

Gas Phase Chemistry of Superheavy Elements

A. Türler*

Institut für Radiochemie, Technische Universität München, D-85748 Garching, Germany

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The knowledge and understanding of the chemistry of the superheavy elements, especially of the early transactinides Rf, Db, and Sg and their compounds, both experimentally and theoretically, is nowadays quite extensive. While rapid chemical separations in aqueous solution were (and are) the method of choice for detailed investigations of Rf and Db, the development of gas-phase chemical separation methods have allowed first chemical studies of increasingly heavier transactinide elements such as Bh and Hs. In all cases, the separated transactinide element was unequivocally identified by observing the characteristic nuclear decay properties of one of its isotopes. The current paper will review the progress made in gas phase chemical separations of transactinide elements and highlight future perspectives.

1. Introduction

The discovery of new elements and their correct placement in the periodic table have originally been the domain of chemists. Indeed, the discovery of new elements up to mendelevium (Md, $Z = 101$) was accomplished by chemical means.¹ The decreasing production cross sections, that nowadays are of the order of one picobarn or even less for the heaviest known nuclei, and the rapidly diminishing half-lives made manual chemical investigations of elements beyond $Z = 105$ virtually impossible. Thus, the synthesis and identification of new elements has completely shifted to nuclear physics and led to the discovery of more than ten new elements. However, the placement of a new element in the periodic table is not only based on its proton number but also on its chemical properties, which are determined by its electronic structure. Relativity which is important in determining the nuclear shell structure and thus the decay properties of superheavy elements (SHE), is extremely important in defining the chemical properties. Therefore, not only the physics but also the chemistry of SHE is extremely interesting and rewarding to be studied. With $Z = 104$, Rf, starts a new series of d-elements, the so-called transactinides (see Figure 1). Since the liquid drop fission barrier also disappears around $Z = 104$, the term SHE is often used as a synonym for transactinide elements.

Despite the numerous difficulties involved in chemically isolating one single, relatively short-lived atom from a plethora of unwanted by-products of the nuclear production reaction, remarkable progress was made in recent years. This progress can be attributed to the discovery of enhanced nuclear stability close to the vicinity of the previously predicted deformed shells at $Z = 108$ and $N = 162$,² which provided chemists with sufficiently long-lived isotopes of seaborgium (Sg, $Z = 106$),³ bohrium (Bh, $Z = 107$)⁴ and even hassium (Hs, $Z = 108$).⁵ By developing fast, automated, and sensitive techniques chemists have discovered or significantly contributed to the characterization of the new nuclides ^{265,266}Sg,⁶ ^{266,267}Bh,⁷ and ^{269,270}Hs.⁸ As in experiments of our nuclear physics colleagues, the production of a heavy nucleus was detected by registering its nuclear decay, which for many super-heavy nuclei consists of unique alpha-particle decay chains quite often terminated by spontaneous fission (SF). The knowledge and understanding

of the chemistry of SHE, especially of the early transactinides Rf, Db, and Sg and their compounds, both experimentally and theoretically, are nowadays quite extensive as documented by the first textbook entitled "The Chemistry of Superheavy Elements" edited by Schädel.⁹ While rapid chemical separations in aqueous solution were (and are) the method of choice for detailed investigations of Rf and Db,^{10,11} the development of gas-phase chemical separation methods have allowed first chemical studies of all transactinide elements up to Hs.¹²⁻¹⁴ The discovery of longer-lived (half-lives of several seconds) isotopes of elements 110 through 114 in the ⁴⁸Ca-induced reactions on actinide targets at the Flerov Laboratory of Nuclear Reactions in Dubna has opened fascinating new perspectives to experimentally study the chemistry of even the heaviest elements in the periodic table.¹⁵ Currently, experiments are conducted to elucidate the chemical properties of element 112 (E112)¹⁶⁻¹⁸ and also element 114 (E114) in their elemental state. There are already indications that E112 behaves chemically not at all similarly to its lighter homologue Hg. Since all of the decay chains of the newly discovered neutron-rich nuclides end in an uncharted area of the chart of nuclides a chemical identification of one of the members of these decay chains could clearly pinpoint the atomic number of the newly synthesized elements. Therefore, a chemical separator system can be regarded as a somewhat slow, but efficient Z-separator. Since chemical separator systems are nearly independent on the production reaction, thick targets and very asymmetric reactions can be employed to access neutron-rich heavy nuclei.

Periodic Table of the Elements

| | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
|----|----|-------------|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|-----|-----|--------|-----|-----|-----|-----|-----|-----|----|----|----|----|----|----|--|--|
| 1 | | | | | | | | | | | | | | | | | 18 | | | | | | | | | | | | | | | | | |
| H | | | | | | | | | | | | | | | | | He | | | | | | | | | | | | | | | | | |
| 3 | 4 | | | | | | | | | | | 5 | 6 | 7 | 8 | 9 | 10 | | | | | | | | | | | | | | | | | |
| Li | Be | | | | | | | | | | | B | C | N | O | F | Ne | | | | | | | | | | | | | | | | | |
| 11 | 12 | | | | | | | | | | | 13 | 14 | 15 | 16 | 17 | 18 | | | | | | | | | | | | | | | | | |
| Na | Mg | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | Al | Si | P | S | Cl | Ar | | | | | | | | | | | | | | | | | |
| 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 34 | 35 | 36 | | | | | | | | | | | | | | | | | |
| K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr | | | | | | | | | | | | | | | | | |
| 37 | 38 | 39 | 40 | 41 | 42 | 43 | 44 | 45 | 46 | 47 | 48 | 49 | 50 | 51 | 52 | 53 | 54 | | | | | | | | | | | | | | | | | |
| Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe | | | | | | | | | | | | | | | | | |
| 55 | 56 | 57-71 | 72 | 73 | 74 | 75 | 76 | 77 | 78 | 79 | 80 | 81 | 82 | 83 | 84 | 85 | 86 | | | | | | | | | | | | | | | | | |
| Cs | Ba | Lanthanides | | | | | | | | | | | | | | | | 87 | 88 | 89-103 | 104 | 105 | 106 | 107 | 108 | | | | | | | | | |
| Fr | Ra | Actinides | | | | | | | | | | | | | | | | 109 | 110 | 111 | 112 | 113 | 114 | 115 | 116 | 118 | | | | | | | | |
| | | | | | | | | | | | | | | | | | | Mt | Ds | Rg | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | | | | La | Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu | | |
| | | | | | | | | | | | | | | | | | | Ac | Th | Pa | U | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Md | No | Lr | | |

Figure 1. Periodic table of the elements. See text for detailed explanations.

*Corresponding author. E-mail: Andreas.Tuerler@radiochemie.de. FAX: +49-89-289-12204.

Figure 1 displays a modern periodic table of the elements. Elements whose chemical behavior has not yet been experimentally investigated are shown below their expected positions. The element names are those accepted, or in the case of element 111 (roentgenium, Rg), recommended by IUPAC. Provisional names such as ununbium (Uub, $Z = 112$) are not indicated.

In the following the observed chemical properties of Hs and the expected behavior of heavier elements, the available chemical separation techniques, and the latest results of recent chemistry experiments on E112 are presented.

2. Chemical Properties of SHE and their Compounds

Studies of transactinide elements by chemical means rely strongly on predictions of their chemical properties. In order to plan a separation scheme, the stability of compounds and their physicochemical properties have to be judged on the basis of predictions. Traditionally, the chemical properties of an unknown element and its compounds were predicted by exploiting the fundamental relationships of the physicochemical data of the elements and their compounds within the groups and the periods of the periodic table. Since relativistic effects are increasing proportionally with Z^2 , extrapolations of chemical properties from lighter homologue elements must fail at some point. Here, the only alternative are fully relativistic calculations. Generally, three relativistic effects are observed. First, due to the high probability density near the highly charged nucleus the $s_{1/2}$ and $p_{1/2}$ orbital radii are contracting and the binding energies are increasing. These are called "direct" relativistic effects.¹⁹ Second, the spin-orbit splitting produces two levels for each 1 quantum number. Third, due to the increased screening of the nuclear charge by the $s_{1/2}$ and $p_{1/2}$ orbitals the d and f orbitals are expanding spatially and are energetically destabilized. This was named an "indirect" relativistic effect,¹⁹ but this effect directly influences the outermost electrons that are largely responsible for the chemical behavior of an atom. At present it is not possible to directly compute physicochemical properties of a molecule. All-electron calculations of molecules containing transactinide elements are exceedingly difficult due to the large number of electrons involved. Nonetheless, also due to the enormously increasing computing power, theoretical calculations have progressed now to the point that a number of relevant atomic and molecular properties can be computed. This paper will focus on some aspects of the expected chemical properties of elements with $Z \geq 108$. Comprehensive reviews on the calculated chemical properties of the early transactinides can be found in the literatures.^{20, 21}

Sometimes Mother Nature is rather kind to chemists and provides them with favorable and very clear cut cases. Such a case constitutes the chemistry of Hs. If Hs has any resemblance to its lighter homolog element Os then it should also form molecules of the type MO_4 ($M = Os, Hs$). Due to the perfect tetrahedral symmetry of OsO_4 , this compound is very volatile, and only interacts very weakly with non-reducing surfaces, similar to a noble gas. Relativistic molecular orbital calculations by Pershina et al.²² confirmed that indeed HsO_4 must be a very stable molecule and that its volatility should be very similar to its lighter homologue compound OsO_4 . This exceptional chemical property distinguishes Os and Hs from other d-elements and allows a clear assignment to group 8 of the periodic table. Thus, experimentalists successfully took on the daunting task to build a separator system that allowed the isolation of Hs as volatile HsO_4 .

An illustrative example of the increasing influence of relativistic effects is shown in the case of the so-called coinage metals Cu, Ag, Au, and Rg ($Z = 111$). In Figure 2, the ground state electronic configurations and the first excited states of Cu,

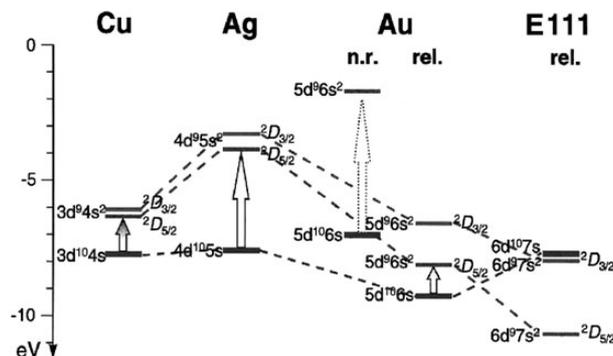


Figure 2. Energy levels of group 11 elements Cu, Ag, Au, and E111 (Rg). In the case of Au also the calculated non-relativistic energy level scheme is shown. The calculated relativistic energy levels for E111 are taken from Ref. 23.

Ag, Au, and Rg²³ are shown. For Au also the hypothetical non-relativistic case has been calculated. Cu, Ag, and Au all have the same $d^{10}s^1$ ground state configuration. As can be clearly seen, the spin-orbit splitting of the d^9s^2 first excited state is increasing with the proton number. A possible reason for the red color of Cu and the colorless appearance of Ag lies in the substantially higher first excited state of Ag which leads to an absorption which no longer lies in the visible region. If this trend would continue, Au should be a colorless metal which is less noble than Cu and Ag due to its lower ionization energy. However, the relativistic stabilization of the s-orbitals and the increasing spin-orbit splitting make Au a yellow metal with a more noble character than Cu or Ag. The strong relativistic stabilization of the filled s^2 -orbital and the further increased spin-orbit splitting lead to an inversion of states in Rg. Thus Rg is expected to have a $6d^9 7s^2$ ground state; the higher ionization energy compared to Au (≈ 10.6 eV vs. 9.21 eV) and the lower electron affinity (≈ 1.55 eV vs. 2.31 eV) will probably make Rg an even nobler metal. The trends observed in group 11 are also persisting in groups 12 through 14.

Another chemically very favorable case constitutes E112 as an expected homolog of Hg. E112 is expected to have an ionization potential which is more than 1.5 eV higher than that of Hg.²⁴ Similar to Hg, E112 should not have a bound anion.²⁴ Therefore, E112 is expected to be rather inert in its elemental state. It is well known that Hg is a very volatile element, but it interacts strongly with other metals such as Zn or Au to form amalgams. Yakushev et al. demonstrated that single atoms of Hg can quantitatively be adsorbed on a Au surface from a stream of He.¹⁶ First relativistic calculations of dimers Hg–Au and E112–Au indicate a lower, but still sizeable binding energy of the E112–Au dimer.²⁵ Therefore, current experiments focus on the property whether E112 also forms strong metal bonds with Au or whether E112 is so inert, that it behaves more like a heavy noble gas such as Rn.

Similar considerations apply to E114, which also has a higher ionization potential and no electron affinity, rendering it chemically less metallic and more inert compared to its lighter homolog Pb. Qualitatively these trends were realized early on, already in 1975 Pitzer²⁶ published a short paper with the title "Are elements 112, 114, and 118 relatively inert gases?". Molecules of the type MX_4 ($X = F, Cl$) were calculated to be thermodynamically stable for $M = Pb$, whereas with $M = E114$ the +2 oxidation state will be favored.²⁷

3. Experimental Techniques

A chemistry experiment with a transactinide element can be divided into four basic steps: synthesis of the transactinide element, rapid transport of the synthesized nuclide to the chemical apparatus, fast chemical isolation of the desired nuclide and preparation of a sample suitable for nuclear spec-



Figure 3. The GSI rotating target wheel.

troscopy, and detection of the nuclide via its characteristic nuclear decay properties.

In order to gain access to the longer-lived isotopes of transactinide elements, exotic, highly radioactive target nuclides such as ^{244}Pu , ^{243}Am , ^{248}Cm , ^{249}Bk , ^{249}Cf , or ^{254}Es are bombarded with intense heavy ion beams such as ^{18}O , ^{22}Ne , ^{26}Mg , or ^{48}Ca . On the one hand as intense beams as possible are to be used; on the other hand the destruction of the very valuable and highly radioactive targets has to be avoided. A rotating ^{248}Cm target with a rotating vacuum window that can stand pressure differences of up to 1.5 atm has recently been used in heavy element chemistry experiments at the Gesellschaft für Schwerionenforschung (GSI). This rotating target carrying up to 6 mg of target material has allowed the use of high-intensity beams for heavy element chemistry experiments.⁹ A picture of a rotating ^{248}Cm target after irradiation with up to 1 μA of a ^{26}Mg beam (a factor of four larger than possible with a fixed target) is shown in Figure 3. The target wheel is synchronized with the time structure of the accelerator (UNILAC) in order to spread one beam pulse over the area of one target segment.

Reaction products recoiling out of the target are stopped in a recoil chamber filled with helium gas. Non-volatile products such as Sg or Bh are adsorbed on aerosol particles of about 100 nm diameter and transported through a capillary over relatively long distances to the chemistry apparatus. As aerosol materials potassium chloride (KCl) or carbon are often used. Aerosol particles of suitable size can be generated by sublimation of KCl that is heated in flowing He to about 640°C. Carbon aerosols are generated by spark discharge in flowing He. Unfortunately, high transportation yields cannot be reliably maintained over long time periods, also the yield is strongly dependent on the beam current and usually decreasing with increasing beam intensity.

Basically, four different approaches which involve the direct detection of the nuclear decay of the isolated nuclides have been successful in studying the chemical properties of transactinide elements. Two of the systems work in the liquid phase, whereas the other two are designed to investigate volatile transactinide compounds in the gas phase. The predominant share of today's knowledge about the chemical behavior of Rf, Db, and Sg in aqueous solution was obtained with the Automated Rapid Chemistry Apparatus (ARCA).⁹ This micro-computer controlled set-up allows fast repetitive separations on miniaturized chromatography columns. Depending on the chemistry, the columns are filled with ion exchange resin or organic extractants on an inert support material. Often several thousand separations are performed. After chemical separation the fraction containing the transactinide element is evaporated and the sample placed in an α -SF spectroscopy system. This last step, which was performed manually, has now also been automated in a set-up called

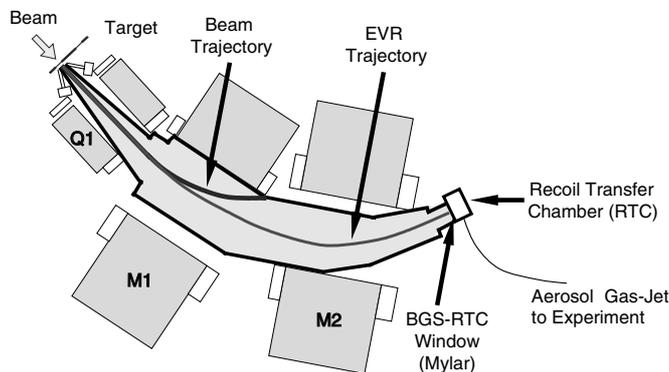


Figure 4. Schematic of the recoil transfer chamber (RTC) coupled to the Berkeley Gas-filled Separator (BGS). The separator delivers a clean beam of evaporation residues (EVR) to the RTC. The RTC is separated from the separator which is operated at a pressure of about 1 mbar by means of a thin mylar window of typically $> 1 \mu\text{m}$ thickness. This thin window is supported by a thin wire grid. For chemical studies with the SISAK system, the RTC is flushed with an aerosol gas-jet and stopped EVR's are rapidly transported to the continuously operating liquid-liquid extraction system.

AIDA developed in Japan.¹⁰

A continuously operating liquid-liquid extraction system using miniaturized centrifuges and liquid scintillation flow through detection cells (SISAK) was recently successful to separate and identify 4-s ^{257}Rf .²⁸ The latest version of SISAK is very well adapted to study nuclides with half-lives as short as 1 s. In order to suppress the large background created by β -particles, a recoil chamber was coupled to the Berkeley Gas-filled Separator (BGS) (Figure 4). Coupling a chemistry set-up with a recoil separator may open new frontiers in direct chemical reactions with a large variety of compounds, since one no longer has to deal with the harsh ionizing conditions created by the passage of the primary beam. Furthermore contaminants that cannot be effectively removed due to their chemical similarity to SHE, such as Po or Rn isotopes, are largely removed by the recoil separator.

In order to study elements beyond Sg, faster and much more efficient chemistry set-ups had to be used. Such systems are gas-phase chromatographic separations. Since transactinide nuclei are usually stopped in gas, a fast and efficient link to a gas chromatography system can be established; either by direct transport of volatile species or volatile compounds that were formed in-situ in the recoil chamber, or by a transport with aerosol particles. Despite the fact that the transition metals (groups 4 to 11) are very refractory, there exist few stable inorganic compounds that are appreciably volatile at experimentally manageable temperatures below 1100°C. These are the halides and oxyhalides of groups 4 to 7, the oxide hydroxides of groups 6 and 7, and the oxides of group 8. Moreover, elements 112 to 118 are expected to be rather volatile in the elemental state and thus gas-phase separations will play a crucial role in investigating the chemical properties. Early on, gas-phase chemistry played an important role in the investigations of SHE. The technique was pioneered by Zvara and co-workers in Dubna to investigate Rf- and Db-halides which were formed in-situ behind the target and detected by latent fission tracks left in a thermochromatography column.⁹

Later the On-Line Gas-chemistry Apparatus (OLGA) was developed and successfully used to study halides and oxyhalides of elements Rf,⁹ Db,⁹ Sg,¹² and also Bh.¹³ A schematic of the OLGA set-up coupled to the Rotating wheel Multidetector Analyzer (ROMA) is shown in Figure 5. Aerosols carrying reaction products from the target to the OLGA set-up are collected on a quartz wool plug inside the reaction oven kept at 1000°C. Reactive gases are introduced in order to form volatile compounds. The chromatographic separation takes place downstream in the adjoining isothermal section of the column.

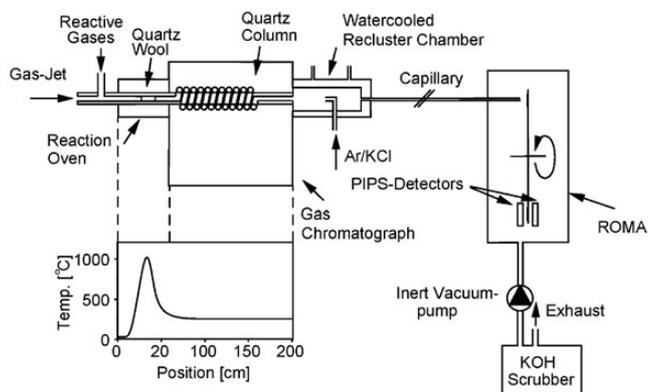


Figure 5. Schematic of the OLGA set-up coupled to the ROMA detection system.

At isothermal temperatures $\geq 300^\circ\text{C}$ most of the halides and oxyhalides of Rf, Db, Sg, and Bh are volatile and travel through the column essentially without delay, while less volatile compounds are retained much longer and are removed by decay of the interfering nuclide. At the exit of the column the isolated molecules are attached to new aerosol particles and transported to a detection system. Thus all investigated nuclides were unambiguously identified by registering α -particle decay chains.

The OLGA set-up was sensitive to cross sections of the order of 100 pb. In order to assess nuclides that are produced with few picobarn cross sections the overall efficiency had to be improved by at least one order of magnitude. This was accomplished by introducing the in-situ formation of volatile compounds and their condensation and detection in a thermochromatography detector, as in the early experiments by Zvara [see Ref. 9 and references cited therein]. Sufficiently volatile reaction products such as Hg or E112 can be transported directly with the flowing gas. In experiments with Hs, recoiling atoms were converted in-situ with an admixture of O_2 gas to the volatile HsO_4 . Instead of an isothermal temperature profile as in OLGA, a negative longitudinal temperature gradient is established along the column. Thus compounds are deposited in the chromatography column according to their volatility, forming distinct deposition peaks. If the column consists of silicon detectors then the nuclear decay of the separated nuclide can be registered. The detector number indicates the temperature at which the volatile compound was deposited.

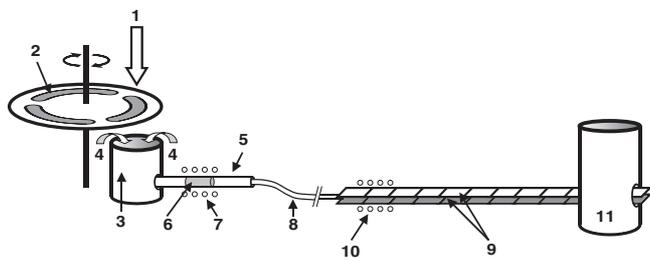


Figure 6. Schematic of the experimental set-up used for Hs chemistry. The beam (1) passes through the rotating vacuum window ($3.68 \text{ mg/cm}^2 \text{ Be}$) and the target (2) assembly (^{248}Cm $239 \mu\text{g/cm}^2$, $692 \mu\text{g/cm}^2$, and $730 \mu\text{g/cm}^2$ on $2.82 \text{ mg/cm}^2 \text{ Be}$). Hs nuclei formed in fusion reactions recoil out of the target into a gas volume (3) and are flushed with a He/O_2 mixture (4) to a quartz column (5) containing a quartz wool plug (6) heated to 600°C by an oven (7). There, Hs is converted to HsO_4 which is volatile at room temperature and transported with the gas flow through a perfluoroalkoxy (PFA) capillary (8) to the Cryo On-Line Detector (COLD) registering the nuclear decay (α and spontaneous fission) of the Hs nuclides. The array consisted of 36 detectors arranged in 12 pairs (9), each detector pair consisted of 3 PIN diode sandwiches. Always 3 individual PIN diodes (top and bottom) were electrically coupled. A thermostat (10) kept the entrance of the array at 20°C ; the exit was cooled to -170°C by means of liquid nitrogen (11). Depending on the volatility of HsO_4 , the molecules adsorbed at a characteristic temperature. Figure from Ref. 14.

Thus, every detected nuclide reveals also chemical information. A schematic of the In-situ Volatilization and On-line detection apparatus (IVO)²⁸ is shown in Figure 6. The IVO set-up was successfully used to study the chemical properties of HsO_4 .¹⁴ The overall efficiency (including detection of a complete 3 member α -particle decay chain) is of the order of 30 – 50%.

Similar set-ups were used in first attempts to chemically identify E112. If E112 is chemically similar to Hg it should be adsorbed on Au or Pd surfaces. In test experiments short-lived Hg isotopes could be isolated in the elemental form from other reaction products and transported in He quantitatively through a 30 m long Teflon™ capillary at room temperature. Adsorption of Hg nuclides on silicon detectors, proved experimentally not feasible, since Hg was adsorbed on quartz surfaces only at temperatures of -150°C and below. However, Hg adsorbed quantitatively on Au, Pt, and Pd surfaces at room temperature. As little as 1 cm^2 of Au or Pd surface was sufficient to adsorb Hg atoms nearly quantitatively from a stream of 1 L/min He.¹⁶ Therefore, detector chambers containing a pair of Au or Pd coated PIPS detectors were constructed. Eight detector chambers (6 Au and 2 Pd) were connected in series by Teflon™ tubing. The detector chambers were positioned inside an assembly of 84 ^3He filled neutron detectors (in a polyethylen moderator) in order to simultaneously detect neutrons accompanying spontaneous fission events (see Figure 7).^{16, 17} In the latest experiment aiming at measuring the volatility of E112, one row of the silicon detectors of the Cryo On-Line Detector (COLD) was removed and replaced by a Au surface. A negative temperature gradient was established reaching from room temperature down to -187°C .¹⁸

3.1. Recent Results on the Chemistry of Hassium. In the course of an experiment to produce the nuclides $^{269,270}\text{Hs}$ in the reaction $^{248}\text{Cm}(^{26}\text{Mg}, 4n)$ and $^{248}\text{Cm}(^{26}\text{Mg}, 5n)$ conducted in May of 2001 at GSI, valid data was collected during 64.2 h.^{8, 14} During this time 1.0×10^{18} ^{26}Mg beam particles passed through the ^{248}Cm target. The IVO set-up was used to synthesize volatile HsO_4 , which were adsorbed in the COLD detector. Only α -lines originating from ^{211}At , $^{219,220}\text{Rn}$, and their decay products were identified. While ^{211}At and its decay daughter ^{211}Po were deposited mainly in the first two detectors, $^{219,220}\text{Rn}$ and their decay products accumulated in the last three detectors, where the temperature was sufficiently low to partly adsorb Rn. During the experiment, seven correlated decay chains were detected (see Figure 8). All decay chains were observed in detectors 2 through 4 and were assigned to the decay of either ^{269}Hs or the yet unknown ^{270}Hs . The characteristics of the three decay chains agreed very well with the decay properties of ^{269}Hs and its daughter nuclides observed in two

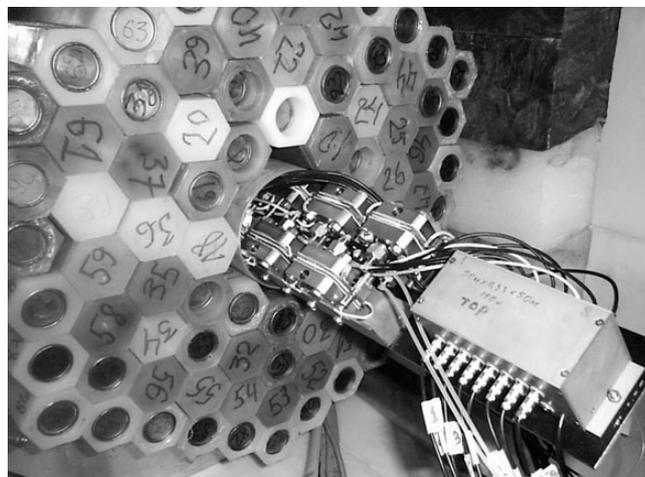


Figure 7. Detector arrangement for the detection of $^{283}112$ consisting of pairs of Au and Pd coated PIPS detectors inside an assembly of 84 ^3He filled neutron detectors.¹⁶

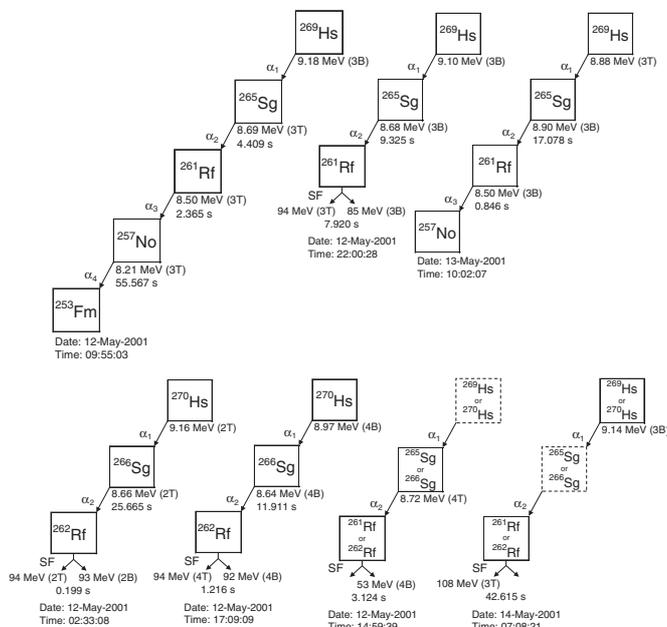


Figure 8. Observed decay chains attributed to the decay of ^{269}Hs and ^{270}Hs produced in the reaction $^{26}\text{Mg} + ^{248}\text{Cm}$ Ref. 8.

decay chains of $^{277}112$.⁵ The unusual α -decay energy of 8.52 MeV, which fits well into the systematic of ground-state α -decay energies, as well as a rather large spontaneous fission branch could be confirmed for the nuclide ^{261}Rf .⁵ The previously very well established decay properties of ^{261}Rf ($T_{1/2} = 78$ s, $E_{\alpha} = 8.28$ MeV, SF < 10%) must therefore be assigned to a long-lived isomeric state. Two additional decay chains were tentatively attributed to the decay of ^{270}Hs . The last two decay chains were incomplete and a definite assignment to ^{269}Hs or ^{270}Hs could not be made. The tentative assignment of two decay chains to ^{270}Hs is based on the following reasoning: according to the measurements of Lazarev et al.³ the daughter nuclide of ^{270}Hs , ^{266}Sg decays at least partially by emitting α -particles of 8.63 ± 0.05 MeV to ^{262}Rf which decays with a short half-life ($T_{1/2} = 2.1 \pm 0.2$ s) by spontaneous fission.^{3,30} The nuclide ^{262}Rf is known to fission symmetrically.³⁰ In both decay chains the α -decay energy attributed to ^{266}Sg is in agreement with literature data.³ The short correlation times of both SF events and the symmetric energy division among the fragments point to ^{262}Rf as terminating nuclide. Nevertheless, only measurements of the complete excitation function of the $^{26}\text{Mg} + ^{248}\text{Cm}$ reaction will provide more definite answers. An assignment of all observed decay chains to only ^{269}Hs cannot be ruled out. No additional three-member decay chains with a total length of 300 s were registered in detectors 2 to 10. The background count-rate of α -particles with energies between 8.0 and 9.5 MeV was about 0.6 h^{-1} per detector, leading to very low probabilities of 7×10^{-5} and 2×10^{-3} for any of the first five chains and any of the last two chains, respectively, being of random origin. In addition, four fission fragments with energies > 50 MeV that were not correlated with a preceding α -particle were registered in detectors 2 through 4. Assuming an overall efficiency of $\approx 40\%$, production cross sections of 4 pb for α -decaying ^{270}Hs and of 6 pb for α -decaying ^{269}Hs were calculated at a beam energy of 143.7–146.8 MeV (with an estimated accuracy of a factor of ≈ 3).

The longitudinal distribution of the 7 decay chains originating from Hs is depicted in Figure 9. The maximum of the Hs distribution was found at a temperature of -44 ± 6 °C. The distribution of $^{172}\text{OsO}_4$ ($T_{1/2} = 19.2$ s) measured before and after the experiment showed a maximum in detector 6 at a deposition temperature of -82 ± 7 °C. The higher deposition temperature of about 40 °C and the thus about 7 kJ/mol higher adsorption enthalpy seem to indicate a slightly lower volatility of HsO_4

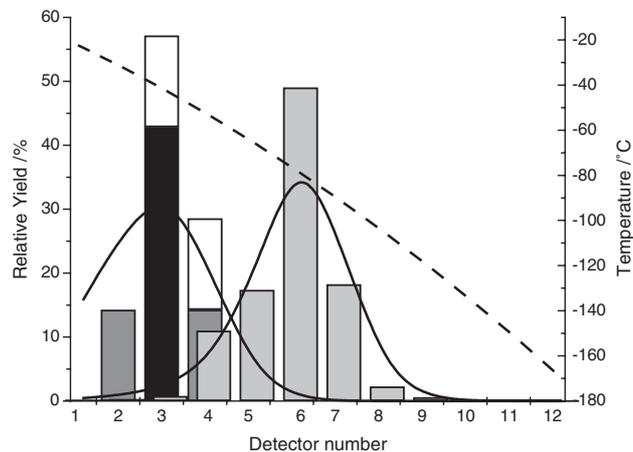


Figure 9. Relative yields of HsO_4 and OsO_4 for each of the 12 detector pairs. Measured values are represented by bars: $^{269}\text{HsO}_4$: black; $^{269}\text{HsO}_4$ or $^{270}\text{HsO}_4$: dark grey; $^{172}\text{OsO}_4$: light grey; $^{269}\text{HsO}_4$ or $^{270}\text{HsO}_4$: white. The dashed line indicates the temperature profile (right-hand scale). The maxima of the deposition distributions were evaluated as -44 ± 6 °C for HsO_4 and -82 ± 7 °C for OsO_4 . Solid lines represent results of a Monte Carlo simulation of the adsorption process.

compared to its lighter homologue OsO_4 . This experimental result was somewhat unexpected, since according to both classical extrapolations and relativistic molecular calculations, HsO_4 was predicted to be about as volatile as OsO_4 . Nevertheless, the high volatility of the Hs oxide species clearly suggests that it is HsO_4 since, by analogy with the known properties of the Os oxides, all other Hs oxides are expected to be much less volatile and unable to reach the detector system. The observed formation of a volatile Hs oxide (very likely HsO_4) provides strong experimental evidence that Hs behaves chemically as an ordinary member of group 8 of the periodic table.

3.2. Recent Results on the Chemistry of E112. A first attempt to chemically identify one of the long-lived isotopes of E112, namely $^{283}112$ (SF, $T_{1/2} \approx 3$ m),³¹ in the elemental state was made by Yakushev et al.¹⁶ using the $^{48}\text{Ca} + ^{238}\text{U}$ production reaction. It should be noted that in very recent experiments at the Dubna gas-filled separator, this long-lived SF activity could no longer be identified. Instead $^{283}112$ decayed by α -particle emission ($E_{\alpha} = 9.54$ MeV, $T_{1/2} \approx 6$ s) to short-lived $^{279}110$ (SF, $T_{1/2} \approx 0.3$ s).¹⁵

In an experiment conducted in January of 2000 a total beam dose of 6.85×10^{17} ^{48}Ca ions was accumulated. The chemical yield for the simultaneously produced ^{185}Hg ($T_{1/2} = 49$ s) was 80%. If E112 behaved chemically like Hg and all efficiencies measured for Hg were also valid for E112, detection of 2–4 SF events could be expected assuming the cross section value for the production of $^{283}112$ measured in.¹⁶ However, no SF events were observed. Therefore, no unambiguous answer as to the chemical and physical properties of E112 was obtained.

In the next experiment, the question whether E112 remained in the gas phase and passed over the Au surfaces was addressed.¹⁷ For this purpose, a special ionization chamber to measure SF fragments of nuclei remaining in the gas was added at the exit of the Au coated PIPS detector array. A total beam dose of 2.8×10^{18} ^{48}Ca ions were accumulated. Again zero SF events were registered on the Au and Pd coated PIPS detectors, confirming the result of the first experiment. However, 8 SF events accompanied by neutrons were registered in the ionization chamber, while only one background count was expected. Therefore, the majority of the SF events were attributed to the decay of a nuclide of E112, since there are no other known volatile nuclides decaying by SF. From these experiments it appears that the interaction of E112 with a Au or Pd surface is much weaker than for Hg. In the light of the latest results from Dubna the question arises whether the observed SF events could be attributed to the decay of ^{279}Ds , the daughter of 6 s $^{283}112$. Calculations of the

transport time of a volatile nuclide from the target to the ionization chamber show that indeed this scenario cannot be excluded with certainty, but the experiment was designed to be most sensitive for a 3-min nuclide.

Obviously, in a next step, the adsorption temperature of E112 on Au surfaces has to be measured experimentally. This was done with a modified version of the cryo thermochromatography detector in an experiment conducted recently at GSI.¹⁸ A 1.5 mg/cm² thick ²³⁸U target was bombarded with 2.8×10^{18} ⁴⁸Ca particles. A total of 11 events with energies > 40 MeV were registered with an estimated background of about 3 events. Seven events were registered at the cold end of the detector where also Rn was deposited. However, none of these events was correlated with a preceding α -particle. Therefore, the detected events cannot yet be conclusively attributed to the decay of E112 or its daughter.

4. Summary and Outlook

The spectacular results obtained at Flerov Laboratory in Dubna³² using ⁴⁸Ca ion beams and actinide targets to synthesize isotopes of elements 112, 114, 115, and 116 give chemists the historic opportunity to experimentally investigate the chemistry of even the heaviest known elements. Especially since some of the nuclides and their decay products seem to have half-lives of the order of seconds to even hours. In the last couple years, chemists have made a quantum leap and are now working with nuclides that can be produced with picobarn (10^{-36} cm²) cross sections only, as demonstrated by the first chemical investigations of hassium. There are indications that the chemical investigation of E112 and also E114 seem to reveal strong relativistic effects that significantly alter the chemical behavior of these elements compared to their lighter homologues. The unambiguous identification of the separated nuclides by measuring their decay properties yields additional valuable information about the nuclear structure of SHE. In order to reduce interferences from the plasma created by the beam and from undesired by-products of the nuclear reaction, chemists are investigating possibilities to couple their equipment with recoil separators. First experiments with the recoil transfer chamber coupled to the BGS were very successful. At GSI components of the dismantled HECK separator³³ are being used to set-up a dedicated separator that suits the needs of chemistry.

Due to the decreasing production cross sections, also chemists have to rely on future accelerators that will deliver even higher beam intensities. A substantial amount of beam time is required for each heavy element experiment. Target designs that allow the irradiation of exotic radioactive materials with highest possible beam intensities must be developed. Intense, neutron-rich radioactive heavy ion beams will be the only way to approach the predicted $N = 184$ neutron shell and produce long-lived SHE. Prospects to experimentally study the chemical properties of all currently known elements in the periodic table, even though only single atoms can be produced, are fascinating and challenging our creativity.

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