

## STATUS AND PERSPECTIVE OF CHEMICAL STUDIES OF HEAVIEST ELEMENTS

H.W. GÄGgeler

*Paul Scherrer Institut  
5232 Villigen, Switzerland*

During the last decade the elements hassium (Hs, Z=108), copernicium (Cn, Z=112), and flerovium (Fl, Z=114) have been studied for the first time by chemical means. Hassium as a member of group eight of the periodic table proved to form a volatile molecule with oxygen,  $\text{HsO}_4$ . Copernicium and flerovium both behaved like a volatile noble metal. While  $\text{HsO}_4$  turned out to be less volatile compared to the nearestby homologue in the same group of the periodic table,  $\text{OsO}_4$ , Cn and Fl were both significantly more volatile compared to their homologues Hg and Pb, respectively, in their elemental state. All first ever chemical studies were performed with very few atoms: seven in case of Hs, five with Cn and three with Fl, respectively.

### Introduction

The investigation of chemical properties of heaviest elements has developed to a frontier research discipline in chemistry because investigations have to be performed at a single-atom-at-a-time level. This restriction enables to learn how to tackle chemical studies under such extreme conditions. Several modern analytical techniques have now reached the sensitivity down to the single atom (ion) level besides radiometric methods such as e.g. studies in ion traps, atomic force microscopy etc. In heaviest element research one is confronted with extremely low production rates at modern heavy ion accelerators down to a level of single atoms-per-day only. Moreover, produced nuclides exist in form of very short lived isotopes with half lives reaching values below one second. Therefore, the chemists are confronted with the question what can we learn about chemical properties under such conditions. Let's remind us that the term "chemical property" is usually defined for the behavior of a large number of atoms or molecules under certain chemical conditions. If we want to describe, however, the behavior of single atoms or molecules we have to introduce reaction probabilities for single participants, usually applying Monte Carlo models. But even after having studied the chemical behavior of very few single atoms in a given chemical environment we still have to solve the

question what information we can infer on presumed macro amounts of the exotic element under study.

So far two approaches have been applied, first a comparison of the observed behavior in an experiment with a theoretical prediction. The underlying chemical theory has first to be validated with “conventional” chemical elements that were investigated in a similar way as the exotic ones, i.e. at a micro chemical level. The second approach is purely empirical: in model studies with homologous elements of the exotic element under study empirical correlations are established between the micro chemical observations and known macro chemical properties. It is then assumed that such a correlation also holds for the exotic element, thus enabling to deduce a “macro chemical” property even though the number of atoms or molecules under study was very small.

For a general overview on both possibilities to analyze chemical properties of single atoms or molecules we refer to reviews [1 - 4].

### Recent progress in chemical studies of heaviest elements

Figure 1 depicts the actual periodic table. Elements that are displaced from the corresponding period have been discovered – or claimed to have been discovered – but no chemical information exists yet.

Periodic Table																	
1																	18
1 H	2 He																
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar										
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57-71 Lanthanides	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89-103 Actinides	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og

Figure 1: Periodic table of the chemical elements. Elements displaced from their position indicate that no chemical information exists yet.

This means that the heaviest element which has been chemically investigated is flerovium (Fl,  $Z=114$ ). Element 113 is currently under investigation but no

publication exists yet on the outcome of these experiments. Element copernicium (Cn,  $Z = 112$ ) has been studied several times already. Then there is a lack of chemical knowledge for the elements roentgenium (Rg,  $Z = 111$ ), darmstadtium (Ds,  $Z = 110$ ), and meitnerium (Mt,  $Z = 109$ ). Below Mt, all elements have been chemically investigated at least once.

This manuscript discusses the chemical experiments conducted in the last decade with the elements hassium (Hs,  $Z = 108$ ), Cn, and Fl. All these first ever chemical investigations were performed using the gas adsorption thermochromatography technique. This technique was introduced by I. Zvara in Dubna for the chemical study of the first transactinides rutherfordium (Rf,  $Z = 104$ ) and dubnium (Db,  $Z = 105$ ) [5] – and later for seaborgium (Sg,  $Z = 106$ ) [6]. It consists of a chromatography column along which a stationary negative temperature gradient is applied. The products under study are continuously injected into this column from the high temperature side and then transported along the column towards lower temperatures. The species adsorb onto the surface of the column at a given deposition temperature that is a measure of the volatility: the lower the deposition temperature the higher the volatility. Applying basic principles of gas adsorption chromatography one can then deduce from the observed deposition temperature a corresponding adsorption enthalpy.

The chromatography set-up used for the recent investigations, however, was much improved compared to that applied in the historic experiments from Zara et al. (see Fig. 2 for the first chemical study of hassium). The main improvement is that the signals used to analyze deposited atoms or molecules inside the chromatography column were measured on-line [7]. Hence, the chromatography column consisted of an array of individual detectors that enable assay of decaying nuclides via their  $\alpha$ - or spontaneous-fission (SF) decay. In other words, the detector surfaces serve as chemical sensors for the atoms or molecules under study.

### **Chemical study of hassium**

In the Hs experiments, the products formed in a complete fusion reaction between  $^{26}\text{Mg}$  projectiles and a  $^{248}\text{Cm}$  target at an energy corresponding to the Bass fusion barrier were stopped in a gas mixture consisting of helium and oxygen. The isotope used for chemical investigation was 15s  $^{269}\text{Hs}$  formed in the 5n reaction. Oxygen served as chemical agent to form, *in-situ*, the very volatile molecule  $\text{HsO}_4$  which could then be continuously transported to a detector array that covered a temperature gradient from  $-20^\circ\text{C}$  down to

-170°C. Measured was the position, hence the temperature at which the HsO<sub>4</sub> molecules were deposited.

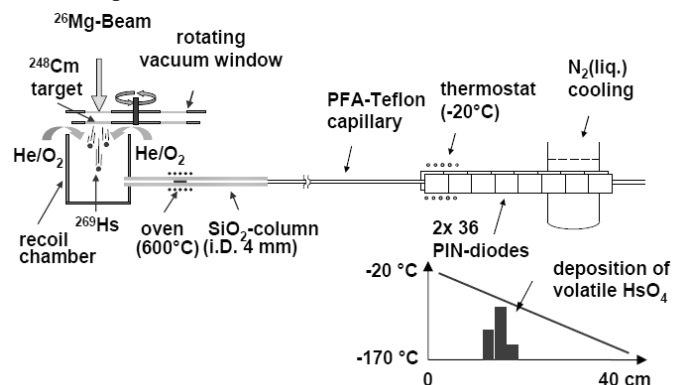


Figure 2: Example of the thermochromatography set-up used for the chemical study of Hs (see text).

Figure 3 shows the result of the first study. Based on seven molecules it was possible to show that HsO<sub>4</sub> is less volatile compared to OsO<sub>4</sub>, the identical compound of the homologous element in group eight of the periodic table [8].

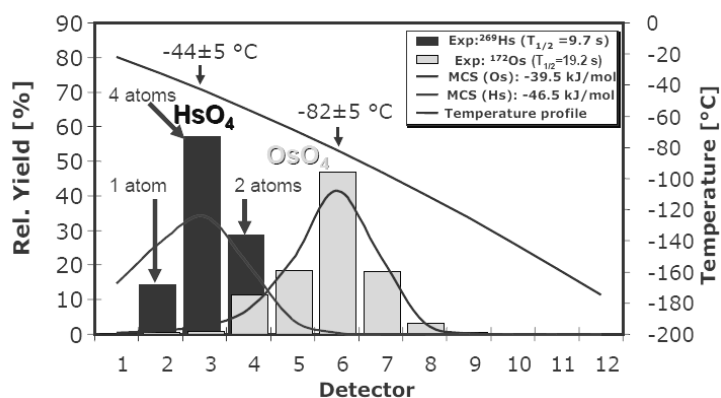


Figure 3: Deposition of seven molecules of HsO<sub>4</sub> inside the chromatography column compared to that measured for OsO<sub>4</sub> which was also studied under micro chemical conditions [8].

Using an empirical correlation between micro chemical adsorption enthalpies of d-element oxides and/or oxide-hydroxides with their respective sublimation enthalpies (see Fig. 4) it becomes possible to predict from the measured

adsorption enthalpy of  $-46.5$  kJ/mol for  $\text{HsO}_4$  a sublimation enthalpy of  $59$  kJ/mol.

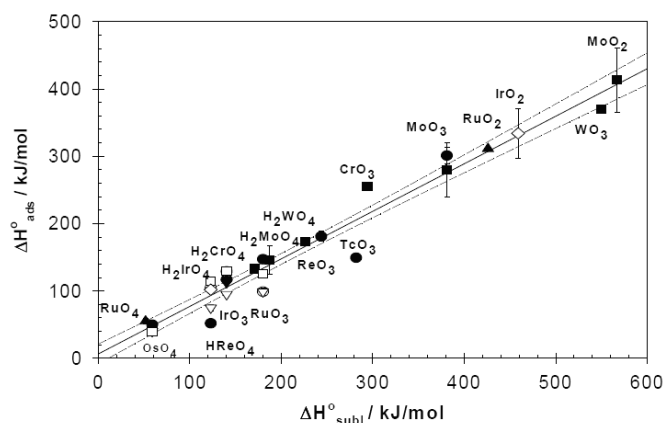


Figure 4: Correlation between micro chemical adsorption enthalpies of oxides and/or oxide-hydroxides of d-elements with their respective sublimation enthalpies (from [9]).

This experimental technique was then used to search for new isotopes of hassium in the same reaction but at different beam energies. Indeed, the two new isotopes,  $^{270}\text{Hs}$  and  $^{271}\text{Hs}$  could be discovered. They have half-lives of about  $25$  s and  $10$  s, and decay via  $\alpha$ -emission with energies of  $8.88$  MeV and  $9.13/9.30$  MeV, respectively [10,11].

### Chemical study of copernicium and flerovium

With element 112 (Cn) the  $6d$  electronic shell is filled. This situation drastically changes the chemical behavior: elements between atomic number 112 and 118 are expected to be volatile in the elemental state. This opens up new perspectives to study their chemical behavior in a state that does not require any chemical reaction prior to detection. Copernicium and flerovium were for the first time chemically investigated using the reactions between  $^{48}\text{Ca}$  projectiles and  $^{242,244}\text{Pu}$  targets which form in complete fusion reactions flerovium isotopes (see e.g. [12]). This rather exceptional strategy, to study also copernicium in this combination and not in a fusion reaction that directly forms the element of choice (as would be possible in the reaction  $^{48}\text{Ca}$  on a  $^{238}\text{U}$  target) was triggered by the fact that the reaction cross section for direct formation of Cn is about a factor of five lower compared to the cross section for production of Fl, i.e. about  $1\text{pb}$  vs.  $5\text{pb}$ , respectively [12]. In several experimental attempts it turned out that the applied gas thermochromatography technique was not sufficiently sensitive to be used at a cross section level of  $1$

pb [13], while for the latter reaction several atoms were observed after several weeks of beam time (see below).

This drawback required to apply a strategy where in the studies of Cn the firstly formed isotope of Fl decayed by  $\alpha$ -emission faster than the time needed to transport the products from the accelerator to the detector array. This was achieved by first forming 0.5 s  $^{287}\text{Fl}$  in the  $^{242}\text{Pu}(^{48}\text{Ca}; 3n)^{287}\text{Fl}$  reaction (Fig. 5). Products were then transported to the detector array within about 2.2 s, hence, ensuring decay of this isotope of Fl to a level of about 5 %, resulting in an injection of its daughter  $^{283}\text{Cn}$  into the detector with a yield of about 67 % [17].

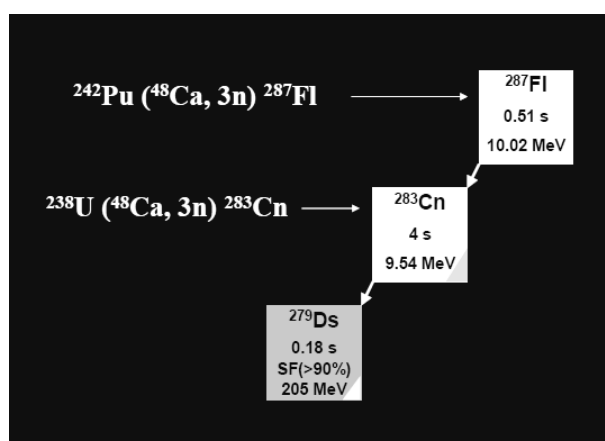


Figure 5: Synthesis of Fl and Cn in the reactions  $^{48}\text{Ca}$  on  $^{238}\text{U}$  and  $^{242}\text{Pu}$  targets, respectively. Cn can be produced in the first reaction with about 1 pb. Therefore, the chemical studies of both elements were performed with the second reaction that has a approx. five times higher cross section (see e.g. [12]).

For the chemical study a set-up was used which is very similar to that applied in the hassium experiments (see Fig. 2). The only changes concerned the gas system and the detector surfaces: since the atoms were studied in their elemental state no oxygen was required to be added to the inert carrier gas helium and secondly, in order to study the possible metallic character of the formed atoms the surface of the detectors were covered by a thin layer of the noble metal Au. As can be easily shown, atoms that behave like noble metals have a strong interaction with such an Au surface while atoms that behave similar to a noble gas exhibit very weak interaction. This statement can be nicely approved using a few atoms of Hg and Rn. Hg atoms attach to Au surface at a very high temperature (about 180 °C), while Rn atoms adsorb on Au surface at very low temperature (about -170 °C). These temperature values are

of course depending on experimental conditions such as gas flow rate, temperature gradient etc. In the course of three experiments five atoms of copernicium were detected [14, 15]. Four atoms were deposited between  $-5^{\circ}\text{C}$  and  $-39^{\circ}\text{C}$  on the Au covered detectors. Slightly different regimes inside the detector array with respect to temperature range and gas flow velocity were applied in the three experiments.

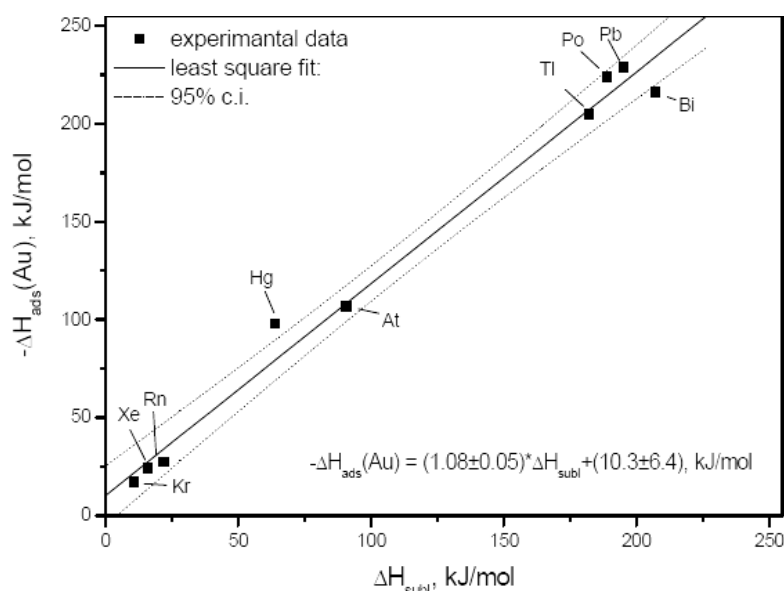


Figure 6: Correlation between adsorption enthalpies of some noble gases and of 5p-elements on a Au surface with their respective sublimation enthalpy (from [16]).

The observed deposition pattern could be well described using a Monte Carlo model assuming an adsorption enthalpy  $\Delta H_{\text{ads}} = -52^{+20}_{-4}$  kJ/mol ( $1\sigma$  uncertainty). The fifth atom was observed at  $-124^{\circ}\text{C}$  on that part of the detector array which was covered by a thin layer of ice that formed below  $-110^{\circ}\text{C}$  due to some residual water vapor. For p- and s-elements model studies showed that microchemically measured adsorption enthalpies on a Au surface correlate reasonably well with the corresponding sublimation enthalpies (see Fig. 6). Using the correlation of Fig. 6 the sublimation enthalpy for copernicium results as  $\Delta H_{\text{subl}} = 39^{+23}_{-10}$  kJ/mol. This value is rather low, indicating that Cn is a highly volatile noble metal. However, its volatility is in full agreement with expectation based on the volatility trend within group 12 of the periodic table (see Fig. 7). In the course of the experiments to study copernicium, also one atom of flerovium was detected. This was very unexpected since only 5% of all

$^{289}\text{Fl}$  atoms should reach the detector array (see above). A second and third atom of flerovium were then observed using the reaction  $^{244}\text{Pu}(^{48}\text{Ca};4n)^{288}\text{Fl}$ . Due to the higher half-life for  $^{288}\text{Fl}$  of 0.8s this isotope should reach the detector with about 15% yield [17]. It decays via  $\alpha$ -emission with an energy of 9.95 MeV, followed by the SF decay of 0.1s  $^{284}\text{Cn}$ .

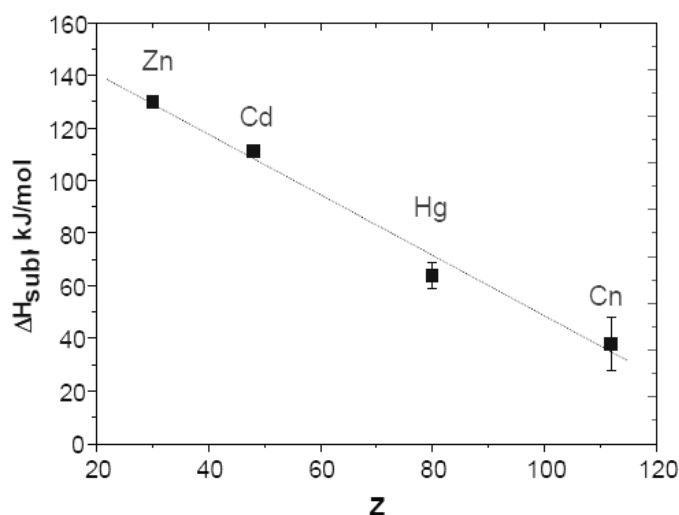


Figure 7: Trend of the sublimation enthalpy as a measure of the volatility for elements of group 12 of the periodic table.

Fig. 8 shows the position of the three atoms of flerovium together with three (out of the five) atoms of Cn observed during the same experiments [17].

The resulting adsorption enthalpy for Fl on a Au surface resulted in  $-34^{+20}_{-3}$  kJ/mol which transforms into a sublimation enthalpy of  $\Delta H_{\text{subl}} = 22^{+23}_{-2}$  kJ/mol using the empirical correlation depicted in Fig. 6.

This value is surprisingly low – even lower than expected based on an extrapolation of sublimation enthalpies within group 14 (see Fig. 9). Whether this high volatility is a result of relativistic effects that are expected to cause a very high splitting between the filled electronic  $6p_{1/2}$  shell from the empty  $6p_{3/2}$  shell by about 4 eV remains unclear.

The result of this experiment was met with some criticism [18]. Therefore, actually additional experiments are being performed, both at GSI Darmstadt as well as at FLNR to confirm or disprove the current picture.

In this respect, the experimental interpretation of the volatility of flerovium has to be considered preliminary.



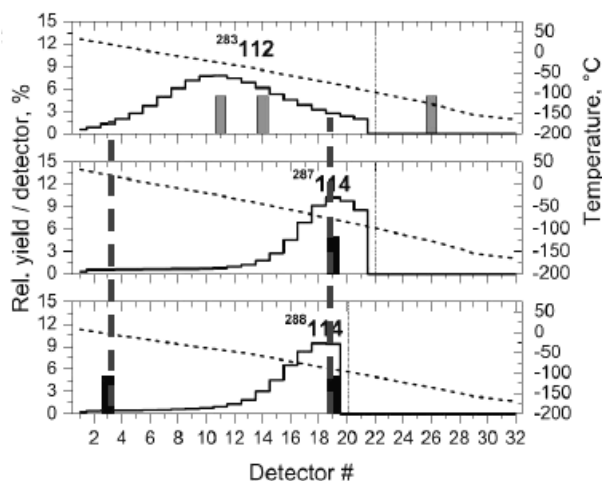


Figure 8: First row: position of three atoms of Cn observed in the  $^{242}\text{Pu}(^{48}\text{Ca};3n\alpha)^{283}\text{Cn}$  reaction. Second row: single atom of Fl observed in the reaction  $^{242}\text{Pu}(^{48}\text{Ca};3n)^{287}\text{Fl}$  where the three atoms of Cn from the first row were detected. Third row: two atoms of Fl observed in the reaction  $^{244}\text{Pu}(^{48}\text{Ca};4n)^{288}\text{Fl}$ . Dashed black lines: temperature gradient along the detector array. Solid black line: Monte Carlo model used to describe the adsorption of Cn and Fl. In case of Fl it was assumed that the “high temperature” event at  $-5^\circ\text{C}$  is due to a decay during transport. As indicated by the vertical dashed lines, within chromatographic resolution inside the detector array, all three events from Fl still fit inside the Monte Carlo deposition pattern of Cn. The thin vertical lines indicate the onset of ice formation on the surface of the Au covered detectors (deduced from [17]).

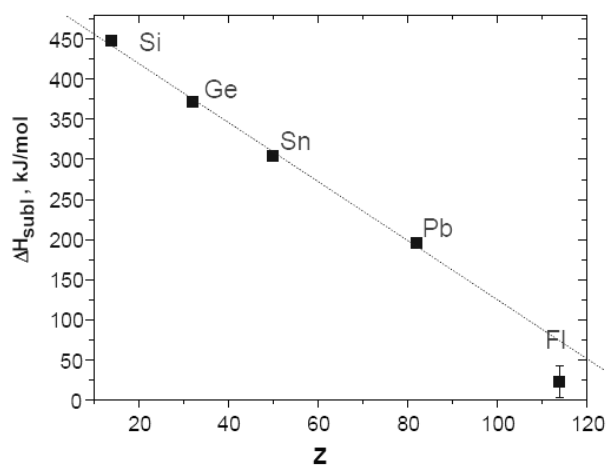


Figure 9: Trend of sublimation enthalpies for elements of group 14 of the periodic table.

## References

1. H.W. Gäggeler, A. Türler, Gas phase chemistry of Superheavy Elements, in: *The Chemistry of Superheavy Elements*, Matthias Schädel (Ed.), Kluwer Academic Publishers, ISBN 1-4020-1250-0 (2003).
2. Ivo Zvara, *The Inorganic Radiochemistry of Heavy Elements*, Springer, ISBN 978-1-4020-6601-6 (2008).
3. M. Schädel, *Radiochim. Acta* **100**, 579 (2012).
4. H.W. Gäggeler, *Radiochim. Acta* **99**, 503 (2011).
5. I. Zvara, Y.T. Chuburkov, R. Caletka, M.R. Shalaevski, B.V. Shilov, *J. Nucl. Energy* **21**, 601 (1967).
6. S.N. Timokhin, A.B. Yakushev, H. Xu, V.P. Perelygin, I. Zvara, *J. Radioanal. Nucl. Chem. Lett.* **212**, 31 (1996).
7. C.E. Düllmann, B. Eichler, R. Eichler, H.W. Gäggeler, D.T. Jost, D. Piguët, A. Türler, *Nucl. Instr. Meth.* **A479**, 631 (2002).
8. C.E. Düllmann, W. Brüche, R. Dressler, K. Eberhardt, B. Eichler et al., *Nature* **418**, 859 (2002).
9. B. Eichler, R. Eichler Gas-Phase Adsorption Chromatographic Determination of Thermochemical Data Empirical Methods, in: *The Chemistry of Superheavy Elements*, Matthias Schädel (Ed.), Kluwer Academic Publishers, ISBN 1-4020-1250-0 (2002).
10. J. Dvorak, W. Brüche, M. Chelnikov, R. Dressler, C.E. Düllmann et al., *Phys. Rev. Lett.* **97**, 242501 (2006).
11. J. Dvorak, W. Brüche, M. Chelnikov, R. Dressler, C.E. Düllmann et al., *Phys. Rev. Lett.* **100**, 132503 (2008).
12. Yu.Ts. Oganessian, *J. Phys. G.: Nucl. Part. Phys.* **34**, R165-R242 (2007)
13. R. Eichler, W. Brüche, R. Buda, S. Bürger, R. Dressler et al., *Radiochim. Acta* **94**, 181 (2006).
14. R. Eichler, N.V. Aksenov, A.V. Belozerov, G.A. Bozhikov, V.I. Chepigin et al., *Nature* **447**, 72 (2007).
15. R. Eichler, N.V. Aksenov, A.V. Belozerov, G.A. Bozhikov, V.I. Chepigin et al., *Angw. Chem. Int. Ed.* **47**, 3262 (2008).
16. R. Eichler, *Radiochim. Acta* **93**, 245 (2005).
17. R. Eichler, N.V. Aksenov, Y.V. Albin, A.V. Belozerov, G.A. Bozhikov et al., *Radiochim. Acta* **98**, 133 (2010).
18. Ch.E. Düllmann, *Radiochim. Acta* **99**, 515 (2011).