Superheavy element chemistry at GARIS

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Abstract. A gas-jet transport system has been installed to the RIKEN GAs-filled Recoil Ion Separator, GARIS to start up SuperHeavy Element (SHE) chemistry. This system is a promising approach for exploring new frontiers in SHE chemistry: background radioactivities from unwanted by-products are suppressed, a high gas-jet transport yield is achieved, and new chemical reactions can be investigated. Useful radioisotopes of ^{261}Rf^{a,b}, ^{262}Db, and ^{265}Sg^{a,b} for chemical studies were produced in the reactions of ^{248}Cm(^{18}O,5n)^{261}Rf^{a,b}, ^{248}Cm(^{19}F,5n)^{262}Db, and ^{248}Cm(^{22}Ne,5n)^{265}Sg^{a,b}, respectively. They were successfully extracted to a chemistry laboratory by the gas-jet method. Production and decay properties of ^{261}Rf^{a,b}, ^{262}Db, and ^{265}Sg^{a,b} were investigated in detail with the rotating wheel apparatus for α- and spontaneous fission spectrometry. Present status and perspectives of the SHE chemistry at GARIS are also briefly presented.

1. Introduction

Studies on chemical properties of SuperHeavy Elements (SHEs, atomic number $Z \geq 104$) are extremely interesting and challenging research subjects in modern nuclear and radiochemistry [1, 2]. SHEs are produced at accelerators in heavy-ion induced nuclear fusion reactions. Due to short half-lives and low production rates of SHEs, any chemistry experiment must be done on a one-atom-at-a-time basis. Thus, rapid and efficient radiochemical procedures must be devised. So far, by coupling a gas- or liquid-chromatography apparatus to a target/recoil-catcher chamber through a gas-jet transport line, chemical properties of SHEs have been investigated for elements 104 (Rf) to 108 (Hs), and recently elements 112 (Cn) to 114 (Fl) [1–3]. At the same time, these successful experiments have definitely demonstrated the limitations of the conventional gas-jet technique just behind the target. Large amounts of background radioactivities from unwanted reaction products become unavoidable for identifications of SHEs with larger Z, especially $Z \geq 106$. High-intensity beams from advanced heavy-ion accelerators give rise to a problem in that the plasma formed by the beam in the target/recoil-catcher chamber significantly reduces gas-jet extraction yields. To overcome these limitations, a coupling of SHE chemistry to a recoil separator for nuclear physics studies has been considered [4].

In 2002, the pioneering SHE experiment with the Recoil Transfer Chamber (RTC) coupled to Berkeley Gas-filled Separator (BGS) at Lawrence Berkeley National Laboratory was first noteworthy [5]. The isotope of ^{257}Rf separated from the large amount of α-decaying products was identified with a liquid scintillator after a liquid-liquid solvent extraction with SISAK. The BGS/RTC system was then applied to a development of the Cryo-Thermochromatographic Separator (CTS) with $^{169-173}$OsO$_4$ as a homologue of HsO$_4$ [6]. Further, the production of Zr and Hf isotopes with the BGS/RTC system was investigated

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using the $^{nat}Ge(^{18}O,xn)^{85}Zr$, $^{74}Se(^{18}O,\alpha 3n)^{85}Zr$, $^{112}Sn(^{50}Ti,4n)^{158}Hf$, $^{116}Sn(^{50}Ti,4n)^{162}Hf$, $^{120}Sn(^{50}Ti,5n)^{165}Hf$, and $^{124}Sn(^{50}Ti,5n)^{169}Hf$ reactions [7]. The solvent extraction of ^{85}Zr and ^{169}Hf with crown ethers [8] and the gas-chromatographic separation of volatile ^{85}Zr and $^{162,165,169}Hf$ complexes with hexafluoroacetylaceton [9] were conducted as model experiments of Rf.

At GSI Helmholtzzentrum für Schwerionenforschung, a gas-filled recoil separator, the TransActinide Separator and Chemistry Apparatus (TASCA) was built in 2009. In the commissioning of the separator, different RTCs were tested with Pb and Os isotopes produced in the $^{152}Gd(^{40}Ar,xn)^{192-x}Pb$ and $^{nat}Ce(^{40}Ar,xn)^{175-177}Os$ reactions, respectively [10]. The electrodeposition behaviour of $^{175-177}Os$ on Pd and Ni electrodes was investigated with an electrolytic cell as a model experiment of Hs. In the final phase of the TASCA commissioning, the fluoride complexation of Rf in a diluted hydrofluoric acid was studied by anion-exchange chromatography with the Automated Rapid Chemistry Apparatus (ARCA) using $^{261}Rf^a$ produced in the $^{244}Pu(^{22}Ne,5n)^{261}Rf^a$ reaction. Further, volatile carbonyl complexes of $W(CO)_6$ and $Os(CO)_5$ were synthesized at TASCA using W and Os isotopes produced in the $^{144}Sm(^{24}Mg,4;5n)^{163,164}W$ and $^{152}Gd(^{24}Mg,5;6n)^{170,171}Os$ reactions, respectively [11]. Recently, Fl isotopes were produced in the $^{244}Pu(^{48}Ca,4;3n)^{288,289}Fl$ reactions, and the adsorption behaviour of Fl and their α-decay product $^{284,285}Cn$ on Au or SiO_2 surface were studied by isothermal gas chromatography and thermochromatography together with Pb, Hg, and Rn [12]. The Dubna Gas-Filled Recoil Separator (DGFRS) was also used for gas-phase chemistry of Fl [13].

At the RIKEN RI Beam Factory, a gas-jet transport system was installed to the GAs-filled Recoil Ion Separator (GARIS) to start up the SHE chemistry at RIKEN. The performance of the system was systematically investigated using ^{88}Nb, ^{170}Ta, ^{206}Fr, ^{245}Fm, and ^{255}No produced in the $^{nat}Ge(^{19}F,xn)^{88}Nb$, $^{nat}Gd(^{19}F, xn)^{170}Ta$, $^{169}Tm(^{40}Ar,3n)^{206}Fr$, $^{208}Pb(^{40}Ar,3n)^{245}Fm$, and $^{238}U(^{22}Ne,5n)^{255}No$ reactions, respectively [14–16]. An accurate and precise excitation function is necessary for effective production of SHE nuclides with extremely low production yields and for planning of long-term experiments with a costly heavy-ion accelerator. The decay properties such as α-particle energy and half-life are also essential to unambiguously assign SHE nuclides and to derive their chemical information. Especially, the half-life value is a direct measure for chemical constants such as equilibrium constant and adsorption enthalpy. Thus, using the GARIS gas-jet system, useful radioisotopes of $^{261}Rf^{a,b}$, ^{262}Db, and $^{265}Sg^{a,b}$ for chemical studies were produced in the $^{248}Cm(^{18}O,5n)^{261}Rf^{a,b}$, $^{248}Cm(^{19}F,5n)^{262}Db$, and $^{248}Cm(^{22}Ne,5n)^{265}Sg^{a,b}$ reactions, respectively. Production and decay properties of those isotopes were investigated in detail using a rotating wheel apparatus for α and spontaneous fission (SF) spectrometry [17–20]. In this paper, the recent studies on the production and decay properties of $^{261}Rf^{a,b}$, ^{262}Db, and $^{265}Sg^{a,b}$ are summarized together with the SHE chemistry programs at GARIS.

2. Production of ^{261}Rf, ^{262}Db, and ^{265}Sg

2.1 GARIS gas-jet system

A schematic of the GARIS gas-jet setup is shown in Fig. 1. The ^{18}O, ^{19}F, and ^{22}Ne beams were extracted from the RIKEN linear accelerator for the production of $^{261}Rf^{a,b}$, ^{262}Db, and $^{265}Sg^{a,b}$, respectively. The $^{248}Cm_2O_3$ targets of about 300 $\mu g\,cm^{-2}$ thickness were prepared by a molecular-plating method on a 2-μm Ti backing foil. The eight arc-shaped targets were mounted on a rotating wheel of 100-mm diameter, and the wheel was rotated during the irradiation at 1000 rpm. The EVaporation Residues (EVRs) of interest were separated in-flight from the beam particles and the majority of the nuclear transfer products through
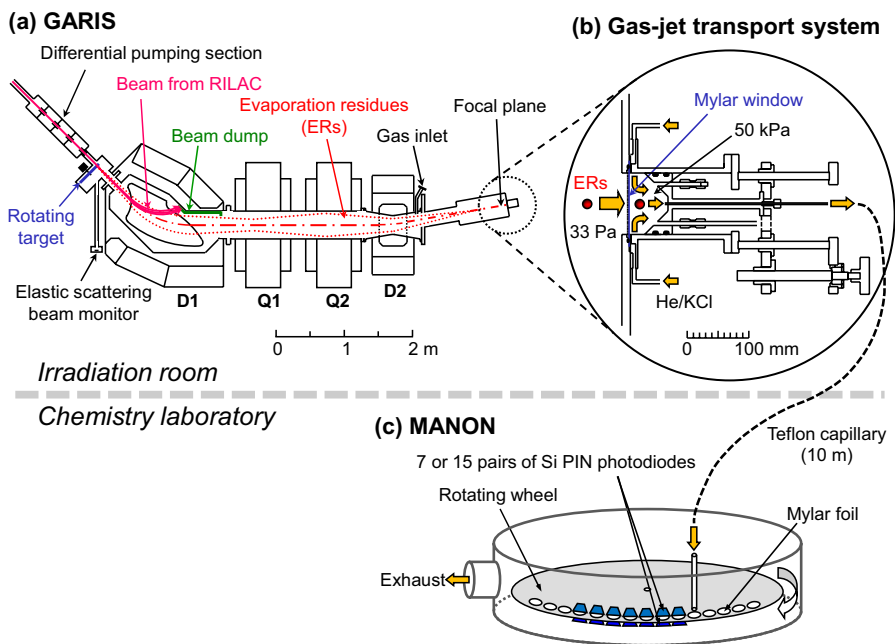
Figure 1. (a) RIKEN GAs-filled Recoil Ion Separator (GARIS). (b) Gas-jet transport system coupled to GARIS. (c) The rotating wheel apparatus MANON for α and SF (Spontaneous Fission) spectrometry at the chemistry laboratory.

D1 (D: dipole), Q1 (Q: quadrupole), Q2, and D2 electromagnets, and were guided to a focal plane of GARIS. GARIS was filled with He gas at a pressure of 33 Pa. The transmissions of GARIS were $(7.8 \pm 1.7)\%$ [17, 18], $(8.1 \pm 2.2)\%$ [20], and $\sim13\%$ [19] for ^{261}Rf^{a,b}, ^{262}Db, and ^{265}Sg^{a,b}, respectively. At the focal plane, the EVRs passed through a Mylar vacuum window foil of 0.5-μm (^{261}Rf^{a,b} and ^{262}Db) or 0.7-μm (^{265}Sg^{a,b}) thickness which was supported by a honeycomb-hole grid with 84% transparency. In the gas-jet chamber (100-mm inner diameter $\times$ 20-mm depth), the EVRs were thermalized in He gas, attached to aerosol particles of potassium chloride (KCl), and were continuously transported through a Teflon capillary (2.0-mm inner diameter $\times$10-m length) to a chemistry laboratory, where the Measurement system for Alpha-particle and spontaneous fissioN events ON line (MANON) was equipped. The flow rate of the He gas was $2.0 \, \mathrm{l\,min^{-1}}$, and the inner pressure of the gas-jet chamber was about 50 kPa. The gas-jet transport efficiency and average transport time were 50% and 3 s, respectively [17, 18].

In MANON, the aerosol particles were deposited on a Mylar foil of 0.5-μm thickness, 40 of which were set on the periphery of a rotating wheel. The wheel was stepped to position the foils between seven or fifteen pairs of Si PIN photodiodes. The step interval of MANON was set to 30.5, 2.0, 15.5, and 20.5 s to effectively detect ^{261}Rf^{a}, ^{261}Rf^{b}, ^{262}Db, and ^{265}Sg^{a,b}, respectively, with their different half-lives. Each Si PIN photodiode had an active area of $18 \times 18 \, \mathrm{mm^2}$ and a 38% counting efficiency. The α-energy resolution for the samples deposited on the Mylar foil was about 50-keV full width at half maximum in the top detectors and about 100 keV in the bottom detectors; the latter was larger because of energy degradation in the Mylar foil. All events were recorded in an event-by-event mode together with time information.

2.2 Production and decay properties of ^{261}Rf, ^{262}Db, and ^{265}Sg

2.2.1 ^{261}Rf^{a,b}

Rutherfordium-261 with a half-life of $T_{1/2} = 68$ s was produced in the ^{248}Cm(^{18}O,5n)^{261}Rf reaction [17]. The beam energy was 95.5 MeV in the middle of the ^{248}Cm$_2$O$_3$ target, and the average beam intensity was 5 particle μA (pμA). In the α-particle spectrum measured with MANON, α peaks of ^{261}Rf and its daughter ^{257}No were clearly identified under low background conditions. The radioactivities due to decays of Po, At, Rn, Fr, Ra, Ac, and Th isotopes, which were largely produced in the transfer reactions on the lead impurity in the target [21], were fully removed by the GARIS gas-jet system.

Although the 68-s ^{261}Rf (^{261}Rf^a) had been known for many decades in the ^{248}Cm(^{18}O,5n)^{261}Rf reaction since 1970 [21], the 3-s isomeric state ^{261}Rf^b found on the decay chains from ^{277}Cn and ^{269}Hs had not been observed as an evaporation residue. Under a low background condition attained with the GARIS gas-jet system, ^{261}Rf^b was successfully identified based on α-α correlations linking α decays of ^{261}Rf^b and its known daughter ^{257}No [18]. The α-particle energy of ^{261}Rf^b was measured to be 8.52 ± 0.05 MeV. The half-life was determined to be 1.9 ± 0.4 s based on both 8.52-MeV α and SF decays. The α and SF branches are $b_\alpha = 0.27 \pm 0.06$ and $b_{SF} = 0.73 \pm 0.06$, respectively. The cross section for the ^{248}Cm(^{18}O,5n)^{261}Rf^b reaction is $\sigma(^{261}$Rf$^b) = 11 \pm 2$ nb at 95.1 MeV, which gives a cross-section ratio of $\sigma(^{261}$Rf$^a)/\sigma(^{261}$Rf$^b) = 1.1 \pm 0.2$.

2.2.2 ^{262}Db

Dubnium-262 was produced in the ^{248}Cm(^{19}F,5n)^{262}Db reaction at beam energies of 97.4 and 103.1 MeV: at the latter energy, the excitation function calculated by the HIVAP code [22] exhibits the maximum cross section. The beam intensity was 4 pμA. Based on the genetically correlated 73 α-α and two α-SF decay chains of ^{262}Db and its known daughter nuclide ^{258}Lr, two α lines at $E_\alpha = 8.46 \pm 0.04$ and 8.68 ± 0.03 MeV with α intensities $I_\alpha = 70 \pm 5\%$ and $30 \pm 5\%$, respectively, were assigned to ^{262}Db, though three energies of $E_\alpha = 8.45$ ($I_\alpha = 75\%$), 8.53 (16%), and 8.67 MeV (9%) had been adopted for ^{262}Db in [23]. The half-life of $T_{1/2} = 33.8^{+4.4}_{-3.5}$ s obtained for ^{262}Db confirmed the literature data [23]. The SF branch of $b_{SF} = 52 \pm 4\%$ is fairly larger than that adopted in [23] ($b_{SF} = {\sim}33\%$). The average α-particle energy of $E_\alpha = 8.61$ MeV and the half-life of $T_{1/2} = 3.54^{+0.46}_{-0.36}$ s were obtained for ^{258}Lr, and they agree with the literature values [23]. The EC decay was observed in ^{258}Lr for the first time with $b_{EC} = 0.026 \pm 0.018$. The decay pattern for the chain ^{262}Db $\to$ ^{258}Lr $\to$ ^{258}No is shown in Fig. 2a. The production cross sections for the ^{248}Cm(^{19}F,5n)^{262}Db reaction were $\sigma(5n) = 2.1 \pm 0.7$ and $0.23^{+0.18}_{-0.11}$ nb at 103.1 and 97.4 MeV, respectively. They were reproduced by the HIVAP code [22].

No correlated α-α or α-SF pair was observed for the four-neutron evaporation product ^{263}Db and its α-decay daughter ^{259}Lr. The upper-limit cross sections of $\sigma(4n) \leq 0.064$ nb at 103.1 MeV and $\leq$0.13 nb at 97.4 MeV derived for the ^{248}Cm(^{19}F,4n)^{263}Db reaction are rather smaller than the HIVAP prediction.

2.2.3 ^{265}Sg^{a,b}

Two isomeric states of ^{265}Sg, i.e., ^{265}Sg^a and ^{265}Sg^b, proposed in [24] were produced in the ^{248}Cm(^{22}Ne,5n)^{265}Sg reaction at the beam energy of 117.8 MeV [19]. The beam intensity was 3 pμA. Based on the correlated α-α(-α) and α-SF decay chains, 18 and 24 events were assigned to ^{265}Sg^a and ^{265}Sg^b, respectively. The half-life and α-particle energy of ^{265}Sg^a were measured to be $T_{1/2} = 8.5^{+2.6}_{-1.6}$ s and $E_\alpha = 8.84 \pm 0.05$ MeV, respectively, and those of
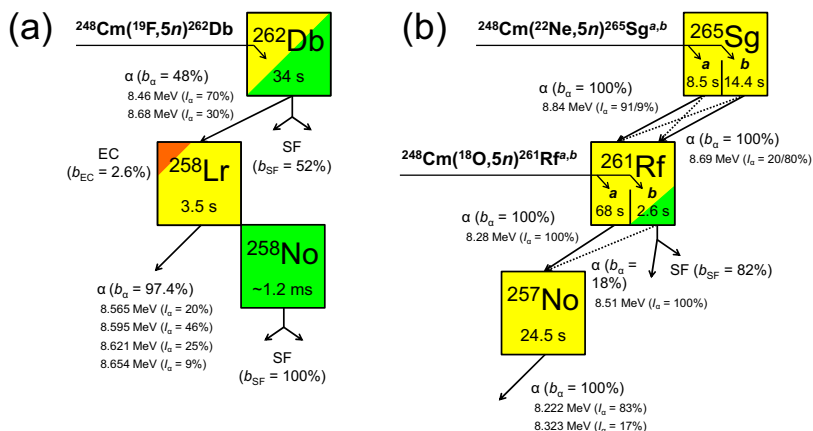
Figure 2. Decay patterns for the chain (a) ^{262}Db $\rightarrow$ ^{258}Lr $\rightarrow$ ^{258}No and (b) ^{265}Sg^{a,b} $\rightarrow$ ^{261}Rf^{a,b} $\rightarrow$ ^{257}No.

^{265}Sg^b were $T_{1/2} = 14.4^{+3.7}_{-2.5}$ s and $E_\alpha = 8.69 \pm 0.05$ MeV. As a daughter product of ^{265}Sg^{a,b}, the decay properties of ^{261}Rf^b were also derived: $T_{1/2} = 2.6^{+0.7}_{-0.5}$ s, $E_\alpha = 8.51 \pm 0.06$ MeV, and $b_{SF} = 0.82 \pm 0.09$. These results confirmed and refined the complicated decay pattern suggested for the decay chain ^{269}Hs $\rightarrow$ ^{265}Sg^{a,b} $\rightarrow$ ^{261}Rf^{a,b} $\rightarrow$ ^{257}No in [24] as shown in Fig. 2b. The production cross sections for ^{265}Sg^a and ^{265}Sg^b were reliably determined to be $\sigma = 180^{+80}_{-60}$ and 200^{+60}_{-50} pb at 117.8 MeV, respectively.

3. SHE chemistry at GARIS

The GARIS gas-jet system is expected to open new chemical studies that were not accessible before. In the gas-phase chemistry, the beam-free condition in the gas-jet chamber makes it possible to synthesize a large variety of chemical compounds. Even *et al.* [25] succeeded in the synthesis of the first carbonyl complex of SHEs, Sg(CO)$_6$ using the pre-separated ^{265}Sg^{a,b} with GARIS. A next-generation experiment to investigate the stability of the metal carbon bond in Sg(CO)$_6$ is ready with a thermal decomposition setup [26].

So far, aqueous chemistry studies of SHEs have been carried out for Rf, Db, and Sg mainly using batch-wise column chromatography apparatuses such as the Automated Rapid Chemistry Apparatus (ARCA) and the Automated Ion-exchange separation apparatus coupled with the Detection system for Alpha spectroscopy (AIDA) [1, 2]. However, there have been no reports on the aqueous chemistry of Sg and the heavier SHEs after the pioneering studies on fluoride complexation and hydrolysis of Sg in the 1990s [1, 2]. Toward the aqueous chemistry of Sg and element 107, Bh, Komori *et al.* [27] have been developing a rapid solvent extraction apparatus coupled to the GARIS gas-jet system. This new chemistry system consists of a continuous dissolution apparatus (Membrane DeGasser: MDG) [28], the Flow Solvent Extractor (FSE) consisting of a Teflon capillary and a phase separator, and a flow liquid scintillation detector for α/SF-spectrometry. The performance of MDG and FSE was investigated in the extraction system of HNO$_3$/tri-*n*-octylamine in toluene using ^{92,94m}Tc and ^{181}Re produced in the ^{nat}Mo(d,xn) and ^{nat}W(d,xn) reactions, respectively, at the RIKEN AVF cyclotron [27]. It was found that the extraction equilibrium of Tc and Re in 1 M HNO$_3$ can be obtained with a 0.5-mm i.d. × 40-cm capillary at a flow rate of 1 ml min^{-1} for both aqueous and organic solutions. The time required for the solutions to pass through the 40-cm capillary is calculated to be 2.4 s. This is short enough to conduct the solvent extraction

of ^{266}Bh ($T_{1/2} = \sim 10$ s) produced in the ^{248}Cm(^{23}Na,5n)^{266}Bh reaction at GARIS. The flow liquid scintillation detector is under development.

4. Summary

The GARIS gas-jet system was developed to open the next generation SHE chemistry. Useful radioisotopes of ^{261}Rf^{a,b}, ^{262}Db, and ^{265}Sg^{a,b} for chemical studies were successfully extracted to the chemistry laboratory, and the production and decay properties of those isotopes were investigated. These results clearly demonstrated that the GARIS gas-jet method is a promising approach for exploring new frontiers in SHE chemistry: the background radioactivities from unwanted reaction products are strongly suppressed, the intense primary heavy-ion beam is absent in the gas-jet chamber, and hence the high gas-jet transport yield is achieved. Further the beam-free conditions make it possible to investigate new chemical systems. The first chemistry behind GARIS, the chemical synthesis and gas-chromatographic separation of Sg(CO)$_6$ were successful. The novel rapid solvent extraction apparatus is under development toward the aqueous chemistry of the heaviest SHEs such as Sg and Bh.

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