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Chemical properties of element 106 (seaborgium)

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The synthesis, via nuclear fusion reactions, of elements heavier than the actinides, allows one to probe the limits of the periodic table as a means of classifying the elements. In particular, deviations in the periodicity of chemical properties for the heaviest elements are predicted as a consequence of increasingly strong relativistic effects on the electronic shell structure[1–7]. The transactinide elements have now been extended up to element 112 (ref. 8), but the chemical properties have been investigated only for the first two of the transactinide elements, 104 and 105 (refs 9–19). Those studies showed that relativistic effect render these two elements chemically different from their lighter homologues in the same columns of the periodic table (Fig. 1). Here we report the chemical separation of element 106 (seaborgium, Sg) and investigations of its chemical behaviour in the gas phase and in aqueous solution. The methods that we use are able to probe the reactivity of individual atoms, and based on the detection of just seven atoms of seaborgium we find that it exhibits properties characteristic of the group 6 homologues molybdenum and tungsten. Thus seaborgium appears to restore the trends of the periodic table disrupted by relativistic effects in elements 104 and 105.

Calculations of the electron configurations of heavy atoms[1–5] have predicted that sudden changes in the structure of the electron shells may appear due to strongly increasing relativistic effects. These relativistic effects are proportional to the square of the nuclear charge, which attracts electrons in spherically symmetric orbitals (*s* and $p_{1/2}$) most strongly to the nucleus. This, in turn, means that the nuclear charge is more efficiently screened, thus allowing expansion of the non-spherical *d* and *f* orbitals. Because the chemical behaviour of an element is strongly dependent on the electronic configuration, such relativistic effects can lead to unexpected chemical properties[6,7].

Studies of the chemical properties of elements 104 (rutherfordium, Rf) and 105 (hahnium, Ha; the name dubnium has also been proposed, but has yet to be approved by the International Union of Pure and Applied Chemistry) were full of surprises[18,19]. The non-tantalum-like behaviour of hahnium in aqueous solution[10,11,20], for example, and its similarity to niobium and/or protactinium, depending on its chemical environment, demonstrated that the chemical properties cannot be reliably extrapolated from the trends observed in its lighter homologues. Such surprises have also been seen in thermo-chromatographic[9,21] and gas-chromatographic experiments[12,13,15,16]. Therefore, it is of interest to investigate whether the chemical properties of element 106 (seaborgium, Sg) resemble those of the lighter homologues in group 6 (molybdenum and tungsten) or those of the pseudo-group-6 element uranium.

We synthesized the most neutron-rich seaborgium isotopes[22,23], ^{265}Sg and ^{266}Sg, in a nuclear fusion reaction between ^{22}Ne ions from the GSI UNILAC accelerator and a ^{248}Cm target with a rate of the order of one atom per hour (ref. 24). The ^{265}Sg and ^{266}Sg nuclei were knocked out of the target foil and were stopped in helium gas loaded with tiny (0.1–1 μm) solid particles (aerosols). Within about three seconds, the helium transported the reaction products—attached to aerosols—along capillary tubes to two different sets of chemical devices. To provide conclusive evidence that a seaborgium atom had passed through the chemical separation procedures, the experiments were designed to detect the characteristic α-decay chains of the isotope ^{265}Sg, and the corresponding daughter nuclides ^{261}Rf and ^{257}No (ref. 24). In addition, fission fragments were measured from spontaneous fission decay, which would arise from ^{262}Rf, the α-decay product of ^{266}Sg. An earlier attempt to perform a chemical separation of element 106 fell short of unambiguously showing that the observed, by itself unspecific, spontaneous fission decay originated from an isotope of element 106 (ref. 25). We have applied two chemical separation techniques, one probing the formation of volatile oxychlorides in a gas-chromatographic experiment, and another one probing the formation of oxo- or oxyfluoride complexes in aqueous solution by liquid chromatography.

In classical gas chromatography, a substance under investigation is introduced into a flowing stream, and the time taken for the sample to emerge from chromatographic system is measured. In our experiment, in contrast, the nuclear reaction products were continuously supplied and separated in OLGA III—the on-line gas chemistry apparatus[17]. This technique uses the half-life of the

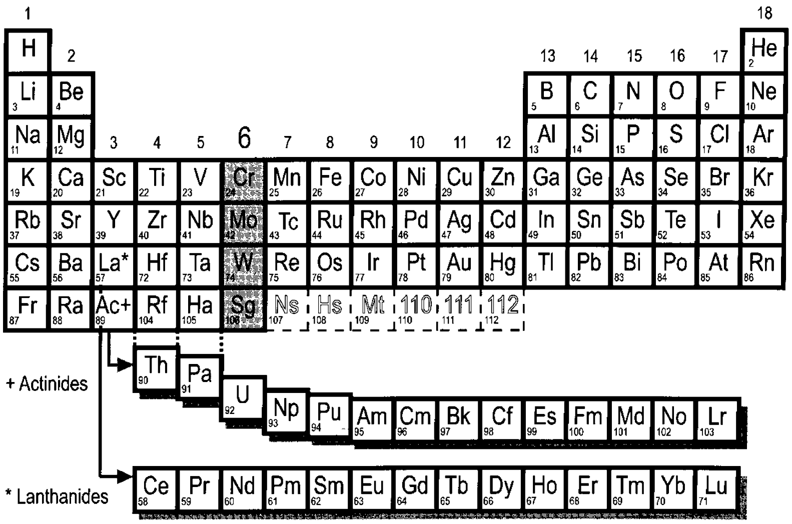

Figure 1 Periodic table of the elements. The arrangement of the actinides reflects the fact that the first actinide elements still resemble, to a decreasing extent, the chemistry of the other groups: Th the fourth group below Hf, Pa the fifth group below Ta, and U the sixth group below W. The known transactinide elements 104 to 112 take the positions from below Hf in group 4 to below Hg in group 12. Element 106, seaborgium (Sg), the heaviest element chemically investigated, is placed in group 6.

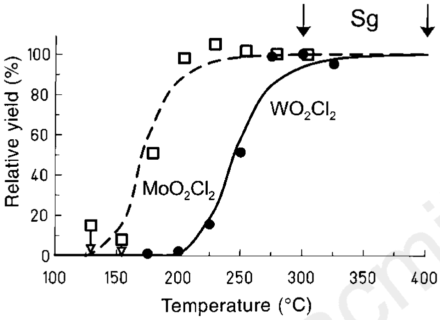

Figure 2 Measured relative yields of the compounds MoO_2Cl_2 (open squares) and WO_2Cl_2 (filled circles) versus temperature of the gas-chromatographic column. The lines are the result of Monte Carlo simulations which model the behaviour of the compounds during separation. Arrows indicate the temperatures at which seaborgium was separated.

nuclide under investigation as an 'internal' clock for the chromatographic process. Just half of the atoms introduced into the gas-chromatographic column will emerge from the other end when the time taken for an atom to pass through the column (retention time) corresponds to the nuclide's half-life. In this way, yields (that is, the ratio of the quantity introduced into the column to the quantity detected after the column) can be converted into retention times when the column is run at various temperatures. Figure 2 shows the behaviour of compounds of the short-lived isotopes of the homologues molybdenum and tungsten under the experimental conditions used for the separation of seaborgium. Reactive gases—chlorine saturated with thionyl chloride, and a little oxygen—were added to the chemically inert carrier-gas helium. Given a sufficiently high temperature, the volatile oxychloride compounds form. Thermodynamic calculations indicate the formation of dioxydichlorides as the most stable compond. Figure 2 shows that MoO_2Cl_2 is more volatile than WO_2Cl_2 because the former passes through the chromatography column at a lower temperature. The experiment with seaborgium atoms was carried out at temperatures of 300 and 400 °C, high enough for detection of the volatile oxychlorides—assuming that these seaborgium compounds do not exhibit unexpectedly low volatilities.

In the course of the OLGA experiment, the chemically separated volatile compounds leaving the end of the quartz gas-chromatography column are deposited on aerosol particles and rapidly transported in a gas stream to a detector. Here, about six seconds after their formation, the seaborgium compounds are deposited on thin foils, mounted on a revolving wheel. The wheel is rotated in a ten-second cycle so as to position the samples between detector pairs, which detect the α-particles and spontaneous-fission fragments, and measure their characteristic energies and time sequences. With OLGA III, it was possible for the first time to detect unambiguously three α-decay chains of ^{265}Sg after solid/gas-phase chemical separation (Fig. 3). An additional α-decay, which was followed 2.8 seconds later by a spontaneous fission, can be assigned to the decay of the neighbouring isotope ^{266}Sg.

Our chemical results show that, under the given conditions, element 106 forms a volatile oxychloride at 300 and 400 °C. At each temperature, two α-decay chains were observed. Thermodynamic calculations indicate that SgO_2Cl_2 is formed, in analogy to MoO_2Cl_2 and WO_2Cl_2. This agrees with the expected behaviour from an extrapolation in group 6 of the periodic table and with theoretical calculations[7].

Further chromatographic separations were carried out with single seaborgium atoms to determine its ion valency and complex formation in aqueous solution[24]. Using the separation apparatus ARCA[26] (automated rapid chemistry apparatus), investigations with molybdenum and tungsten showed that hexavalent ions could be eluted from cation exchange columns with dilute nitric/hydrofluoric acid. This chemical system makes use of characteristic differences in the formation of cationic, neutral and anionic complexes with F^- ions between elements of groups 3, 4, 5 and 6. Di- and trivalent actinides, group 4 elements, and the pseudo-group-6 element uranium, present as UO_2^{2+}, are retained on the cation exchange resin. However, the group 6 elements molybdenum and tungsten form anions of the type MO_4^{2-}, MO_3F^- or $MO_2F_3^-$ (where M indicates a metal ion)[27]. Moreover, the formation of a neutral compound like MO_2F_2 can not be excluded. Anionic and neutral species readily elute from the column.

Theoretical calculations of the electronic structure and redox potentials predict that, within the series of MO_4^{2-} ions formed in aqueous solution, SgO_4^{2-} will be the most stable[28]. From this, we expect that in very dilute hydrofluoric acid seaborgium forms SgO_4^{2-} which should follow the lighter homologues molybdenum and tungsten in the chemical separation.

During the course of more than 5,000 liquid-chromatographic separations (elution time, 10 seconds each), it was possible to detect three α-decay chains of the daughter nuclei of ^{265}Sg—namely, the α-decay of ^{261}Rf and ^{257}No—in the seaborgium fraction[24] (Fig. 3). They constitute unambiguous proof that seaborgium has passed

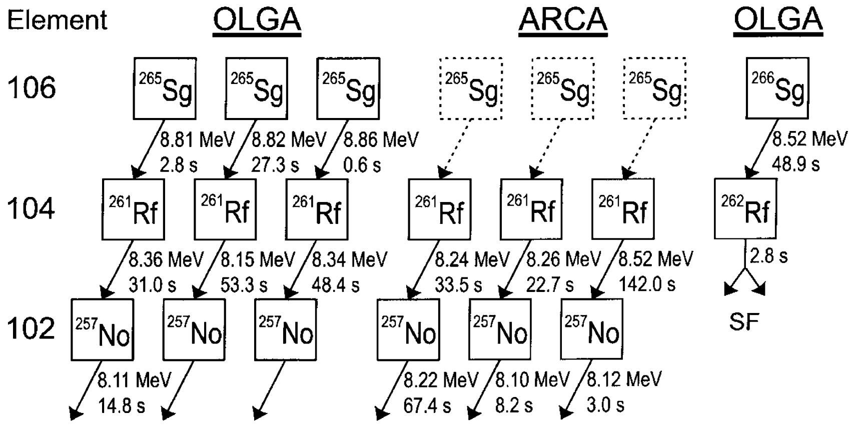

Figure 3 The observed nuclear decay chains from the seaborgium isotopes ^{265}Sg and ^{266}Sg, which allowed an unambiguous identification of seaborgium after chemical separation with ARCA (automated rapid chemistry apparatus) and OLGA (on-line gas chemistry apparatus). The α-decay energies are given in MeV, and the observed life-times in seconds.

through the column, given that both of these nuclides could only be present in the seaborgium fraction due to the α-decay of ^{265}Sg. Isotopes of the elements 104 and 102 formed directly or from decay of seaborgium before chemical separation were chemically separated. With a 90% probability, the parent nuclei had already decayed into the daughter nucleus ^{261}Rf in the time between the end of chemical separation and the commencement of measurement about 28 seconds later. This is very likely in view of the short life-times measured for the ^{265}Sg decays with OLGA (Fig. 3).

The first liquid-chromatographic separation of element 106 shows that at least a substantial fraction of the formed seaborgium behaves similarly to its lighter homologues molybdenum and tungsten, that is, that its behaviour is typical of a hexavalent ion belonging to group 6 of the periodic table. Presumably, seaborgium forms $\mathrm{SgO_4^{2-}}$ or a neutral complex.

Both our isothermal gas chromatographic and liquid chromatographic separations clearly indicate that seaborgium behaves similarly to its lighter homologues molybdenum and tungsten, and its behaviour is typical for a group 6 element of the period table. These results support the assumption that the chemistry of elements 107 to 112 will be homologous to that of the group 7 to 12 elements rhenium to mercury—if increasingly strong relativistic effects do not alter the chemical properties to such an extent that they are no longer predictable from such simple extrapolations, as seen for elements 104 and 105. ☐

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Vegetation and climate change in northwest America during the past 125 kyr

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Vegetation records spanning the past 21 kyr in western North America display spatial patterns of change that reflect the influence of variations in the large-scale controls of climate[1]. Among these controls are millennial-scale variations in the seasonal cycle of insolation and the size of the ice sheet, which affect regional climates directly through changes in temperature and net radiation, and indirectly by shifting atmospheric circulation. Longer vegetation records provide an opportunity to examine the regional response to different combinations of these large-scale controls, and whether non-climatic controls are important. But most of the longer North American records[2,3] are of insufficient quality to allow a robust test, and the long European records[4–9] are in regions where the vegetation response to climate is often