

## Aqueous Chemistry with Seaborgium (Element 106)

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After the first aqueous chemistry experiments with seaborgium (element 106) where 5072 individual separations had allowed unambiguous identification of Sg [1-3], two more series of experiments have been carried out to extend the knowledge about the chemical behavior of Sg in aqueous media. Seaborgium was previously eluted from cation exchange columns like its homologs molybdenum and tungsten in 0.1 M HNO<sub>3</sub>/5x10<sup>-4</sup> M HF. Its chemical form was presumably a neutral or anionic oxygen containing fluoride. However, species containing no fluoride could not be excluded. Therefore, we repeated the first experiments without HF, using only 0.1M HNO<sub>3</sub> [4], to probe the influence of fluoride ions.

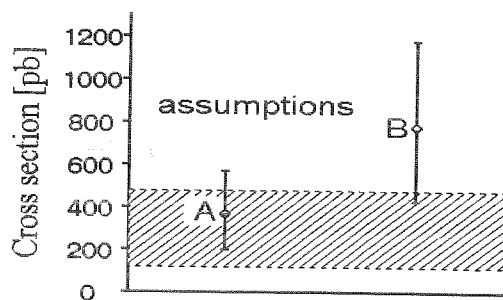
In an additional series of separations we used the well-known complexing agent  $\alpha$ -hydroxy-isobutyric acid ( $\alpha$ -HIB, 0.05M unbuffered), as eluent.

Like in the first experiments, we used the reaction  $^{22}\text{Ne} + ^{248}\text{Cm}$  to produce  $^{265}\text{Sg}$  (and  $^{266}\text{Sg}$ ). The  $^{248}\text{Cm}$  targets (700-820  $\mu\text{g}/\text{cm}^2$  electrodeposited on 2.7 mg/cm<sup>2</sup> Be foils) were spiked with 22  $\mu\text{g}/\text{cm}^2$   $^{152}\text{Gd}$ ; so one could easily monitor the transport- and chemical yield of tungsten, the light homolog of seaborgium, produced in the Gd + Ne reaction. Every eighth sample was therefore measured by  $\gamma$ - spectroscopy after 6 minutes of  $\alpha$ - spectroscopy. The He-jet technique was used to continuously transport all evaporation residues attached to KCl aerosols to the chemistry laboratory in 20 m distance from the irradiation position. 50% of the reaction products could be collected with a delay of 4.8 s, and more than 90% are transported within 8 s.

The Automated Rapid Chemistry Apparatus (ARCA) enabled us to perform cyclic column liquid- chromatographic separations with a cycle time of 45 s. A separation takes typically less than 10 s; the manual sample preparation by evaporation to dryness allows to start measurement 38-45 s after the end of collection. In the new series of experiments, we changed the detector setup to get a better counting efficiency. We were able to spray the effluent containing the separated Sg sample through 60  $\mu\text{m}$  capillaries onto 400-500  $\mu\text{g}/\text{cm}^2$  titanium foils mounted on aluminum frames, and to dry the samples by IR- light and hot He gas. The Ti foils were inserted between pairs of 450 mm<sup>2</sup> PIPS detectors and assayed for  $\alpha$ - particles and fission fragments with 66% detection efficiency. Compared to the first experiment, this increases the probability to detect correlated pairs of mother- daughter decays by a factor of 4.8. Some disadvantage of this method is, that the  $\alpha$ - particles penetrating the Ti- foil lose at least 200 keV. Since the angle of penetration is not known, the resolution (FWHM) deteriorates from 40 keV to about 250 keV. In addition, some

acids dissolve parts of the foil. So, even the front part yields a typical resolution of 60 keV.

In this series of 4032 separations with  $\alpha$ -HIB, we unexpectedly had a contamination of 15% Rf in the seaborgium fractions; in addition, background events from Pb, Bi, and actinides were by far more than usually detected. This contamination is critical because in our experiment, the detection of Sg is based on the detection of a Rf- No- decay-chain where Rf is formed as  $\alpha$ -decay daughter of Sg. When Rf is not retained on the cation exchange columns, Rf can falsify the Sg results by feigning Sg decays. Because of the unusual high background we found 14 correlations fitting into the right energy- and time- window. Two independent methods, a statistical simulation, and the measurement of anticorrelated events between detectors that did not assay the same samples agreed in the result that on the average 6.5 events were background. From the remaining 7.5 events we can calculate a cross section of  $370^{+200}_{-170}$  pb under the assumption (A) that all Sg was eluted from the cation exchanger. With the opposite assumption (B), that all Sg is retained on the column and all measured events stem from the Rf contamination a too high cross section of  $780^{+400}_{-350}$  pb would be the result. The best known value for a  $^{22}\text{Ne}(^{248}\text{Cm},5n)^{265}\text{Sg}$  cross section at our irradiation energy of 120MeV is 240pb, with an error of a factor of 2 [5]. So our results are compatible with the assumption A that Sg behaves like its lighter homologs and is eluted with  $\alpha$ -HIB, see the following figure.



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## Physico-Chemical Characterization of Seaborgium as Oxide Hydroxide

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The goal of the present gas chemistry experiment of the seaborgium-collaboration is to show that Sg forms low volatile oxide hydroxides. This is a continuation of experiments with seaborgium oxychlorides [1].

The **HI**gh-Temperature on-line **GA**s chromatography Apparatus **HITGAS** developed for studying low volatile oxide hydroxides is shown schematically in Fig. 1. Considering the low rate of the basic reactions of the gas chromatography of group 6 oxide hydroxides in quartz glass columns [2], reasonable short open tubular chromatography columns were used and directly coupled with the GSI **RO**tating **W**heel **M**ultidetector Analyzer **ROMA**: The chromatography furnace was flanged onto the ROMA and a separate deposition chamber was placed between column and rotating wheel. In test experiments with short-lived Mo- and W-isotopes retention times as short as 8 s and chemical yields of about 60 % were achieved [3,4]. On-line alpha spectroscopy was carried out with a resolution of 25 keV. However, 1  $\mu$ m collection foils, to be applied in  $4\pi$  alpha spectroscopy, which were stable in pure He carrier gas, were immediately destroyed when the reactive gas H<sub>2</sub>O/O<sub>2</sub> was added. Considering the results of the test experiments and potential interferences of Po-isotopes, we decided to study <sup>266</sup>Sg ( $T_{1/2} = 21$  s) instead of the shorter-lived <sup>265</sup>Sg ( $T_{1/2} = 7.4$  s) and detect it in  $2\pi$  geometry by registration of <sup>266</sup>Sg  $\alpha$ -decay and time correlated spontaneous fission events of the <sup>262</sup>Rf daughter.

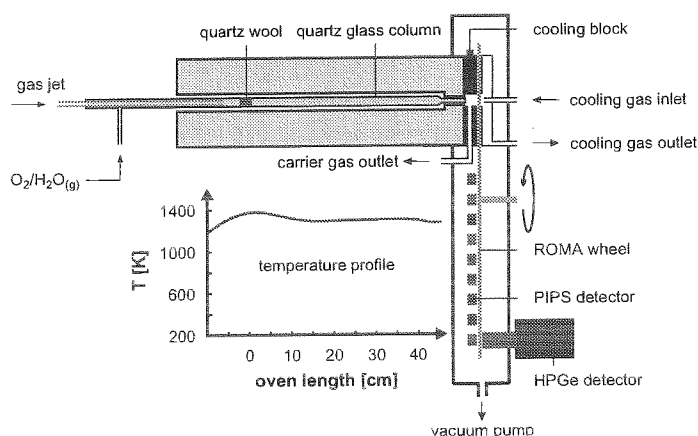


Figure 1: HITGAS, schematically

The seaborgium experiments were performed at the GSI accelerator UNILAC with a mixed <sup>248</sup>Cm/<sup>152</sup>Gd target (820  $\mu$ g/cm<sup>2</sup> <sup>248</sup>Cm, 85  $\mu$ g/cm<sup>2</sup> <sup>152</sup>Gd, GSI) at a <sup>22</sup>Ne beam energy of 118-120 MeV. Assuming a cross section of 80 pb for the reaction <sup>248</sup>Cm(<sup>22</sup>Ne,4n)<sup>266</sup>Sg, the production rate was about one <sup>266</sup>Sg atom per hour. A He/MoO<sub>3</sub>-jet was used to transport the nuclear reaction products with a gas flow rate of 2 l/min to the HITGAS. The temperature of the chromatography columns was 1325 K in the reaction and 1300 K in the isothermal zone. At

the column entrance, 0.5 l/min O<sub>2</sub>, moistened at 323 K with H<sub>2</sub>O, were added as reactive gas. 25  $\mu$ m Al-foils were used to collect the species under study. The ROMA was operated with a cycle-time for collection and detection of 10 s. 15 equidistantly positioned PIPS detectors were used to detect spontaneous fission and  $\alpha$ -decay events [5]. Short-lived W-isotopes were monitored with a HPGe detector. The yield of W and the separation of interfering spontaneously fissioning actinides were watched continuously. The quartz-glass columns were replaced when the spontaneous fission rates were above 2 cph and/or W-yields were lower than 40 %.

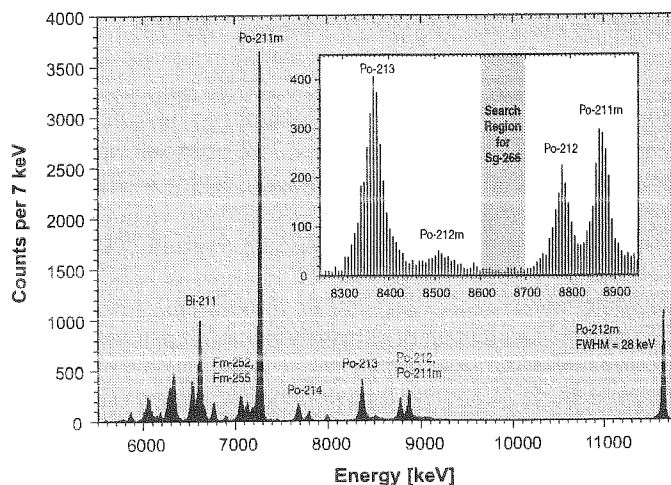


Figure 2: Summary alpha spectrum of 43 h beam time

The spectrum in Fig. 2 was summarized from the single spectra of 10 PIPS detectors, accumulated during 43 h beam time. We detected two correlated <sup>266</sup>Sg-<sup>262</sup>Rf-decay chains:

Table 1: Correlated decay events

Chain	E [MeV]	life time <sup>266</sup> Sg [s]	life time <sup>262</sup> Rf [s]
1	8.66	84.9	7.0
2	8.70	4.8	3.7

A statistic evaluation of the background events in the spectra yielded 0.4 random chains.

The results show the formation of a low volatile seaborgium oxide hydroxide as typical for group 6 elements.

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# Fluoride Complexation of Rutherfordium (Rf, Element 104)

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It had been shown experimentally [1] that  $^{261}\text{Rf}$  is not eluted from the cation exchange (CIX) column under the condition of previously performed seaborgium (Sg, element 106) experiments [2,3] and that  $^{261}\text{Rf}$  can only appear in the Sg sample as a result of the decay of  $^{265}\text{Sg}$ . Further, the distribution coefficient ( $K_d$ ) of  $^{261}\text{Rf}$  on a cation exchange resin at a higher HF concentration (0.1 M  $\text{HNO}_3$ /0.01 M HF) had been studied [1]. At this concentration, despite Zr and Hf being eluted, Rf is still retained on the column.

Now, the  $K_d$  values of Rf at HF concentrations of 0.03 M and 0.05 M (both in 0.1 M  $\text{HNO}_3$ ) have been determined to establish at which concentration the  $K_d$  drops down indicating that neutral or anionic complexes of Rf are being formed.

In addition, experiments using an anion exchanger (AIX) have been performed. It is expected that Rf will form anionic complexes resulting in high  $K_d$  values at high HF concentrations, while the pseudo-homologue Th does not form anionic fluoride complexes.  $^{261}\text{Rf}$  was produced in the  $^{248}\text{Cm}(^{18}\text{O},5n)$  reaction at the PSI Philips Cyclotron.

A  $730 \mu\text{g}/\text{cm}^2$   $^{248}\text{Cm}$  target was bombarded with a 0.5  $\mu\text{A}$   $^{18}\text{O}^{5+}$  beam. The target contained 10% Gd thus producing simultaneously short-lived Hf isotopes. Rf and Hf were transported by a He(KCl) gas jet and collected for 90 s by impaction on a slider in the Automatic Rapid Chemistry Apparatus ARCA II. The residue was dissolved in 200  $\mu\text{l}$  0.1 M  $\text{HNO}_3$ /x M HF (x variable) and fed onto the ion exchange column. The effluent was evaporated to dryness as sample 1. In order to elute remaining Rf from the column, a second fraction (200  $\mu\text{l}$ ) was collected which is known to elute group 4 elements from the column (i.e. 0.1 M  $\text{HNO}_3$ /0.1 M HF (CIX) or 5 M  $\text{HNO}_3$ /0.01 M HF (AIX)). This fraction was prepared as sample 2. 78-s  $^{261}\text{Rf}$  was detected by  $\alpha$ -spectroscopy. The counting time was 12 min. Every 8th pair of samples was monitored by additional  $\gamma$ -spectroscopy to determine the distribution of Hf.

The data (see figures) show that Rf behaves differently from Zr and Hf and seems to resemble Th on both AIX and CIX (dotted lines). On the CIX, the fall of the  $K_d$  values for Rf occurs between 0.01 M and 0.1 M HF, i.e. at one order of magnitude higher HF concentrations than for Zr and Hf. It is remarkable, that the  $K_d$  values of Zr and Hf on the AIX rise in the same HF concentration range where they fall on the CIX indicating that the formation of anionic complexes takes place simultaneously with the decrease of cationic complexes. Conversely, the Rf data

on the AIX suggest that Rf forms neutral complexes of the type  $[\text{RfF}_4]$ .

A first attempt of interpretation could be that the ionic radii of  $\text{Zr}^{4+}$  and  $\text{Hf}^{4+}$  are very similar due to the lanthanide contraction resulting in a similar complexation behaviour, while in Rf, the actinide contraction is surpassed by the relativistic expansion of the d orbitals. A third beam time at the PSI will be used to verify and complete the AIX data.

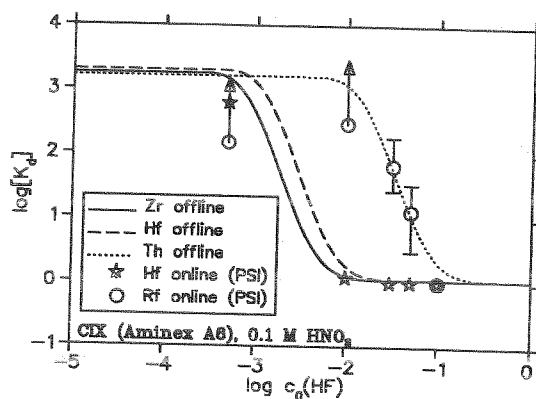


Figure 1: Sorption of Zr, Hf, Th and Rf on a CIX resin (Aminex A6) at various HF concentrations.

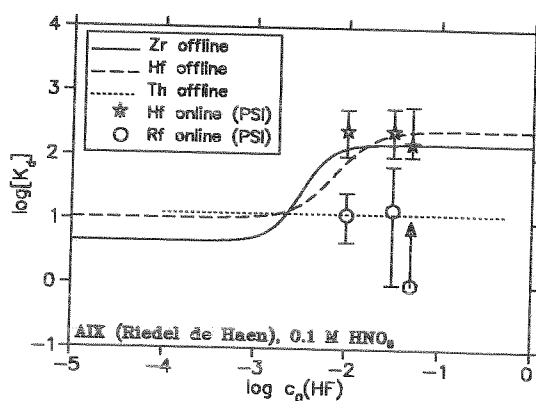


Figure 2: Sorption of Zr, Hf, Th and Rf on an AIX resin (Riedel de Haen) at various HF concentrations.

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## Ionization Potentials of Seaborgium

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The knowledge of the electronic structure of an atom is an indispensable ingredient for the understanding of its physical and chemical behavior. It is also a very helpful starting point for any kind of chemical interpretation. Though for element 106, Sg, first chemical experiments<sup>1</sup> have been conducted, its atomic electronic structure has not been investigated in detail. It is now absolutely necessary to continue the type of study for element 106 which has been already done for elements 104 and 105.<sup>2,3</sup> Some values of the ionization potentials (IP) and ionic radii (IR) for the lighter elements were also not available earlier. Thus, in this paper, we present first accurate atomic structure calculations for the neutral and positively charged states of Sg, as well as for its lighter homologs in group 6, Cr, Mo and W.

The calculations have been performed within the multiconfiguration Dirac-Fock (MCDF) approximation.<sup>3</sup> We have considered a large number of configuration state functions (for the neutral and charged states of Sg) constructed for all possible angular momenta and parities arising from various electronic configurations formed by the valence  $ns$ ,  $np_{1/2}$ ,  $np_{3/2}$ ,  $(n-1)d_{3/2}$ ,  $(n-1)d_{5/2}$  single particle wave functions. Here,  $n$  is the principal quantum number. (E.g., 1289 positive parity states for the 10 electronic configurations of the neutral Sg were taken into account).

As a result, the electronic states, electronic transition energies including IP (Table 1) and the  $R_{\max}$  values (location of the maximum of the charge density) of the valence orbitals (Table 2) have been calculated for various charge states of the elements of interest. Since the MCDF excitation energies are too small in comparison with experiment, an extrapolation procedure described in ref. 2 was used to give the "empirical" values. This extrapolation is based on the experimental and MCDF values for the other three group 6 elements. The  $R_{\max}$  values have been used to obtain the IR. The quadratic extrapolation was applied to obtain the "empirical" IR of Sg (Table 2).

The results have shown the trend in the values of the MCDF excitation values to be in good agreement with experiment. There is also very good agreement for excitation energies within the same charge state: these differences are about 0.01 eV. The "empirical" IP have an accuracy of 0.5 eV and the "empirical" IR of 0.005 nm in comparison with experimental values.<sup>5</sup> These calculations show that the MCDF method is quite adequate for describing the IP and IR given.

Knowledge of the electronic states of Sg as well as the IR and IP will be used to predict physico-chemical properties studied experimentally. These properties are: the stability of oxidation states, redox potentials, heats of hydration and sublimation, the extraction of Sg complexes from aqueous solutions by organic solvents. Similar calculations are foreseen for elements heavier than Sg.

Table 1. Ionization potentials (eV) for group 6 elements

Potential	Transition	Calc.	Exp. <sup>5</sup>	Emp.
Cr(0→1+)	$d^5s^1 \rightarrow d^5$	6.02	6.76	6.84
Mo(0→1+)	$d^5s^1 \rightarrow d^5$	6.26	7.09	7.08
W(0→1+)	$d^4s^2 \rightarrow d^4s^1$	6.97	7.86	7.79
Sg(0→1+)	$d^4s^2 \rightarrow d^3s^2$	7.03	-	7.85
Cr(1+→2+)	$d^5 \rightarrow d^4$	15.15	16.48	16.36
Mo(1+→2+)	$d^5 \rightarrow d^4$	15.07	16.16	16.28
W(1+→2+)	$d^4s^1 \rightarrow d^4$	14.81	-	16.02
Sg(1+→2+)	$d^3s^2 \rightarrow d^3s^1$	15.85	-	17.06
Cr(2+→3+)	$d^4 \rightarrow d^3$	29.76	30.96	30.89
Mo(2+→3+)	$d^4 \rightarrow d^3$	26.08	27.13	27.21
W(2+→3+)	$d^4 \rightarrow d^3$	24.73	-	27.21
Sg(2+→3+)	$d^3s^1 \rightarrow d^3$	24.61	-	25.74
Cr(3+→4+)	$d^3 \rightarrow d^2$	48.04	49.16	49.16
Mo(3+→4+)	$d^3 \rightarrow d^2$	39.17	46.40	40.29
W(3+→4+)	$d^3 \rightarrow d^2$	36.87	-	37.99
Sg(3+→4+)	$d^3 \rightarrow d^2$	34.28	-	35.40
Cr(4+→5+)	$d^2 \rightarrow d^1$	68.58	69.46	69.55
Mo(4+→5+)	$d^2 \rightarrow d^1$	53.44	54.49	54.41
W(4+→5+)	$d^2 \rightarrow d^1$	50.30	-	51.27
Sg(4+→5+)	$d^2 \rightarrow d^1$	46.31	-	47.28
Cr(5+→6+)	$d^1 \rightarrow \text{core}$	89.59	90.63	90.68
Mo(5+→6+)	$d^1 \rightarrow \text{core}$	67.70	68.83	68.79
W(5+→6+)	$d^1 \rightarrow \text{core}$	63.59	-	64.68
Sg(5+→6+)	$d^1 \rightarrow \text{core}$	58.15	-	59.24

Table 2. Calculated  $R_{\max}$  and "empirical" IR (nm) for Sg

State	Orbital	$R_{\max}$	Empirical IR
Sg(4+)	$6d_{3/2}$	0.0870	0.082
Sg(5+)	$6d_{3/2}$	0.0822	0.077
Sg(6+)	$6p_{3/2}$	0.0665	0.065

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# Redox Reactions for Group 6 Elements, including Seaborgium, in Aqueous Solutions

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The question about stable oxidation states of an element is one of the most important since many other physical and chemical properties depend upon the oxidation state. This is particularly valid for the transactinides, the 6d elements, where relativistic effects on the valence electron shells are very strong. The relative stability of the oxidation states of element 104, Rf, and element 105, Db has been predicted by us on the basis of multiconfiguration Dirac-Fock (MCDF) atomic calculations<sup>1,2</sup> Redox potentials for Sg were, however, not given until now, though this information was urgent. Previous predictions for Sg based on extrapolations within the Periodic Table were also not unanimous in the conclusion: +4 oxidation state as the most stable was predicted by Penneman and Mann,<sup>3</sup> while +6 oxidation state was predicted by Cunningham.<sup>4</sup> In the present work, a complete set of redox reactions for group 6 elements including Sg in aqueous acid solutions is considered, and estimates of the potentials are made using ionization potentials (IP) calculated within the multiconfiguration Dirac-Fock (MCDF) approximation (see the previous report).

The method of estimates is based on the correlation between the IP and redox potentials which is seen from the following equations. The free energy of a reduction reaction  $M^{z+x} + ne \leftrightarrow M^{z+}$  is

$$\Delta G^\circ = -nFE^\circ,$$

where F is the Faraday number and  $E^\circ$  is the standard reduction potential. At the same time, from the Born-Haber cycle it follows that

$$E^\circ(M^{z+x}/M^{z+}) = 1/n[\Delta IP + \Delta H_{\text{hydr}}] - \text{const.}$$

One of those correlations is shown in Fig. 1 demonstrating a decrease in the stability of the +4 oxidation state of Sg. Additionally, thermodynamic equations were used to estimate potentials provided a correlation was not reliable.

A complete scheme of the redox potentials for group 6 compounds is shown in Fig. 2. These data indicate that the stability of the +6 oxidation state increases in the group, while the relative stability of the +5, +4 and +3 states decreases. In contrast to the expectations<sup>3</sup>, there will be no enhanced stability of the +4 state of Sg. This is easily seen from the ionization process:  $\text{Sg}(d^4s^2) \rightarrow \text{Sg}^+(d^3s^2) \rightarrow \text{Sg}^{2+}(d^3s^1) \rightarrow \text{Sg}^{3+}(d^3) \rightarrow \text{Sg}^{4+}(d^2) \rightarrow \text{Sg}^{5+}(d^1) \rightarrow \text{Sg}^{6+}(\text{core})$ . Our present MCDF calculations have shown that after the first d electron is ionized, there is an inversion of the s and d levels, so that for the  $\text{Sg}^+$  state, the d level is deeper than the s level. Thus, next two ionized electrons are s, and not d. Upon reaching the  $\text{Sg}^{4+}$  state, the electronic configuration of Sg is therefore  $6d^2$  and not  $7s^2$ . Since the d levels of Sg are more destabilized than those of W,

the +4 state of Sg will be even less stable than +4 state of W. Thus, there is no relativistically stabilized  $7s^2$  pair resulting in the preferential stability of +4 state of Sg. The same is valid for the +3 oxidation state of element 105, Db. Thus, no deviation from the Mendeleev-type periodicity is observed for oxidation states in group 6 elements in going over to the 6d element, Sg.

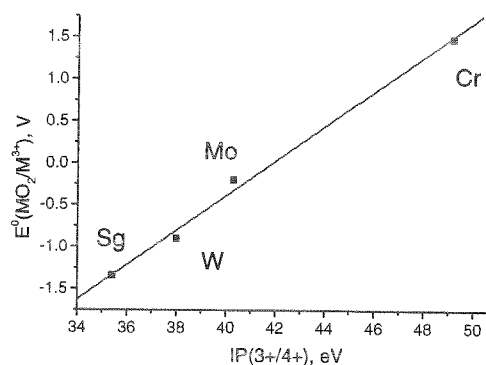
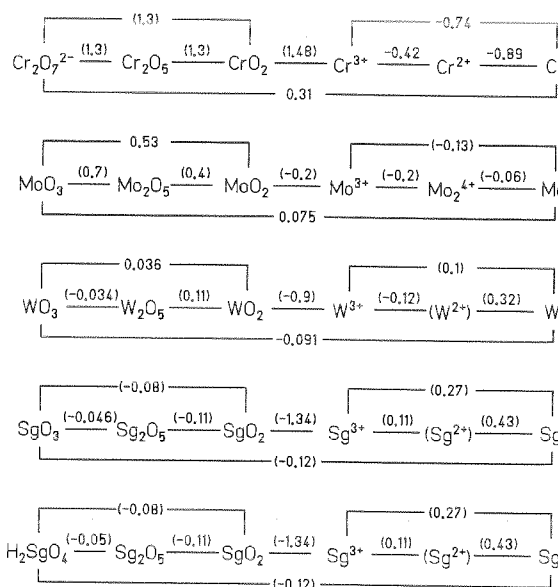


Fig. 1. Correlation between reduction potentials  $E^\circ(\text{IV/III})$  and  $\text{IP}(3+ \rightarrow 4+)$ .



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# Heavy ion induced columnar defects: A sensitive probe for the 2D/3D behaviour of vortex matter in high-temperature superconductors

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GSI Darmstadt: for HTS collaborations see Ref [1] - [4]

High-temperature superconductors (HTS) lead to many new phenomena of vortex matter not encountered in conventional superconductors. Of special importance is the decoupling of vortex lines into segments. In highly anisotropic materials vortices may behave as independent stacks of two-dimensional (2D) pancakes rather than three-dimensional (3D) flux lines. Correlated disorder in the form of well oriented columnar defects by heavy ion irradiation is a powerful method of exploring the nature of pinning and vortex dimensionality in HTS. See Ref. [1] for some of our recent results that were obtained in collaboration with different groups.

Columnar defects increase the longitudinal correlation of flux lines in Bi-2212 single crystals and a finite line tension is reached. Contrary to this no anisotropic pinning is observed in the transport measurements with epitaxial Bi-2212 films after heavy ion irradiation [2].

In order to further elucidate the effect of columnar defects on vortex behaviour in Bi-2212, the techniques of Muon-spin rotation ( $\mu$ SR) and small angle neutron scattering (SANS) are ideal methods since these are able to investigate magnetic field distributions inside superconducting materials and to measure the microscopic behaviour within the bulk of the sample. On the other hand these measurements require crystals with a thickness of at least a few hundred micrometers which is far beyond the range of UNILAC beams. Ions from the heavy ion synchrotron SIS with relativistic energies can easily penetrate several millimeters of material. The problem with the higher energetic beams from the SIS is the decreasing electronic energy loss with increasing ion velocity. At some energy the electronic energy loss drops below the threshold value and the ions will no more create columnar defects in the entrance part of the crystal. Clearly U-ions should be used to obtain columnar defects of maximum length. It turned out from comparative measurements of thin films irradiated at the UNILAC and at the SIS as well as from TEM micrographs, that columnar defects of sufficient length were obtained with 17.7 GeV U-ions.

We have irradiated several sets of Bi-2212 crystals with U-ions at the SIS under various conditions. Results are taken from Ref. [3]. Fig. 1 shows the temperature dependence of the normalised  $\mu$ SR linewidth. The data points are clearly shifted after the heavy ion irradiations, but are identical within the experimental uncertainties irrespective of whether the field is applied parallel or perpendicular to the tracks. This implies that the degree to which thermal fluctuations are suppressed by the defects, an indirect measure of the pinning strength, does not depend greatly on the orientation of the field to the tracks. The degree of straightness of the vortex lines, however, is found to be quite different. This is concluded from the asymmetry of the measured magnetic field probability distribution, that indicates relatively straight lines, but only if the magnetic

field is parallel to the columnar defects and not, if the field is perpendicular to the tracks. The  $\mu$ SR measurements are complemented with SANS data, supporting these results.

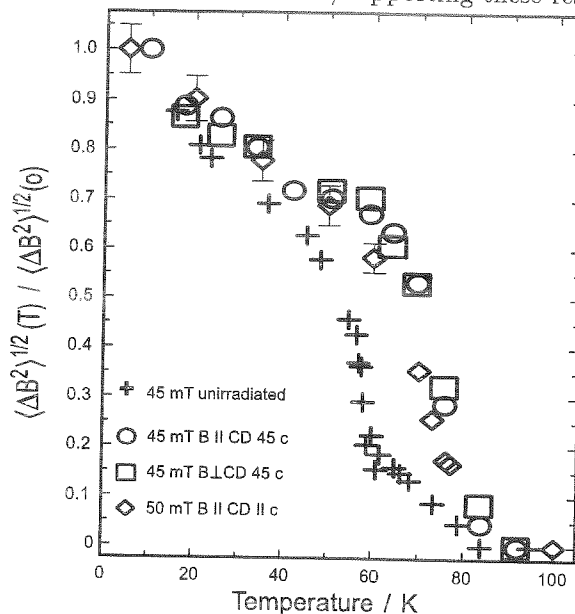


Figure 1: The normalised temperature dependence of the  $\mu$ SR linewidth for a Bi-2212 sample with columnar defects at  $45^\circ$  to the c-axis ( $B_\phi = 100$  mT), where a field of 45 mT is applied both parallel and perpendicular to the tracks. Also shown is the measurement of a sample with the same defect density, but having the columnar defects parallel to the c-axis and a field of 50mT parallel to the defects. Data of an unirradiated sample are shown for comparison.

Contrary to the Bi-2212 material, YBCO is much less anisotropic and the 3D vortices are locked-in to the columnar defects. But using vector magnetometry with high angular resolution, a narrow dip was found in the irreversible magnetic moment for the field direction parallel to the columns [4] in single crystals. Possible explanations for the underlying vortex dynamics are discussed in the paper.

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# ON-LINE CHROMATOGRAPHY OF SHORT-LIVED Hf ISOTOPES WITH THE MULTI-COLUMN TECHNIQUE

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The first aqueous chemistry of Seaborgium required accumulation of 5000 single experiments with the Automated Rapid Chemistry Apparatus ARCA. This experiment showed that Seaborgium, in 0.1 M HNO<sub>3</sub>/ 5\*10<sup>-4</sup> M HF, forms neutral or anionic oxyfluorides [1], but the experiment did not determine a distribution coefficient. In future experiments with Seaborgium and other transactinides, we plan to determine K<sub>d</sub>-values on anion and cation exchangers in HNO<sub>3</sub>/HF solutions using the multi-column technique [2] via activities of a long-lived descendant.

In this technique, the KCl aerosol particles transporting the activities in a gas-jet are continuously dissolved in a degasser unit in an aqueous solution which is continuously pumped through three consecutive columns.

The first column (F) acts as a filter for all decay products of the interesting element and is passed by the latter. The second column (C) is the true chromatographic column where the element of interest experiences a retention time, t<sub>R</sub>, being of the order of its nuclear half life, t<sub>1/2</sub>. The daughter nuclides that are formed during the retention time of the element of interest on column C are strongly retained on column D (daughter activity A<sub>D</sub>). The part of the element of interest that passes C is also passing the third column D without notable retention. The final eluate (E) is sampled in order to collect the residual atoms as well as its decay products (daughter activity A<sub>E</sub>).

After the experiment, the activities of the decay products on column D and in the final eluate E are measured and the retention time is obtained according to:

$$t_R = \frac{t_{1/2}}{\ln 2} \ln \left( \frac{A_D + A_E}{A_E} \right) \quad (1)$$

The distribution coefficient, K<sub>d</sub>, of the element of interest in column C may then be obtained as:

$$K_d = (t_R - t_0) \frac{V}{m} \quad (2)$$

where

t<sub>0</sub> = column hold-up time due to its dead volume [s]

V = flow rate of the mobile phase [ml\*s<sup>-1</sup>]

m = mass of the stationary phase [g].

This way, the nuclear half-life of the studied isotope is used as an internal clock.

The degasser unit has been developed and tested at the Mainz TRIGA reactor. It has been shown that the dissolution of the aerosol can be performed quantitatively, but only at the expense of a very high pressure in the target chamber. As a result of many experiments, the dissolution yield in the degasser unit is now over 80% at a tolerable pressure in the target chamber of 1.7 bar at a gas-flow rate of 2 L/min.

To prepare such experiments with Seaborgium, we have studied the chemical behavior of its homolog tungsten on anion exchangers in HNO<sub>3</sub>/HF solutions using the multi-column technique [3].

We describe an on-line test of the system with 76-s <sup>165</sup>Hf produced in the <sup>158</sup>Dy(<sup>12</sup>C, 5n) reaction at the UNILAC. In order to separate <sup>165</sup>Hf and its decay products, we used a combination of the cation exchanger DOWEX 50WX8 (in column F and D) and anion exchanger DOWEX 1X8 (in column C) in HPLC quality. In the solution 0.1 M HNO<sub>3</sub>/ 0.01 M HF, lanthanides, the decay products of hafnium, form cations, and hafnium has a retention time on the anion exchanger in the range of the nuclear half life and no notable retention on cation exchangers.

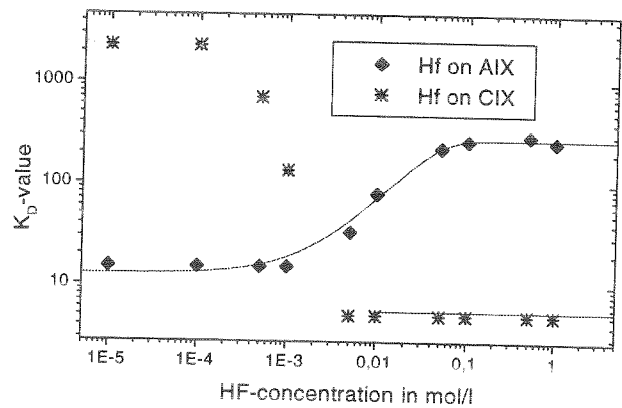


Abb. 1 K<sub>d</sub>-values of Hf in 0.1 mol/l HNO<sub>3</sub>/ variable HF on anion exchanger (AIX) and cation exchanger (CIX)

The K<sub>d</sub>-values from the experiment with 0.1 M HNO<sub>3</sub>/ 0.01 M HF on the AIX are:

93.6 ± 12.0 ml/g (from the 120-keV line of <sup>165</sup>Lu)

93.8 ± 26.7 ml/g (from the 204-keV line of <sup>165</sup>Lu)

111.4 ± 12.0 ml/g (second experiment)

in agreement with the batch value 82±2 ml/g (carrierfree <sup>175</sup>Hf). The errors on the K<sub>d</sub> values given are mainly due to the statistical errors of the gamma measurement and can be reduced. We have learnt that it is important to use a HPLC pump in the present experiments to ensure a pulse-free flow of the solution through the three columns. Further work with the degasser is needed as the hold-up time of the activity in the degasser must be reduced.

Next experiments with rutherfordium will be performed with 0.1 M HNO<sub>3</sub>/ ≥ 0.1 M HF. Within this concentration range, the K<sub>d</sub>-value of rutherfordium on a cation exchanger is zero, while on an anion exchanger it can be adjusted to about 100 [4].

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# Modifications of the Automated Rapid Chemistry Apparatus ARCA II for a Sg (Element 106) reduction experiment

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Tungsten (W) as a homologue of seaborgium (Sg) is used to develop a reduction experiment for Sg. Previous off line studies [1] with carrier free amounts of W showed the possibility to reduce W(VI) to W(III) with solid Al at increased temperature (80°C). While W(III) runs through an anion exchange column in diluted HCl/HF as a cation, W(VI) forms anionic oxyfluoro complexes and sticks to the resin. In off line experiments, 4 M HCl/0.01 M HF was used to strip a second fraction from the column to ensure that all activity was recovered.

For the on-line experiments with solid reducing agents, the head of ARCA was modified (see figure). W (mainly <sup>170</sup>W) produced on-line at the Philips Cyclotron of the Paul Scherrer Institut or at the UNILAC at Darmstadt, respectively, was transported to ARCA with a He/KCl gas jet system. After a collection time of 120 s, the KCl spot was dissolved in 333 μl of a mixture of 0.1 M HCl and 0.1 M HF. Fractions were eluted under varied conditions (see below) and monitored by γ-spectroscopy.

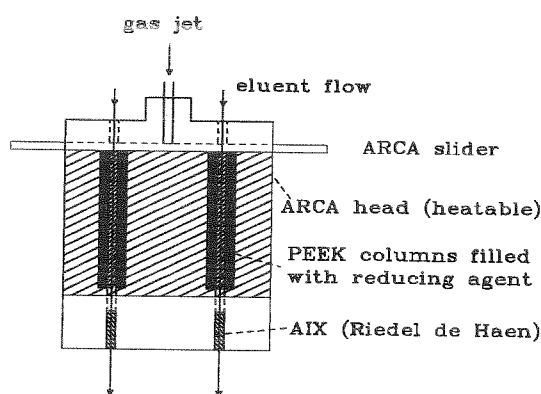


Fig.1: Modified ARCA head as used in exp. 3 and 4. The Ti head in exp. 1 and 2 contained no PEEK inlays.

To simulate a Sg experiment (which has to be a 1-step experiment due to the short half live) no strip fraction was taken. Instead, reference values were obtained using 'empty' reducing columns in which the dead volume was diminished by a piece of PE capillary.

For each experiment are given 4 values: Elution through a) the the empty head (showing the absorption on the head material), b) through the reducing agent (RA) only (showing absorption in both head and RA), c) through AIX without RA (showing the efficiency of the W(VI) separa-

a known  $K_d$  instead of c)), one can calculate the overall yield of W(III) (last column of the table).

Exp. #	head material	reducing agent	resin	% eluted	% reduced
1a	Ti	none	none	39	-
1b	Ti	Al	none	17	-
1c	Ti	none	AIX	5*	-
1d	Ti	Al	AIX	11*	10*
2a	Ti	none	none	64	-
2b	Ti	Al	none	41	-
2c	Ti	none	AIX	7	-
2d	Ti	Al	AIX	31	30
3a	PEEK	none	none	100	-
3b	PEEK	Al	none	85	-
3c	PEEK	none	AIX	10*	-
3d	PEEK	Al	AIX	67*	64*
4a	PEEK	none	none	100	-
4b	PEEK	Zn	none	98	-
4c	PEEK	none	AIX	13	-
4d	PEEK	Zn	AIX	< 5	0

Table 1: Yields of eluted W under different conditions. All yields are given relative to a direct catch from the gas jet (=100%). Asterisks indicate that the values were not measured but calculated using known  $K_d$  values.

Experiment 1 showed that W absorption on the Ti surface is quite strong, thus resulting in overall reduction yields too low for a Sg experiment. For experiment 2, the HF concentration was risen to 0.3 M, resulting in weaker absorption but in rapid dissolution of the reducing agent Al. Using a PEEK head in experiments 3, the absorption in the head was reduced to a minimum, but the rapid dissolution of Al was still unsatisfying. The weaker RA Zn (Exp.4) showed almost no dissolution, but also no reducing effects. This is remarkable, because the potential difference for the reduction of W(VI) with Zn indicates that the reduction is thermodynamically possible ( $\Delta E_0 < -0.5$  V). Obviously, it is kinetically hindered. The lower yield in experiment 4d) with respect to 4c) indicates even a stabilisation of the 6+ state, but the difference is insignificant taking values from different runs to estimate the error.

The results show, that a reduction of on-line produced W is possible at least to an overall yield of 64%. This would be sufficient for a Sg reduction experiment. The aim of forthcoming experiments is to find a finally useful RA. Possibilities are either varying the particle size of Al (preventing rapid dissolution) or choosing another RA (for example Ti, whose redox potential in HF solutions is between those of Al and Zn).

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# CORA - a New Control Program for the Roma Detection System

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A new computer program has been developed for the control of the GSI Rotating Wheel Multi Detector Apparatus (ROMA) running under the Windows 95 and Windows NT 4.0 operating systems. It can be fitted to a lot of detection tasks in a highly flexible way.

The ROMA detection apparatus [1] has been used successfully in a lot of chemical investigations of heavy elements. In preparation of our seaborgium experiment at GSI in summer 1998 [2] a new control program had to be written, because the old computer code was not able to fulfill our experimental demands. The new program is written entirely in C++ using the Borland C++ Builder 1.0 programming environment.

The program has to carry out the following tasks:

- control of the wheel movements;
- start and stop of the nuclear spectroscopy data acquisition;
- sending information about the actual ROMA status to the nuclear spectroscopy data acquisition hardware;
- processing control requests of the data acquisition hardware (e. g. switching in „daughter mode“ [3]);
- processing user input before and during an experiment (e. g. experiment and wheel setup dialog boxes).

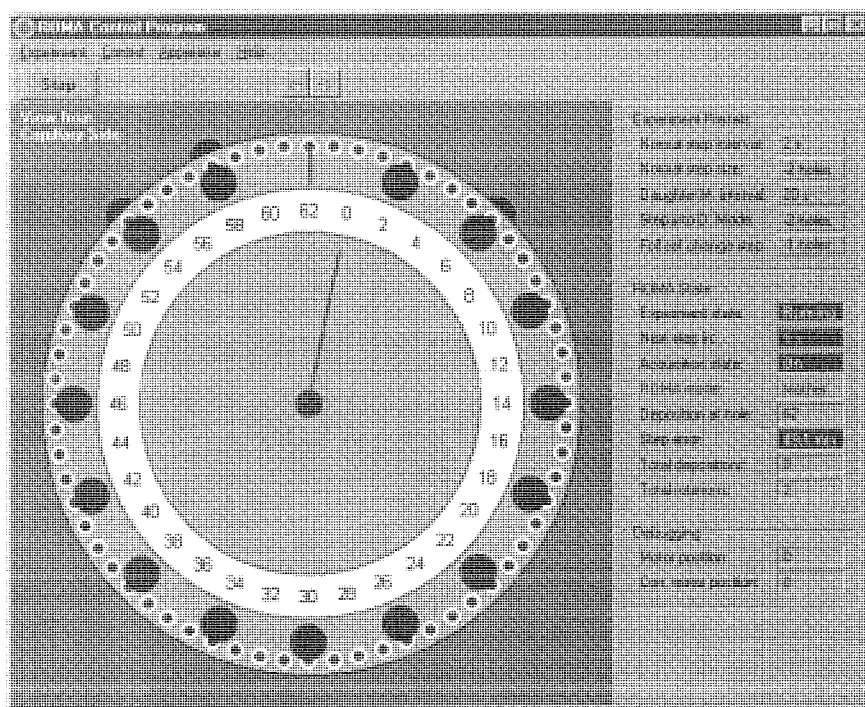


Fig. 2: Main Window of the Program

The program consists mainly of four software modules as shown in Fig. 1. *Hardware\_IO.dll* implements an interface for all interactions with the hardware. The other parts, organizing the experiment on a more abstract level, are using exclusively this interface for controlling the hardware.

Thus, the program can be adapted to similar detection systems with very low programming effort: Only *Hardware\_IO.dll* must be adapted to the other hardware, there is no need to rebuild the program. This is planned for the new GSI multi detector apparatus, which is currently in development.

The program has a very comfortable user interface; Fig. 2 shows the Main window. It is almost self-explanatory. Even not experienced users can access control in an easy way using dialog boxes. Critical hardware settings are hidden, but all program settings can be modified in initialization files (Windows 3.x style) with a normal editor.

It is possible to control the experiment-related parts of the program solely by the digital I/O interface without user input. Thus, the program can be used in fully automated systems.

## Acknowledgments

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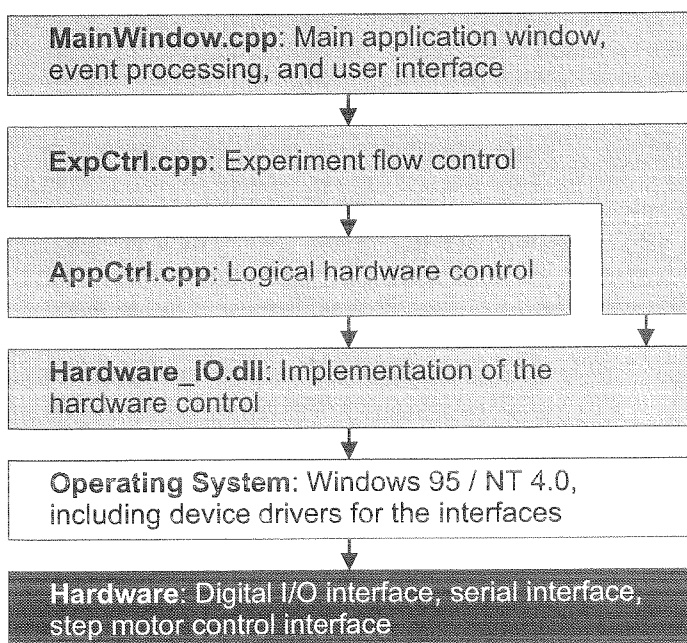


Fig. 1: Simplified Layer Scheme of the Program