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Heavy-element chemistry —Status and perspectives

A. Türler[a]

Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland and Bern University, CH-3012 Bern, Switzerland

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Abstract. In the past ten years, nuclear chemists have made considerable progress in developing fast on-line separation techniques, which allowed to chemically characterize the first four transactinide elements Rf (rutherfordium, $Z = 104$), Db (dubnium, $Z = 105$), Sg (seaborgium, $Z = 106$), and recently also Bh (bohrium, $Z = 107$). In all cases the isolated nuclides were unambiguously identified by observing genetically linked decay chains. Nuclides with production cross-sections of less than 100 pb and half-lives as short as a few seconds have been chemically isolated. Thus, chemists have discovered or significantly contributed to the characterization of the nuclear-decay properties of a number of transactinide nuclei. New techniques with greatly improved overall efficiencies should allow chemists to extend their studies to even heavier elements such as Hs (hassium, $Z = 108$) and to the recently discovered superheavy elements with $Z = 112$ and 114, which can be produced only with picobarn cross-sections.

PACS. 27.90.+b $A \geq 220$ – 23.60.+e Alpha decay

1 Introduction

The discovery of new elements, being originally the domain of chemistry, has completely shifted in the past 30 years to nuclear physics. Not only the decreasing production cross-sections, but also the rapidly diminishing half-lives made chemical investigations of elements beyond $Z = 105$ virtually impossible. This situation changed with the discovery of the relatively long-lived isotopes ^{265}Sg and ^{266}Sg by Lazarev *et al.* [1]. Their enhanced nuclear stability was attributed to the close vicinity to the previously predicted deformed shells $N = 162$ and $Z = 108$. By developing fast and sensitive techniques, chemists were able to chemically investigate isotopes of the first four transactinide elements Rf, Db, Sg, and recently also Bh. In all cases, observing genetically linked decay chains unambiguously identified the isolated nuclides. Thus, chemists have discovered or significantly contributed to the characterization of the new nuclides ^{263}Db [2], ^{265,266}Sg [3,4], and ^{266,267}Bh [5,6]. The advantages of chemical separator systems in comparison to kinematic separators arise from the possibility of using thicker targets, high beam intensities spread over larger target areas, and in providing access to nuclides emitted under large angles and low velocities. Therefore, chemical separator systems are also ideally suited to study transfer and (HI, αxn) reaction products.

However, as fascinating as heavy nuclei are by themselves, they are surrounded by electrons, which define their chemical properties. Due to the influence of relativistic effects the chemical properties of the heaviest elements might deviate considerably from what one might expect by just extrapolating from the behavior of lighter homologue elements. Today, chemists have to face the challenge to work with nuclides that can be produced only with picobarn cross-sections. A first step in this direction will be made in an experiment to chemically characterize Hs (hassium, $Z = 108$). A completely new technology should allow to chemically isolate element 108 with an overall efficiency (including detection) between 30 and 50%.

With the recent synthesis of superheavy nuclides produced in the reactions ^{48}Ca+^{238}U and ^{48}Ca+^{242,244}Pu [7], much longer-lived nuclei than the previously known neutron-deficient isotopes of the heaviest elements have been identified. This discovery should allow chemists to explore the periodic table up to the heaviest known elements. Since all of the decay chains of the newly discovered nuclides end in an unknown region 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. In addition to the extremely low production cross-sections, also the chemical behavior of elements 112 and 114 might present extraordinary challenges, since these elements are expected to deviate significantly from the known behavior of their lighter homologues.

In this paper, the latest results of chemical investigations of elements Sg ($Z = 106$) and Bh ($Z = 107$), and prospects to extend these studies to even heavier elements, *e.g.* Hs ($Z = 108$) and 112, are presented.

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[a] e-mail: `andreas.tuerler@psi.ch`

2 Chemistry with transactinide nuclei

The numerous difficulties involved in the production and rapid chemical isolation of few single atoms of a transactinide element from a plethora of other reaction products and the subsequent detection of the nuclear decay required the development of unique separation methods. A chemistry experiment with a transactinide element can be divided into four basic steps: i) the synthesis of the transactinide nuclide, ii) a rapid transport to the chemical apparatus, iii) a fast chemical isolation of the desired nuclide and the preparation of a sample suitable for nuclear spectroscopy, and iv) the detection of the nuclide via its characteristic nuclear-decay properties. To date, three different techniques have successfully been used to investigate the chemical properties of transactinides.

2.1 Gas-phase chemistry

As early as 1966, Zvara and co-workers [8] at the Joint Institute for Nucelar Research (JINR) in Dubna, Russia, exploited the fact that, similar to the elements in groups 4, 5 and 6 of the periodic table, the elements Rf, Db, and Sg should form stable and highly volatile halides and/or oxyhalides. Thus, a good chemical separation can be accomplished from the non-volatile heavy actinide halides/oxyhalides using gas chromatography. On this basis, the heavy-element group of Gäggeler at PSI developed the so-called OLGA-technique (On-Line Gas chromatography Apparatus), which in its current version is able to continuously isolate transactinide nuclei with half-lives as short as seconds and to register, time-resolved, α-particle and spontaneous fission (SF) decays of final products [9]. The most recent version, OLGA III, is shown in fig. 1.

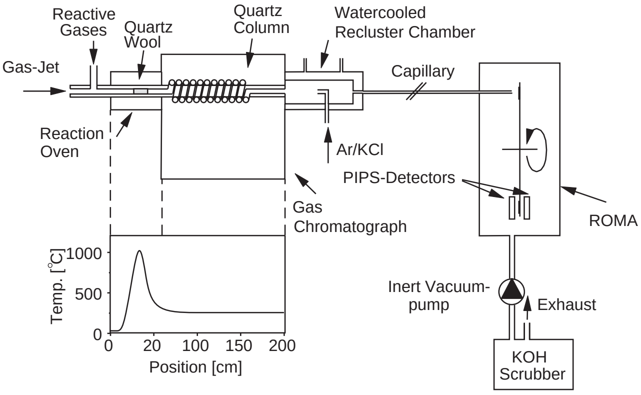

Fig. 1. Schematic of OLGA connected to ROMA.

Nuclear-reaction products, recoiling from a target, are stopped in He gas loaded with aerosols, and —adsorbed to their surface— continuously transported through a thin capillary to the OLGA device. The aerosols carrying the reaction products are collected on quartz wool 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. At temperatures of $\geq$ 300 °C most of the halides or oxyhalides of transactinide elements Rf, Db, Sg, and Bh are volatile and travel through the column essentially without delay, while less volatile compounds are retained much longer. Thus, most of the nuclides interfering with the detection of the transactinide nuclide decay in the column. At the exit of the column the isolated molecules are attached to the surface of new aerosol particles in a so-called recluster chamber and quickly transported to a detection system such as the rotating wheel system ROMA (ROtating wheel Multidetector Analyzer) [10].

2.2 Aqueous-phase chemistry

Aqueous-phase chemical separations take advantage of the fact that the highest stable oxidation states of the first transactinide elements (Rf^{4+}, Db^{5+}, Sg^{6+}) differ from the +3 oxidation state of the heavy actinides. First aqueous chemical separations with Rf were performed as early as 1970 by Siliva *et al.* [11] at Lawrence Berkeley National Laboratory (LBNL). These separations were performed manually and in a discontinuous, batch-wise manner. A first fully automated apparatus was developed by Hulet *et al.* [12] in 1980. The very successful ARCA II (Automated Rapid Chemistry Apparatus) was developed by Schädel and Kratz [13] (GSI and Mainz University) and was used to investigate the chemical properties of Rf, Db, and also Sg in aqueous solution [14]. As in gas-phase chemistry experiments, nuclear-reaction products are transported with the aid of aerosols from the irradiation position to a collection site. Usually, salt aerosol particles (NaCl, KCl) are used, which are easily dissolved in aqueous media. After a collection cycle, the aerosols are dissolved and the solution is quickly passed through a miniaturized HPLC (High Performance Liquid Chromatography) column, where the separation of the transactinide element from unwanted reaction products takes place. The effluent from the column is collected on hot Ta disks and quickly dried. The Ta disks are then manually forwarded to the counting chambers of a α-particle and SF spectroscopy system. Usually, counting starts about 40 to 50 s after the end of collection. Quite often, several thousand separations are performed in one beam time. With ARCA II the nuclide ^{263}Db was discovered in the reaction ^{249}Bk(^{18}O, 4n) [2].

Another very fast and efficient technique, which proved successful in studying the chemistry of Rf, is the continuous liquid-liquid extraction system SISAK (Short-lived Isotopes Studied by the AKuve technique) [15]. This on-line technique, which was used to study nuclides with half-lives as short as 0.8 s, is based on multi-stage solvent extraction separations using high-speed centrifuges for phase separation. A specialty of the SISAK system is the use of liquid scintillation spectroscopy to detect α-particles as well as SF events. Of crucial importance is a very efficient suppression of β-decays by pulse shape analysis. Due to β-β pile-up events, the required sensitivity to study nuclides with production cross-sections of nanobarns was not quite reached. By using the Berkeley Gas-filled Separator (BGS) as a preseparator for nuclear-fusion products, first successful chemical investigations were conducted with ^{257}Rf produced in the reaction ^{208}Pb(^{50}Ti, 1n) [16].

3 Observed nuclear-decay properties

3.1 Experiments with ^{265,266}Sg

Due to the lack of an initial implantation signal in the silicon detectors, the half-lives of ^{265}Sg and ^{266}Sg could not be measured in the discovery experiment [1]. Only their α-decay energies were determined with an energy resolution of about 100 keV. In subsequent experiments OLGA was used to continuously isolate Sg within a few seconds and to study its chemical properties [3,17] as well as the nuclear-decay properties of ^{265}Sg and ^{266}Sg [4]. As in the discovery experiment, ^{265}Sg and ^{266}Sg were produced in the fusion reaction ^{248}Cm(^{22}Ne; 4n, 5n) at beam energies of 121 and 123 MeV. ^{265}Sg and ^{266}Sg were identified by observing time-correlated α-α-(α) and α-SF decay chains. A total of 13 correlated decay chains of ^{265}Sg (with an estimated number of 2.8 random correlations) were identified. Deduced decay properties were $T_{1/2}(^{265}\mathrm{Sg}) = 7.4^{+3.3}_{-2.7}$ s (68% c.i.) and $E_\alpha = 8.69$ MeV (8%), 8.76 MeV (23%), 8.84 MeV (46%) and 8.94 MeV (23%). An upper limit for SF of $\leq 35\%$ was established for ^{265}Sg. A production cross-section of about 240 pb for the α-decay branch in ^{265}Sg was estimated.

The decay properties of ^{266}Sg are of special interest due to its proximity to the predicted deformed closed shells $Z = 108$ and $N = 162$ [18,19]. However, there is no direct experimental evidence for the deformed shape of these nuclei. A promising way to experimentally confirm the deformed nature of these nuclei would be the observation of the first-excited state 2+ of an even-even nucleus in α-decay. The energy of such a state was calculated as 40-50 keV [18,19]. Since the discovery experiment [1], where 6 decays of ^{266}Sg were registered, additional 7 decays have been observed in various other experiments [4,20–22]. All decays attributed to ^{266}Sg are listed in table 1. From these data the following decay properties have been deduced: $T_{1/2}(^{266}\mathrm{Sg}) = 21.1^{+19}_{-8.2}$ s, $E_\alpha = 8.72 \pm 0.03$ MeV (54 ± 35%) and $E_\alpha = 8.59 \pm 0.04$ MeV (46 ± 32%) [22]. However, it should be noted that most of the low-energy events have been observed in the work of Lazarev *et al.* [1]. The half-life of the daughter nuclide $T_{1/2}(^{262}\mathrm{Rf}) = 1.88^{+0.64}_{-0.50}$ s is in good agreement with the half-life of 2.1 ± 0.2 given by Lane *et al.* [23].

Table 1. α-particle decay of ^{266}Sg to ^{262}Rf.

No.	$E_\alpha(^{266}\mathrm{Sg})$ (MeV)	FWHM (keV)	t_{decay} (s)	Δt (s)	Ref.
1	8.54	100		0.215	[1]
2	8.59	100		0.748	[1]
3	8.60	100		0.191	[1]
4	8.60	100		2.011	[1]
5	8.69	100		0.360	[1]
6	8.74	100		6.453	[1]
7	8.52	100	48.938	2.756	[4]
8	8.79	50	15.117	1.734	[4]
9	8.74	50	3.46	2.40	[4]
10	8.69	100	3.809	0.875	[20]
11	8.66	30	84.9	7.0	[21]
12	8.70	30	4.8	3.7	[21]
13	8.72	50	13.62	4.68	[22]

3.2 Experiments with ^{266,267}Bh

In order to investigate the chemical properties of Bh, longer-lived isotopes than the previously known ^{261}Bh ($T_{1/2} = 11.8$ ms), ^{262}Bh ($T_{1/2} = 102$ ms), $^{262\mathrm{m}}$Bh ($T_{1/2} = 8$ ms) and ^{264}Bh ($T_{1/2} = 440$ ms) had to be discovered [24]. Significantly longer-lived Bh isotopes with half-lives of the order of several seconds were expected close to the $N = 162$ closed neutron shell [25,26]. Two new, neutron-rich isotopes, ^{266}Bh and ^{267}Bh, were produced in bombardments of a ^{249}Bk target with 123 MeV and 117 MeV ^{22}Ne ions at the LBNL 88-Inch cyclotron [5]. The nuclides were identified by observing correlated α-particle decays from the Bh isotopes and their Db and Lr daughters, using a rotating wheel detection system. A total of 5 decay chains were observed for ^{267}Bh and one decay chain for ^{266}Bh. ^{267}Bh decayed by emission of 8.83 ± 0.03 MeV α-particles with a half-life of about 20 s. One atom of ^{266}Bh was observed, decaying by the emission of a 9.29 MeV α-particle within 0.87 s. The relatively long half-life of ^{267}Bh made this nuclide an ideal candidate for first ever chemical investigations of Bh. Assuming that α-decay is the dominant decay mode, the ^{249}Bk(^{22}Ne, 4n)^{267}Bh cross-section is 58^{+33}_{-15} pb at 117±1 MeV and 96^{+55}_{-25} pb at 123±1 MeV. In subsequent experiments, carried out at the PSI Philips cyclotron, ^{267}Bh was produced in the reaction ^{249}Bk(^{22}Ne, 4n) at 118 MeV beam energy. Single atoms of bohrium were continuously isolated in the form of volatile oxychloride molecules using the OLGA technique. The decay of ^{267}Bh was registered using a rotating-wheel detection system. A total of 6 decay chains of ^{267}Bh were identified after chemical separation. The spectrum of all registered α-particles attributed to the decay of ^{267}Bh is shown in fig. 2 (the number of events unrelated to the decay of ^{267}Bh was estimated to be 2.4). Two α-decay lines with $E_\alpha = 8.73$ MeV (18%) and 8.85 MeV (82%) were attributed to the decay of ^{267}Bh. The line shown is a superposition of Gaussian distributions assuming FWHM = 35 keV for events that were detected in the detectors facing the samples and FWHM = 75 keV for events detected in the detectors registering α-particles from the back side of the sample through a thin polyethylene foil. Using all 11 decays a new more accurate half-life of $T_{1/2}(^{267}\mathrm{Bh}) = 15.2^{+7.1}_{-4.5}$ s is calculated. Both experiments were not sensitive to a possible spontaneous fission branch in either ^{266}Bh or ^{267}Bh. The observation of a three-memeber α-decay chain starting with ^{267}Bh together with the data from [2] and [27] provides strong evidence for the existence of an isomeric state in ^{259}Lr and possibly also in ^{263}Db.

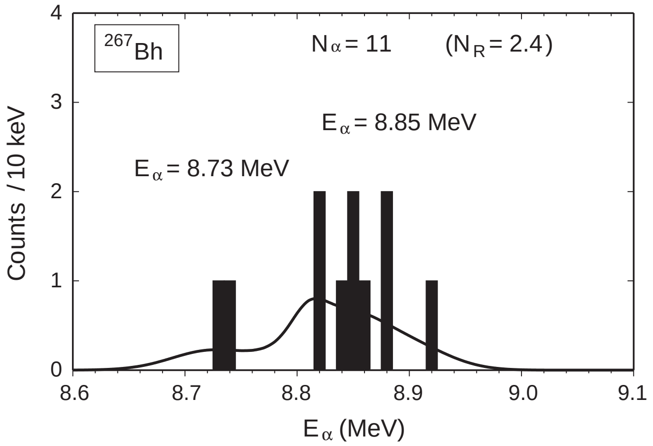

Fig. 2. Spectrum of α-particles of ^{267}Bh [5,6].

4 Future chemistry experiments

In order to extend chemical studies to Hs, the overall efficiency of the separation and detection process has to be improved by about one order of magnitude. Since the overall efficiency in the Bh experiment for the detection of a two-member decay chain was only about 4%, there is room for improvement. Also, one order of magnitude can be gained by using much higher beam intensities and rotating targets in chemistry experiments. Such an arrangement is currently being set up at GSI by the group of Schädel. Using a beam of 1 particle$\cdot\mu$Ampere and a target with a thickness of 2×10^{18}, atoms $\cdot$ cm^{-2} a cross-section of 1 pb still corresponds to the production of 1 atom per day.

Future chemistry experiments will concentrate on elements Hs and 112. Hassium is expected to form very volatile tetroxides, like its lighter homologue Os. Experiments with short-lived Os isotopes have shown that OsO_4 can easily be synthesized *in situ* in the target chamber and transported through Teflon capillaries, thus bypassing several inefficient and time-consuming steps. This technique was nicknamed IVO (In-situ Volatilization and On-line detection) [28]. Chemical yields $\geq$ 50% have been realized. In combination with a cryo thermochromatography detector [29], as is constructed at LBNL and PSI, overall yields (including detection of a 3-member decay chain) of 30–50% will be possible. The nuclide ^{269}Hs with half-life of about 10 s can be produced in the so far not yet investigated reaction ^{248}Cm(^{26}Mg, 5n)^{269}Hs for which a cross-section of the order of about 7 pb has been calculated [14].

An experiment to isolate element 112 in the elemental state has been performed by Yakushev *et al.* [30] at Flerov Laboratory of Nuclear Reactions (FLNR). In the preparatory work, short-lived Hg nuclides were transported in He from the target chamber to a detection system which consisted of a series of chambers that contained pairs of PIPS detectors. The surfaces of these detectors were coated with thin layers of Au or Pd. Hg is deposited quantitatively on these detectors. In an experiment using the nuclide ^{283}112 ($T_{1/2} \approx 3$ m, 100% SF) produced in the reaction ^{238}U(^{48}Ca, 3n) no SF events were detected. Assuming that element 112 behaved chemically like Hg and with the cross-section determined by Oganessian *et al.* [7] one could have expected detection of $3.4^{+4.3}_{-2.2}$ SF events. Thus, the experiment did not provide an unambiguous answer as to the chemical properties of element 112. Nevertheless, the experiment undoubtedly showed that a chemical identification of spontaneously fissioning nuclei produced with picobarn cross-sections is possible.

This paper presents the results obtained by a large group of chemists from Bern University, PSI (Villigen), LBNL (Berkeley), FLNR (Dubna), GSI (Darmstadt), Mainz University, Oslo University, Chalmers University (Göteborg) and Research Center Rossendorf. The experiments were performed at the heavy-ion accelerator complexes of PSI, GSI, LBNL and FLNR. We are indebted to the Office of Science, Office of Basic Energy Research, Division of Chemical Sciences, of the U.S. Department of Energy, for making the ^{248}Cm and the ^{249}Bk target material available through the transplutonium element production program at the Oak Ridge National Laboratory. This work was supported in part by the Swiss National Science Foundation.

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