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Names of the authors: Nadine Mariel Chiera; Robert Eichler; Dave Piguet; Alexander Vögele; Andreas Türlér.

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Affiliation(s) and address(es) of the author(s):

Nadine Mariel Chiera: University of Bern, 3012 Bern, Switzerland & Paul Scherrer Institute, 5232 Villigen, Switzerland. e-mail: nadine-mariel.chiera@psi.ch

Robert Eichler: University of Bern, 3012 Bern, Switzerland & Paul Scherrer Institute, 5232 Villigen, Switzerland. e-mail: robert.eichler@psi.ch

Dave Piguet: Paul Scherrer Institute, 5232 Villigen, Switzerland. e-mail: david.piguet@psi.ch

Alexander Vögele: Paul Scherrer Institute, 5232 Villigen, Switzerland. e-mail: alexander.voegel@psi.ch

Andreas Türlér: University of Bern, 3012 Bern, Switzerland & Paul Scherrer Institute, 5232 Villigen, Switzerland. e-mail: andreas.tuerler@psi.ch

E-mail address of the corresponding author: robert.eichler@psi.ch

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Microscopic interaction of single atomic elemental Hg with a sulfur surface

N.M. Chiera^{1,2}, R. Eichler^{1,2}, D. Piguet², A. Vögele², A. Türlér^{1,2}

¹ *Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, 3012*

Bern, Switzerland

² *Laboratory of Radiochemistry, Paul Scherrer Institute, Villigen PSI Ost, 5232 Villigen,*

Switzerland.

Abstract

In preparation of chemical investigations of the superheavy elements (SHEs) copernicium and flerovium, model experiments with ¹⁹⁷Hg were conducted. The interaction of elemental mercury on a sulfur surface was investigated by off-line isothermal gas chromatography. Although the formation of HgS_(s) is thermodynamically favored, a strong kinetic hindrance is observed at room temperature, and thus only adsorption interactions could be addressed. A dependence of the adsorption interaction strength on the allotropic transformations of the sulfur surface was observed. The high temperatures needed to promote the chemical interaction of Hg with S prevent sulfur from being a suitable chromatographic surface for SHEs experiments with the state-of-the-art gas phase technology.

Keywords

mercury, adsorption, sulfur surface, isothermal gas chromatography, superheavy elements.

Introduction

In the last decades, the Periodic Table has been expanded with the synthesis and the discovery of new elements. Recently, the discovery of the missing elements of the seventh row of the periodic table with $Z = 113, 115, 117$, and 118 has been accepted by the IUPAC [1, 2]. Recurring trends of chemical properties are established along rows and groups of elements in the periodic table. For the transactinide elements ($Z \geq 104$), also referred to as superheavy elements (SHEs), this periodicity reaches its limits. In fact, with increasing nuclear charge, direct and indirect relativistic effects on the valence electron shells can strongly influence the electronic configurations of heavy elements, and thus, their chemical properties [3].

An exceptionally favorable case, which allows for studying multiple SHEs at the same time, is the production of flerovium (Fl) and its alpha-decay daughter copernicium (Cn) in ^{48}Ca induced nuclear fusion reactions with Pu isotopes [4]. Since both elements are characterized by short half-lives and a high volatility, gas chromatography is used [5]. While gas adsorption studies on Au surfaces revealed Cn as a very volatile noble metal [6], contradictory observations prevented so far an unambiguous determination whether Fl behaves as a noble volatile metal [7] or if it interacts with Au forming a weak physisorption bond, typical of a noble-gas-like element [8]. These discrepancies in the experimental results demanded the development of a chemical system, which unambiguously allows for the chemical characterization of Fl.

In preparation and design of experiments involving transactinide elements, extrapolative predictions [9], which describe trends along groups of the Periodic Table, can be used as a “first hint” on exploring the chemical behavior of a transactinide in various simple chemical systems. The interaction of group 12 and group 14 elements with halogens and chalcogenes is well known. However, According to theoretical calculations [10], a negative affinity of Fl to O_2 was predicted, indicating that Fl might not form stable oxides. For chlorides, tetravalent Fl compounds are predicted to be unstable, while theoretical calculations among the divalent compounds indicate that FlCl_2 might be stable [11]. Red cinnabar ($\alpha\text{-HgS}$) and galena (PbS), also called lead glance, are natural mineral forms of

lead and mercury demonstrating a high thermodynamic stability. The stability trends of sulfide formation along groups 12 and 14 suggest the formation of more stable sulfides of Fl in comparison to the sulfides formed by Cn. Unfortunately, no data is available from theoretical studies on the interaction between Cn, Fl and heavy chalcogenes. However, the experimental advantages of studying this system are several: In such chemical systems, the chemical behavior of Cn and Fl can be explored with both SHEs in their elemental states. Since both elements are volatile at room temperature, no additional steps are required for their transport in the gas phase from the point of production to the chemical setup. No reactive gases have to be added to the carrier gas, thus the synthesis of volatile by-products or other interfering species is avoided. Another important advantage is the principal possibility of covering the active surface of PIN diodes with a thin sulfur layer for an on-line detection of the formed compounds using the COLD setup [12, 13].

Hence, in this work, sulphur was chosen as stationary chromatographic material for gas adsorption studies [5]. A sulfur surface is expected to separate Cn and Fl, resulting in: 1) an unambiguous exhibition of the chemical character of Fl; and 2) the confirmation of the periodic trend of chemical properties in groups 12 and 14.

Model experiments with lighter homologues are fundamental for the design of chemical experiments with the SHEs [14]. In this work, isothermal model experiments with carrier free amounts of Hg (copernicium's lighter homologue) and sulfur surfaces were conducted. The affinity of mercury towards sulfur is known, and the formation of $\text{HgS}_{(s)}$ is thermodynamically favored [15]. Therefore, this chemical system is an ideal model system to model the kinetics and thermodynamics of the adsorption and reaction of a volatile noble metal with sulfur surfaces. The low volatility of Pb – flerovium's lighter homologue – prevents its use from gas-solid adsorption model experiments. In facts, its deposition temperature on quartz is at about 500°C, or higher [16], meaning that the chromatographic column with the sulfur surface should be kept at temperatures higher than sulfur's sublimation point, rendering thus the gas/solid study of the Pb/S interaction impossible.

Additionally, the study of the reactivity of microscopic amounts of Hg towards a sulfur surface provides useful information about the possible application of elemental sulfur in the capture of gaseous mercury, which is for example produced in coal-fired power plants

[17-19], or in the capture of radioactive isotopes of Hg escaping from accelerator driven spallation source installations [20] and from other nuclear facilities [21].

In order to obtain thermodynamic information, the experimental results were compared to simulations applying a microscopic model of the adsorption chromatographic process at zero Hg surface coverage based on a Monte Carlo approach [22].

Experimental

The coating of quartz columns (i.d. = 0.4 cm, l = 10 cm) with a homogeneous sulfur film was achieved through evaporation and fast quenching of sulfur vapors at ambient pressure, applying a similar technique as described in [23]. The sketch of the setup is shown in Fig. 1. A photomicrograph of a typical sulfur surface obtained with the applied vapor transport deposition technique is presented in Fig. 2.

The carrier free radioactive tracer ^{197}Hg ($t_{1/2} = 64$ h; main γ -line: 77 keV (18.7%)), was produced by irradiation of natural Tl (purity > 99.999%, Sigma-Aldrich) with fast neutrons at the spallation neutron source SINQ at the Paul Scherrer Institute. The volatilization of ^{197}Hg was performed by heating the bulk of Tl up to 350°C. The radioactive tracer was then transported by a He-flow (99.9990 vol.-% purity) to the sulfur coated columns kept at room temperature (see schematic in Fig. 3). The experimental conditions at which the different sets of runs were carried out are summarized in Table 1. Since Hg does not adsorb on quartz at room temperatures [24], all the evaporated Hg was transported to the chromatographic column covered with sulphur. The ^{197}Hg eventually not adsorbed on the sulfur surface was captured in a charcoal trap positioned at the exit. The detection and quantification of ^{197}Hg in each centimeter of the column was performed by γ -ray spectrometry using a HPGe-detector positioned behind a lead collimator (window size 1.0x1.0 cm², lead thickness 1 cm), coupled to the data acquisition and analysis system Canberra Genie2k[®].

Fig. 1 Sketch of the preparation setup for sulfur coated quartz columns: A mixed gas flow ($\text{He} = 130 \text{ ml/min}$, $\text{N}_2 = 50 \text{ ml/min}$, 99.9990 vol.-% purity) regulated by a mass flow controller (1) is passed through a Ta getter (2) kept at 950°C in order to remove O_2 and traces of H_2O . The high purity gas mixture is then passed through the sulfur evaporation oven kept at 400°C (3), and the “cracking oven” (4) kept at 700°C , in order to promote the cracking of the evaporated eight crowned sulfur molecular species into short chained ones. The evaporated sulfur is then rapidly quenched through liquid nitrogen cooling (5), obtaining in this manner a thin sulfur film deposited on the inner walls of the quartz tube (6). The sulfur eventually not deposited is captured in a charcoal trap (7).

Fig. 2 Photomicrograph of a typically obtained sulfur surface (scale bar: 0.4 mm). A 50 W tungsten microscope light was used for back-illumination. The ratio of the dark spots (covered surface) on the yellow background (uncovered surface) allowed for an estimation of $35 \pm 5\%$ coverage of the stationary surface with sulfur.

Fig. 3 Experimental off-line deposition setup: A helium gas flow rate of 25 ml/min, controlled by a Series 5850E Brooks Instruments mass flow controller (1) passes through a quartz tube (3). The irradiated Tl sample is positioned inside this quartz tube, within the

resistive oven (2). By heating this oven to 350°C the carrier free ^{197}Hg is volatilized and transported to the sulfur coated column (4). A charcoal trap (5) positioned behind the sulfur column captures the ^{197}Hg eventually not adsorbed by sulfur.

Table 1 Experimental conditions for the three different Hg adsorption experimental sets.

	#runs	He gas flow (ml/min)	Temperature (°C)	Sulfur coverage ^a (%)	Time (min)
Set 1	2	25	23	35 ± 5	30
Set 2	5	25	23	35 ± 5	60
Set 3	1	25	23	35 ± 5	90
	1	25	23	30 ± 5	30 ^b

a: the coverage was deduced from optical microscopy estimating the ratio of the dark spots (covered surface) on the yellow background (uncovered surface). b: the experiment was carried out for 30 minutes with a sulfur column aged for 2 days.

Results and Discussion

The average ^{197}Hg deposition pattern for Set 1 is given in Fig. 4a, grey bars. Assuming the adsorption interaction of Hg on sulphur being relevant for this deposition, a Monte Carlo simulation was performed, allowing for the estimation of a most probable adsorption enthalpy of -70 kJ/mol (Fig. 4a, red line). This estimation was performed by minimizing the sum of the squares of the offsets of the simulated curve from the experimental ones (X^2) at varied adsorption enthalpies, $-\Delta H_{\text{ads}}^{\text{S}}(\text{Hg})$, as presented in Fig. 4b. Given the rather low significance of the X^2 minimum on the higher adsorption enthalpy side, a lower adsorption enthalpy limit $-\Delta H_{\text{ads}}^{\text{S}}(\text{Hg}) > 65 \pm 1$ kJ/mol at 95% c.i. is preferably stated. The lower limit obtained in the performed isothermal experiment means that the interaction between Hg and the sulfur surface is likely to be stronger. The uncertainty of the enthalpy limit was calculated including a $\pm 5\%$ variation of the sulfur coverage of the quartz

column surface, i.e., the simulations were performed at 30%, 35%, and 40% sulfur coverage. This procedure revealed a variance in the adsorption enthalpies of ± 1 kJ/mol. Hence, the uncertainty of the sulfur coverage determination of the quartz surface does not strongly determine the overall deposition pattern.

Fig. 4 a) Average deposition pattern of ^{197}Hg (grey bars) in Set 1 at $T = 23^\circ\text{C}$ applying a He gas flow of 25 ml/min; experimental time: 30 minutes. The Monte Carlo simulation (red line) is shown as well, assuming $-\Delta H_{\text{ads}}^{\text{S}}(\text{Hg}) = 70$ kJ/mol and a 35% sulfur surface coverage as deduced from optical microscopy. **b)** Estimation of the best simulation curve fitting the experimental data of Set 1, applying a χ^2 test. For $-\Delta H_{\text{ads}}^{\text{S}}(\text{Hg}) = 70$ kJ/mol the lowest χ^2 value, corresponding to $\chi^2 = 27$, is obtained.

A broadening of the initial deposition with time was observed for Set 2 (Fig. 5a, grey bars). This indicates that there is no HgS formation. In fact, in case of an irreversible process (i.e., the formation of HgS molecules, with Hg being strongly or irreversibly bound to the sulfur surface), the ^{197}Hg deposition pattern would not change from Set 1 to Set 2. Hence, a kinetic hindrance preventing the formation of HgS molecules is concluded, suggesting a reversible adsorption process and thus, justifying the applied Monte-Carlo based data analysis approach.

The simulation shown in Fig. 5a (black line) depicts a deposition pattern expected from a reversible process with an interaction enthalpy $-\Delta H_{\text{ads}}^{\text{S}}(\text{Hg}) = 70 \text{ kJ/mol}$ at the experimental conditions applied in Set 2. The observed experimental ^{197}Hg deposition of Set 2 is not well described. Hence, a Monte-Carlo simulation of a diffusion controlled deposition better fitting the experimental data was performed (Fig. 5a, red line); using the X^2 method described above only an upper adsorption enthalpy limit could be deduced as $-\Delta H_{\text{ads}}^{\text{S}}(\text{Hg}) < 66 \pm 1 \text{ kJ/mol}$ at 95% c.i. (Fig. 5b). Again, the uncertainty of the enthalpy limit was calculated on the basis of a $\pm 5\%$ variation of the sulfur coverage of the quartz column surface.

Fig. 5 a) Average deposition pattern of ^{197}Hg (grey bars) in Set 2 at $T = 23^\circ\text{C}$ applying a He gas flow of 25 ml/min; experimental time: 60 minutes. The Monte Carlo simulations of a diffusion controlled deposition (red line) are shown, assuming $-\Delta H_{\text{ads}}^{\text{S}}(\text{Hg}) = 66$ kJ/mol and a 35% sulfur surface coverage. For comparison, the Monte Carlo simulation of the expected deposition pattern for a reversible adsorption process with $-\Delta H_{\text{ads}}^{\text{S}}(\text{Hg}) = 70$ kJ/mol after an experimental time of 60 minutes is depicted as well (black line). **b)** Estimation of the best simulation curve fitting the experimental data of Set 2 applying a χ^2 test. For $-\Delta H_{\text{ads}}^{\text{S}}(\text{Hg}) = 66$ kJ/mol the lowest χ^2 value, corresponding to $\chi^2 = 197$, is obtained.

For Set 3, an even lower retention of ^{197}Hg by the sulfur surface was observed (Fig. 6). Monte Carlo simulations were performed. The χ^2 method allowed deducing an upper limit adsorption interaction enthalpy of $-\Delta H_{\text{ads}}^{\text{S}}(\text{Hg}) < 63 \pm 1$ kJ/mol, with a most probable adsorption enthalpy of -62 kJ/mol (Fig. 7).

Fig. 6 ^{197}Hg deposition pattern in the third set of experiments: **a)** On a sulfur surface at $T = 23^\circ\text{C}$ applying a He gas flow of 25 ml/min, with an experimental deposition time of

90 minutes; **b)** On a sulfur surface aged for two days at laboratory conditions (i.e., $T = 25^{\circ}\text{C}$ and $P = 1$ bar). The experiments were carried out at $T = 23^{\circ}\text{C}$, applying a He gas flow of 25 ml/min, with an experimental deposition time of 30 minutes.

Fig. 7 Estimation of the best simulation curve fitting the experimental data applying the X^2 method. **a)** In Set 3a, the lowest X^2 value, corresponding to $X^2 = 240$, is obtained for $-\Delta H_{\text{ads}}^{\text{S}}(\text{Hg}) = 63 \text{ kJ/mol}$; **b)** In Set 3b, the lowest X^2 value, corresponding to $X^2 = 7$, is obtained for $-\Delta H_{\text{ads}}^{\text{S}}(\text{Hg}) = 62 \text{ kJ/mol}$.

The different Hg deposition pattern on the sulfur surface for the experimental Sets 1, 2, and 3, is the consequence of a changing reactivity of the sulfur on the chromatographic surface with time. At room temperature and standard pressure conditions, the most stable allotrope is the orthorhombic α -sulfur, composed of cycloocta-S crown shape molecules (S_8 -rings). In this work, the inner coverage of the quartz columns with a thin sulfur layer is obtained through the quenching of sulfur vapor composed of S_x ring-shaped or branched molecules of different length, mostly $x = 2$ [26]. The fast quenching leads to the deposition of a phase in which the reactive vapor components are preserved [25]. Due to sulfur's high tendency of catenation, and upon warming (i.e., permitting the column to reach room temperature), these components recombine, yielding a metastable polymeric sulfur phase composed of long helices of polymeric sulfur mixed with other molecular species [26].

The composition of this metastable mixture changes with time, since at standard conditions the sulfur chains and the unstable sulfur rings recombine to form stable S₈-rings, followed by their rearrangement into the well-known orthorhombic α -sulfur structure. Depending on the storage conditions (e.g., light exposure, temperature) and on the presence of impurities, this overall conversion can occur in a range of time from a few minutes to months [26, 27]. The different ratio of polymeric chains / S₈-rings composing the sulfur surface leads to a varied reactivity towards Hg. This is reflected in the different adsorption enthalpy values $-\Delta H_{\text{ads}}^{\text{S}}(\text{Hg})$ found. Since the sulfur polymeric chains, being bi-radical, are chemically more reactive [28, 29], it can be assumed that the only species strongly interacting with Hg at room temperature, but still through a reversible adsorption process, are likely the sulfur chains. Instead, between Hg and the S₈-ring molecules only a weak physisorption interaction is established. Since the physisorption interaction does not strongly depend on the type of surface, it is assumed that the adsorption of Hg on the S₈-rings is similar to the interaction of Hg on a pure quartz surface (i.e., $-\Delta H_{\text{ads}}^{\text{S-rings}}(\text{Hg}) = 42$ kJ/mol). Considering the different reactivity of the polymeric sulfur chains and the S₈-rings, Monte Carlo simulations of the ¹⁹⁷Hg deposition pattern in Set 1 were performed in order to quantify the adsorption interaction strength between Hg and the polymeric sulfur chains, i.e., the $-\Delta H_{\text{ads}}^{\text{S-chains}}(\text{Hg})$. In these new simulations the “polymeric chains ratio”, meant as the percentage of the total sulfur surface composed by polymeric chains, was introduced. In this manner, the surface composition variation (i.e., the preservation of polymeric chains, not converted into S₈-rings) was taken into account. In order to estimate the goodness of the fit, the X^2 method was applied. As shown in Fig. 8, the lowest X^2 values are obtained for $-\Delta H_{\text{ads}}^{\text{S-chains}}(\text{Hg}) > 70$ kJ/mol. For a sulfur surface predominantly made of polymeric chains (i.e., from 60% to 100% polymeric chains ratio), a $-\Delta H_{\text{ads}}^{\text{S-chains}}(\text{Hg}) = 70$ kJ/mol is deduced.

1

Fig. 8 Monte Carlo simulations for Set 1, in dependence on $-\Delta H_{\text{ads}}^{\text{S-chains}}(\text{Hg})$ and on the sulfur surface composition (i.e., polymeric chains ratio), for a 35% sulfur coverage of the quartz column surface. The best fitting (i.e., lowest X^2 values, in blue), are obtained for $-\Delta H_{\text{ads}}^{\text{S-chains}}(\text{Hg}) > 70$ kJ/mol. In case of a sulfur surface composed purely of polymeric chains, i.e., 0% conversion ratio, a $-\Delta H_{\text{ads}}^{\text{S-chains}}(\text{Hg}) = 70$ kJ/mol can be deduced. Regardless of the sulfur surface composition, the probability of an interaction enthalpy $-\Delta H_{\text{ads}}^{\text{S-chains}}(\text{Hg}) < 65$ kJ/mol is small.

The deduced interaction enthalpy values $-\Delta H_{\text{ads}}^{\text{S-chains}}(\text{Hg}) = 70$ kJ/mol and $-\Delta H_{\text{ads}}^{\text{S-rings}}(\text{Hg}) = 42$ kJ/mol can be introduced in the Monte Carlo simulations of the data obtained in Sets 2 and 3 of the experiments. In this manner it appears possible assessing the polymeric chains / S_8 -rings transformation, determining the reactivity of the sulfur surface. For example, applying these simulations to the ^{197}Hg deposition pattern in Set 2, a sulfur surface composed for a 28% of sulfur polymeric chains was deduced (Fig. 9).

Fig. 9 Average deposition pattern of ^{197}Hg (grey bars) in Set 2 at $T = 23^\circ\text{C}$ applying a He gas flow of 25 ml/min; experimental time: 60 minutes. The Monte Carlo simulations (red line) are shown, assuming $-\Delta H_{\text{ads}}^{\text{S-chains}}(\text{Hg}) = 70 \text{ kJ/mol}$ and a $-\Delta H_{\text{ads}}^{\text{S-rings}}(\text{Hg}) = 42 \text{ kJ/mol}$. A sulfur surface composed of 28% sulfur polymeric chains was deduced, for a total 35% sulfur coverage of the quartz column surface.

A kinetic hindrance in the adsorption interaction Hg/S₈-rings cannot be excluded. It can be assumed that in case of a “fresh” sulfur surface the activation enthalpy to promote the adsorption interaction of Hg towards the sulfur polymeric chains is low and the thermal energy is high enough to overcome the activation energy barrier. Instead, an increase of the activation barrier in the adsorption interaction of Hg towards the S₈-rings leads to a weaker apparent interaction. In this case, the Hg adsorption on an aged sulfur surface might be promoted by increasing the temperature of the sulfur surface. In other works the removal of Hg from the gas phase was studied applying sulfur-impregnated adsorbents, most of them obtained through the sulfurization of carbon surfaces, e.g. in [30-36]. It was suggested that the adsorption of Hg on these mixed sorbents depends on the allotropic state of the

deposited sulfur [37], and on the temperature at which the adsorption is carried out, with a clear HgS molecular formation at $T \approx 140^\circ\text{C} - 150^\circ\text{C}$ [38, 39]. The observations in this work confirm this kinetic hindrance for the HgS molecule formation even on a single atomic level. The latter reactions are thus only promoted by providing heat, i.e. by breaking the S-S bonds of the sulfur molecular species. Those temperatures cannot be applied in our gas-solid interaction study; since in fact the starting interaction at 140°C would be above sulfur's melting point.

Conclusions

Here, the reactivity of single atomic elemental Hg towards an elemental sulfur surface at room temperature was studied. The formation of HgS molecules is prevented by kinetic hindrance at the applied experimental temperatures. Instead, a reversible adsorption interaction was observed. The technique used in this work allows for an efficient Hg deposition, until the surface (composed initially mostly of polymeric chains) rearranges itself into the more thermodynamically stable, but less reactive, S_8 -rings allotropes. This spontaneous rearrangement of the sulfur species depends on the time, on the light exposure, and on the presence of impurities [26, 27]. The interaction of Hg towards a “fresh” surface (made prevalently of sulfur polymeric chains) is thermodynamically favored, with an estimated $-\Delta H_{\text{ads}}^{\text{S-chains}}(\text{Hg}) > 70 \pm 1 \text{ kJ/mol}$. The conversion of these reactive species into stable S_8 -rings leads to a weak physisorption interaction, comparable to that of Hg on a quartz surface. The ageing of the surface can be then monitored by studying the Hg deposition pattern.

Regardless of the nature of the adsorption mechanism of Hg on the sulfur surface, the estimated adsorption interaction enthalpy of single atomic Hg with an aged sulfur surface is very close to the condensation enthalpy of elemental Hg. This observation indicates that elemental sulphur will not strongly promote the deposition of gaseous Hg at ambient conditions, except if large sulfur surfaces are provided. The extreme conditions needed to keep the deposited polymeric sulfur surface unchanged (e.g. high temperatures) together with the spontaneous creation of preferential rearrangement spots on the surface, renders

the Hg deposition pattern on the polymeric S_{∞} difficult to reproduce, excluding the usage of this allotrope as a chromatographic surface. The chemical formation of Hg-S molecules needs temperatures above 140°C, as suggested in other works in which sulfur impregnated carbon and macroscopic amounts of Hg were used [38, 39]. This temperature limitation rules out sulfur as a convenient stationary chromatographic surface for on-line gas adsorption studies involving the superheavy elements Cn and Fl, since the detection of these SHEs in gas thermochromatographic experiments is typically done using silicon PIN-diodes, which have as semi-conductors an upper working temperature limit of about 40°C [40]. Isothermal on-line gas experiments, where the detection occurs outside the chromatographic column, are excluded as well since the temperature needed to promote the chemical reaction is above sulfur's melting point (115.2°C). As a further step, experiments with selenium surfaces - sulfur's homologue - are envisaged.

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