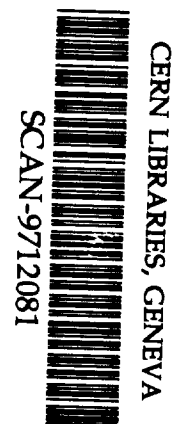


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## Fast Chemical Separation Procedures for Transactinides

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### Introduction

For several reasons experimental investigations of chemical properties of transactinide elements are extremely difficult. First, such elements at the uppermost end of the periodic table can be produced only at a single atom at a time level which requires highest possible sensitivity. Second, based on the usually short half-lives of presently known isotopes fast and if possible continuous techniques are required for their study. Finally, very unique detection systems are needed which permit unequivocal proof that the separated species are indeed from single atoms of transactinide elements.

Fast separation of short-lived radioactive nuclides has a long tradition in the study of physical and chemical properties. Earliest applications were made with gaseous species such as thoron (i.e.  $^{220}\text{Rn}$ ) [1] using an electrometer for the determination of its half-life of about one minute.

A rapid development of fast chemical separation techniques occurred after the discovery of nuclear fission [2]. The detailed study of the large number of mostly short-lived fission products required access to faster and faster techniques reaching the present-day limit in an investigation of the 0.8 s nuclide  $^{110}\text{Tc}$  using the continuous extraction technique SISAK [3]. For reviews on rapid chemical methods for identification and study of short-lived nuclides, mostly from nuclear fission, we refer to [4-9].

Here we restrict the review solely to techniques which have so far successfully been used for investigations of transactinide elements. First, the requirements are discussed which are specific to isolation and identification of these elements. Then a short overview is given on early work, mostly performed between 1965 and 1980, followed by a description of the gas chemical and aqueous phase separation procedures used in recent years in chemical studies with the elements rutherfordium (Rf, Z=104), dubnium (Db, Z=105), and seaborgium (Sg, Z=106). Finally, techniques are presented which have been developed for transactinide element studies but were not successful so far.

### Requirements

As mentioned already, separation techniques for heaviest elements have to be fast, efficient and applicable to single atoms.

#### Speed

The required separation speed follows from the relatively short half-lives of isotopes of transactinide elements. In addition, for identification of separated products the nuclides should at least partly decay via emission of  $\alpha$ -particles. For rutherfordium the most often used production reaction is  $^{248}\text{Cm} (^{18}\text{O}, 5n) ^{261}\text{Rf}$ .  $^{261}\text{Rf}$  has a half-life of 78 s [10]. For dubnium it is  $^{249}\text{Bk} (^{18}\text{O}, 5n) ^{262}\text{Db}$ , which has a half-life of 35 s [11]. In recent studies with seaborgium [12], the reaction  $^{248}\text{Cm} (^{22}\text{Ne}, 5n) ^{265}\text{Sg}$  was used.  $^{265}\text{Sg}$  has a half-life of 7 s [13]. For the still heavier elements bohrium (Bh, Z=107) and hassium (Hs, Z=108) the following production reactions have been proposed:

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$^{249}\text{Bk}$  ( $^{22}\text{Ne}$ , 5n)  $^{266}\text{Bh}$  [14] or  $^{254}\text{Es}$  ( $^{16}\text{O}$ , 5n)  $^{265}\text{Bh}$  [15].  $^{265}\text{Bh}$  and  $^{266}\text{Bh}$  are expected to decay via  $\alpha$ -emission with half-lives of about 0.4 and 19 s respectively [15]. Hassium might be produced in the reaction  $^{248}\text{Cm}$  ( $^{26}\text{Mg}$ , 5n)  $^{269}\text{Hs}$ .  $^{269}\text{Hs}$  has a half-life of about 9 s and decays also via  $\alpha$ -emission [16]. According to recent calculations [17] the half-lives of isotopes of still heavier elements accessible in fusion reactions between actinide targets and heavy ion beams fall below one second, the only exception being perhaps meitnerium (Mt,  $Z=109$ ).

The isotopes used so far for chemical studies have by far not the longest half-lives. If it were possible to produce more neutron rich species, due to strong shell effects at the neutron numbers  $N=162$  and  $N=184$ , very long lived isotopes are predicted to exist. For even-even nuclides calculated values are e.g.  $T_{1/2} = 3,5$  h for  $^{266}\text{Sg}$ ,  $1,3 \times 10^6$  y for  $^{290}\text{Sg}$ , or  $3,2 \times 10^4$  y for  $^{292}\text{Hs}$  [17,18]. It will be a challenge for the future to get access to such nuclides using radioactive beam facilities. Such devices should deliver very neutron-rich beams of radioactive particles (see e.g. [19]).

### Sensitivity

Isotopes of transactinide elements with half-lives significantly longer than one second have been produced solely in hot-fusion reactions. In such reactions heavy actinide targets, e.g.  $^{244}\text{Pu}$ ,  $^{248}\text{Cm}$ ,  $^{249}\text{Cf}$  or  $^{254}\text{Es}$  are bombarded with projectiles such as  $^{18}\text{O}$  or  $^{22}\text{Ne}$  at energies close to the nuclear interaction barrier. After fusion, due to a relatively high excitation energy, the compound nuclei typically evaporate 4 to 5 neutrons in order to form evaporation residues. Since with the emission of every neutron a much higher probability for prompt fission exists, cross sections for final products are many orders of magnitude lower compared to those of the primary compound nuclei. The above mentioned mostly used reactions have therefore rather low production cross sections, being:  $\approx 5$  nb for  $^{248}\text{Cm}$  ( $^{18}\text{O}$ , 5n)  $^{261}\text{Rf}$  [10],  $\approx 6$  nb for  $^{249}\text{Bk}$  ( $^{18}\text{O}$ , 5n)  $^{262}\text{Db}$  [20], and 0,4 nb for  $^{248}\text{Cm}$  ( $^{22}\text{Ne}$ , 5n)  $^{265}\text{Sg}$  [13]. For future production of Bh and Hs via e.g.  $^{249}\text{Bk}$  ( $^{22}\text{Ne}$ , 5n)  $^{266}\text{Bh}$  or  $^{248}\text{Cm}$  ( $^{26}\text{Mg}$ , 5n)  $^{269}\text{Hs}$  cross sections on the order of 50 pb and 5 pb may be expected [21].

For several reasons target thicknesses are limited to about 0.5 to 1 mg/cm<sup>2</sup> in experiments to produce heaviest elements. Due to the high energy loss of heavy ion projectiles in matter maximum beam intensities passing through such targets without damage are about  $3 \times 10^{12}$  p/s (0.5  $\mu\text{A}$ ).

As a consequence, production rates amount to 9-26 atoms per hour of beam time and nanobarn cross section. Hence chemical studies with Rf and Db are possible with about one atom per minute. In case of the recently investigated behaviour of Sg this number reduced to several atoms per hour. Future experiments with Hs will require an additional improvement in sensitivity since production rates will be reduced to a few atoms per day.

### Single atom chemistry and detection

Two aspects deserve special attention in chemical studies with single atoms. First, the separation procedure has to be applicable to single atoms or molecules and, second, detection and identification of final products has to be highly specific.

The question arises whether at ultra-low concentrations the species behave in a chemical process as expected. Guillaumont et al. [22] pointed out that under such conditions the classical law of mass action is no longer valid. If the population of species being part of a chemical reaction reaches the ultimate limit of one, which is always the case in transactinide chemistry, the equilibrium constant  $K$  has to be calculated from probabilities rather than concentrations that the single atom (or molecule) is in a given state or phase. If, however, in a chromatographic process the single atom is subjected to a repetitive partition experiment the average behaviour is correctly described by the "classical" value of  $K$  [22]. For a discussion of thermodynamics at sub-tracer scale we refer to [23-26]. In an experimental study with polonium at a level of 5000 to 40 atoms it could be shown that the electrochemical

deposition on silver and the coprecipitation with elementary tellurium or with arsenic sulfide behaved as expected [27].

On the other hand, one should keep in mind that in radiochemical separations with minute amounts quite often unexpected chemical behaviour is observed. Such surprises are mostly caused by impurities such as colloids which tend to adsorb single atoms or molecules forming what has been named pseudo-radiocolloids. This topic has been discussed by Lieser et al. [28,29].

The second aspect covers detection of single atoms. Even though several techniques have proven to be able to detect single atoms or molecules such as AFM or ion trap techniques, none of these have yet reached a performance to be applicable if only a very few atoms of a short-lived isotope are available for study. Still best suited for detection of single atoms is using the signature of its radioactive decay. This approach has been developed to highest performance in the discovery experiments of the heaviest elements. As an example, meitnerium has been discovered on the basis of one single atom [30]. The basis for this exceptional achievement is the fact that isotopes of heaviest elements predominantly decay via  $\alpha$ -decay chains to long-lived isotopes of actinide elements. This favourable situation permits to detect with every decaying atom several quantities such as decay energies and life times of the mother, daughter, grand-daughter etc. nuclides. If position sensitive silicon detectors are used, the significance can even be improved. This requires, of course, list-mode data acquisition systems.

In some chemical studies spontaneously-fissioning nuclides were used for identification of separated products. Recent examples are studies of dubnium bromide [20] or seaborgium oxychloride [31]. If no additional property such as e.g. the half-life is measured [20], the assignment of the spontaneous-fission activity to a given nuclide and, hence, to the corresponding element is very difficult.

One obvious drawback in using radioactivity for detection of separated single atoms or molecules is the fact that no information on speciation may be gained from the measured signal. So far, information on separated species was obtained only indirectly. In gas phase chemical separations usually thermochemical predictions are compared with the measured retention i.e. volatility behaviour (see e.g. [32,33]). Whether in future speciation of single molecules is possible using e.g. mass spectrometry [34] or ion trap technique [35] remains open.

In aqueous phase separations measured  $K_D$  values permit a determination of the ionic charge of the separated complex [36-38].

### **Techniques used in the first chemical studies of transactinides**

Chemical studies of the first transactinide element Rf has been carried out in Dubna [39] in the reaction  $^{22}\text{Ne} + ^{242}\text{Pu}$ . Frontal gas chemical separation was applied to isolate volatile chlorides of this element. A very ingenious technique was used for formation of volatile species: from the target recoiling reaction products were stopped in a thermalization gas ( $\text{N}_2$ ) and then subjected to a *in-situ* chlorination with  $\text{NbCl}_5$  or  $\text{ZrCl}_4$  vapour. Formed chloride molecules were continuously transported within about 200 ms through an isothermal glass column kept at 250 to 300 °C. Behind the column the  $\text{N}_2$  carrier gas containing the volatile species passed along mica fission track detectors for identification of spontaneously fissioning reaction products. Indeed, some activity was found which was assigned to an isotope of Rf, the main argument being that none of the actinide elements known to have spontaneously fissioning isotopes form chloride molecules which are volatile at such low temperatures.

In later experiments the same group used the thermochromatography technique to determine the adsorption behaviour of volatile Rf halide molecules and compared its deposition temperatures with similar measurements of the homolog Hf [40,41]. They concluded that Rf (then named kurchatovium (Ku) by the dubna scientists) is an ordinary member of group 4 and behaves very similar to Hf. Since the detection of separated transactinide molecules based on the by itself unspecific spontaneous-fission decay-mode, some of these early studies were subject to critical comments (see e.g. [42,43]).

Later, but for the first time aqueous chemical studies with Rf were performed at LBL in Berkeley [44]. They used what has ironically be named the „SRAFAP“ technique (Students Running As Fast As Possible [45]: in each chemical experiment from the target recoiling atoms were collected in a NH<sub>4</sub>Cl-coated platinum foil. This catcher foil was then removed from the irradiation position and transferred to the chemistry laboratory. Here, the NH<sub>4</sub>Cl was dissolved in 0.1 M alpha hydroxyisobutyrate at pH = 4 and eluted through a cation exchange column to separate Rf (and homologs) from actinides. Final samples were forwarded to  $\alpha$ -spectrometry and assayed for the decay of the then known isotope <sup>261</sup>Rf.

The first fully automated apparatus for chemical studies of transactinides was used by Hulet et al., 1980 [46]. Reaction products were transported with a pneumatic transport system to a collecting site, then pneumatically transferred to a chromatography column, where in HCl solutions of different concentrations the extraction of Rf chloride complexes in a quaternary amine was investigated. Final samples were again automatically forwarded to  $\alpha$ -counting devices and assayed for the decay of <sup>261</sup>Rf.

### Techniques successfully used in recent years for chemical studies of transactinides

#### Gas-jet systems

Unique to all chemical investigations performed in recent years is the thermalization of primary reaction products in a gas - mostly helium - followed by a continuous transport to a chemistry device. While in the thermochromatographic studies performed in Dubna the chemistry device was directly connected to the thermalization chamber all other investigations used a continuous carrier gas transport through capillaries. This technique is called a gas-jet system. In order to achieve high transport yields the products have first to be attached to small particles of typically 0.1  $\mu\text{m}$  diameter [47]. Particles of this size exhibit optimum transportation yields caused by two counteracting loss mechanisms: Brownian motion (loss rate decreases as a function of particle size) and gravitational effects (loss rate increases as a function of particle size) [47,48]. As particle material liquid (see e.g. [49]) as well as solid particles (see e.g. [50]) have been used. While liquid aerosol particles showed somewhat higher transport yields, presumably due to smaller inlet losses [49], solid particles have exclusively been used in transactinide chemical studies. The reason is that highly soluble salt particles such as e.g. KCl can easily be coupled to aqueous phase procedures. Typical yields achieved with salt particles such as KCl, MgCl<sub>2</sub>, PbCl<sub>2</sub> or ZnBr<sub>3</sub> over a few meter transportation length were about 60 - 80 % [50]. Transport distances were as long as 700 m [51].

Decisive for achieving a high gas-jet yield is a fast attachment of primary reaction products to the particles. With a <sup>211</sup>Pb generator the transfer rate of primary products to solid particles of different size was investigated. These rates were about 10<sup>-3</sup> cm<sup>3</sup>s<sup>-1</sup> per <sup>211</sup>Pb atom for 30 nm size particles, 10<sup>-2</sup> cm<sup>3</sup>s<sup>-1</sup> for 100 nm or 3x 10<sup>-1</sup> cm<sup>3</sup>s<sup>-1</sup> for 1  $\mu\text{m}$ , respectively [52]. Under real experimental conditions at a nuclear facility particle concentrations of 10<sup>5</sup> to 10<sup>6</sup> cm<sup>-3</sup> were needed to achieve optimum attachment of reaction products resulting in high yields [49].

Salt particles of optimum size and concentration can easily be produced: the substance is placed in a ceramic boat and heated in a tubular oven in the carrier gas to an optimum temperature which is typically several ten degrees below the melting point. Most convenient are NaCl or KCl particles [53,54]. For gas chemical studies, in recent years mainly carbon particles have been used. They can be produced via spark discharge between two rods [55]. Due to the high ionization potential of He, a self confining plasma could be obtained only with well defined geometries of both electrodes [56]. Carbon particles have the advantage that already with trace amounts of oxygen carbon dioxide is formed at elevated temperatures in gaschromatographic devices.

While most of the parameter studies have been carried out with radionuclide generators or with short-lived fission products at reactors, application of the gas-jet technique to heavy ion accelerators is hampered by plasma effects induced by the beam particles in the thermalization gas. A systematic study performed with Ne<sup>5+</sup> beams showed decreasing yields with increasing beam intensities. With KCl as particle materials 90 % yield was observed

at 10 nA beam current. The value reduced to only 45 % at 2  $\mu$ A [57]. At higher beam intensities also increased formation of electrically charged particles was observed. As a consequence, better transportation yields were found if stainless-steel capillaries were used instead of polyethylene or teflon. On the other hand, the yield drop for higher intensities was found to be independent of the microstructure (27 MHz vs. 108 MHz) and macrostructure (macro pulse between 2 ms and 6 ms) of the beam.

#### The On-Line Gas chemistry apparatus OLGA

As described above, on-line gas chemical separations with transactinides have been performed as early as in 1966 [39]. The applied thermochromatography technique is however not suited for real time detection of separated species. Therefore, in subsequent years, coupling of gas jet transportation systems to thermochromatography devices was used to separate and detect long-lived nuclides only (see e.g. [58,59]). In order to overcome this disadvantage, OLGA, an On-Line isothermal Gas chromatography Apparatus was developed which permits on-line detection of separated species. OLGA (I) was used to separate species volatile in the carrier gas at maximum temperatures of about 1000 °C ([60,61], see Fig. 1). Reaction products were collected on a quartz wool plug inserted in a quartz chromatography column. With a first oven this collector position was kept at a temperature of about 1000 °C. Volatile species then entered a second oven kept at an isothermal, but up to 1000 °C variable temperature. Behind the column ejecting atoms or molecules were adsorbed on a water cooled rotating wheel. From time to time, this wheel was rotated by a given angle in order to transport the freshly deposited species in front of surface barrier detectors to assay  $\alpha$ -events and spontaneous-fission activities.

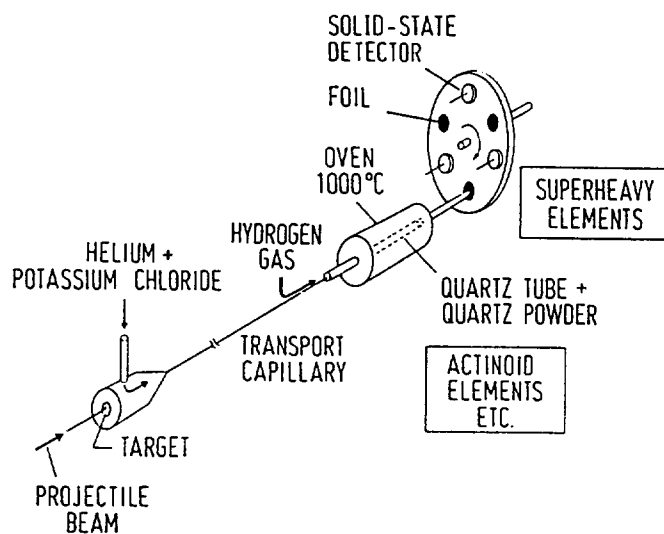


FIGURE 1

OLGA (I) device used to search for volatile superheavy elements produced in heavy ion reactions. Products attached to KCl particles were injected together with little amounts of  $H_2$  in a quartz column mounted inside of a tubular oven which could be heated up to 1000 °C. Volatile species leaving the column were adsorbed on thin metal foils mounted along the circumference of a wheel for  $\alpha$ - and spontaneous-fission counting with surface barrier detectors (from G. Herrmann, *Angewandte Chemie*, 27/11, p.1425 (1988)) [61].

With such a device chromatographic yield curves as depicted in figure 2 are measured. Shown is the shape of the chromatographic yield curve as a function of varying temperatures of OLGA. From the observed change of the yield from low to high values retention times may be deduced: at e.g. 50 % yield the corresponding temperature

corresponds to a retention time which is equal to the half-life of the nuclide. This means that the nuclear decay time can be used to determine a "chemical" time, the retention time.

This technique was first tested with polonium, due to its anticipated chemical similarity with superheavy elements around atomic number 114 [60]. For production the reaction  $^{208}\text{Pb} (\alpha, 1n) ^{211\text{m}}\text{Po}$  was used.  $^{211\text{m}}\text{Po}$  is an  $\alpha$ -emitter ( $E_\alpha = 7.27$  MeV) and has a half-life of 25.5 s.

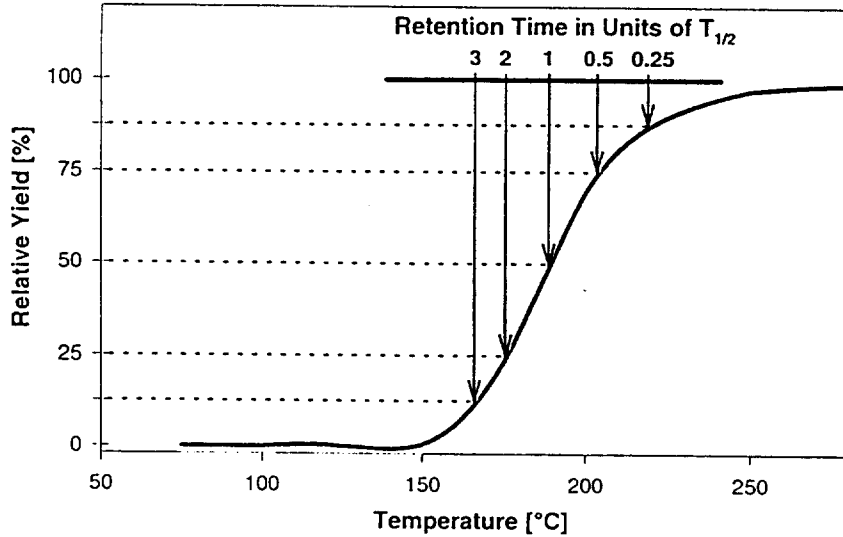


FIGURE 2

Yield curve measured with OLGA for a volatile species labeled with a short-lived nuclide. The retention time in the chromatographic column at the temperature where the yield is 50 % of the maximum value is equal to the half-life of the nuclide. Some other values for retention times at different temperatures may be inferred accordingly.

Under certain model assumptions, from measured retention times the adsorption enthalpy of the volatile species on the surface of the chromatography column may be deduced. Based on the assumption that the gaseous adsorbate is an ideal gas and that the reference state of the adsorbent is zero coverage, the corrected partition coefficient  $k_i$  is given by [62]:

$$k_i = \frac{a}{v} \frac{V}{A} \exp\left(\frac{-\Delta H a^\circ}{RT}\right) \left(\exp \frac{\Delta S a^\circ}{R}\right) \quad (1)$$

where  $a$  and  $v$  are the surface and the volume per unit length of the column,  $A$  and  $V$  the standard molar surface and standard molar volume, and  $\Delta H a^\circ$  and  $\Delta S a^\circ$  the adsorption enthalpy and adsorption entropy, respectively. Assuming mobile adsorptions of a monoatomic gas the standard state is  $V/A = 1$  cm (see [62]).

The migration of a species in ideal isothermal gas chromatography is given by [63]:

$$\frac{dz}{dt} = \frac{u}{1 + k_i} \quad (2)$$

where  $z$  is the direction of migration,  $t$  is the time and  $u$  the linear velocity of the gaseous phase. The linear velocity  $u$  is given by

$$u = \frac{\bar{V}_0 T}{\emptyset T_0} \quad (3)$$

where  $\bar{V}_0$  is the gas flow rate ( $\text{cm}^3/\text{s}$ ) at standard condition (STP),  $T$  is the column temperature,  $T_0 = 298$  K and  $\emptyset$  is the cross section of the column.

Inserting (1) and (3) into (2) and integrating along  $Z$  leads to

$$t_r = (Z_1 - Z_2) \left\{ \frac{T_0 \left[ 1 + \frac{a}{v} \frac{V}{A} \exp\left(\frac{-\Delta H a^\circ}{RT}\right) \exp\left(\frac{\Delta S a^\circ}{R}\right) \right]}{V_0 T} \right\} \quad (4)$$

Measurements of the retention times at different temperatures allows then to determine the adsorption enthalpy and entropy. However, since usually only one retention time at  $t_r = T_{1/2}$  is determined, the adsorption entropy has to be estimated in order to deduce the adsorption enthalpy. For mobile adsorption the adsorption entropy is given by [62]:

$$\Delta S a^\circ = R \ln \frac{A}{V v_B} \left( \frac{kT}{2\pi m} \right)^{1/2} + \frac{1}{2} R \quad (5)$$

with  $k$  = Boltzmann constant,  $m$  = atomic mass of the adsorbate,  $R$  = gas constant and  $v_B$  = characteristic frequency of the adsorbent. For quartz surfaces usually  $v_B = 5 \times 10^{12} \text{ s}^{-1}$  is taken [62].

To conclude, from the measured 50 % yield temperature at which  $t_r = T_{1/2}$  and assuming ideal gas condition the adsorption enthalpy may be obtained using eq. (4).

With the device shown in Fig. 1 an extensive search for "polonium-like" superheavy elements produced in the reaction  $^{48}\text{Ca} + ^{248}\text{Cm}$  was performed [64,65].

After the failure to discover superheavy elements, OLGA (I) was modified to become applicable for chemical studies of the first transactinide elements. Since these elements do not form volatile species at 1000 °C in the He/H<sub>2</sub>-carrier gas, halogenating agents had to be added to the position of the quartz wool plug in order to form volatile halides, mainly chlorides and bromides. The required hot and highly corrosive gases (e.g. HCl, Cl<sub>2</sub>, HBr) however caused damage to the detectors of the wheel system. Therefore, an additional step was added. Behind the chromatography column the volatile species were injected in a recluster chamber and attached to new aerosol particles. Through a capillary the separated species could then be transported to a counting device. This system was named OLGA II [51]. A very similar apparatus was later also built at LBL, the **Heavy Element Volatility Instrument HEVI** [66].

As an alternative to the hitherto used rotating wheel systems for detection of separated species, in OLGA II a type device was used. In a first collection position the particles were deposited on the surface of a commercial magnetic tape via inertial impaction. At preset times the tape could be moved to transport the deposited activity in front of six consecutive PIPS' detectors. Advantage of such a tape system compared to a rotating wheel device is the significantly reduced background count-rate caused by long-lived nuclides. Disadvantage is the restriction to a  $2\pi$  counting geometry since commercially available tapes are too thick to enable  $\alpha$ - or spontaneous-fission detection from the rear side. Rotating wheel devices such as the LBL - MG device [67] can be equipped with very thin ( $\approx 40 \mu\text{g}/\text{cm}^2$ ) organic foils at window positions along the circumference of the wheel.

OLGA II and HEVI were used to study the retention times of RfCl<sub>4</sub> [10], RfBr<sub>4</sub> [68], and DbBr<sub>5</sub> (or DbOBr<sub>3</sub>) [20] in quartz columns.

The disadvantage of OLGA II and HEVI was their short isothermal section of the quartz chromatography column of only about 20-30 cm length. This resulted in poor chromatographic resolutions as exemplified in Fig. 3 for TaBr<sub>5</sub> using  $^{167}\text{Ta}$  with  $T_{1/2} = 78 \text{ s}$  [20]. The left side shows a fit through the data assuming ideal gas chromatography, i.e. using eq. (4). The resulting  $\Delta H a^\circ$  value is -88 kJ/mol. Obviously, the fit fails to follow the data at low temperatures. If, however, a Monte Carlo model is used which describes the migration of single atoms or molecules under real gas flow conditions a significantly improved description of the measured data can be obtained. This Monte Carlo model was introduced by Zvara [69] and adapted to isothermal gas chromatography by Türlér et al. [70]. With this model the down stream displacement of a species is described as follows: whenever the atom or



molecule encounters the surface of the chromatographic column a series of adsorption - desorption processes occurs without displacement. The single surface interaction can be described by the Frenkel equation,

$$\tau = \tau_0 e^{\frac{Q}{RT}} \quad (6)$$

with

$\tau$  = interaction time at temperature T,

$\tau_0 = v_B^{-1}$  (see above) and

Q = enthalpy of interaction

Then, occasionally the molecule diffuses far enough from the wall to perform a long down stream displacement before encountering the surface again. In such a way the numerous interactions of a species with a surface are replaced by a much smaller number of down stream "jumps". As is evident from Fig. 3 the proposed Monte Carlo model perfectly describes the data. The relatively high yield at the lowest temperature is due to a non-negligible probability that the TaBr<sub>5</sub> molecules perform "big jumps" which are longer than the isothermal section of OLGA II.

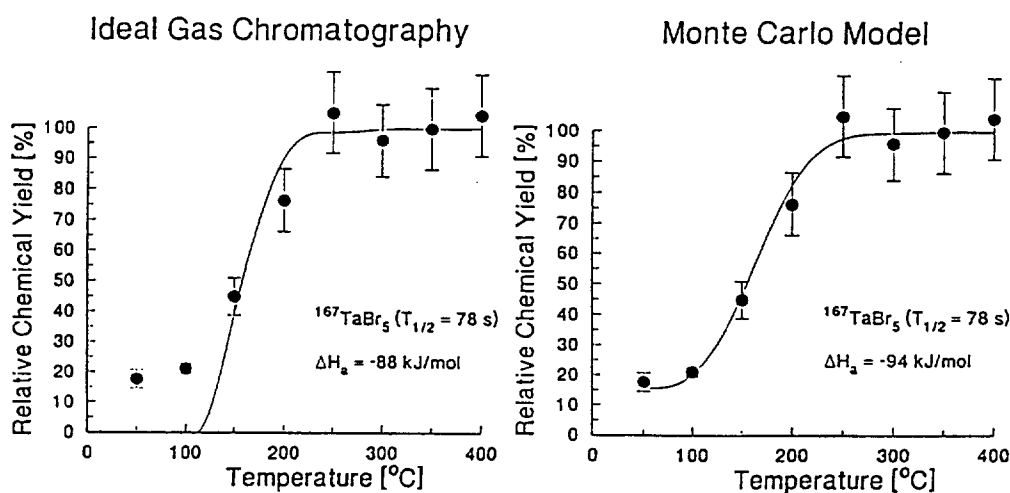


FIGURE 3

Measured yield curves for <sup>167</sup>TaBr<sub>5</sub> with OLGA II (from [20]). The solid line in the left part depicts an attempt to describe the measured yields with eq. (4). The solid line on the right side is a fit through the data using the Monte Carlo model proposed by Zvara [69] (see text).

In order to improve the chromatographic resolution, OLGA III was built with much longer (1.8 m) quartz chromatography columns [71]. To achieve better temperature stability a commercial gas chromatograph (Carlo Erba) with a maximum temperature of 500 °C instead of a tubular furnace was used. Moreover, to reduce the chemical separation time, which was about 20 to 30 s for OLGA II or HEVI, a smaller recluster chamber surrounded by a water cooling jacket was designed [72]. Fig. 4 depicts OLGA III as it was applied for recent transactinide studies. Chemical separation times determined with chlorinated short-lived Nb isotopes from fission of <sup>235</sup>U were about 1 s at 440 °C, 2 s at 350 °C, 5 s at 270 °C, and 10 s at 210 °C [73]. With OLGA III the retention times of RfCl<sub>4</sub> [13], DbCl<sub>5</sub> and DbOCl<sub>3</sub> [11] and SgO<sub>2</sub>Cl<sub>2</sub> [75] in quartz columns were investigated.

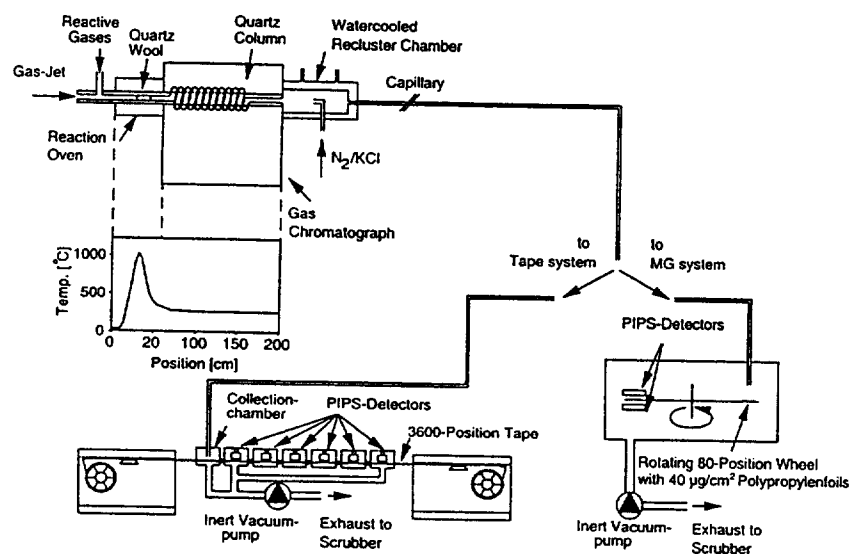


FIGURE 4

OLGA III as it was used for chemical studies of Rf, Db and Sg. Products were transported from the accelerator with a helium/carbon particles gas-jet to a quartz chromatography column kept at 900 to 1000 °C. To this position the reactive gas was added, e.g. 0.2 vol-% O<sub>2</sub>, 12 vol-% Cl<sub>2</sub> and 1.7 vol-% SOCl<sub>2</sub> for studies with Sg [12,75]. Behind the reaction oven followed a 1.8 m long and 1.5 mm diameter quartz column, positioned in a commercial gas chromatograph. Behind the column ejecting volatile species were stopped in a recluster chamber and attached to new aerosol particles. The products were then transported at room temperature to a counting device, a rotating wheel system or a stepwise moving tape.

#### On-line multi-column liquid chromatography

For chemical studies of transactinide elements in aqueous solution, a very elegant and inexpensive separation scheme has been proposed [36,37,76,77,79]. It bases on the fact that most short-lived isotopes of transactinide elements decay via  $\alpha$ -emission(s) to long-lived actinides. In Fig. 5 the basic principle of the technique is outlined. Reaction products attached to soluble aerosol particles are dissolved in a „degasser unit“ [78] and continuously fed on top of a first column (A). This column acts as a filter for all elements having atomic numbers lower than the transactinide element of interest. Then, the eluate is forwarded to a second column (B) where the transactinide element experiences a retention time being on the order of its life time. Behind this column a third column (C) acts as a filter adsorbing all decay products of the transactinide element produced during the passage through column B but lets the residual atoms of the transactinide element pass without notable retention. The final eluate is sampled (or passed through an additional column D) in order to collect the residual atoms of the transactinide as well as its decay products. After the experiment, the decay products of the transactinide element on column C and in the final eluate (or on a column D) are isolated and their activities measured from which the retention time  $t_r$  of the separated species may be obtained according to:

$$t_r = \frac{T_{1/2}}{\ln 2} \ln \left( \frac{A_{(C)} + A_{(D)}}{A_{(D)}} \right) \quad (7)$$

where

$A_{(C)}$  = activity of the decay product on column C

$A_{(D)}$  = activity of decay product in the eluate (or on column D)

The distribution coefficients  $K_D$  of the transactinide element in column B may then be obtained according to:

$$K_D = (t_r - t_0) \frac{V}{M} \quad (8)$$

where

$t_0$  = retention time of the eluent

$V$  = mass flow rate of the eluent, and

$M$  = mass of the stationary phase.

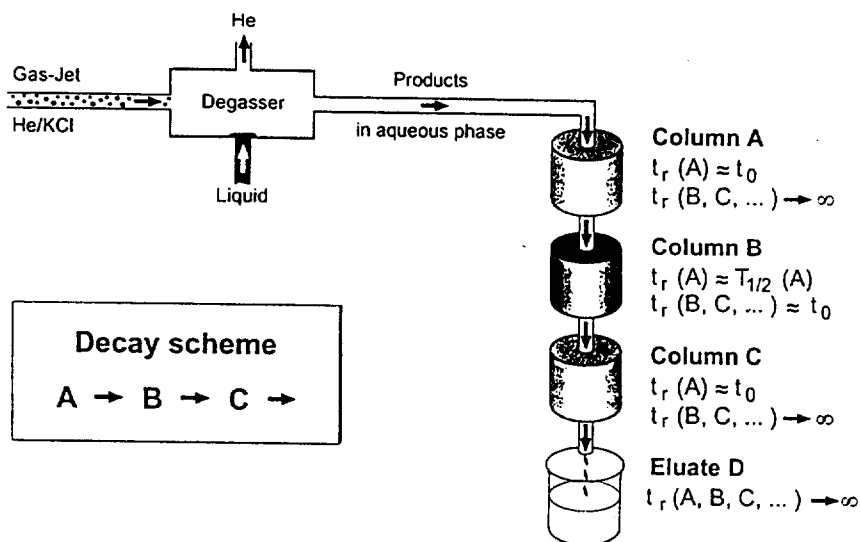


FIGURE 5

On-line multi-column technique to determine  $K_D$  values of ionic or neutral species in chromatographic columns. After a transfer of the products attached to salt particles via a degasser unit into aqueous phase, the liquid flow passes through three columns. After the experiment, column C and eluate D are chemically analyzed for the decay product(s) of the transactinide element to be studied. As an example, for rutherfordium using the 78 s  $^{261}\text{Rf}$ , column A serves to adsorb all actinides, column B to retain Rf for about one minute, and column C to adsorb  $^{257}\text{No}$ ,  $^{253}\text{Fm}$  and  $^{253}\text{Es}$  with essentially no retention for Rf, [38,76,79].

So far, this technique has solely been used to study anionic complexes of Rf on different exchange columns [38,76,79]. It is interesting to note that measurements of  $K_D$  values at various concentrations of a counter ion permits a determination of the ionic charge of the separated complex. As an example, the different slopes of a linear fit through  $K_D$  values measured at different nitric acid concentrations for fluoride complexes of W and Hf allowed to determine the ionic charges to be one (most likely  $\text{WOF}_5^-$ ) and two ( $\text{HfF}_6^{2-}$ ), respectively [36]. For Rf eluted through the ion exchange column Wofatit HS36 in  $\text{HNO}_3/\text{HF}$  solutions, the measured  $K_D$  values at two  $\text{HNO}_3$  concentrations resulted in a slope of two, giving strong evidence for the complex  $\text{RfF}_6^{2-}$  [38].

Under typical eluent flow rates between about 1 and 5 ml/min, the range of  $K_D$  values which can be measured with this technique is limited to approximately 10 to 100 [79].

#### Automated rapid aqueous chemical separations

A gas jet transport system in combination with high performance liquid chromatography is a powerful tool in heavy element research because of its speed, selectivity and high chemical yield.

A microcomputer controlled Automated Rapid Chemistry Apparatus ARCA was developed [80] to search for superheavy elements [65,81] and to study heaviest actinides [82].

The main parts of ARCA are an aerosol particle (mostly KCl) collector, a high performance liquid chromatography (HPLC) system, a collector for the eluent and a detector system. Extremely important for the

versatility of ARCA was to use inert materials such as teflon, Kel-F, glass or saphir for all parts which get into contact with the solvent. A minor disadvantage then is the pressure limitation to about 10 bar due to these materials. While ARCA (I) had separation times of several minutes the totally newly developed version ARCA II [83] permitted separations in the ten second range. This device was recently successfully used for a first ever aqueous chemical study of seaborgium with the 7 s  $^{265}\text{Sg}$  [12, 84].

The main part of ARCA II is shown in Fig. 6. In order to nearly continuously collect reaction products a duplicate design was chosen. In the sampling position the aerosol particles containing the reaction products are collected on a 35  $\mu\text{m}$  pore size polyethylene frit [80] or an impactor surface [84]. After a preset time the sample is moved pneumatically in front of either one of two tiny chromatography columns (typical size 2 x 8-23 mm, depending on the required separation factors). The columns are mounted in magazines carrying 20 fillings each, which enables the application of one column per separation. Hence, with two magazines a total of 40 separations may be performed prior to a reload.

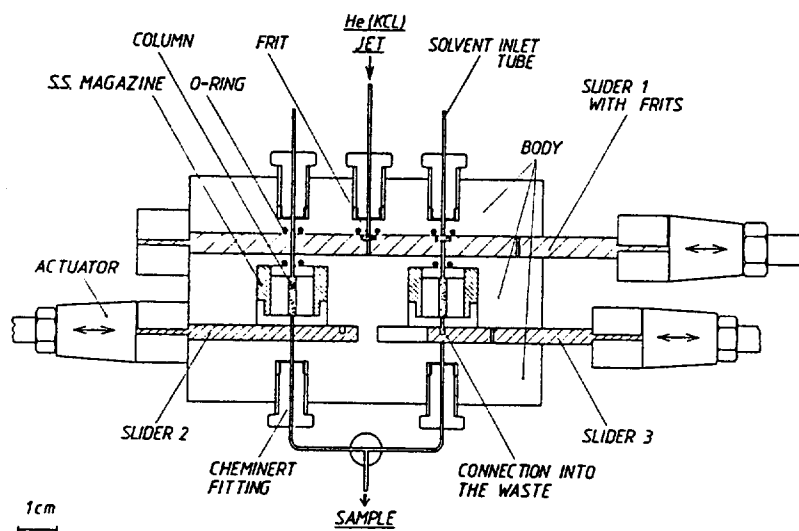


FIGURE 6

The main part of ARCA II (from Schädel et al. [83]). Products attached to KCl particles are sampled for a given time on a frit. Then slider one moves the sample on top of one of the two chromatography columns for elution with a liquid entering through the solvent inlet tube. Meanwhile, the next sample is already collected for chromatography on the second column.

The most time consuming step of this technique is the sample preparation from the eluent for  $\alpha$ -spectroscopy or spontaneous-fission counting. In ARCA II a fast evaporation device is used consisting of an eight position turntable to collect the relevant liquid fraction on Ta discs. These Ta plates have shallow dips of about 1 mm depth in the middle to confine the drops. The discs are heated close to 100 °C. For additional heating a quartz lamp with a median spectral radiation wavelength of 900 nm as well as a 4 l/min He gas flow, preheated to 300 °C, is applied to the sample. A microprocessor controlled time regime optimizes the drying procedure. A typical time needed for the chemical separation of a given fraction in the column is about 10 s, followed by the sampling and drying procedure lasting about 30 s. Achieved chemical overall yields were between 75 and 95 %. After preparation the Ta discs are mounted within a few seconds in counting chambers. Then - mostly in a 2  $\pi$  geometry - the final samples are assayed for  $\alpha$ -decay and spontaneous-fission using PIPS detector. Typical  $\alpha$ -resolutions achieved are  $\leq 50$  keV.

ARCA II was first applied to chemical studies of Db using reversed phase chromatography with TiOA (triisooctylamine) on an inert support [85,86]. With HCl/HF of different concentrations elution positions of Db

relative to those of Nb, Ta and Pa were determined. Also investigated was the extraction behaviour of Db into diisobutylcarbinol [87] and the cation exchange behaviour with  $\alpha$ -hydroxyisobutyric acid [88].

In more recent applications, the extraction behaviour of fluoride-, chloride- and bromide complexes of the elements Nb, Ta, Pa and Db into aliphatic amines was studied [89] as well as the chromatographic behaviour of Rf in the system HCl/TBP (tributylphosphate) [90]. In the latter work, ARCA II was for the first time used to determine  $K_D$  values. From the fraction of Rf passing through a TBP coated Voltalef column in a 8 M HCl solution relative to a stripping with 2 M HCl, the  $K_D$  value for Rf could be determined and was found to be intermediate between those of Hf and Zr [90].

#### Continuous liquid-liquid extraction with SISAK - on the threshold of success

SISAK (Short-lived Isotopes Studied by the AKuve technique, see e.g. Skarnemark et al., [91]) is a well established on-line technique for studies of radioactive nuclides with half-lives as low as 0.8 s [3]. It is based on multi-stage solvent extraction separations using high-speed centrifuges for phase separations. The main parts of a SISAK separation device are a gas jet, a degasser, ultracentrifuge units and a detection system.

The gas jet (mostly with KCl particles) transports the products to a degasser unit which dissolves the particles and the products of interest in an aqueous solution. This solution is then continuously fed in a centrifuge unit together with an organic extractant. Separation of the two phases is achieved continuously in usually less than one a second. If required, additional extraction (or backextraction) units may be added. For applications of SISAK to transactinide elements new centrifuge units made from PEEK (PolyEtherEtherKetone) were developed [92]. This inert material allows to also perform extractions from HF solutions.

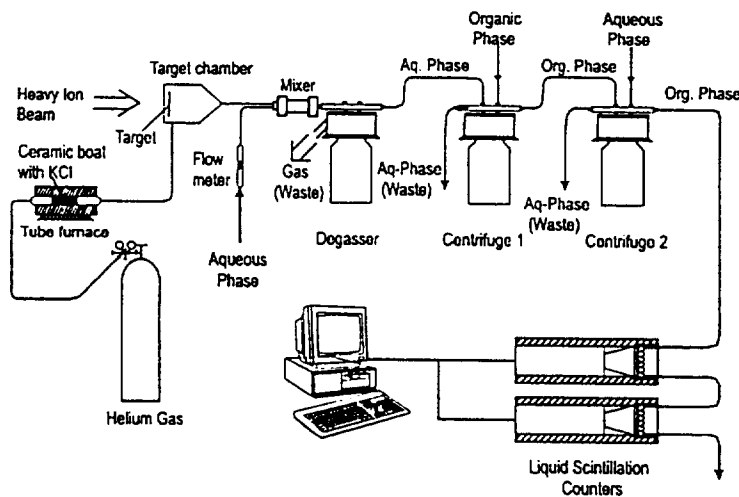


FIGURE 7

SISAK set-up as it was used in transactinide research (from Malmbeck, [106]).

A typical SISAK experimental set-up is depicted in Fig. 7. In order to apply SISAK to transactinide element studies the extraction device has to be coupled to a continuous flow detection system. To achieve this goal, liquid scintillation spectroscopy units were built [93] which allow to continuously measure  $\alpha$ - as well as spontaneous-fission events using the pulse shape discrimination technique (Fig. 8). Several such units are operated in series to increase the counting time interval. Measured  $\alpha$ -resolutions were about 300 keV [93]. In addition, the continuous flow can be stopped in case an  $\alpha$ -event from the decay of a mother nuclide is detected in one of the counting cells. During a preset waiting time, the system is then able to detect consecutive decay events from daughter nuclides.

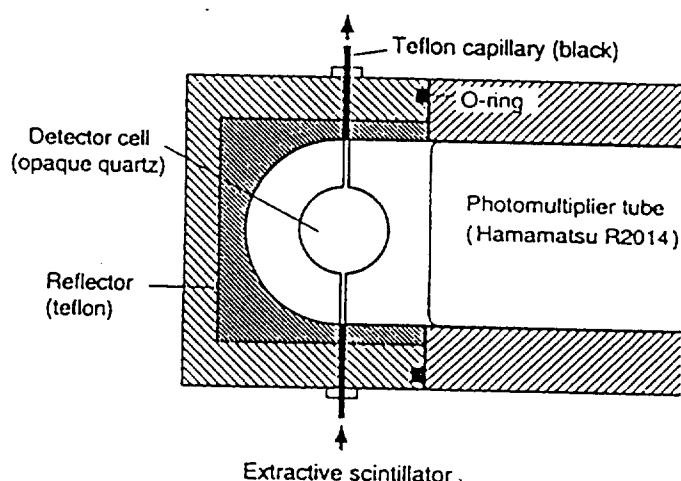


FIGURE 8

Detector for scintillation spectroscopy in organic solutions flowing through a spherical opaque quartz cell coupled to a photomultiplier (from Wierczinski et al. [93]).

For the investigation of transactinide elements various chemical separation schemes have been worked out [94]. Several successful on-line tests were performed with the corresponding homologous elements. Then experiments with Rf, Db and Sg [95-97] have been made. Unfortunately, these experiments failed of unambiguously identifying transactinide nuclides after chemical separation. The main limitation was the sensitivity which corresponded to several nanobarn. The main reason for this rather poor detection limit is a too high background count-rate in the  $\alpha$ -spectra from  $\beta$ -particles pile-up due to a non-perfect pulse-shape discrimination. Future effort will therefore be devoted to improvements of pulse shape analysis [98]. The entire separation technique in its " $\alpha$ -detection version" is very fast, as has recently been shown in the separation and detection of the 0.8 s  $\alpha$ -decaying nuclide  $^{224}\text{Pa}$  [97].

### Summary and outlook

After a first period of chemical studies of the transactinide elements Rf and Db ending about 1980, a period followed which was characterized by manifold attempts to search for superheavy elements with atomic numbers around 114. For these search experiments fast and partly continuous chemical separation techniques were developed which could - after minor adaptations - be used for improved chemical studies of transactinide elements.

Recent chemical studies used two different versions of on-line gas chemistry as well as three types of aqueous phase separation procedures. In gas phase this was thermochromatography and isothermal chromatography. The first technique has the advantage of being very fast in the production of the volatile species and the disadvantage of not being applicable to real time detection of separated species. With the second (OLGA or HEVI) technique on-line detection of separated species is possible.

In aqueous phase the three options are i) manual chemical separations, ii) on-line multi column separations and iii) automated separations using high performance liquid chromatography (ARCA). Even though not explicitly mentioned in this article, still several recent chemical studies of transactinide elements used manual chemical separations. Usually, the gas-jet was applied to transport and collect the products on a frit or an impactor foil which was then subjected to an analytical separation procedure. A recent example is first ever aqueous chemical study of dubnium [99].

The second, multicolumn technique has the advantage of being inexpensive and fast with separation times of several seconds. The shortcoming is certainly that only decay products of the element of interest are measured.

The third technique (ARCA) has the advantage to be coupled to a fast detection system but the disadvantages of being a discontinuous technique and relatively slow, with an overall separation time of about 30 s.

Future technical efforts will certainly focus on more efficient and even faster separation devices as well as improved detection systems. One should keep in mind that overall yields of the presently applied techniques are rather poor, a few percent only. The main reason is that still too many steps are needed to process a single atom from its „birth“ at the accelerator to its detection via its decay. It is therefore much required to reduce the number of processes involved in the chain from production to detection or to push the yields of each step to the ultimate limit of 100 %.

With the OLGA III technique the separation should be sufficiently fast for future studies of the two or possibly three elements above Sg. This may not be the case for ARCA where strong efforts are needed to reduce the overall separation time significantly below 30 s. It might be desirable to connect ARCA to a on-line detection cell. Such an attempt has indeed been made but failed [100]: the eluent passed in form of a thin ( $\approx 10 \mu\text{m}$ ) liquid film along the surface of a large ( $2700 \text{ mm}^2$ ) PIPS detector for continuous  $\alpha$ -counting. However, such large area silicon detectors turned out to be too wafy causing poor energy resolutions and inhomogeneous flow patterns.

Common to all automated techniques are their still relatively poor separation factors from  $\alpha$ -decaying contaminants which hamper the detection of the transactinide elements. Therefore, it was proposed [74] to couple a on-line physical (gas-filled magnetic) separator to a on-line chemistry device. Combining these two techniques decontamination factors unrivaled in magnitude could be achieved.

Whether the multicolumn technique is applicable to elements above Rf depends on the existence of appropriate daughter nuclides. As an example, studies with the presently known longest-lived isotope of seaborgium,  $^{266}\text{Sg}$  with  $T_{1/2} = 20 \text{ s}$ , are not possible since this nuclide decays to the short-lived spontaneously-fissioning nuclide  $^{262}\text{Rf}$ . However, application of this technique to the nuclides  $^{262}\text{Db}$  and  $^{265}\text{Sg}$  seems feasible, since they decay (at least partly) to the long-lived fermium isotopes  $^{254}\text{Fm}$  and  $^{253}\text{Fm}$ , respectively.

A special challenge will be the development of a chemical separation procedure for Hs, since this element presumably forms a very volatile tetroxide  $\text{HsO}_4$ . A cryogenic device named OSCAR (On-line Separation and Condensation Apparatus) has been constructed which is able to continuously condensate and detect volatile species on the surface of a silver disc cooled to liquid nitrogen temperature [101]. This device was very similar to a previous apparatus developed for on-line detection of short-lived radon isotopes [102] and gaseous superheavy nuclides [103]. Another approach for separation of Hs has been developed at Dubna using other reducing surfaces such as a thin layer of lead evaporated on top of a silicon detector. Such a detector proved to nearly quantitatively adsorb the homologous element Os, most likely in form of the dioxide [104]. A search for  $\alpha$ -decaying isotopes of Hs having half-lives longer than about 50 ms, which was the separation time of the technique, from the reaction  $123 \text{ MeV } ^{22}\text{Ne} + ^{249}\text{Cf}$  remained negative at a cross section limit of about 0.1 nb [105].

In a recent proposal [74] on-line detection of  $\text{HsO}_4$  in a thermochromatographic device was proposed where the walls of the column consist of silicon detector stripes covering a temperature gradient between room temperature and liquid nitrogen temperature.

Finally, ion trap techniques have been proposed for future chemical studies, coupled to a on-line separator for decontamination from beam particles and most of the reaction products [35].

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