A.: Extraction of osmium tetroxide and evidence for anionic osmium(VIII) species. *J. Inorg. Nucl. Chem.* **34**, 375 (1972).
22. Galbács, Z.M., Zsednai, A., and L. 1. Csanyi: The acidic behavior of osmium(VIII) and osmium(VI). *Transition Met. Chem.* **8**, 328 (1983).
23. Firestone, R.B.: Nuclear data sheets update for $A = 181$. *Nucl. Data Sheets* **62**, 101 (1991).
24. Düllmann, Ch.E.: Chemical investigation of Hs (Hs, $Z = 108$). Thesis, University of Bern, 2002.
25. Poláková, D., Alstad, J., Bjørnstad, T., Opel, K., and Omtvedt, J. P.: Measurement of transport time through the continuous liquid-liquid extraction system SISAK. (To be published).
26. Torgov, V.G., Shulman, R.S., and Marochkina, L.Y.: Extraction of osmium tetroxide with organic solvents. *Zh. Neorg. Khim.* **30**, 434 (1985).
27. Düllmann, Ch. E.: Physical separators for the heaviest elements. *Nucl. Instrum. Methods Phys. Res., B* **266**, 4123 (2008).
28. Ekberg, C., and Skarnemark, G.: Uncertainty evaluation for one-atom-at-a-time studies of transactinides. *J. Radioanal. Nucl. Chem.* **263**, 71 (2005).
29. Samadani, F., Alstad, J., Bjørnstad, T., Düllmann, Ch. E., Eberhardt, K., Even, J., Gates, J.M., Hild, D., Jäger, E., Khuyagbaatar, J., Kratz, J.V., Krier, J., Nilssen, J., Ottesen, H.B., Qureshi, S., Roth, Ch., Schädel, M., Schausten, B., Schulz, F., Türlér, A., Wiehl, N., Yakushev, A., and Omtvedt, J.P.: Test of SISAK extraction-system for Hs with α -emitting Os. (To be published).

Paper III

Test of SISAK extraction-system for Hs with α -emitting Os

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Abstract. A pilot SISAK experiment for chemical investigation of Hs, using α -emitting Os isotopes, was performed to test the entire SISAK setup with double α -detector arrays. This liquid-liquid extraction system is designed to study the distribution of HsO₄ between NaOH solution and toluene and was developed in an initial stage using γ -emitting Os isotopes at the Oslo Cyclotron Laboratory (OCL). The α -emitting osmium isotopes were produced in a natural-composition Ce target in the gas-filled separator TASCA (TransActinide Separator and Chemistry Apparatus), using a ⁴⁰Ar¹¹⁺ beam from the linear accelerator at the GSI Helmholtzzentrum für Schwerionenforschung GmbH. At the focal plane of the separator a recoil transfer chamber transferred Os-ions in a 10% O₂ and 90% He gas-mixture as volatile osmium tetroxide. The volatile tetroxide was carried with the gas to the SISAK system, where the distribution ratio between NaOH solution and toluene is measured by liquid scintillation α -spectroscopy incorporating pulse-shape discrimination of disturbing β - and γ -activity. The result of the experiment was in a good conformity with the results from the Oslo experiments and verified that such an experiment with Hs is feasible in principle. This was the first on-line SISAK run at TASCA and thus also provided valuable experience in how future SISAK experiments can be performed at TASCA.

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1. Introduction

Experimentally verified knowledge of the chemical behaviour of the heaviest elements, the transactinide elements ($Z \geq 104$), is scarce because they can only be produced in heavy-ion induced nuclear fusion-reactions with extremely small cross-sections. Furthermore, their half-lives are so short that with current facilities only a single atom is available at a given moment in time, usually with hours or even days until the next atom is produced. Even under such very challenging conditions, many experiments have been performed to probe into the chemical properties of these elements. A good review of this field is given in e.g. the book edited by M. Schädel [1].

There are many reasons for why such difficult, time consuming and expensive experiments should be performed. The most basic reason is perhaps human curiosity: The elements are fundamental for our understanding of matter around us and the millions of different compounds they build. Exploring properties of unknown elements is in this perspective important and receive widespread attention. It is of course hard to see any practical application of transactinide elements, but a thorough understanding, including theoretical calculations, of their chemical behaviour will not only apply to the transactinides, but lead to a better understanding of the structure of *all* atoms. This is the *scientific* reason for undertaking experimental studies of the transactinides. In particular, the influence of the relativistic part of the wave functions needed to accurately describe the chemical behaviour of atoms is dependent on the velocity of the atomic electrons. The velocity depend on the nuclear charge, thus the transactinide elements contain electrons with very high velocities and is therefore an excellent test bed for accurate theoretical calculations. In this perspective it is important to design experiments targeted at highlighting properties and behaviour that can also be investigated in theoretical calculations. The work reported here used this as a guideline for developing an experiment aimed at investigating solution chemistry of element 108, hassium, using the SISAK [2, 3] liquid-liquid extraction (LLE) system.

Generally, it is easier to perform gas-phase than liquid-phase experiments on the transactinide elements (the experimental setup tend to be mechanically less complex and more stable, and the transport time in gas-phase is usually faster). Until recently, hassium was the heaviest element which ever had been investigated chemically (the first chemistry experiments on element 112, recently named copernicium, and element 114 were recently reported [4, 5]). The experiment on Hs, performed at the GSI Helmholtzzentrum für Schwerionenforschung GmbH (abbreviated GSI), was performed in gas phase using ^{269}Hs produced in the hot fusion reaction $^{248}\text{Cm}(^{26}\text{Mg}, 5n)^{269}\text{Hs}$. It proved that Hs form a volatile tetroxide when contacted

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with a He/O₂ gas mixture, analogous to its lighter homologues in group 8 [6]. This strongly indicates that its position in group 8 (below Os) is correct, in accordance with the expected systematics of the Periodic Table. The volatility of HsO₄ provide the advantage that most unwanted by-products produced in nuclear reactions with the ²⁶Mg beam are not gases or volatile. Therefore, they will not be carried with the gas stream.

The only other type of chemistry experiment ever performed with Hs was investigation of how HsO₄ reacts with moisturized NaOH [7]. The results showed that Hs reacts with NaOH analogous to Os and presumably forms Na₂[HsO₄(OH)₂]. However, although it was a very successful experiment, it was not sensitive enough to clearly verify that the reaction between HsO₄ and hydroxide was weaker than the analogue reaction with OsO₄, as predicted by theoretical calculations [8].

So far, no Hs experiment in liquid phase has been attempted. It would however be advantageous to complement the knowledge obtained from gas-phase experiments with data from solution chemistry. As described in a previous article [9] a system to study the affinity of HsO₄ to hydroxide in aqueous solution was developed, based on the automated liquid-liquid extraction (LLE) system SISAK¹. SISAK is a fast solvent extraction system working in a continuous manner (the input and output gas- and liquid streams are kept flowing uninterrupted and at fixed rates). Basically it consists of static mixers and small centrifuges. The mixers are PEEK (Poly EtherEtherKeton) tubes filled with PEEK wool. In the mixers small droplets of the immiscible phases are formed, ensuring fast transfer of the extractable species in order to obtain equilibrium conditions for the LLE. The SISAK centrifuges then separates the phases rapidly and efficiently. The activity in the outgoing, organic phase is measured directly by adding a scintillator cocktail. The emitted α -particles are then measured by liquid scintillation (LS) detection in cells coupled directly to the SISAK system. Details can be found in [10, 11] and references therein.

The successful Rf SISAK experiments [12], performed at Lawrence Berkeley National Laboratory in California, proved that the SISAK system and its liquid scintillation detectors is sufficiently sensitive to detect α -emitting nuclides in chemical experiments with event rates of one atom per four hours. In favourable cases the sensitivity should be good enough to detect radionuclides with one event per day or even less.

¹ SISAK is an acronym for "Short-lived Isotopes Studied by the AKufve technique", where AKUFVE is a Swedish acronym for an arrangement for continuous investigations of distribution ratios in liquid-liquid extraction.

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The development of the SISAK extraction system for Hs was based on hassium's known chemical properties. As already mentioned, hassium's lighter homologue Os was used as model for hassium to develop the system. The transport of Os nuclides was based on the in situ formation of OsO_4 in a He and O_2 gas mixture. The SISAK apparatus was then used to study the distribution of OsO_4 between NaOH solution and toluene. OsO_4 is known to form hydroxyl complexes in NaOH solution. The distribution ratio of Os between the two phases was obtained as a function of NaOH concentrations. By slope analysis of the extraction curve (distribution ratio vs. OH^- concentration) the equilibrium constants for the complex formation were calculated [9].

The development work for the hassium LLE system was performed with γ -emitting osmium-isotopes, produced at the Oslo Cyclotron Laboratory (OCL) at the University of Oslo. However, for a hassium experiment α -detection is necessary, but the particle beams available at OCL cannot produce α -emitting Os-nuclei. Therefore, it was not possible to perform a realistic full-scale test of the complete system in Oslo; such an experiment must be performed at a larger cyclotron facility. Fortunately, it was possible to perform such a test experiment using a ^{40}Ar beam delivered by the linear accelerator UNILAC (UNIVERsAL Linear AC-celerator) at GSI. Thus, a test of the full SISAK setup [10] with double α -detector arrays to detect activity in both the organic and aqueous phases, similar to how a Hs-experiment would be performed, was performed at GSI as a "proof-of-principle" experiment and to learn the restraints and requirements necessary to perform a hassium SISAK experiment there. The experiment and its results are described below.

2. Experimental Procedure

The experiment was performed at the GSI heavy-ion accelerator laboratory in Darmstadt, Germany. Short lived, α -emitting osmium isotopes were produced in a cerium target irradiated with a ^{40}Ar beam from the UNILAC. The products (referred to as "Evaporation Residues" or EVRs) are "shot out" from the target due to their momentum and enters a gas-filled separator named TransActinide Separator for Chemistry Apparatus (TASCA) [13, 14]. Here beam particles and most unwanted reaction products are suppressed on basis of their magnetic rigidity, see e.g. [15] for a review of this method. Right behind the focal plane of the separator a "Recoil Transfer Chamber" (RTC) is positioned to collect the selected EVRs and transfer them to a chemistry apparatus with a gas-transport system. For the experiment described in this article, oxygen was added to the

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normally inert carrier gas² (He), in order to oxidise osmium to volatile osmium tetra-oxide. The gas-transport system [16] is commonly referred to as a "gas-jet".

The gas-filled separator is operated in the 0.5-2 mbar pressure range. The pressure in the gas-jet depend on the requirements of the chemistry apparatus it is connected to; For liquid-phase experiments the pressure must in most cases be well above 1 bar in order to force the gas to be mixed with the liquid. For SISAK, a target chamber pressure between 1.3 and 1.8 bar is usual. Therefore, a window is necessary to separate the near vacuum zone of the preseparator and the much higher pressure in the transfer chamber. The window must be solid enough to withstand the pressure difference, but at the same time thin enough to allow EVRs through. This challenge is overcome by using a support grid on the separator side of the window. The method of using a transfer chamber behind a gas-filled separator, to reduce the very high amount of unwanted reaction products in transactinide chemistry experiments, was originally proposed by Ken Gregorich at Lawrence Berkeley National Laboratory (LBNL). Uwe Kirbach and co-workers implemented the RTC method for use at the LBNL Berkeley Gas-filled Separator (BGS) [17], and in 2000 the first transactinide chemistry experiment behind a gas-filled preseparator, using 4-s ²⁵⁷Rf, was successfully performed at LBNL by Omtvedt et al. [12] using the SISAK liquid-liquid extraction system.

Partially based on the experience gained from the BGS RTC, a similar system was implemented for the GSI TASCA separator. Since TASCA can be operated in two modes, as a function of the polarity of the focusing quadrupole magnets [13], two RTCs had to be developed: One for the relatively large focal image obtained in the "High Transmission Mode" (HTM) and one for the much smaller focal image of the "Small Image Mode" (SIM). HTM has the highest transmission yield through TASCA, but SIM makes it possible to build RTCs with significantly smaller volumes, which is important to quickly flush out short lived nuclei. Details of the construction and commissioning of the TASCA RTCs can be found in [18] for HTM and [19] for SIM.

Below specific details of the general system components, as used in the pilot experiment to test the SISAK hassium-

² Usually, the EVRs will not easily form a volatile compound as osmium do in the experiment described in this work. Hence, they will not be transported with the carrier gas. Thus, for most other elements, the inert carrier gas has to be seeded with aerosol particles, to which the ions (EVRs) will adsorb and thus be carried away with the gas. A typical aerosol is potassium chloride, which can easily be produced by heating solid potassium chloride to around 640-660° C inside a quartz tube in which the carrier gas passes through.

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chemistry with α -emitting osmium-isotopes, is described in detail.

2.1. Target and production of ^{172}Os

A 240.0 MeV $^{40}\text{Ar}^{11+}$ beam with intensity of about 200 particle nA from the linear accelerator UNILAC at GSI irradiated a rotating natural-composition Ce (88.48 % ^{140}Ce ; 11.08% ^{142}Ce) target mounted on a wheel with three arc-shaped target sections [20], producing $^{172-175}\text{Os}$ nuclides. The target-wheel rotation is synchronised with the UNILAC beam pulses, which are 5 μs long with up to 50 pulses per second³ to ensure that only the target are hit and not the spokes in between.

The cross-section for the Ar-induced reaction is not experimentally known. Therefore, the HIVAP [21] code was used to estimate the cross-sections for the different osmium isotopes likely to be produced. Of these, only $^{172-174}\text{Os}$ have useful α -branches, although still very small. Cross sections, α -branches and half-lives (from [22]) are shown in Table 1, together with deduced relative decay and α -emission rates. As can be clearly seen, the dominant α activity comes from

Table 1 The branching percentage and decay data of $^{172-174}\text{Os}$ isotopes.

Isotope	^{172}Os	^{173}Os	^{174}Os
Cross-section (mbarn)	17.8 [#]	20.9 [#]	8.8 [#]
Beam energy (MeV, Lab)	240	240	240
Relative production rate (%)	37	44	19
α branch (%)	1.02 ^S	0.021 ^S	0.020 ^S
Half-life (s)	19.2 ^S	22.4 ^S	45 ^S
Relative α -disintegration rates:			
At target (%)	97.5	2.1	0.4
After 60 s decay (%)	95.8	2.8	1.4

[#] Calculated with the HIVAP code [21].

^S Half lives and α -branching from [22].

^{172}Os . A beam energy of 242.8 MeV (lab frame) was selected to maximize the production of ^{172}Os (according to the HIVAP code), the 2.8 MeV extra in comparison to the values in Table 1 is to compensate for energy loss in the target backing before the beam enters the Ce target material. ^{173}Os and ^{174}Os have increasingly higher cross-sections at lower beam energies.

³ The number of pulses depends on what other experiments are run simultaneously at the UNILAC, up to 6 different experiments can be run in parallel: One experiment will generally be “main beam” using most of the pulses, the others in “parasitic mode” take one or a few pulses per second or less. The experiment described in this article was performed in main-beam mode.

2.2. TASCA Separator and RTC

The gas-filled separator TASCA was used to separate osmium isotopes from unwanted nuclear by-products. For this test experiment, HTM operation [13] was selected, although for a hassium experiment SIM will probably give higher yield due to more efficient RTC flushing and shorter transport times. But since this experiment was run in tandem with another chemistry experiment requiring HTM, it was decided to run both in HTM. The magnet setting and other parameters used for TASCA are specified in Table 2, the magnet currents were empirically optimised to maximise the yield of ^{172}Os .

Table 2 TASCA parameters

Parameter:	
Fill gas	He
Pressure	1 mbar
Dipole magnet current	395 A
Quadrupole magnet currents	355 A
Magnetic rigidity	1.52 Tm

The Recoil Transfer Chamber (RTC) for HTM was mounted immediately behind the focal plane of the separator. The RTC and the window separating it from the separator's low-pressure zone are described in detail in [18, 19]. The RTC was swept out with an O_2/He mixture (10% O_2). The Os nuclides recoiling out of the target foil are stopped in the gas and oxidized to volatile tetroxide due to the presence of O_2 . To ensure complete and fast oxidation an oven was placed immediately after the RTC. It consisted of a quartz tube with a quartz wool-plug heated to about 677°C . Two heating sections, each of about 8 cm width, were used to ensure uniform heating along the total length of the wool plug.

The volatile tetroxide exiting the oven was then transported through a 26 meter long (i.d. = 1.0 mm) Teflon tube to the SISAK apparatus.

2.3. Chemistry system SISAK

An overview of the applied SISAK set-up is shown in Fig. 1. The chemistry and the extraction setup is explained in detail in the paper describing the development of the extraction system [9], performed at OCL. Only a general overview will be given here. Details about the SISAK centrifuges can be found in [2, 3], and references therein.

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OsO₄ from the carrier gas is dissolved in NaOH solution in a static mixer. After the mixer the gas is separated from the liquid phase using a SISAK degasser unit. The effluent of the degasser is then contacted with pure toluene in a second static mixer and the two phases are separated from each other by a SISAK centrifuge unit.

In order to deduce the distribution ratio of OsO₄ between the two phases, the amount of ¹⁷²Os in both phases must be measured. This is easy for the organic phase, as it can be directly mixed with a scintillator cocktail and measured by Liquid Scintillation (LS) α -spectroscopy. Before entering the detector cells, any oxygen in the solution must be removed because it interferes with the scintillator's ability to distinguish between α and β particles (performed by electronic Pulse Shape Discrimination (PSD)). Therefore, oxygen is purged from the solution by flushing with argon. Subsequently the gas is removed with a dedicated SISAK degasser, which also helps to pump the solution through the detection cells (therefore frequently referred to as a "booster"). The detection principle and spectroscopy requirements are described in detail in [11].

In contrast to the organic phase, the aqueous output from the centrifuge cannot be measured directly. This is because

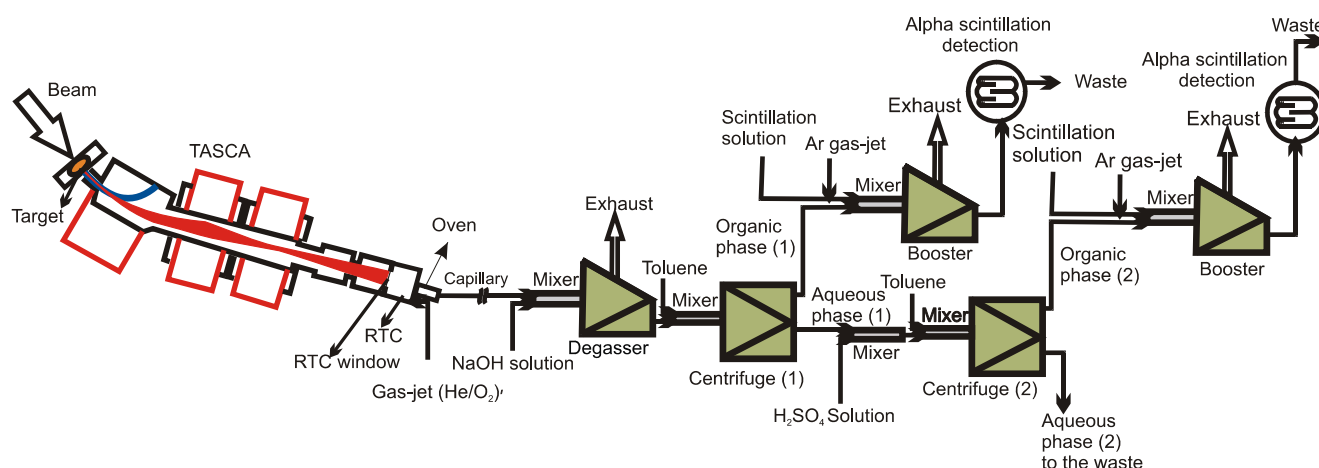


Fig. 1 The schematic set-up of the SISAK apparatus behind TASCA for measuring of distribution of ¹⁷²OsO₄ between NaOH solutions and toluene as a pilot experiment for chemical investigation of Hs experiment.

water and aqueous-phase components quench the scintillation process [11]. Consequently, to accurately measure the α -activity in the aqueous phase, a second extraction stage is needed to transfer the Os content of the aqueous phase into a second organic phase. This is achieved by acidification of the aqueous phase, which regenerates OsO₄, followed by mixing with toluene. The OsO₄ is efficiently extracted into the toluene, with a yield of (90 $\pm$ 3)% [9]. After separation of the phases in a second centrifuge, the organic phase can be

measured in the same way as the first organic phase (in a separate detector array with its own Ar-flushing and booster). Thus, the activity in the *second organic* phase represents the activity in the *aqueous phase after the first extraction*. The aqueous phase effluent of the second stage is discarded.

Flow rates and the most important experimental parameters are given in Table 3.

2.4. Chemicals and Recycling

NaOH was procured from Carl Roth GmbH + Co.KG with purity greater than 99%. The purity of H₂SO₄ was greater than 95% and delivered from the same company. 1-methyl naphthalene was delivered by SIGMA-ALDRICH with

Table 3 Experimental conditions during Os extraction

RTC, oven and gas jet	
10% O ₂ in He, total flow	1.0 L/min
RTC pressure	1.82 bar
Oven 1 temperature (outside tube)	685±2 °C
Oven 2 temperature (outside tube)	670±2 °C
Quartz wool plug temperature [#]	677±5 °C
SISAK	Flow
<i>First extraction stage:</i>	
Aq.: 0.0005 M or 0.005 M NaOH	0.2 mL/s
Org. 1: Pure toluene	0.2 mL/s
Scint. 1: 50% M-napht + 3 g/L 2M-POPOP	0.2 mL/s
Ar flushing gas	0.5 L/min
<i>Second extraction stage:</i>	
Acid: 0.001 M H ₂ SO ₄	0.1 mL/s
Org. 2: Pure toluene	0.2 mL/s
Scint. 2: 50% M-napht + 3 g/L 2M-POPOP	0.2 mL/s
Ar flushing gas	0.5 L/min

[#] Estimated from calibration

purity greater than 90%. The 1-methyl-naphthalene was distilled before use (using a vacuum distillation setup and Ar atmosphere). Dimethyl POPOP was of scintillation grade and was delivered by Fluka. The purity of toluene was higher than 99.5% and procured from Carl Roth GmbH + Co.KG.

The scintillation cocktail was prepared as a solution of 50 vol-% 1-methyl naphthalene, 3 g/L dimethyl POPOP (1,4-Bis(4-methyl-5-phenyl-2-oxazolyl)benzene) in toluene. It was mixed with the organic phases in a 1:1 ratio, thus the scintillation cocktail in the detection cells contained 25 vol-% 1-methyl naphthalene and 1.5 g/L dimethyl POPOP.

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The on-line SISAK experiment consumes rather large volumes of chemicals and produces large amounts of waste during the experiment, which was running continuously for several days. To reduce the chemical consumption the organic solution effluent was distilled and reused. First toluene was (to a large extent) removed in a RotaVapor with a 20 L flask. Methyl-naphthalene was then removed by vacuum distillation under inert atmosphere. Dimethyl POPOP was then separated as a precipitate after cooling and purified by washing with toluene (which subsequently could be reclaimed in the RotaVapor).

2.5. Yield measurements

Os (and Hs) atoms can be lost or delayed due to adsorption on tube and equipment surfaces. Furthermore, the transport time through the setup is of paramount importance, as decay losses usually is the most dominant factor in the overall yield. Clearly, for a future hassium experiment with production rate of only a few atoms per day, a high yield is absolutely necessary.

The pilot experiment described in this work was not set up to minimise transport time, but to demonstrate SISAK's capability to accurately measure the sodium hydroxide - toluene distribution of the volatile group-4 tetroxides by on-line α -measurements. The experiment was performed at lower liquid flow-rates than what a transactinide experiment would be using. In addition, the equipment was placed far away from TASCA, using a 26 m capillary. Nevertheless, it is of interest to measure the yield from the (HTM) RTC to the SISAK apparatus. This was done by γ measurements of the amounts of ^{173}W and ^{174}Re on an aluminium catcher foil placed directly behind the RTC entrance-window and comparing it to the amount found in a NaOH sample taken directly from the SISAK degasser. Tungsten and rhenium ions/atoms will not be transported without an aerosol-particle seeded gas-jet, thus the amount found in the NaOH solution must be decay products of osmium-isotopes after they have been dissolved the liquid in the degasser. It is assumed that also the ^{173}W and ^{174}Re on the Al catcher-foil is decay products of respectively ^{173}Os and ^{174}Os . It cannot be totally excluded that part of the tungsten and rhenium produced directly in the target will be transmitted through the TASCA separator and enter the RTC, but both the magnet settings and beam energy is unfavourable for the tungsten and rhenium isotopes. Directly produced tungsten and rhenium would result in that the calculated yield will be too low. A high yield would indicate that this is not a problem.

All γ -measurements was performed with a HPGe-detector with 80% efficiency (as compared to a "standard" 3" NaI-

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detector for ^{60}Co 1332 keV-rays). The Al foil was dissolved in a strong NaOH solution with the same volume as the samples from the degasser to ensure equal measuring geometry. The sampling-counting procedure was 10 min beam, 2.5 min pause to prepare the sample, and finally 10 min counting. The number of counts for a given nuclei in each spectrum were calculated from the sum of selected γ -ray peaks. For ^{173}W the 131 keV, 458 keV and 623 keV γ -rays were used, for ^{174}Re 113 keV and 243 keV were used.

The amount of ^{173}Os and ^{174}Os reaching the degasser depend, in addition to the overall yield, on the decay loss during the transport from the RTC to SISAK. Thus, decay correction must be performed. This demands that the transport time must be known. This was measured by two different methods: Directly using beam pulses and indirectly by observing the relative change in isotopic ratio between the two isotopes.

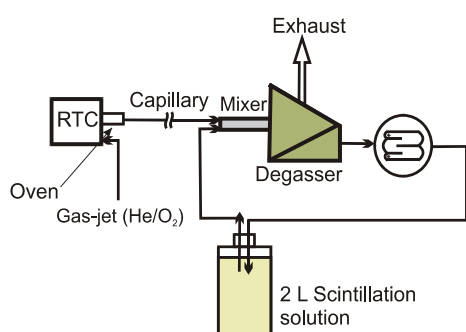


Fig. 2 Schematics for the set-up used for transport-time measurements.

The setup for directly measuring the transport time using beam pulses is shown in Fig. 2. For this experiment the liquid flow rate was increased to 0.4 mL/s, as the mean transport time through the degasser and into the detection cell is known from earlier experiments to be about 2.5 s [23] for this flow rate. The gross activity (mainly from β -particles and their γ - and annihilation-radiation) in the LS detection cell was measured as a function of time after the start of a 10-s beam pulse. The mean transport-time, i.e. the average time a particle will use from the RTC to the detection cell is taken as the time it takes for 50% of the activity to reach the detector cell. As starting point, the middle point of the beam pulse is used (when 50% of the activity has been produced).

The amount of activity produced in a 10-s beam pulse is too low to provide accurate data. Thus, the experiment is repeated continuously and the data added together until satisfactory statistics is obtained. The loop cycle time is selected long enough to ensure that all activity from the initial

beam-pulse has been detected. This is important, as otherwise the 50% point cannot be accurately calculated.

3. Results and discussion

3.1. Determination of α activity

The liquid scintillation detectors are sensitive to β particles and γ radiation in addition to α particles. Thus, Pulse Shape Discrimination (PSD) was used to distinguish α -particles from other events. Details of the data analysis method, together with the detector system, are described in detail in [11]. This method works very well for transactinide experiments, where a physical preseparator have been used to remove most of the unwanted background. It would otherwise result in a β/γ count-rate so high that all data would be completely masked by pile-up events.

For the current experiment, where only a small fraction of the activity decays by α emission, there is a rather high amount of β/γ activity. Thus, much more β 's and γ 's are present in the spectrum than usual; a small fraction of these

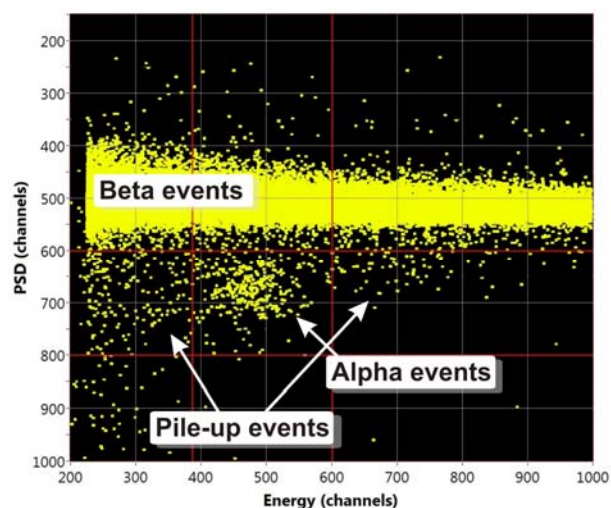


Fig. 3 A typical matrix of Pulse-Shape Discrimination vs. energy obtained from the extraction experiments described in this work.

will result in pile-up events. An example of this can be seen in Fig. 3. In the analysis, the amount of pile-ups in the α -PSD region was corrected for by measuring the amount on either side of the α -energy region. Since there are more low-energy events, there will be correspondingly more pile-up events to the left of the α region than to the right. The amount of pile-ups in the α region was calculated by linear interpolation of the amounts to the left and right.

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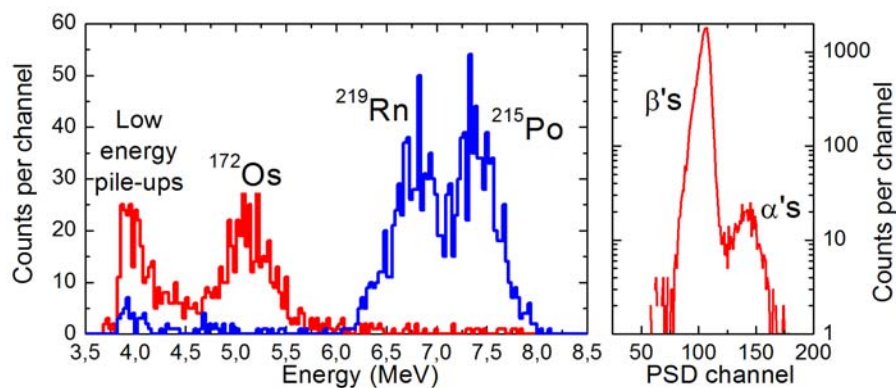


Fig. 4. Energy (left panel) and PSD (right panel) spectra from the detector cell measuring on the organic phase from the first extraction stage. Data from extraction from 0.0005 M NaOH. A calibration spectrum from ^{219}Rn emanation from an ^{227}Ac source is inserted in the energy spectrum (left panel) for comparison.

The energy resolution and quality of a typical α -spectrum is illustrated in Fig. 4 for data measured on the (first) organic phase. The data is shown together with a calibration spectrum generated by a ^{227}Ac emanation source, which provides ^{219}Rn and ^{215}Po α 's [11]. The energy spectra were projected from data gated on the α part of the PSD spectrum. In the right panel the PSD spectrum for the energy region 2.9 to 5.7 MeV, corresponding to the ^{172}Os α -peak, is shown. Usually, there is hardly any counts between the α and β PSD peaks, but in this case the separation is not so good due to the higher amount of β 's and γ 's. In addition, the separation is less good for low energy α 's, as emitted by ^{172}Os . Transactinide α 's typically have energies from 9 MeV and upwards.

3.2. Distribution ratios

Distribution ratio of OsO_4 between NaOH solution and toluene was measured at two concentrations of NaOH in the aqueous solution. A distribution ratio of unity has the lowest uncertainty for a given number of counts. Thus the NaOH concentration of 5×10^{-4} M was selected since it results in a distribution ratio close to unity, as found in experiments at OCL. The other concentration used was 0.005 M. The results obtained from the TASCA experiment measured with the SISAK on-line α detectors are compared to results from OCL measured with γ emitting Os-nuclei in Fig 5. As can be clearly seen, the results are in good agreement.

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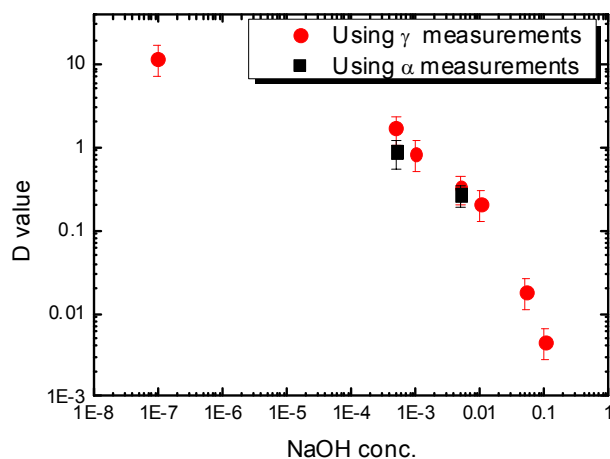


Fig. 5. A comparison of the results from the experiment at GSI with α -emitting Os to the SISAK experiment at OCL using γ -emitting Os.

3.3. Yield Measurements

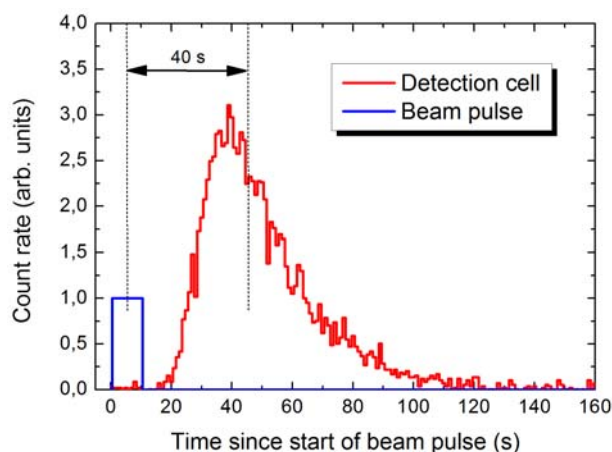


Fig. 6. Measured transport-time from the RTC to a SISAK detection cell coupled directly to the degasser.

Using the setup described in Section 2.5 and Fig. 2, 10 s beam pulses were used to measure the amount of activity, as a function of time since start of the beam pulses, in a detection cell placed immediately after the degasser. The result is shown in Fig. 6. From this curve the average transport time is found to be 40 ± 3 s (zero is defined as the middle of the beam pulse, i.e. after 5 s). Liquid flow rate was 0.4 mL/s, gas flow 1 L/min (He with 10% O), resulting in a RTC pressure of 1.8 bar.

The average transit time through a SISAK mixer/degasser is about 2.5 s [23], thus the average transport time from the RTC to the SISAK apparatus was 38.5 s, with an estimated uncertainty of ± 4 s.

The long tail of the transport-time curve is, most likely, in a large part due to the large volume of the HTM RTC. In the SIM RTC, with a much smaller volume and more efficient flushing, the tailing should be reduced. For short lived activity this is important, as most activity in the tail will decay before reaching the detectors.

The transport time was also measured indirectly: The amount of ^{173}W and ^{174}Re activity on an aluminium catcher-foil, placed directly behind the RTC window, and in 120 mL 0.0005-M NaOH samples from the degasser were compared. Sample and measurement times were 10 min., with a 2.5 min pause in between. The sum of the counts in the selected γ -ray peaks (see section 2.5) representing ^{173}Os and ^{174}Os were divided by the beam integrals for normalisation.

Table 3 Measured activity at the RTC entrance window and in the effluent from the degasser.

	^{173}W , representing ^{173}Os	^{174}Re , representing ^{174}Os
Al-catcher foil	1519 ± 20	3802 ± 28
0.0005 M NaOH	601 ± 12	792 ± 13

The experiment was repeated three times and the average results are given in Table 3.

Since ^{173}Os and ^{174}Os have sufficiently different half-lives, the change in the ratio between them can be used to calculate the transport time. Using the data from Table 3, a transport time of 41 ± 3 s results, which is in reasonable agreement with the directly measured transport time. The average between the two methods is 40 ± 3 s.

The transport yield from the RTC to the entrance of the chemistry apparatus can then be calculated from Table 3, using 40 s transport time. This gives $(53 \pm 5)\%$ from the ^{173}Os data, and $(45 \pm 5)\%$ from ^{174}Os . These numbers include the yield loss in the transfer of activity from the gas to the liquid phase in the degasser. The later yield is not known for the volatile OsO_4 , since such yields normally is determined by measuring the activity transferred to the liquid phase by the mixer/degasser assembly in comparison to the amount of activity from aerosol particles caught on a filter in which the gas jet passes. Obviously, the volatile OsO_4 will not be retained by the filter. For aerosol-carried particles the mixer/degasser yield is around 80%. Assuming this is representative for the tetroxide also, the RTC and gas-jet transfer yield to the chemistry apparatus is around $(60 \pm 10)\%$ (uncertainty only roughly estimated). From experiments at OCL, using the same gas-flows and pressures as used in the work described here, it is known that the gas-

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jet loss in a 20 m capillary is about 50%. However, when transporting the volatile OsO_4 , this loss is much lower and we usually observe yields of more than 90% (including the loss in the mixer/degasser). This indicates that the large RTC is not very suitable for SISAK experiments, as most of the loss must have occurred in the recoil chamber. This can either be due to insufficient depth, i.e. a fraction of the EVRs was shot into the back wall, or due to inefficient flushing-out of the RTC.

The measured average transport-time from the RTC to SISAK is about four half-lives of ^{269}Hs . (In addition it will take between 15 and 20 s to travel through SISAK.) Clearly, this is too long for a 10-s nuclide produced at a rate of a few per day. Transport through a 26 m gas capillary is rather fast, thus most of the 40 s the OsO_4 uses, on average, to travel from the RTC to the SISAK apparatus is most likely due to inefficient flushing of the RTC. As mentioned in the introduction, using the SIM RTC will improve this significantly.

4. Conclusion

In this work it was demonstrated that it is possible to obtain liquid-liquid extraction data for hydroxyl complexes of OsO_4 by on-line α -measurements using SISAK and liquid scintillation spectroscopy. The obtained data agree well with data measured by γ -spectroscopy at the Oslo Cyclotron Laboratory. The experiment provided valuable experience for future SISAK experiments behind TASCA and highlighted parameters which need to be changed or improved in order to do the best possible transactinide experiments with SISAK at GSI.

The most important issue to address before a hassium experiment can be performed is the transfer yield and decay loss (long transport time). Even though the transmission through TASCA is about a factor 2/3 lower when using the SIM RTC (in comparison to the HTM unit), this will by far be outweighed by the much shorter average transport time when using the SIM RTC. In addition, it is likely that the yield, not including transport time gains, will also increase for the SIM RTC.

Increasing the gas-flow rate is also known to increase the gas-jet yield, but the limiting factor here is the fragile RTC window and gas-liquid transfer yield (which decreases when the gas-liquid ratio becomes very unfavourable for the liquid). A new type of degasser, using membrane technology, is under development to address these issues. One of the design goals is to enable operation at a lower gas pressure than the current degasser. Unlike the current de-

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gasser, it has no moving parts. Thus, it is more robust and requires less attention than the current units. The overall aim is to develop a version of SISAK which will run with a minimum of attention for long periods and can maybe even be placed inside the TASCA cave to minimise transport losses.

It is interesting to estimate the required length of a liquid-liquid extraction experiment on hassium. This is dictated by the minimum number of events required to obtain a statistical significant result. The number of events needed to determine a specific distribution ratio with a certain accuracy is calculated in [24]: If a standard deviation of 50% for the

Table 4 Estimated yield factors for a future hassium experiment using ^{269}Hs .

Yield factor	
TASCA transmission (in SIM)	0.4
RTC window loss due to grid support	0.8
RTC flush out and gas-transfer yield	0.8
5 s RTC to chemistry apparatus transport [#]	0.7
10 s SISAK transport time [§]	0.5
SISAK mixer/degasser yield	0.8
$^{269}\text{Hs} - ^{265}\text{Sg}$ chain detection probability [§]	0.9
Overall	0.065

[#] Assumes that chemistry apparatus is mounted close to TASCA and SIM RTC.

[§] Assumes 50% improvement on current transport-time by optimization of SISAK and improved degassers.

[§] Assumes 100% α -branch in both ^{269}Hs and ^{265}Sg .

distribution ratio is accepted, then 16 atoms needs to be detected for a distribution ratio of 1.

Two hassium isotopes have half-lives long enough to be suitable for chemistry experiments: 9.7 s ^{269}Hs [25] and 22 s ^{270}Hs [26]. However, the later was calculated indirectly from α -decay energy and is rather uncertain. In addition, for LS spectroscopy, it is not possible to detect fission decay reliable enough to identify members of a decay chain. Thus, ^{270}Hs , with its fission-decaying ^{266}Sg daughter, is not suitable for SISAK and LS detection. In a hassium experiment, ^{269}Hs is therefore the most suited isotope and is used here for decay loss estimates and detection efficiency. The relevant yields are given in Table 4. As can be seen, when the relevant factors are multiplied, only 6.4% of the events is actually detected. For the 16 required events this demands about 250 ^{269}Hs nuclei to be produced. For the $^{248}\text{Cm}(^{26}\text{Mg},5n)^{269}\text{Hs}$ reaction the cross section is about 7 pb [26] and in past chemistry experiments at GSI with this reaction about 8 ^{269}Hs nuclei was produced per day (based on 1,5 μA (DC) intensity of ^{26}Mg particles and 3.4 μg of ^{248}Cm target). This would require 31 days of experiment time. In addition, at least 25% must be added to compensate

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for maintenance and down-time due to breakage. I.e. about 40 days is needed. This is probably unrealistic with respect to obtaining beam-time, manpower and funding. However, the UNILAC is operated in pulsed mode in such a way that the beam is only present 25% of the time (5 μ s pulse and 15 μ s pause). Plans are under way to construct a new machine which provides true DC beam and this would increase the beam intensity with a factor 4. The targets can withstand this, as the limiting factor is the instantaneous beam intensity and not the average intensity. With such a machine, the SISAK hassium experiment described here can be performed in about 10 days of beam time, which is realistic.

Acknowledgements. We thank the GSI UNILAC linear accelerator operators for providing stable and intense beam. We thank the Norwegian Research Council (NFR) for financing of this project (No. 177538).

References

1. Schädel, M., in *The Chemistry of Superheavy Elements*. Kluwer Academic Publishers, Dordrecht, 2003, ISBN 1-4020-1250-0.
2. Persson, H., Skarnemark, G., Skalberg, M., Alstad, J., Liljenzin, J. O., Bauer, G., Haberberger, F., Kaffrell, N., Rogowski, J., and Trautmann, N.: *Radiochim. Acta* **48**, 177 (1989).
3. Omtvedt, J. P., Alstad, J., Eberhardt, K., Fure, K., Malmbeck, R., Mendel, M., Nahler, A., Skarnemark, G., Trautmann, N., Wiehl, N., and Wierczinski, B.: *Journal of Alloys and Compounds* **271**, 303 (1998).
4. Eichler, R., Aksenov, N. V., Albin, Y. V., Belozarov, A. V., Bozhikov, G. A., Chepigin, V. I., Dmitriev, S. N., Dressler, R., Gaggeler, H. W., Gorshkov, V. A., Henderson, R. A., Johnsen, A. M., Kenneally, J. M., Lebedev, V. Y., Malyshev, O. N., Moody, K. J., Oganessian, Y. T., Petrushkin, O. V., Piguet, D., Popeko, A. G., Rasmussen, P., Serov, A., Shaughnessy, D. A., Shishkin, S. V., Shutov, A. V., Stoyer, M. A., Stoyer, N. J., Svirikhin, A. I., Tereshatov, E. E., Vostokin, G. K., Wegrzecki, M., Wilk, P. A., Wittwer, D., and Yerebin, A. V.: *Radiochim. Acta* **98**, 133 (2010).
5. Eichler, R., Aksenov, N. V., Belozarov, A. V., Bozhikov, G. A., Chepigin, V. I., Dmitriev, S. N., Dressler, R., Gaggeler, H. W., Gorshkov, V. A., Haenssler, F., Itkis, M. G., Laube, A., Lebedev, V. Y., Malyshev, O. N., Oganessian, Y. T., Petrushkin, O. V., Piguet, D., Rasmussen, P., Shishkin, S. V., Shutov, A. V., Svirikhin, A. I., Tereshatov, E. E., Vostokin, G. K., Wegrzecki, M., and Yerebin, A. V.: *Nature* **447**, 72 (2007).

Author	Title	File Name	Date	Page
F. Samadani a,*, J. Alstada, T. Bjørnstada, Ch.E. Düllmannb, K. Eberhardt, J. Evend, J.M. Gatesb, D. Hild, E. Jägerb, J. Khuyagbaatarb, J.V. Kratzd, J. Krierb, J. Nilssena, H.B. Ottesena, S. Qureshia, Ch. Rothd, M. Schädelb, B. Schaustenb, F. Schulza, A.	A SISAK extraction system for chemical study of Hs	Article_2_TASC A-Os_experiment_v26_11Aug2010_f_JPO.doc	12.08.2010	18 (21)

6. Dullmann Ch, E., Bruchle, W., Dressler, R., Eberhardt, K., Eichler, B., Eichler, R., Gaggeler, H. W., Ginter, T. N., Glaus, F., Gregorich, K. E., Hoffman, D. C., Jager, E., Jost, D. T., Kirbach, U. W., Lee, D. M., Nitsche, H., Patin, J. B., Pershina, V., Piguet, D., Qin, Z., Schadel, M., Schausten, B., Schimpf, E., Schott, H. J., Soverna, S., Sudowe, R., Thorle, P., Timokhin, S. N., Trautmann, N., Turler, A., Vahle, A., Wirth, G., Yakushev, A. B., and Zielinski, P. M.: *Nature* **418**, 859 (2002).
7. von Zweidorf, A., Angert, R., Bruchle, W., Burger, S., Eberhardt, K., Eichler, R., Hummrich, H., Jager, E., Kling, H. O., Kratz, J. V., Kuczewski, B., Langrock, G., Mendel, M., Rieth, U., Schadel, M., Schausten, B., Schimpf, E., Thorle, P., Trautmann, N., Tsukada, K., Wiehl, N., and Wirth, G.: *Radiachim. Acta* **92**, 855 (2004).
8. Pershina, V.: *Radiachim. Acta* **93**, 373 (2005).
9. Samadani, F., Alstad, J., Bjørnstad, T., Stavsetra, L., and Omtvedt, J. P.: *Developing a Sisak Extraction System for Chemical Studies of Element 108, Hassium*, Accepted for publication in *Radiachim. acta*, 2010, to be published.
10. Omtvedt, J. P., Alstad, J., Bjørnstad, T., Dullmann, C. E., Gregorich, K. E., Hoffman, D. C., Nitsche, H., Opel, K., Polakova, D., Samadani, F., Schulz, F., Skarnemark, G., Stavsetra, L., Sudowe, R., and Zheng, L.: *European Physical Journal D* **45**, 91 (2007).
11. Stavsetra, L., Gregorich, K. E., Alstad, J., Breivik, H., Eberhardt, K., Folden, C. M., Ginter, T. N., Johansson, M., Kirbach, U. W., Lee, D. M., Mendel, M., Omtvedt, L. A., Patin, J. B., Skarnemark, G., Sudowe, R., Wilk, P. A., Zielinski, P. M., Nitsche, H., Hoffman, D. C., and Omtvedt, J. P.: *Nuclear Instruments & Methods in Physics Research Section a-Accelerators Spectrometers Detectors and Associated Equipment* **543**, 509 (2005).
12. Omtvedt, J. P., Alstad, J., Breivik, H., Dyve, J. E., Eberhardt, K., III, C. M. F., Ginter, T., Gregorich, K. E., Hult, E. A., Johansson, M., Kirbach, U. W., Lee, D. M., Mendel, M., Nähler, A., Ninov, V., Omtvedt, L. A., Patin, J. B., Skarnemark, G., Stavsetra, L., Sudow, R., Wiehl, N., Wierczinski, B., Wilk, P. A., Zielinski, P. M., Kratz, J. V., Trautmann, N., Nitsche, H., and Hoffman, D. C.: *Journal of Nuclear and Radiochemical Sciences* **3**, 121 (2002).
13. Semchenkov, A., Bruchle, W., Jager, E., Schimpf, E., Schadel, M., Muhle, C., Klos, F., Turler, A., Yakushev, A., Belov, A., Belyakova, T., Kaparkova, M., Kukhtin, V., Lamzin, E., and Sytchevsky, S.: *Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms* **266**, 4153 (2008).

Author
 F. Samadani a*, J.
 Alstada, T. Bjørnstad,
 Ch.E. Düllmannb, K.
 Eberhardt, J. Evend, J.M.
 Gatesb, D. Hild, E.
 Jägerb, J. Khuyagbaatarb,
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 _f_JPO.doc

Date

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Page

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14. Schadel, M.: European Physical Journal D **45**, 67 (2007).
15. Düllmann, C. E.: Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms **266**, 4123 (2008).
16. Trautmann, N., Aronsson, P. O., Bjornstad, T., Kaffrell, N., Kvale, E., Skarestad, M., Skarnemark, G., and Stender, E.: Inorg Nucl Chem Lett **11**, 729 (1975).
17. Kirbach, U. W., Folden, C. M., Ginter, T. N., Gregorich, K. E., Lee, D. M., Ninov, V., Omtvedt, J. P., Patin, J. B., Seward, N. K., Strellis, D. A., Sudowe, R., Turler, A., Wilk, P. A., Zielinski, P. M., Hoffman, D. C., and Nitsche, H.: Nuclear Instruments & Methods in Physics Research Section a-Accelerators Spectrometers Detectors and Associated Equipment **484**, 587 (2002).
18. Even, J., Balloi, J., Bruchle, W., Buda, R. A., Düllmann, C. E., Eberhardt, K., Gorshkov, A., Gromm, E., Hild, D., Jäger, E., Khuyagbaatar, J., Kratz, J. V., Krier, J., Liebe, D., Mendel, M., Nayak, D., Opel, K., Omtvedt, J. P., Reichert, P., Runke, J., Sabelnikov, A., Samadani, F., Schädel, M., Schausten, B., Scheid, N., Schimpf, E., Semchenkov, A., Thörle-Pospiech, P., Toyoshima, A., Türlér, A., Vicente Vilas, V., Wiehl, N., Wunderlich, T., and Yakushev, A.: *The Recoil Transfer Chamber - an Interface to Connect the Physical Preseparator Tasca with Chemistry and Counting Setups*, In preparation for publication in Radiochim. acta, 2010, to be published.
19. Omtvedt, J. P., Düllmann, C. E., Even, J., Hummrich, H., Opel, K., Kratz, J. V., Lahiri, S., Jäger, E., Nayak, A., Sabelnikov, A., Samadani, F., Schädel, M., Schausten, B., Schimpf, E., Semchenkov, A., Toyoshima, A., Türlér, A., Wiehl, N., and Yakushev, A.: *Tasca Recoil Transfer Chamber for Chemistry Experiments with Very Short-Lived Transactinide Elements*, In preparation for publication, 2010, to be published.
20. Eberhardt, K., Bruchle, W., Düllmann, C. E., Gregorich, K. E., Hartmann, W., Hubner, A., Jager, E., Kindler, B., Kratz, J. V., Liebe, D., Lommel, B., Maier, H. J., Schadel, M., Schausten, B., Schimpf, E., Semchenkov, A., Steiner, J., Szerypo, J., Thorle, P., Turler, A., and Yakushev, A.: Nuclear Instruments & Methods in Physics Research Section a-Accelerators Spectrometers Detectors and Associated Equipment **590**, 134 (2008).
21. Reisdorf, W. and Schadel, M.: Zeitschrift Fur Physik a-Hadrons and Nuclei **343**, 47 (1992).
22. Firestone, R. B., Shirley, V. S., Baglin, C. M., Chu, F., and Zipkin, J.: *Table of Isotopes*. John Wiley & Sons, Inc., (1996).
23. Polakova, D., *personal communication* (2010).

Author F. Samadani a*, J. Alstada, T. Bjørnstada, Ch.E. Düllmannb, K. Eberhardt, J. Evend, J.M. Gatesb, D. Hild, E. Jägerb, J. Khuyagbaatarb, J.V. Kratzd, J. Krierb, J. Nilssena, H.B. Ottesena, S. Qureshia, Ch. Rothd, M. Schädelb, B. Schaustenb, F. Schulza, A.	Title A SISAK extraction system for chemical study of Hs
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24. Ekberg, C. and Skarnemark, G.: Journal of Radioanalytical and Nuclear Chemistry **263**, 71 (2005).
25. Morita, K., Morimoto, K., Kaji, D., Akiyama, T., Goto, S. I., Haba, H., Ideguchi, E., Katori, K., Koura, H., Kudo, H., Ohnishi, T., Ozawa, A., Suda, T., Sueki, K., Tokanai, F., Yamaguchi, T., Yoneda, A., and Yoshida, A.: J Phys Soc Jpn **76** (2007).
26. Dvorak, J., Bruchle, W., Chelnokov, M., Dressler, R., Düllmann, C. E., Eberhardt, K., Gorshkov, V., Jäger, E., Krücken, R., Kuznetsov, A., Nagame, Y., Nebel, F., Novackova, Z., Qin, Z., Schadel, M., Schausten, B., Schimpf, E., Semchenkov, A., Thorle, P., Turler, A., Wegrzecki, M., Wierczinski, B., Yakushev, A., and Yerein, A.: Physical Review Letters **97** (2006).

Author	Title	File Name	Date	Page
F. Samadani a*, J. Alstada, T. Bjørnstada, Ch.E. Düllmannb, K. Eberhardtd, J. Evend, J.M. Gatesb, D. Hilded, E. Jägerb, J. Khuyagbaatarb, J.V. Kratzd, J. Krierb, J. Nilssena, H.B. Ottesena, S. Qureshia, Ch. Rothd, M. Schädelb, B. Schaustenb, F. Schulza, A.	A SISAK extraction system for chemical study of Hs	Article_2_TASC A-Os_experiment_v26_11Aug2010_f_JPO.doc	12.08.2010	21 (21)

Report I

TASCA Commissioning Completed*

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The TransActinide Separator and Chemistry Apparatus (TASCA) project [1], which is focusing on the separation and investigation of neutron-rich transactinide nuclides produced in actinide-target based reactions, has successfully finished its commissioning; see [2] for an interim report. TASCA is ready for the envisioned research program which includes both chemical investigations of transactinide or superheavy elements (SHE) after pre-separation with the gas-filled separator and nuclear structure and nuclear reaction studies.

The central device of TASCA is a gas-filled separator in a DQQ configuration operated either in the "High Transmission Mode" (HTM, DQ_hQ_v) or in the "Small Image Mode" (SIM, DQ_vQ_h) [1-5]. In the HTM, the unsurpassed transmission of TASCA - at a relatively low dispersion - is exploited. In contrast, the SIM provides unique possibilities due to its small spot size in the focal plane (< 3 cm diam.) at a still relatively high transmission; see Table 1.

Table 1: Important parameters of TASCA, calculated for the reaction $^{48}\text{Ca}(^{244}\text{Pu}, 3n)^{289}114$, in comparison with other gas-filled separators operated in SHE research.

Separator	Con- figu- ration	Trans- mission %	Dis- persion mm/%	Bp (max) Tm
DGFRS	DQ _h Q _v	35	7.5	3.1
GARIS	DQ _h Q _v D	40	9.7	2.16
BGS	Q _v D _h D	49-59	20	2.5
TASCA	DQ _h Q _v	60	9	2.3
TASCA	DQ _v Q _h	35	1	2.3

Table 2 provides a compilation of all nuclear reactions and reaction products applied and detected in the course of the commissioning program together with the mode TASCA was operated in and the fill gas. Also listed are experiments to test and optimize the recoil transfer chambers (RTC) [6], the gas-jet transport of pre-separated products into our Rotating wheel On-line Multidetector Analyzer (ROMA), and its performance, and the coupling and

use of aqueous chemistry set-ups behind TASCA.

Table 2: Nuclear reactions and their products used to commission TASCA; H=HTM, S=SIM, TSp=TASISpec, R=ROMA, C=chemistry, catch=catcher foils.

Product	xn	Beam	Target	Mode	Gas	RTC +R/C
^{30}Si	--	^{30}Si	--	H,S	Vac	
$^{173,175}\text{Os}$	7n	^{40}Ar	^{144}Ce	H	He	C
$^{180-182}\text{Hg}$	2-4n	^{40}Ar	^{144}Sm	H,S	He	C
^{188}Pb	4n	^{48}Ca	^{144}Sm	H,S	He	
^{188}Pb	4n	^{40}Ar	^{152}Gd	H,S	He	
$^{194-196}\text{Pb}$	4-5n	^{40}Ar	^{144}Sm	H,S	He	R
$^{198-199}\text{Bi}$	4-5n	^{22}Ne	^{181}Ta	H,S	He	catch
$^{195-196}\text{Po}$	4-5n	^{48}Ca	^{152}Gd	H	He	R
^{200}At	3n	^{64}Ni	^{141}Pr	TSp	He	
^{200}Fr	5n	^{64}Ni	^{141}Pr	TSp	He	
$^{205-206}\text{Fr}$	5-6n	^{30}Si	^{181}Ta	H	He	
$^{208-211}\text{Ra}$	3-4n	^{54}Cr	^{144}Sm	H,S	He	
$^{208-211}\text{Ra}$	3-6n	^{64}Ni	^{150}Nd	TSp	He	
^{210}Ac	5n	^{40}Ar	^{144}Sm	H,S	He, N ₂	
^{215}Ac	4n	^{22}Ne	^{197}Au	H,S	He, H ₂	
$^{218-x}\text{Th}$	xn	^{64}Ni	^{154}Sm	TSp	He	
$^{224-x}\text{U}$	xn	^{64}Ni	^{144}Sm	TSp	He, H ₂	
^{245}Fm	3n	^{40}Ar	^{208}Pb	H,S	He	R
^{252}No	2n	^{48}Ca	^{206}Pb	H,S	He	R
^{253}No	2n	^{48}Ca	^{207}Pb	TSp	He	
^{254}No	2n	^{48}Ca	^{208}Pb	H,S	He, H ₂	
^{255}No	5n	^{22}Ne	^{238}U	H,S	He, H ₂	R
^{256}No	4n	^{22}Ne	^{238}U	H	He	
^{260}Rf	6n	^{22}Ne	^{244}Pu	H	He, H ₂	
$^{261a,261b}\text{Rf}$	5n	^{22}Ne	^{244}Pu	H	He	R,C
^{262}Rf	4n	^{22}Ne	^{244}Pu	H	He, H ₂	

Extensive studies have been performed in the HTM and SIM to obtain optimized parameter sets for (i) the target thickness and stability, (ii) the gas pressure and the gas filling (He, H₂, and mixtures), (iii) the dipole setting (Bp) and quadrupole focusing, (iv) the RTCs (window material and thickness, support structures, and size and shape of the chamber), (v) gas-jet transport of pre-separated products, and (vi) the coupling and performance of devices

* Work supported by BMBF (06MT247I, 06MT248, 06MZ223I) and GSI-F&E (MT/TÜR, MZJVKR) [#]m.schaedel@gsi.de

like ROMA and the Automated Rapid Chemistry Apparatus (ARCA). Results of many of these parameter studies were compared with TASCA model calculations [7] and very good agreement was achieved. This agreement is of special importance as it allows for the selection of proper settings for magnetic rigidities ($B\rho$) in the dipole magnet and the quadrupole magnets for all nuclear reactions and for all gases and gas mixtures tested at various pressures. It is especially rewarding to see that not only $B\rho$ values were properly chosen to centre product distributions on focal plane detectors (FPD) but also that the measured spatial distributions and, more importantly, the efficiencies were in very good agreement with model calculations. These results confidently demonstrate that we are able to perform trustworthy SHE experiments with TASCA. In the following, we mention a few concluding experiments, some of the highlights and new developments; see [2] for additional information on the parameter studies.

The first efficiency measurements with catcher foils behind the target and in the focal plane showed very good agreement with model calculations for the fairly asymmetric reaction $^{22}\text{Ne}(^{181}\text{Ta},\text{xn})^{198\text{m},199}\text{Bi}$ [2]. To confirm this agreement in a more symmetric reaction, leading to a significantly heavier reaction product, and to obtain a standard reaction to test and check the TASCA performance, detailed studies were performed with well known reactions of ^{48}Ca with $\approx 0.5 \text{ mg/cm}^2$ thick targets of $^{206,207,208}\text{Pb}$ leading to $^{252,253,254}\text{No}$. Assuming cross sections of 0.5 μb , 1.3 μb , and 2 μb [8] for the production of ^{252}No , ^{253}No , and ^{254}No , efficiencies of 54%, 56%, and 50%, respectively, were obtained for the HTM, using a He filling of 0.8 mbar, and a (80x36) mm^2 16-strip FPD. Taking into account uncertainties in cross sections and systematic errors of target thicknesses and beam current measurements, we observe an excellent agreement with model calculations [7] predicting 54%. Equally good is the agreement in the SIM, at a He pressure of 0.8 mbar, where a 30% efficiency was measured for the reaction $^{48}\text{Ca}(^{208}\text{Pb},2\text{n})^{254}\text{No}$.

A new (140x40) mm^2 large, highly efficient FPD, consisting of double-sided silicon strip detectors (DSSSD) in the focal plane and SSDs for the backward box detectors will further increase the TASCA efficiency; see [9] for details of the new detector.

As one of the crucial tests and one of the highlights finalizing the TASCA commissioning program, we studied the isotopes ^{260}Rf , $^{261\text{a}},^{261\text{b}}\text{Rf}$, and ^{262}Rf synthesized in the very asymmetric reaction $^{22}\text{Ne} + ^{244}\text{Pu}$; see [10] for details of the nuclear reactions, for TASCA parameters, and for the interesting nuclear decay results. In essence, the performance of TASCA was as anticipated; everything worked well, including the ^{244}Pu target wheel. Efficiencies and magnetic settings ($B\rho=1.99 \text{ Tm}$ at 0.4 mbar He, HTM) were as expected. As observed in previous experiments [2], it was again possible to reduce the background in the FPD by using a mixture of He and H_2 . This part of the commissioning program showed clearly that TASCA can be applied efficiently for nuclear decay and nuclear

reaction studies of neutron-rich nuclides of SHE synthesized in very asymmetric hot-fusion reactions. Rf isotopes were not only measured in the FPD but were also collected in an RTC and were transported either to ROMA for nuclear decay measurements [10] or to ARCA for chemical investigations [11].

An additional highlight of the experiment was the first transactinide chemistry behind TASCA designed as a proof-of-principle experiment. It was performed in ARCA with pre-separated 78-s $^{261\text{a}}\text{Rf}$; details of the nuclear reaction and the Rf separation in TASCA are described in [10] while all chemical aspects are discussed in [11]. This successful experiment, which studied the formation of Rf-fluoride complexes and their adsorption behaviour on an anion-exchange resin, demonstrated that aqueous-phase transactinide chemistry behind TASCA can now be performed.

The new set-up termed *TASCA Small Image mode Spectroscopy* (TASISpec) [12] exploits advantages of the SIM, i.e. the fact that neutron-rich nuclides of SHE, produced in hot-fusion reactions, can be focused with high efficiency into an area of $< 7 \text{ cm}^2$. This provides the unique possibility to build a compact Si-detector box for α -particle, electron, and fission-fragment measurements, and to pack composite Ge-detectors in very close geometry, resulting in an unprecedented, highly efficient set-up for multi-coincidence measurements with γ -rays and X-rays; see [12] for details. A prototype set-up has been commissioned successfully and first data have been collected for nuclides as heavy as $^{252,253}\text{No}$.

In conclusion, the performance of TASCA as a separator is well understood and is perfectly under control. TASCA as a whole is presently the most versatile and highest efficient instrument in SHE research worldwide. It has entered the region of transactinides or superheavy elements, and is ready to explore the physics and chemistry of the "terra incognita" it was designed and built for.

References

- [1] M. Schädel *et al.*, GSI Sci. Rep. 2005, GSI Report 2006-1, 2006, p. 262, and <http://www.gsi.de/TASCA>
- [2] M. Schädel *et al.*, GSI Sci. Rep. 2007, GSI Report 2008-1, 2008, p. 152.
- [3] M. Schädel, Eur. Phys. J. D 45 (2007) 67.
- [4] A. Semchenkov *et al.*, Nucl. Instr. and Meth. in Phys. Res. B 266 (2008) 4153.
- [5] Ch.E. Düllmann *et al.*, Nucl. Instr. and Meth. in Phys. Res. B 266 (2008) 4123.
- [6] Ch.E. Düllmann *et al.*, GSI Sci. Rep. 2006, GSI Report 2007-1, 2007, p. 146.
- [7] K.E. Gregorich *et al.*, GSI Sci. Rep. 2006, GSI Report 2007-1, 2007, p. 144.
- [8] Yu. Ts. Oganessian *et al.*, Phys. Rev. C 64 (2001) 054606.
- [9] A. Yakushev *et al.*, contribution to this report.
- [10] A. Gorshkov *et al.*, contribution to this report.
- [11] J. Even *et al.*, contribution to this report.
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Report II

Measurements of $^{260-262}\text{Rf}$ produced in $^{22}\text{Ne} + ^{244}\text{Pu}$ fusion reaction at TASCA*

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As a final experiment in the commissioning phase of TASCA the transactinides ($Z \geq 104$) were reached. Production and decay of ^{260}Rf , $^{261a,b}\text{Rf}$ and ^{262}Rf [1,2,3], produced in the asymmetric nuclear fusion reaction $^{244}\text{Pu}(^{22}\text{Ne},\text{xn})$ was studied. Separated reaction products were guided to a Focal Plane Detector (FPD) or into a Recoil Transfer Chamber (RTC), where they were available for transport to either the Rotating wheel On-line Multidetector Analyzer (ROMA) or to the Automated Rapid Chemistry Apparatus (ARCA) for chemical experiments [4].

TASCA was operated in the High Transmission Mode (HTM) [5]. The ^{22}Ne ion beam (average intensity: 0.8 $\mu\text{A}_{\text{part}}$) impinged on a rotating target wheel with 0.4 mg/cm^2 $^{244}\text{PuO}_2$ targets on 2.2 μm Ti backings. Three beam energies in the center of the target, $E_{\text{c.o.t.}}$, of 109 MeV, 116 MeV and 125 MeV, were used for the production of ^{262}Rf , ^{261}Rf and ^{260}Rf , respectively. The transmission of Rf has been optimized in He filling gas. The optimal pressure was 0.4 mbar. The magnetic rigidity, $B\rho$, was determined to be 1.99 T·m. To increase suppression of unwanted products, a He/H₂ (2:1) filling gas at a pressure of 1.5 mbar was used in experiments with the FPDs. Evaporation residues were implanted into a (80 x 36) mm^2 16-strip Position-Sensitive silicon Detector (PSD) or a (58 x 58) mm^2 Double-Sided Silicon Strip Detector (DSSSD). In other experiments, $^{261a,b}\text{Rf}$ passed a 1.2 μm thick (140 x 40) mm^2 Mylar window and was thermalized in 1.2 bar He in the RTC (depth: 17 mm). Rf atoms were then transported to ROMA by an He/KCl jet (gas flow rate: 3.45 L/min) through a 4 m long polyethylene capillary (inner diameter: 2 mm).

The measurement of ^{260}Rf , produced in the 6n evaporation channel at $E_{\text{c.o.t.}} = 125$ MeV yielded 15 time ($\Delta t \leq 200$ ms) correlated EVR-SF events in the PSD. The correlation time analysis yielded a half-life of $21^{+7.3}_{-4.3}$ ms (errors are within the 68% confidence interval). A search for ^{262}Rf decays at $E_{\text{c.o.t.}} = 109$ MeV yielded 7 position and time correlated EVR-SF events observed in the DSSSD, with EVR energies of 0.8 to 3.3 MeV and SF fragment energies of > 100 MeV. The measured $T_{1/2}$ for ^{262}Rf is 210^{+128}_{-58} ms (Fig. 1a), in contradiction with values from [1,2]. In addition, 9 short EVR-SF correlations were registered with $\Delta t \leq 1.5$ ms and EVR energies of 7.5 ± 5.0 MeV. They were attributed to the decay of $^{244\text{mf}}\text{Am}$ ($T_{1/2} =$

0.9 ms). Because of a relatively high counting rate of EVR-like events in the DSSSD a random event analysis was performed for EVR-SF correlations within a Δt of 1 s. The random event number, n_b , was calculated individually for each observed event. It varies between 0.035 and 0.11 and depends on the event position in the DSSSD.

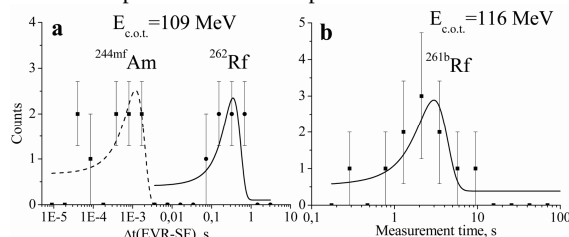


Figure 1: Time distributions of a) EVR-SF correlations from the DSSSD and b) SF decays from ROMA.

^{261}Rf was produced in the 5n channel at $E_{\text{c.o.t.}} = 116$ MeV and was detected in ROMA. Stepping times of 35 s (for ^{261a}Rf) and 2.5 s (for ^{261b}Rf) were used. 149 single α -particles ($E_\alpha = 7.8 - 8.5$ MeV) from ^{261}Rf and ^{257}No were registered; among these 28 α - α correlations. Also, 11 SF-events were registered and are attributed to ^{261b}Rf based on the measured $T_{1/2}$ of $2.2^{+0.9}_{-0.5}$ s. The SF activity assigned in [2] to ^{262}Rf likely originated from the then unknown ^{261b}Rf .

From our results and a cross section of 4.4 nb [6], a transmission of Rf through TASCA to a 140 x 40 mm^2 large area in the focal plane of 10% follows. For ^{261b}Rf , a cross section of $1.8^{+0.8}_{-0.4}$ nb was calculated, respecting decay during transport. With an estimated transmission of 6% to the area of the FPDs, preliminary cross sections for ^{260}Rf and ^{262}Rf of ≈ 1.2 nb and ≈ 250 pb, respectively, follow. ^{261b}Rf was observed for the first time as an EVR. The production ratio of ^{261a}Rf to ^{261b}Rf is about 2.5:1. The data analysis is still in progress.

References

- [1] L. P. Somerville *et al.*, Phys. Rev. C **31**, 1801 (1985).
- [2] M. R. Lane *et al.*, Phys. Rev. C **53**, 2893 (1996).
- [3] Ch. E. Düllmann, A. Türler, Phys. Rev. C **77**, 064320 (2008).
- [4] J. Even *et al.*, this Scientific Report.
- [5] A. Semchenkov *et al.*, NIMB **266**, 4153 (2008).
- [6] Yu. Lazarev *et al.*, Phys. Rev. C **62**, 064307 (2000).

* Work supported by BMBF project 06MT248.

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Report III

Observation of ^{270}Hs in the complete fusion reaction $^{36}\text{S}+^{238}\text{U}^*$

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Superheavy elements ($Z \geq 104$) exist only due to nuclear shell effects. Deformed shell closures at $Z=108$ and at $N=162$ have been predicted theoretically [1] and observed in recent experiments [2]. Three hassium isotopes $^{269-271}\text{Hs}$, have been produced in the complete fusion reaction $^{248}\text{Cm}(^{26}\text{Mg}, \text{xn})^{274-x}\text{Hs}$ at the linear accelerator UNILAC at GSI [2,3]. The excitation function measurement at five different beam energies resulted in maximum cross sections of the 3n, 4n, 5n exit channels of a few pb [3].

Recent theoretical studies, analysing the formation of ^{270}Hs in the 4n channel, using a two-parameter Smoluchowski equation, predict even higher cross sections due to a lower reaction Q-value for the reaction $^{238}\text{U}(^{36}\text{S}, 4\text{n})^{270}\text{Hs}$ (24 pb) and $^{226}\text{Ra}(^{48}\text{Ca}, 4\text{n})^{270}\text{Hs}$ (30 pb) [4]. HIVAP [5] predicts a maximum cross section of 3.5 pb for the reaction $^{238}\text{U}(^{36}\text{S}, 4\text{n})^{270}\text{Hs}$.

Here, we report on first results of an experiment aimed to study the nuclear fusion reaction $^{36}\text{S} + ^{238}\text{U}$, leading to the compound nucleus $^{274}\text{Hs}^*$. For the experiment we used our highly efficient chemical separation and detection system COMPACT which was connected to a Recoil Chamber (RC) installed behind the ARTESIA target wheel in cave X1 [2]. A beam of $^{36}\text{S}^{5+}$ ions was accelerated by the UNILAC up to 7.13 MeV/u and impinged on a rotating ^{238}U target wheel. During the experiment, we used two different sets of ^{238}U targets. The beam passed through a 20.2 μm Be vacuum window, 6 mm of He/O₂ gas mixture (He:O₂ = 9/1), a 12.6 μm Be target backing before entering the ^{238}U target (3 segments of 1.8 mg/cm², 1.5 mg/cm² and 1.6 mg/cm²). The second target set had a Be backing of 8.2 μm and 3 segments containing 1.0 mg/cm² of ^{238}U each. We assumed that only Hs nuclei with a minimum residual range after exiting the target of 10 mm in gas could be transported to the detection system, corresponding to an active layer of the target of 1.0 mg/cm². The energy of the ^{36}S ions was in the range of 175.0 MeV to 181.2 MeV within the first set of target and in the range of 190.4 MeV to 196.1 MeV in the second set [6], corresponding to excitation energies, E^* , of 38 ± 3 MeV and 51 ± 3 MeV [7], near the predicted maxima of the 4n and 5n evaporation channel, respectively. Starting at $E^* = 38$ MeV we irradiated the first target set with a beam dose of $5.74 \cdot 10^{17}$ ions. The second target set was irradiated with a beam dose of $1.03 \cdot 10^{18}$ ions at $E^* = 51$ MeV.

We searched for correlated decay chains, which were defined as an α -decay ($8.0 \leq E_\alpha \leq 9.5$ MeV) followed within 300 s in the same or a neighbouring detector pair by an α -decay in the same energy range or by a SF-like event with at least one fragment above a threshold of 15 MeV. The data analysis revealed one chain at the higher E^* of 51 MeV. A 9.02 ± 0.05 MeV α -particle was observed in bottom detector #24 followed after 23 ms by one 41 MeV fission fragment measured in top detector #24. We attributed this decay chain to the decay of ^{270}Hs produced in the 4n evaporation channel [2].

Because of background from α -decay and SF of heavy nuclides from (multi) nucleon transfer pseudo correlated chains can be found with nonzero probability. We have calculated the probability to observe random decay chains of the types $\alpha \cdot \alpha \cdot \alpha \cdot \alpha$, $\alpha \cdot \alpha \cdot \text{SF}$, and $\alpha \cdot \text{SF}$ satisfying the criteria specified above. 351 and 771 α -particles have been registered in the first and the second run, respectively. They originated mainly from α -decays of ^{212}Po . Also, 6 SF-like events were registered in the first run and 13 events in the second run. None of these were coincident with each other. The results are shown in Table 1.

Table 1: Random rates for different decay chains

decay chain	$E^* = 38$ MeV	$E^* = 51$ MeV
$\alpha \cdot \alpha \cdot \alpha \cdot \alpha$	$7.08 \cdot 10^{-4}$	$3.12 \cdot 10^{-3}$
$\alpha \cdot \alpha \cdot \text{SF}$	$4.61 \cdot 10^{-3}$	$1.67 \cdot 10^{-3}$
$\alpha \cdot \text{SF}$	$1.6 \cdot 10^{-2}$	$4.6 \cdot 10^{-2}$

At $E^* = 38$ MeV the cross section limit for both channels is 2.9 pb. The cross section for the 4n channel at $E^* = 51$ MeV based on the one event is $8_{-0.7}^{+2.6}$ pb and the cross section limit for the 5n channel is 1.5 pb. Errors and limits correspond to 68% confidence level. The measured cross section and limits are lower than those of the reaction $^{248}\text{Cm}(^{26}\text{Mg}, \text{xn})^{274-x}\text{Hs}$ [3], in contrast to calculations from [4]. We plan to continue these measurements in the near future.

References

- [1] Z. Patyk, A. Sobiczewski, Nucl. Phys. A533, 132 (1991).
- [2] J. Dvorak *et al.*, Phys. Rev. Lett. 97, 242501 (2006).
- [3] J. Dvorak *et al.*, Phys. Rev. Lett. 100, 132503 (2008).
- [4] Z. H. Liu, J.-D. Bao, Phys. Rev. C 74, 057602 (2006).
- [5] W. Reisdorf, M. Schädel, Z. Phys. A 343, 47 (1992).
- [6] J.F. Ziegler, Nucl. Instr. and Meth. A 219, 1027 (2004).
- [7] G. Audi *et al.*, Nucl. Phys. A 729, 337 (2003)

* Work supported by BMBF project 06MP2471

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TASCA – A New Tool in the Quest for Superheavy Element Studies

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The TransActinide Separator and Chemistry Apparatus (TASCA) project [1, 2], which is focusing on the separation and investigation of neutron-rich transactinide nuclides produced in actinide-target based reactions, has successfully finished its commissioning and has entered the research program which includes chemical investigations of superheavy elements (SHE) after pre-separation with the gas-filled separator and nuclear structure and reaction studies.

The central device of TASCA is a gas-filled separator in a DQQ configuration operated either in the "High Transmission Mode" (HTM, DQ_hQ_v) or in the "Small Image Mode" (SIM, DQ_vQ_h) [1-5]. In the HTM, the unsurpassed transmission of TASCA is exploited. In contrast, the SIM provides unique possibilities due to its small spot size in the focal plane at a still relatively high transmission.

Extensive studies have been performed to obtain optimized parameter sets for (i) the target thickness and stability, (ii) the gas pressure and the gas filling (He, H₂, and mixtures), (iii) the dipole setting (Bp) and quadrupole focusing, (iv) Recoil Transfer Chambers (RTCs) [6] (window material and thickness, support structures, and size and shape of the chamber), (iv) gas-jet transport of pre-separated products, and (vi) the coupling and performance of devices like ROMA and the Automated Rapid Chemistry Apparatus (ARCA). Results of many of these parameter studies were compared with TASCA model calculations [7] and very good agreement was achieved. These results confidently demonstrate that we are able to perform trustworthy SHE experiments with TASCA.

Efficiency measurements with catcher foils behind the target and in the focal plane showed very good agreement with model calculations for the fairly asymmetric reaction ²²Ne(¹⁸¹Ta,xn)^{198m,199}Bi [2]. To confirm this agreement in a more symmetric reaction and to obtain a standard reaction to test and check the TASCA performance, detailed studies were performed with well known reactions of ⁴⁸Ca with targets of ^{206,207,208}Pb leading to ^{252,253,254}No. Assuming cross sections of 0.5 μb, 1.3 μb, and 2 μb [8] for the production of ²⁵²No, ²⁵³No, and ²⁵⁴No, efficiencies of 54%, 56%, and 50%, respectively, were obtained for the HTM and a (80x36) mm² 16-strip FPD; model calculations [7] predict 54%. Equally

good is the agreement in the SIM where a 30% efficiency was measured for the reaction ⁴⁸Ca(²⁰⁸Pb,2n)²⁵⁴No.

As one of the crucial tests in the TASCA commissioning program, we studied the isotopes ²⁶⁰Rf, ^{261a,261b}Rf, and ²⁶²Rf synthesized in the very asymmetric reaction ²²Ne + ²⁴⁴Pu [9]. The performance of TASCA was as anticipated. Efficiencies and magnetic settings were as expected. Rf isotopes were not only measured in the FPD but were also collected in an RTC and were transported to ROMA for decay measurements [9] and to ARCA for chemical investigations. One highlight of the experiment was the first transactinide chemistry behind TASCA. It was performed in ARCA with pre-separated 78-s ^{261a}Rf and it demonstrated that aqueous-phase transactinide chemistry behind TASCA can now be performed [10].

The new set-up termed *Tasca Small Image mode Spectroscopy* (TASISpec) [11] exploits the small spot in SIM. It provides a unique possibility to build a compact Si-detector box for α-, e⁻, and SF-fragment measurements, and to pack Ge-detectors in close geometry, resulting in a highly efficient set-up for coincidence measurements with γ- and X-rays.

In conclusion, the performance of TASCA as a separator is well understood and, as the most versatile and highest efficient instrument in SHE research, it is ready to explore the physics and chemistry of SHE.

References

- [1] M. Schädel *et al.*, GSI Sci. Rep. 2005, GSI Report 2006-1, **2006**, p. 262, and <http://www.gsi.de/TASCA>
- [2] M. Schädel *et al.*, GSI Sci. Rep. 2008, **2009**, in print.
- [3] M. Schädel, Eur. Phys. J. D **2007**, 45, 67.
- [4] A. Semchenkov *et al.*, Nucl. Instr. and Meth. in Phys. Res. B **2008**, 266, 4153.
- [5] Ch.E. Düllmann *et al.*, Nucl. Instr. and Meth. in Phys. Res. B **2008**, 266, 4123.
- [6] Ch.E. Düllmann *et al.*, GSI Sci. Rep. 2006, GSI Report 2007-1, **2007**, p. 146.
- [7] K.E. Gregorich *et al.*, GSI Sci. Rep. 2006, GSI Report 2007-1, **2007**, p. 144.
- [8] Yu. Ts. Oganessian *et al.*, Phys. Rev. **2001**, C 64, 054606.
- [9] A. Gorshkov *et al.*, GSI Sci. Rep. 2008, **2009**, in print.
- [10] J. Even *et al.*, GSI Sci. Rep. 2008, **2009**, in print.
- [11] L.-L. Andersson *et al.*, GSI Sci. Rep. 2008, **2009**, in print.