Journal of Alloys and Compounds 271–273 (1998) 312–315

First aqueous chemistry with seaborgium (element 106)

Matthias Schädel[1],*

Gesellschaft für Schwerionenforschung mbH, Postfach 110552, D-64220 Darmstadt, Germany

Abstract

Chemical separations of element 106 (seaborgium, Sg) were performed in aqueous solutions. The isotopes ^{265}Sg and ^{266}Sg, produced in the $^{248}Cm+^{22}Ne$ reaction, were continuously transported to the automated liquid chromatography system ARCA. In 0.1 M $HNO_3/5\times10^{-4}$ M HF, Sg was found to be eluted from cation-exchange columns together with the hexavalent Mo- and W-ions, while hexavalent U-ions were strongly retained on the column. Seaborgium was detected by measuring correlated α-decays of the daughter isotopes. For the isotope ^{266}Sg, we have evidence for a spontaneous fission branch. The chemical results show that the most stable oxidation state of Sg in aqueous solution is +6, and that like its homologs Mo and W, Sg forms neutral or anionic oxo- or oxohalide-compounds. Sg exhibits properties very characteristic of group 6 elements, and does not show U-like properties. A second, very recent experiment, performed with pure 0.1 M HNO_3, gave evidence that the F^--anions contributed significantly to the complex formation in the first experiment. © 1998 Elsevier Science S.A.

Keywords: Seaborgium; α-Decays

1. Introduction

All experimental findings about the chemistry of element 104, rutherfordium, Rf, and element 105, hahnium, Ha, show that they constitute the first two transactinide elements; see [1] for a review. However, the chemistry of either element provided many surprises. Therefore, it is of great interest to investigate to what extent the chemical properties of element 106 resemble properties of the lighter homologs in group 6, Mo and W, or rather those of the pseudogroup-6 element U. A brief summary of first results and conclusions from aqueous-phase and gas-phase chromatographic experiments with Sg is given in [2]. More experimental details are given in [3] for the aqueous phase experiments.

^{265}Sg and ^{266}Sg were discovered in the reaction ^{22}Ne on ^{248}Cm [4,5]. α-Particles with energies 8.71 to 8.91 MeV were assigned to ^{265}Sg and a half-life of 2 to 30 s was estimated [4]. Six α-decays ($E_\alpha=8.63\pm0.05$ MeV), followed by spontaneous fission (SF), were attributed to the decay chain $^{266}Sg \xrightarrow{\alpha} {}^{262}Rf \xrightarrow{SF}$. A partial α half-life of 10 to 30 s and an upper limit of 85% SF-branching was estimated for ^{266}Sg [4]; in agreement with theoretical predictions [6].

2. Preparatory tracer experiments

2.1. Choice of the chemical system

The ARCA [7] is a computer-controlled liquid-chromatography system. The following prerequisites are needed for a Sg-experiment with ARCA: (i) Fast access to the Sg fraction, and fast sample preparation for α-spectroscopy, (ii) Bi and Po separation to avoid too many interfering α-events, (iii) separation of trivalent actinides to identify SF-events from ^{266}Sg and ^{262}Rf and (iv) efficiently separated elements 104 and 102. This last item is important because, if fulfilled, then, all Rf and No isotopes, observed in the Sg fraction after chemical separation, can be presumed to be daughter nuclei of Sg precursor nuclei.

We have prepared the following system: formation of anionic, or possibly neutral, oxo- and oxofluoride compounds in dilute nitric/hydrofluoric acid and separation on cation exchange columns. Batch experiments gave low distribution coefficients, K_D, ($K_D\leq6$) for the group 6 elements Mo and W on a cation exchange resin 0.1 M

---

*Corresponding author. Tel.: +49 6159 712460; fax: +49 6159 712903; e-mail: m.schaedel@gsi.de

[1] Darmstadt–Mainz–Dresden–Krakow–Berkeley–Tokai-collaboration

0925-8388/98/$19.00 © 1998 Elsevier Science S.A. All rights reserved.
PII: S0925-8388(98)00078-4

$HCl/1\times10^{-4}$ M HF [8]. Under the same conditions, trivalent ions and the tetravalent Zr and Hf ions form cationic complexes which are strongly adsorbed.

Presumably, Mo and W form anionic complexes of the type MO_3F^-, $MO_2F_3^-$ and $MO_2F_4^{2-}$ at a sufficiently high HF concentration, and, more likely, the oxo-compound MO_4^{2-} in very dilute HF. Moreover, the formation of neutral compounds, like MO_2F_2, cannot be excluded. Theoretical calculations predict that, within the series of MO_4^{2-} ions formed in aqueous solution, SgO_4^{2-} will be the most stable [9].

2.2. On-line tracer separations

Carrier-free tracer activities were obtained as fission products and from heavy-ion reactions. A He(KCl)-jet system was applied to transport the tracers to the ARCA [7]. After collection, tracer activities were dissolved and were washed onto the 8 mm×1.6 mm chromatographic column filled with the cation exchange resin Aminex A6, 17.5±2 μm. Elutions were performed with 1 ml min^{-1} flow rate. Fractions were collected to monitor chemical yields, purities of the chemical separations, and elution curves by applying X-ray and γ-spectroscopy.

We kept the HNO_3 concentration constant at 0.1 M and varied the HF concentration between 5×10^{-4} and 10^{-3} M. Either eluent dissolves and elutes more than 85% of the W within 10 s. In 1×10^{-3} M HF neutral or anionic complexes of Hf are formed which appear in the W fraction. 5×10^{-4} M HF provides conditions for a clean separation of group 6 elements from di- or trivalent actinides, group 4 elements and U [3].

3. Seaborgium experiments

To produce ^{265}Sg and ^{266}Sg, we used the ^{22}Ne on ^{248}Cm reaction; for details see [3]. A 950-μg cm^{-2} ^{248}Cm-target was bombarded with typically 0.5 μA (particle) of 122 MeV ^{22}Ne ions. Reaction products were transported with a He(KCl)-jet to ARCA within 3 s. There, the reaction products were collected for 45 s, and were dissolved afterwards. The overall yield (36%), including He(KCl)-jet transport efficiency, chemical separation, and sample preparation, was frequently checked with ^{169}W, produced on small amounts of ^{152}Gd in the target. Sg was separated in 0.1 M $HNO_3/5\times10^{-4}$ M HF solution. We collected the eluent from the first 10 s. Evaporation of the eluent started with the beginning of elution, and measurements started about 38 s later.

α-Particle and SF-fragment pulse-height analyses were performed on each sample for 360 s using a system of eight 450 mm^2 PIPS detectors. The energy of each event with the time after start of counting and detector identification was stored in list mode. For α-particles, the energy resolution was about 60 keV (FWHM), the energy calibration was accurate to about 15 keV, and the detector efficieny was 33%.

4. Results and discussion

4.1. ARCA-^{265}Sg

In the first main ARCA experiment, 3900 collection and elution cycles were run. A small contamination of $^{211m,212,213}Po$ and ^{214}At prevents assigning single α-decays to the decay of Sg without further information. To identify α-decays of ^{265}Sg and the daughter nuclei ^{261}Rf and ^{257}No, we have searched for correlated α–α decays. All correlated α–α events with energies between 6 and 10 MeV are depicted in Fig. 1. We have searched for the $^{265}Sg \xrightarrow{\alpha} {}^{261}Rf \xrightarrow{\alpha}$ decay in the "parent–daughter" window ("P" in Fig. 1). For the first ("parent") α-particle we accepted energies between 8.50 and 9.10 MeV (*E*1-scale in Fig. 1). For the second ("daughter") α-particle the energy window was open between 8.10 to 8.60 MeV (*E*2-scale in Fig. 1) to include α-particles from the decay of ^{261}Rf and ^{257}No. One correlated event (event No. 3 in Table 1) was observed.

To judge the significance of this one event for being a true decay of ^{265}Sg followed by the decay of ^{261}Rf, we have calculated the number of expected random events by a Monte-Carlo simulation which gives a random rate of 0.56 correlations. For an expectation value of 0.56 the

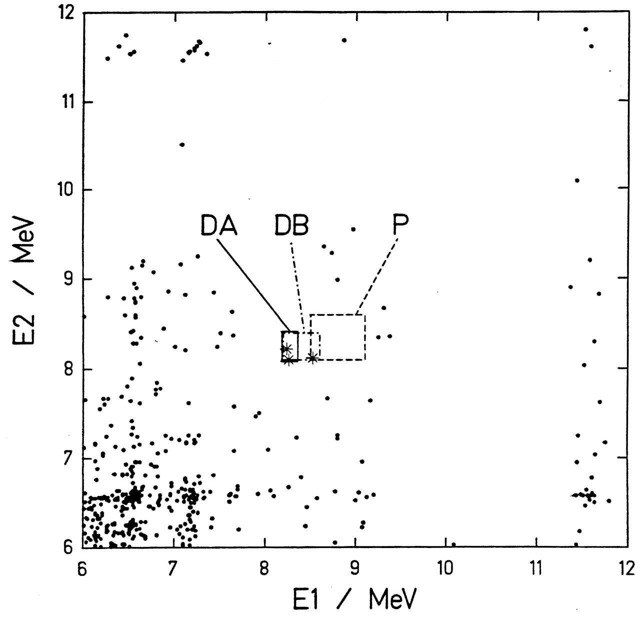

Fig. 1. Correlated α–α events observed in Sg fractions after chemical separation with ARCA. *E*1 represents the α-energy of the α-particle observed first, *E*2 the energy of the subsequent second α-particle. The energy windows are given for our search for the $^{265}Sg \xrightarrow{\alpha} {}^{261}Rf \xrightarrow{\alpha}$ decay ("P"), and for the $^{261}Rf \xrightarrow{\alpha} {}^{257}No \xrightarrow{\alpha}$ decay ("DA" and "DB").

Table 1
^{265}Sg-events from the ARCA experiment with 121-MeV ^{22}Ne on ^{248}Cm

Event No.	$E(1)$ (MeV)	$\Delta t1$ (s)	$E(2)$ (MeV)	$\Delta t2$ (s)
1	8.24	33.5	8.22	67.4
2	8.26	22.7	8.10	8.2
3	8.52	142.0	8.12	3.0

$E(1)$: energy of the first α-particle.
$E(2)$: energy of the second α-particle.
$\Delta t1$: time after start-of-measurement.
$\Delta t2$: time after first α-event.

probability is 32.1% for observing one random correlation, see Table 2. Thus, we have no convincing evidence for the direct observation of a ^{265}Sg α-decay.

In a second energy region, we have looked for the $^{261}\mathrm{Rf} \xrightarrow{\alpha} {}^{257}\mathrm{No} \xrightarrow{\alpha}$ decay (‘‘daughter–daughter’’). For the first α-particle we have investigated two options. Option A is based on the assumption that ^{261}Rf has only one characteristic α-decay with $E_\alpha = 8.28$ MeV. In this option (A) energies between 8.20 and 8.36 MeV are accepted for the first α. Option B is based on the assumption that ^{261}Rf has a second characteristic α-decay energy with $E_\alpha = 8.52$ MeV [10]. In this option (B) α-particles with energies between 8.20 and 8.60 MeV are viewed as possible candidates for the decay of ^{261}Rf. For the second α-particle, from the decay of ^{257}No, an energy window from 8.10 to 8.40 MeV was selected.

The two correlated α–α decays observed in the energy window ‘‘DA’’ (option A) of Fig. 1 are listed in Table 1 as events Nos. 1 and 2. A third correlated α–α decay (event No. 3) was observed in the larger energy window ‘‘DB’’ of Fig. 1 when option B is applied.

A comparison of these numbers of measured events with the expected random correlations, as obtained from the Monte-Carlo simulation, shows that the observed α–α correlations are very likely true α-decays of the ^{265}Sg daughter nuclei ^{261}Rf and ^{257}No. The two events from option A have to be compared with an expectation value of 0.15 for random correlations. This leads to a probability of only 0.96% that the two events are random, see Table 2. Applying option B we have to compare three measured events with an expectation value of 0.27 for random correlations. This gives an even lower probability of only 0.24% that the three events are random correlations, and a high confidence that we have measured the decay of ^{261}Rf and ^{257}No as the daughter nuclei of ^{265}Sg. Isotopes of Rf and No can only be observed as the decay products of Sg because they were chemically separated on the cation exchange column in ARCA. Most likely, the decay of ^{265}Sg was not seen because it decayed in the time interval between the end-of-separation and the start-of-measurement. Decay data, measured in a companion experiment to ARCA with an on-line gas-chromatographic technique [2,11], yielded in a preliminary analysis of three α–α correlations a ^{265}Sg half-life of $(7.1+8.6/-2.5)$ s [2,11].

Table 2
Probability $P(\mu,n)$ to observe a discrete number, n, of random correlations for a given expectation value, μ, of a Poission distribution

Win	μ	$P(\mu,n)$ (%)			
		$n=0$	$n=1$	$n=2$	$n=3$
P	0.56	57.0	32.1	8.95	1.65
DA	0.15	86.1	12.9	0.96	0.05
DB	0.27	76.3	20.7	2.77	0.24

μ is from a Monte-Carlo simulation of the experimental data for a given energy window, Win (see text Fig. 1).

Most recently, a second experiment was performed with 4575 individual separations similar to the first ARCA experiment, except that no HF was added to the 0.1 M HNO_3. Based on our first experiment we had expected five correlated α–α decay chains, but we have observed only one which is likely (50% probability) to be a random event.

4.2. ARCA-^{266}Sg

To identify decays of ^{266}Sg, we have searched for correlated α-SF events from the α-decay of ^{266}Sg followed by a SF from ≈2-s ^{262}Rf [12], and we have analysed single SF-fragment events which may originate from a SF-decay branch in ^{266}Sg. No α-SF correlation was observed in the ARCA experiment. We have measured nine single SF-events after 3900 experiments. A one-component decay analysis of these nine SF-events yields a half-life of $(94+46/-23)$ s (68% c.i.).

A careful analysis of all possible sources of SF-fragment background left with a 68% c.i. $(7.0+4.0/-2.2)$, observed SF-fragments remain as possible candidates for the SF-decay of ^{266}Sg and ^{262}Rf. This corresponds to a cross-section of $(82+46/-26)$ pb if a half-life of 34 s [2,11] is assumed.

As we have not observed the α-decay of ^{266}Sg in the ARCA experiment, we are not able to determine directly a branching ratio for the decay. However, the SF-branch of ^{266}Sg can be estimated, with a very large uncertainty, from the ratio between the partial SF-decay cross-section of $(82+46/-26)$ pb, as determined in the ARCA experiment, and the partial α-decay cross-section of $(50+115/-15)$ pb (68% c.i.) as reported in the OLGA experiment [11]. The ratio of the cross-section probability distributions for the α-decay and the SF-decay yields a most probable SF-branch of 39%. This is smaller than our previously reported value of 62% [3] which, in the data analysis, did not account for the possible SF-decay contribution of the ^{266}Sg α-decay daughter isotope ^{262}Rf. An analysis which includes the latter contribution yields a 0% ‘‘lower limit’’ SF-branch for 48% and a 81% ‘‘upper limit’’ SF-branch for 95% of all combinations of cross-section ratios. If we assume a total half-life of 34 s and a branching ratio of 39%, we calculate a partial SF half-life of 87 s for ^{266}Sg. A ‘‘lower limit’’ of 24 s can be calculated for the partial SF

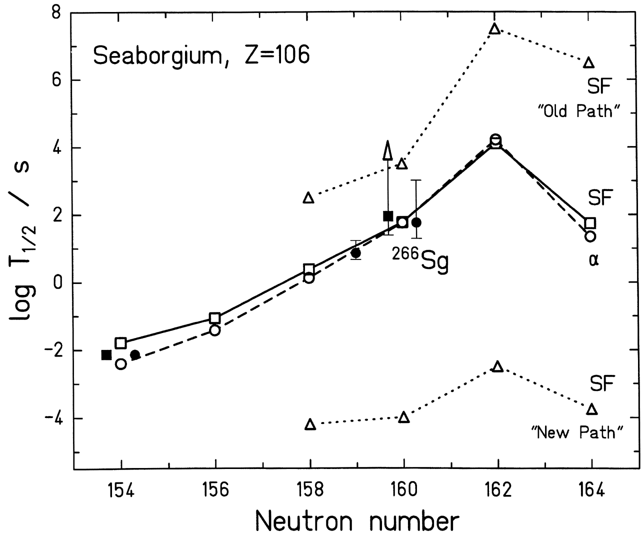

Fig. 2. Measured (solid symbols: squares for SF, dots for α-decay) and calculated partial half-lives (open symbols) for isotopes of element 106. The experimental data for ^{266}Sg are from this work and from [11]; see text for the discussion of the error bars. Calculations are from [6] for α-decay (open circles) and SF (open squares). A different theoretical approach was used in [13] to calculate SF half-lives (open triangles) for two different paths into the fission valley.

half-life from the $T_{1/2}=19$ s "lower limit" total half-life and the 81% "upper limit" of the branching ratio. Fig. 2 shows the region of experimentally determined partial α and SF half-lives (based on the assumption of a total $T_{1/2}=(34+163/-15)$ s) in comparison with those from different theoretical approaches. For ^{266}Sg, the partial SF half-life of $(87+\infty/-63)$ s yields a partial α-decay half-life of $(56+980/-37)$ s.

4.3. Seaborgium chemistry

From the observation of the three correlated α-decay chains of Sg daughters we conclude, that, for the first time, a chemical separation of element 106 was performed in aqueous solution [2,3]. Seaborgium shows a behaviour typical for a hexavalent element located in group 6 of the Periodic Table below Mo and W. From our first experiment [2,3] we concluded, that, presumably, Sg forms the anionic oxo-compound $[SgO_4]^{2-}$ or a neutral complex. The formation of other kinds of anionic compounds, like $[SgO_3F]^-$, $[SgO_2F_3]^-$ or $[SgO_2F_4]^{2-}$ was not excluded from the first results. The most recent experiment strongly indicates that the F^--anions played a significant role in the complex formation of our first experiment and that, contrary to our first interpretation, Sg may form F^--containing compounds at 5×10^{-4} M HF. However, for the lighter homologs, Mo and W, these species are only observed at higher F^--concentrations. Contrary to element 105 in group 5, where a striking similarity of its chemical behaviour to that of the pseudogroup-5 element Pa was observed, these first experiments do not indicate a Sg behaviour similar to that of the pseudogroup-6 element U, which is strongly retained on the column as UO_2^{2+}.

Acknowledgements

This work was performed by W. Brüchle, E. Jäger, M. Schädel, B. Schausten, E. Schimpf, G. Wirth, R. Günther, J.V. Kratz, W. Paulus, A. Seibert, P. Thörle, N. Trautmann, S. Zauner, D. Schumann, M. Andrassy, R. Misiak, K.E. Gregorich, D.C. Hoffman, D.M. Lee, E.R. Sylwester Y. Nagame and Y. Oura.

References

[1] M. Schädel, Radiochim. Acta 70–71 (1996) 207.
[2] M. Schädel, W. Brüchle, R. Dressler, B. Eichler, H.W. Gäggeler, R. Günther, et al., Nature 388 (1997) 55.
[3] M. Schädel, W. Brüchle, B. Schausten, E. Schimpf, E. Jäger, G. Wirth, et al., Radiochim. Acta 77 (1997) 149.
[4] R.W. Lougheed, K.J. Moody, J.F. Wild, J.H. McQuaid, Yu.A. Lazarev, Yu.V. Lobanov, et al., J. Alloys Comp. 213–214 (1994) 61.
[5] Yu.A. Lazarev, Yu.V. Lobanov, Yu.Ts. Oganessian, V.K. Utyonkov, F.Sh. Abdullin, G.V. Buklanov, et al., Phys. Rev. Lett. 73 (1994) 624.
[6] R. Smolańczuk, J. Skalski, A. Sobiczewski, Phys. Rev. C 52 (1995) 1871.
[7] M. Schädel, W. Brüchle, E. Jäger, E. Schimpf, J.V. Kratz, U.W. Scherer, H.P. Zimmermann, Radiochim. Acta 48 (1989) 171.
[8] D. Schumann, St. Fischer, R. Dressler, St. Taut, H. Nitche, N. Trautmann, et al., Radiochim. Acta 72 (1996) 137.
[9] V. Pershina, B. Fricke, Radiochim. Acta 65 (1994) 13.
[10] S. Hofmann, V. Ninov, F.P. Heßberger, P. Armbruster, H. Folger, G. Münzenberg, et al., Z. Phys. A 354 (1996) 229.
[11] A. Türler, Proc. Int. Workshop XXIV on Gross Properties of Nuclei and Nuclear Excitations, Hirschegg, 15–20 January, 1996, p. 29.
[12] M.R. Lane, K.E. Gregorich, D.M. Lee, M.F. Mohar, M. Hsu, C.D. Kacher, et al., Phys. Rev. C 53 (1996) 2893.
[13] P. Möller, J.R. Nix, J. Alloys Comp. 213–214 (1994) 43.