

Physico-chemical characterization of seaborgium as oxide hydroxide

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Summary. Seaborgium (Sg; element 106) was studied in comparison with tungsten in the O₂-H₂O_(g)/SiO_{2(s)}-system using high temperature on-line isothermal gas chromatography. The 21-s nuclide ²⁶⁶Sg was produced in the ²⁴⁸Cm + ²²Ne reaction at a beam energy of 119 MeV. The reaction products were continuously transported by a He(MoO₃)-jet to the chromatography apparatus HITGAS. Group 6 element oxide hydroxide molecules volatile at temperatures above 1000 K were formed at 1325 K by adding humid oxygen as reactive gas. ²⁶⁶Sg was unambiguously detected after gas chromatographic separation by measuring ²⁶⁶Sg-²⁶²Rf mother-daughter α -sf correlations. The experimental results demonstrate the volatility of Sg in humid oxygen, presumably as Sg oxide hydroxide, a behavior typical for both U(VI) and the group 6 elements.

1. Introduction

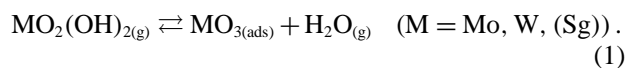
The first chemical studies of Sg revealed chemical properties of a typical group 6 element [1–3]. In gas-chromatographic studies of oxychlorides as well as in liquid-chromatographic separations of oxo- or oxyfluoride complexes, Sg behaved similar to the group 6 homologues Mo and W. This “normal” behavior was not expected a priori, since for the first two transactinide elements, Rf (rutherfordium, element 104) and Db (dubnium, element 105), deviations in the periodicity of chemical properties have been observed, which were attributed to the influence of relativistic effects on chemical properties [4]. Relativistic effects increase with nuclear charge and could be more pronounced for the heavier seaborgium. Therefore, it is meaningful to investigate whether in other chemical systems the typical group 6 properties vary also monotonously in the sequence Cr-Mo-W-Sg.

Here we report first gas-chromatographic studies of seaborgium oxide hydroxide in the O₂-H₂O_(g)/SiO_{2(s)}-system.

2. The chemical system and preparatory experiments

To chemically characterize a transactinide element, available only in quantities of a few atoms of short-lived isotopes, it is favorable to study it simultaneously with trace amounts of well characterized elements, first of all its supposed homologues. As chemical species for such comparative studies with Sg, the trioxides of the group 6 elements were considered [5, 6] because the clear gradation of their chemical properties within the group should facilitate the detection of relativistic effects on chemical properties.

It is well known for Mo and W, that in an O₂/H₂O atmosphere the solid trioxides, MO₃, are in equilibrium with the gaseous oxide hydroxides of the type MO₂(OH)₂. In the case of single atoms, it was assumed, that in the O₂-H₂O_(g)/SiO_{2(s)}-system the gaseous oxide hydroxides undergo a dissociative adsorption process:



The gas chromatography of oxides or oxide hydroxides in quartz-glass columns should be characterized by a high selectivity with regard to the lighter transactinides and actinides, which could disturb the unequivocal identification of Sg. Preparatory experiments were carried out to verify these predictions and to develop the adequate experimental technique for studying Sg.

The behavior of trace amounts of Mo and W in the O₂-H₂O_(g)/SiO_{2(s)}-system was studied by thermochromatography and high temperature on-line isothermal gas chromatography [7–9]. The oxide hydroxides proved to be less volatile than the group 6 oxychlorides. The gas chromatography of group 6 oxide hydroxides in the O₂-H₂O_(g)/SiO_{2(s)}-system was shown to be a typical reaction gas chromatography governed by the surface reactions dissociative adsorption and associative desorption. As typical for reaction gas chromatography, the reaction rate and yield are determined not only by the column temperature but mainly by the limited concentration of the reaction partner H₂O. The chromatographic resolution is not as high as in case of gas

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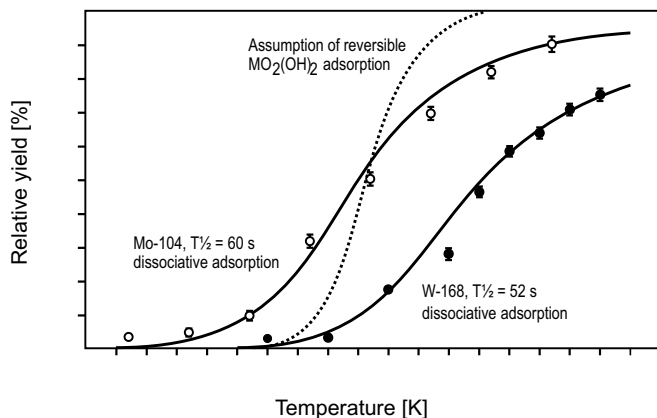


Fig. 1. Isothermal gas chromatography of Mo and W oxide hydroxides in quartz-glass columns using humid oxygen as reactive carrier gas component; (○): relative yields of ^{104}Mo , (●): relative yields of ^{168}W , dashed line: hypothetical curve assuming reversible adsorption of an oxide hydroxide.

chromatographic separations based on reversible adsorption processes. Thermochromatographic peaks are broadened and the yield of isothermal elution chromatography varies only slightly with temperature as shown in Fig. 1 for the isothermal chromatography of ^{104}Mo and ^{168}W . The yield curves were calculated by Monte Carlo simulation with $\Delta H^{\circ}_{\text{diss.ads}} = -54 \text{ kJ/mol}$ for $\text{MoO}_2(\text{OH})_2$ and $\Delta H^{\circ}_{\text{diss.ads}} = -56 \text{ kJ/mol}$ for $\text{WO}_2(\text{OH})_2$. The dashed line was obtained assuming a simple reversible adsorption of hypothetical $\text{Mo}_2(\text{OH})_2$ molecules with $\Delta H^{\circ}_{\text{ads}} = -220 \text{ kJ/mol}$.

In test experiments with Mo and W isotopes the PSI On-Line Gas Chromatography Apparatus OLGA II, which was successfully used to study Rf and Db halides [10], turned out to be unsuitable for Sg studies in the $\text{O}_2\text{-H}_2\text{O}_{(\text{g})}/\text{SiO}_{2(\text{s})}$ -system. Residence times of Mo and W oxide hydroxides of about two min were measured, far too long for studying nuclides with half-lives of about 20 sec. In order to achieve reasonable reaction rates and chemical yields for a Sg experiment under the less favorable conditions of reaction gas chromatography, the experimental parameters as well as the complete experimental set-up had to be optimized. The HIgh Temperature on-line Gas chromatography ApparatuS HITGAS was developed [11]. The most essential changes in comparison to the PSI On-Line Gas Chromatography Apparatus OLGA II and OLGA III, were the use of relatively short chromatography columns and the replacement of the reclustering by a direct coupling of chromatography and detection. This was realized by directly depositing the species leaving the chromatographic column on metal foils mounted on the wheel of the GSI ROTating Wheel Multidetector Analyzer ROMA. This technique has been applied already in earlier search experiments for super heavy elements [12] and experiments modeling bohrium studies [13].

HITGAS was tested in experiments with short-lived W isotopes and lanthanides (as models for actinides). Retention times of W as short as 8 s, chemical yields of, e.g., 53% for the 18.8 sec nuclide ^{166}W , and decontamination factors from lanthanides between 10^2 and 10^3 were achieved [9]. These performance data meet the requirements of a transactinide experiment. On-line alpha spectroscopy, however,

could be carried out only in 2π geometry. $1 \mu\text{m}$ collection foils made of aluminum, which are a prerequisite for 4π alpha spectroscopy, were stable in pure He carrier gas leaving the column with about 1000 K, but were immediately destroyed when the reactive gas $\text{H}_2\text{O}/\text{O}_2$ was added.

3. Experimental

Bearing in mind the challenging character of Sg studies in the $\text{O}_2\text{-H}_2\text{O}_{(\text{g})}/\text{SiO}_{2(\text{s})}$ -system we decided to carry out a first-generation experiment. This experiment should establish whether Sg forms a volatile oxide hydroxide, and whether the experimental technique meets the requirements of a second-generation experiment aimed at a quantitative thermochemical characterization of Sg.

Considering the results of the preparatory experiments and potential interferences of Po-isotopes, we decided to study ^{266}Sg ($T_{1/2} = 21 \text{ s}$) instead of the shorter-lived ^{265}Sg ($T_{1/2} = 7.4 \text{ s}$) despite its lower production cross section and to detect it in 2π geometry by registering ^{266}Sg α -decays followed by time correlated spontaneous fission events of the ^{262}Rf daughter.

3.1 Nuclide production and transport

The Sg studies were performed at the GSI accelerator UNILAC. ^{265}Sg and ^{266}Sg were produced in the $^{22}\text{Ne} + ^{248}\text{Cm}$ reaction. We used two mixed $^{248}\text{Cm}/^{152}\text{Gd}$ targets ($820 \mu\text{g}/\text{cm}^2$ ^{248}Cm , $85 \mu\text{g}/\text{cm}^2$ ^{152}Gd and $730 \mu\text{g}/\text{cm}^2$ ^{248}Cm , $75 \mu\text{g}/\text{cm}^2$ ^{152}Gd , respectively) which were bombarded with $^{22}\text{Ne}^{5+}$ ions at a beam energy of $119 \pm 1 \text{ MeV}$ (middle of the target). A bombarding energy of 119 MeV was chosen as optimum for the production of ^{266}Sg in the $4n$ -channel. The beam current in the seaborgium experiment was about 0.4 particle microamperes ($2.4 \times 10^{12} \text{ s}^{-1}$). This beam current was chosen considering the target stability and transportation yield which dropped significantly at higher beam currents. With a cross section of 60 pb [14] for the reaction $^{248}\text{Cm} (^{22}\text{Ne}, 4n) ^{266}\text{Sg}$, the expected production rate of ^{266}Sg was about 0.8 h^{-1} .

A He/ MoO_3 gas-jet was used to rapidly transport the nuclear reaction products to the chromatography apparatus: Reaction products recoiling from the target were stopped in He gas loaded with MoO_3 particles produced by sublimation from MoO_3 powder at 900 K. The gas-jet was operated at a He-flow rate of 2.0 l/min and a pressure of about 1.5 bar in the recoil chamber. Reaction products, attached to the aerosol particles, were swept out of the recoil chamber into a steel capillary (2 mm i.d.) and transported through it within 1.2 s over a distance of 13.5 m to the chromatography apparatus HITGAS.

3.2 High temperature on-line gas chromatography apparatus HITGAS

Fig. 2 shows a schematic of the apparatus as it was used in the Sg experiments. A five-section chromatography furnace (HTM Reetz GmbH, Berlin) allows to employ differently shaped chromatography columns with outer diameters up to 18 mm at isothermal temperatures up to 1375 K. The

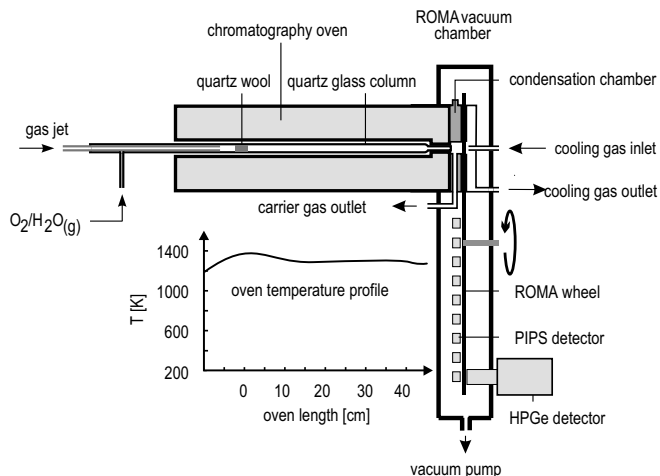


Fig. 2. Schematic of the high temperature on-line gas chromatography apparatus HITGAS.

columns used in the seaborgium experiment were straight open tubular quartz-glass columns with the following specifications: (a) inner diameter 3.5 mm, (b) 6 cm long preheating section, (c) constriction for positioning a quartz wool plug as a high temperature reaction zone, (d) 38 cm long isothermal zone, and (e) capillary outlet. The choice of these column dimensions and the use of a relatively loose, only 15 mm long quartz wool filter as a high temperature reaction zone was a compromise between reaction rate and chemical yield on one hand and separation efficiency (from actinides) on the other. In order to directly couple chromatography and detection, the chromatography furnace was flanged to ROMA and a separate deposition chamber was placed between column outlet and rotating wheel. The deposition chamber allowed to establish an optimum pressure for direct deposition of about 80 mbar and, at the same time, a pressure below 5 mbar in the detection positions of the ROMA chamber. Furthermore, being connected with a cooling thermostat, the deposition chamber cooled the wheel. In order to cool the collection foils and to establish the same pressure at both their front and back sides, a cooling gas chamber was installed at the back side of the ROMA wheel.

The computer program CORA was developed for the ROMA step motor control and the synchronization of the ROMA movement with the nuclear spectroscopy data acquisition system [15]. It is running on a Windows 9x or Windows NT personal computer and uses the Windows user interface. With this program, the stepping of the ROMA and its communication with the acquisition environment can be set up in a very simple manner, no knowledge about the program internals and computer programming are required. The program architecture strictly separates the experiment logic from direct hardware access, so it can be adapted with little effort to other step motor and I/O hardware.

3.3 Seaborgium experiments

For a first series of Sg experiments an overall beam time of 120 h was available. Optimum experimental conditions were established by adding 0.5 l/min O_2 gas saturated with H_2O at 323 K to the gas-jet at the column entrance. The tem-

perature of the chromatography column was 1325 K in the reaction and 1300 K in the isothermal zone. 25 μm Al-foils were used to collect the species under study. The rotating wheel was operated with a cycle-time for collection of 10 s. 15 equidistantly positioned PIPS detectors were used to detect spontaneous fission and α -decay events for a time period of 150 sec after the collection. The yield of short-lived W isotopes, which served as models for group 6 elements, was determined with a HPGe detector, which was mounted in a cylindrical ROMA insert at the rear of the wheel in detection position 2. The separation efficiency from actinides, which is of crucial importance for the unambiguous detection of ^{266}Sg by registering ^{266}Sg α -decays and time correlated spontaneous fission events of the ^{262}Rf daughter, was monitored by summarizing the spontaneous fission event rate over all detectors. The use of the spontaneous fission event rate as a measure of the separation efficiency from actinides is based on the fact, that nearly all spontaneous fission events originate from the decay of heavy actinide nuclides such as, *e.g.*, ^{256}Fm , which are produced in large excess in comparison to all other fissile nuclides in the given beam/target combination.

An experiment run was stopped when the W yield dropped below 40% and/or the spontaneous fission event rate exceeded 2 per hour. With a production cross section of ^{256}Fm of about 0.15 μb [16] and a mean beam current of 0.4 μA , the spontaneous fission event rate of 2 per hour corresponds to a decontamination factor from actinides of about 500. A new run was started after replacing the chromatography column.

The off-line data evaluation started with an extensive data reduction. Because the detectors 11–15 turned out to be very noisy only events registered in detectors 1–10 were used. Applying as main quality criterion the separation efficiency from actinides, all runs with decontamination factors above or equal 330 were considered. As result, the data of 21 runs covering 63.5 h of beam time were taken into consideration and were further evaluated.

4. Results and discussion

The data accumulated during these 63.5 h of beam time corresponded to a total beam dose of 6.32×10^{17} ^{22}Ne ions. All 210 single alpha spectra were energy-calibrated manually using the prominent α -decay lines of Po. The α -spectrum in Fig. 3 is a sum of these 210 spectra. Noticeable is the excellent resolution of 28 keV (FWHM). A negative feature is the high contamination with various Po isotopes. These nuclides are produced most probably from Pb impurities in the target and/or the target assembly. Unfortunately, Po cannot be separated from group 6 elements in the oxide hydroxide system. In future experiments, the only way to reduce the contamination with Po is to avoid its production.

The search for time correlated ^{266}Sg - ^{262}Rf mother-daughter decay chains was carried out in the following way: Alpha events with energies between 8610 and 8750 keV were considered as possible ^{266}Sg mother decays [14]. Because the spectra of the first 10 detectors were used (with a ROMA step time of 10 seconds) the search interval for

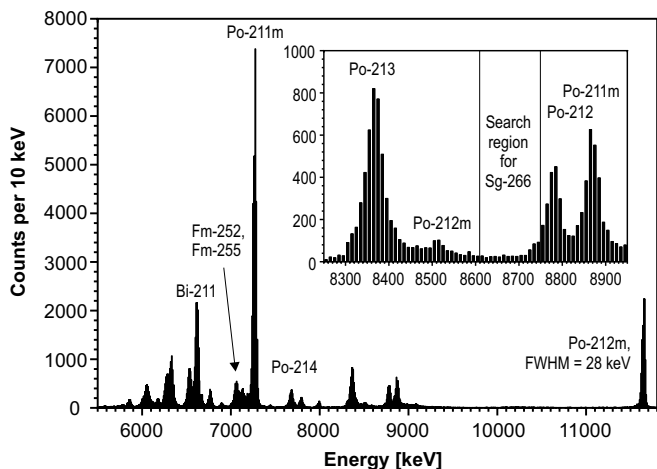


Fig. 3. Sum of alpha spectra of detectors 1–10 accumulated over 63.5 h of beam time.

Table 1. Detected time-correlated alpha-spontaneous fission event chains.

| Chain | E_α [MeV] | life time ^{266}Sg [s] | life time ^{262}Rf [s] |
|-------|------------------|---------------------------------|---------------------------------|
| 1 | 8.66 | 84.9 | 7.0 |
| 2 | 8.70 | 4.8 | 3.7 |

mother events was 100 s. Spontaneous fission decays, which occurred within 10 s after a mother event in the same deposition sample, were considered as possible ^{262}Rf daughter decays. Table 1 lists the detected time-correlated event chains.

In the course of the experiment, 22078 deposition samples were measured. In these samples, 516 alpha events with the ^{266}Sg decay energy and 89 spontaneous fission events were detected.

These data were used to estimate the mean number of random correlations. First, the probability was calculated that two independent decays were detected which mimic the decay sequence for ^{266}Sg . Then, the mean number of samples, containing such decay sequences, was estimated using the Bayes theorem of inverse probability. This led to an expectation value of 0.2 samples containing random correlations. This corresponds to probabilities of 0.82 that no random correlations were observed and 0.16 that one random correlation was observed. Thus, from a purely statistical point of view, the probability that both detected event chains are entirely random is 2%.

In [17] an analysis of all measured ^{266}Sg decay chains with known ^{266}Sg decay time information [14, 18] was carried out. It was shown, that both detected events of the present work fit to the events from other experiments. The obtained half life is 21.1 s, in close agreement with the 21 s from [14].

The two observed Sg events of this work correspond to a production cross section of 60 [−29, +106] pb related to the alpha decay branch of ^{266}Sg . (Assuming one detected event as random, the cross section is 27 [−17, +110] pb.)

Due to the low probability that both observed events are random, we conclude that Sg was volatile under the conditions of the experiment, presumably as Sg oxide hy-

droxide. In the $\text{O}_2\text{-H}_2\text{O}_{(\text{g})}/\text{SiO}_{2(\text{s})}$ -system Sg shows both typical group 6 element properties and an uranium(VI)-like behavior which is also known to form a volatile oxide hydroxide [19].

This first-generation experiment could not answer the question about the influence of relativistic effects on the chemical properties of seaborgium. However, the $\text{O}_2\text{-H}_2\text{O}_{(\text{g})}/\text{SiO}_{2(\text{s})}$ -system as well as the experimental technique have proven to meet the requirements of a long running experiment to study Sg in more detail.

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