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Gas Phase Chromatography of Halides of Elements 104 and 105

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GAS PHASE CHROMATOGRAPHY OF HALIDES OF ELEMENTS 104 AND 105

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GAS PHASE CHROMATOGRAPHY OF HALIDES OF ELEMENTS 104 AND 105

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Abstract

On-line isothermal gas phase chromatography was used to study halides of $^{261}104$ ($T_{1/2}$ = 65 s) and $^{262,263}105$ ($T_{1/2}$ = 34 s and 27 s) produced an atom-at-a time via the reactions $^{248}Cm(^{18}O, 5n)$ and $^{249}Bk(^{18}O, 5n,4n)$, respectively. Using HBr and HCl gas as halogenating agents, we were able to produce volatile bromides and chlorides of the above mentioned elements and study their behavior compared to their lighter homologs in Groups 4 or 5 of the periodic table. Element 104 formed more volatile bromides than its homolog Hf. In contrast, element 105 bromides were found to be less volatile than the bromides of the group 5 elements Nb and Ta. Both 104 and Hf chlorides were observed to be more volatile than their respective bromides.

Introduction

Recently, considerable interest has been shown in the study of the chemistry of the transactinide elements (atomic number > 103) by both experimental and theoretical chemists. At these very high atomic numbers the inner electrons are subjected to such large nuclear charges that they attain

relativistic velocities. These relativistic effects are also felt by the valence electrons to such an extent that the chemical properties may no longer be extrapolated from those of their lighter homologs in the periodic table. Recent extensive theoretical calculations[1-4] have provided chemists with predictions on how the relativistic rearrangements of valence electrons may affect the chemical properties of the heaviest elements and in which compounds these effects should become important. The practical investigation of the chemical properties of the transactinide elements, however, is extremely difficult. Currently, these elements can only be produced by heavy ion fusion reactions at accelerators at a rate of a few atoms per hour of beam time. In addition, even the longest-lived known isotopes of these elements have half-lives of only one minute or less, which further complicates chemical studies. Due to the low production rates and short half-lives very fast chemical procedures, which work continuously or can be performed with a high repetition rate, must be devised to study the chemistry of these elements. Studies of chemical properties have only been performed on elements through 105 so far.

Based on relativistic calculations[5,6] for element 103, KELLER[7] proposed that in the case of element 104 the ground state configuration should be $[Rn]5f^{14}7s^27p^2$ rather than $6d^27s^2$ analogous to the $[Xe]4f^{14}5d^26s^2$ configuration of its lighter homolog Hf. Therefore, he suggested that element 104 might behave like a heavy p-element similar to Pb. In recent accurate Multi-Configuration Dirac-Fock (MCDF) calculations using 468 jj-configurations, GLEBOV et al.[1] determined that the ground state of 104 should be a J = 2 level consisting primarily of the $6d7s^27p$ configuration (80%) with a level only 0.5 eV higher consisting of the $6d^27s^2$ configuration (95%), while the $7s^2p^2$ state is 2.9 eV above the ground state. They concluded that element 104 should show no distinctive p-character, but should behave like Hf, a typical d-element. Recent experimental evidence[8] indicates that element 104 does not exhibit p-element properties.

As early as 1966 ZVARA et al.[9] performed the first gas phase chemistry experiments with 104-halides. Their extensive studies have continued until today. By using thermochromatographic methods, they found[2] that element 104 forms chloride and bromide compounds noticeably more volatile than the corresponding compounds of Hf and Zr. Until the current study no other groups have attempted volatility studies of 104-halides. The results of all chemical studies (gas phase and aqueous) [Refs. 10, 11 for review articles] indicate that element 104 behaves like a group 4 element, thus supporting its assignment as the first transactinide element.

Element 105 is anticipated to be the heaviest group 5 element and, as such, may be expected to have a ground state configuration of $[Rn]5f^{14}6d^37s^2$. By analogy to calculations[7] for Lr, a probable ground state configuration could be $6d7s^27p^2$. However, recent calculations by JOHNSON and FRICKE[12] indicate that the ground state of element 105 is $6d^36s^2$ with the $6d^26s^27p$ configuration about 1 eV above the ground state. First experiments on the volatility of 105 halides have again been performed by ZVARA et al.[13,14] They concluded that element 105 is a homolog of Nb and

Ta. Its chloride appeared to be less volatile than $NbCl_5$ and more similar to $HfCl_4$. The bromide seemed to be less volatile than $NbBr_5$ and $HfBr_4$.[14]

In 1988 on-line isothermal gas chemistry experiments were performed[15] to study the volatility of 105 bromides in empty quartz columns, using $^{262,263}105$. In agreement with the work done in Dubna, the 105 bromides seemed to be less volatile than those of its lighter homolog Nb. However, these experiments were hampered by contaminating Po-activities and poor statistics.

In the current work, the same technique is used[15,16] to study the volatility of 104 and 105 bromides and chlorides and those of their homologs, Hf and Ta. Alpha particles and spontaneous fissions (SF's) from the decay of the isotopes $^{261}104$ and $^{262,263}105$ produced by the $^{248}Cm(^{18}O, 5n)$ and $^{249}Bk(^{18}O, 5n,4n)$ reactions, respectively, were detected directly at the exit of the chromatography system in order to identify those nuclides unambiguously.

Experimental Methods

The nuclides $^{261}104$ and $^{262,263}105$ were produced at the LBL 88-Inch Cyclotron by the $^{248}Cm(^{18}O, 5n)$ and the $^{249}Bk(^{18}O, 5n,4n)$ reactions, respectively. The targets, containing either 0.74 mg/cm^2 of ^{248}Cm in the form of Cm_2O_3 on 2.09 mg/cm^2 Be or 0.54 mg/cm^2 ^{249}Bk in the form of Bk_2O_3 on 2.49 mg/cm^2 Be, were prepared as 6-mm diameter deposits by stepwise electrodeposition of $Cm(NO_3)_3$ or $Bk(NO_3)_3$ from an isopropanol solution. Each deposited layer was converted to the oxide by heating to 500 °C for at least 20 min. The ^{249}Bk target was prepared on August 3rd and the experiments conducted between August 7th and 31st, 1990. Hence, only a small part of the 330-d ^{249}Bk had already decayed into ^{249}Cf. The calculated energies incident on the Cm and the Bk target were 94 MeV and 98 MeV, respectively. At these bombarding energies the nuclide $^{261}104$ is produced with a cross section[17] of about 5 nb and the nuclides $^{262,263}105$ are produced[18] with cross sections of 6 ± 3 nb and 2 ± 1 nb, respectively. $^{261}104$ has a half-life[17] of 65 s and decays[19] > 90% by α-emission and < 10% by SF. $^{262}105$ has a half-life[20] of 34 s and decays[18] 67% by α-emission and 33% by SF. $^{263}105$ has a half-life[18] of 27 s and decays 43% α-emission and 57% by SF. Hence, the total cross sections for α- and SF- decaying $^{262}105$ + $^{263}105$ amounted to about 4.9 nb and 3.1 nb, respectively. Typical ^{18}O beam currents for the experiments were 0.5 pμA.

Short-lived isotopes of the homologous elements Hf ($^{162-164}Hf$) and Ta ($^{164-167}Ta$) were produced by bombarding targets of ^{147}Sm (approx. 0.25 mg/cm^2 on 4.5 mg/cm^2 Be) and $^{nat.}Eu$ (approx. 0.25 mg/cm^2 on 4.5 mg/cm^2 Be) with beams of $^{20}Ne^{6+}$ ions. The targets were prepared in the same manner as described above. The incident beam energies were 120 MeV on the Sm target and 143 MeV on the Eu target, respectively. Actual beam currents were 0.1 pμA. Individual isotopes were detected by their characteristic γ-lines.

A schematic of the target arrangement is shown in Fig. 1. The beam, after being collimated by a water-cooled graphite ring, passed through a 1.8 mg/cm^2 HAVAR isolation foil, separating the target chamber from the vacuum of the beam transfer line, a volume of 0.2 mg/cm^2 nitrogen cooling gas and the Be target substrate before interacting with the target material. The reaction products recoiling out of the target material were stopped in a volume of He loaded with KCl aerosols and transported through a polyethylene capillary of 2-mm i.d. and about 10-m length to the chromatography apparatus at a He flow rate of about 1.5 - 2 l/min. The pressure in the recoil chamber was about 1.3 bar.

A schematic of the **On-Line Gas** chromatography **Apparatus** (OLGA II)[21], which is similar to a previously used set up is shown in Fig. 2. The apparatus consisted of a quartz column (50-cm in length, 6-mm i.d.) with a narrow exit tip (6-cm in length, 1-mm i.d.) situated inside an oven with 5 individually controlled heating sections. Reaction products transported on KCl aerosols were stopped on a quartz wool plug (length about 5-mm) inserted into the column. Section I of the oven at the position of the quartz wool plug was kept at a fixed temperature of 900 °C. Sections II-V which heat the isothermal chromatography section (length 25 cm) and the exit tip of the column were kept at the same temperature for a given experiment. In different experiments this temperature was varied between 100 °C and 800 °C. Due to the high temperature in the first section of the column the isothermal length decreased from about 20 cm (excluding the exit tip) at $T_{isothermal}$ = 700 °C to only about 6 cm at 100 °C. At the position of the quartz wool plug, $HBr_{(g)}$ or $HCl_{(g)}$ were added as reactive agents at a flow rate of 100 ml/min.[21] In some of the experiments, BBr_3 was also added by passing the HBr gas over liquid BBr_3 kept at 0 °C. Volatile bromide or chloride species formed at the position of the quartz wool plug were then transported along the cooler chromatography section of the column, thus undergoing sorption/desorption steps, with retention times indicative of their volatility at the temperature of the isothermal part of the column. Volatile products leave the column through the tip, whereas, due to their longer retention time, nonvolatile species undergo radioactive decay in the chromatography section. Reaction products leaving the chromatography column were thermalized in the recluster chamber (7-cm i.d., 31-cm length) which was flushed with another N_2/KCl or Ar/KCl aerosol gas jet at a rate of 2 l/min.

The separated products, reattached to aerosol particles, were transported along a second capillary (2-mm i.d., 5-m length) to the MG (**M**erry-**G**o-round) rotating wheel system[22] in experiments with element 104, or to the moving tape system,[21] in experiments with element 105. In the MG system, the aerosols carrying the separated activities were deposited on thin polypropylene foils (30-40 μg/cm^2) placed around the periphery of an 80 position wheel. Every minute, the wheel was stepped to move the collected activity successively into place between pairs of PIPS (**P**assivated **I**mplanted **P**lanar **S**ilicon) detectors. This new detector type is chemically inert and offers superior resolution. Six pairs of PIPS detectors registered alpha particles and SF decay. The

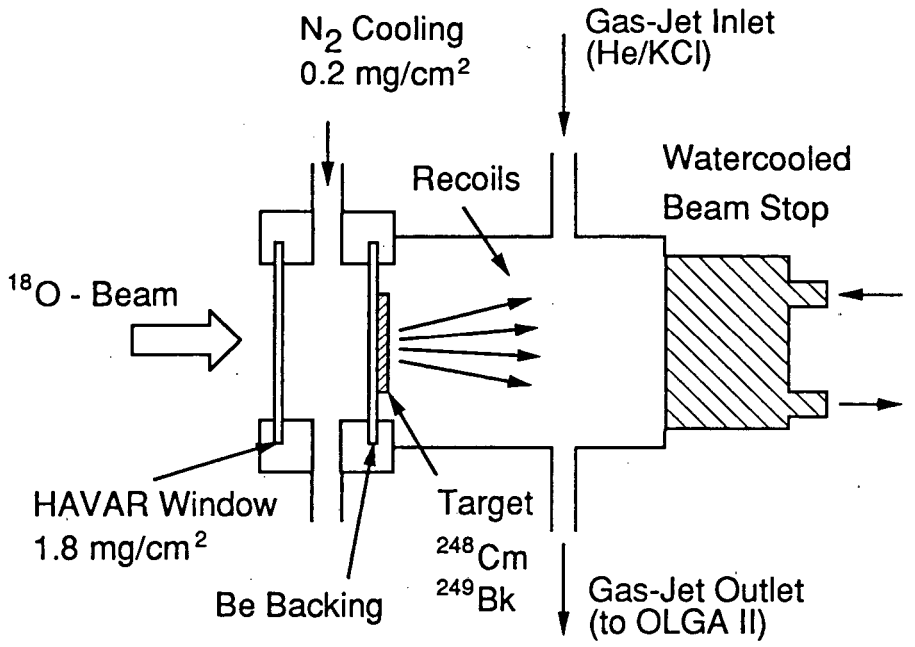

Fig 1. Schematic diagram of the target arrangement. The HAVAR window separates the target system from the accelerator vacuum. The window and the Be target backing are cooled by a stream of N_2. Recoiling reaction products are attached to KCl aerosols and transported in a He stream to the chromatography system OLGA.

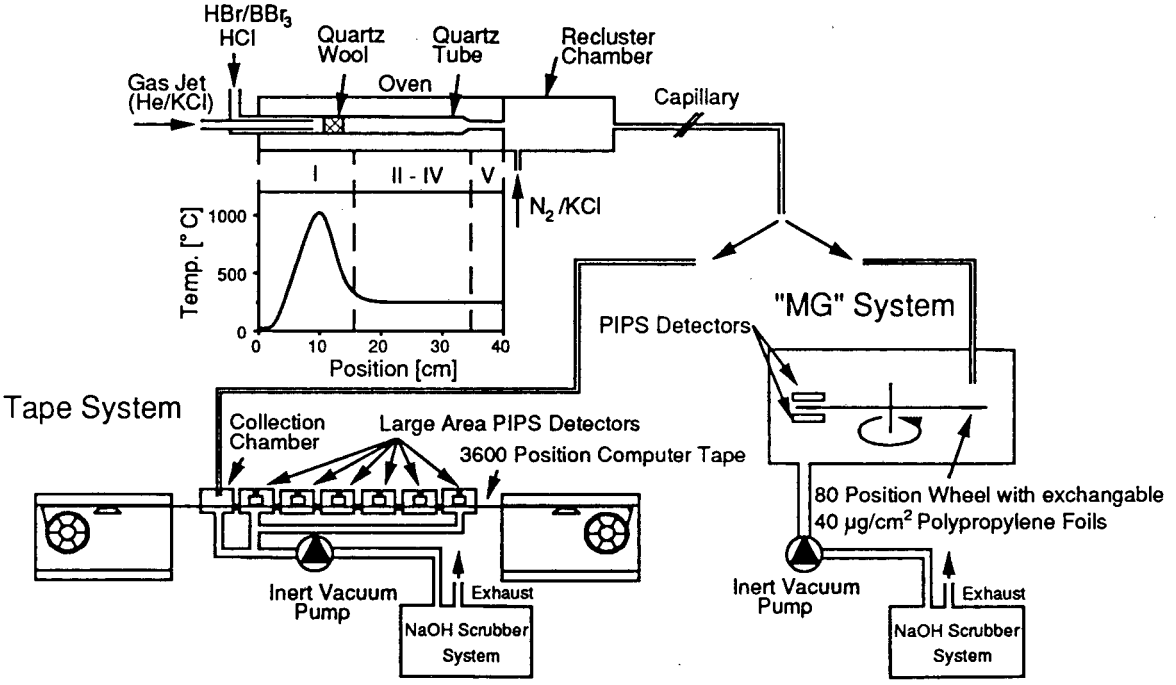

Fig 2. Schematic of OLGA II in combination with the MG-system (for details, see text) used to study volatile 104 halides or in combination with the tape system (for details, see text) used to study volatile 105 bromides.

data were stored on magnetic tape in an event-by-event mode with the MG-RAGS system.[23] Each wheel was replaced after two revolutions. The MG chamber was pumped with an inert vacuum pump; the pump exhaust gases, still containing the reactive agents HBr or HCl, were neutralized in a NaOH scrubber system. The MG wheel system allowed the registration of alpha events from both sides of the deposited spot together with the detection of single and coincident SF events with a detector efficiency of 60%.

To prevent interference from long-lived SF activities in the detection of SF's from $^{262,263}105$, the tape system was developed.[21] The activity was deposited at the collection site on a regular computer tape, and then subsequently stepped in front of 6 large area PIPS detectors. One tape allowed the collection of about 3000 samples, free from activities deposited from previous runs. The detector efficiency was 38% for alpha-particles and 76% for SF's. All alpha- and SF events were recorded and analyzed in an event-by-event mode using the PSI TANDEM data acquisition system.[24] For on-line display the CERN PAW software[25] package was used. Again the system was pumped with an inert vacuum pump and the exhaust gases were neutralized in the scrubber system.

Results and Discussion

Volatility Studies of Hf and 104 Halides

The yield in our studies is defined as the ratio between the activity measured after the chromatography apparatus and the activity measured at the end of the transportation capillary without chromatography. The absolute value of the maximum yield is dependent on the half-life of the nuclide. This can be explained by the time needed for the molecules in the recluster unit to re-attach on new KCl particles before being transported to the detector. This time was estimated to be about 25 s. The maximum yields measured for long-lived nuclides ($T_{1/2} >> 1$ min) were about 60%. Maximum average yields for ^{162}Hf bromides and chlorides were 37.5±2.4% (measurements at 600 °C - 700 °C) and 30.1±1.5% (measurements at 100 °C - 600°C), respectively. No yield could be measured for $^{261}104$ bromides and chlorides since we were unable to identify the alpha lines of this isotope without chemical separation. In order to allow a comparison of the volatility of the group 4 elements, the maximum average yield for each element measured at high temperatures was taken as 100% in order to normalize the data, and obtain relative chemical yields. In Figs. 3 and 4, the relative chemical yields of 41-s ^{162}Hf and 65-s $^{261}104$ bromides and chlorides are shown as a function of the temperature in the isothermal part of the oven.

The relative chemical yield of Hf-bromides dropped to about 60% in the temperature range from 600 °C to 550 °C, remained fairly constant in the range from 550 °C to 400 °C and then

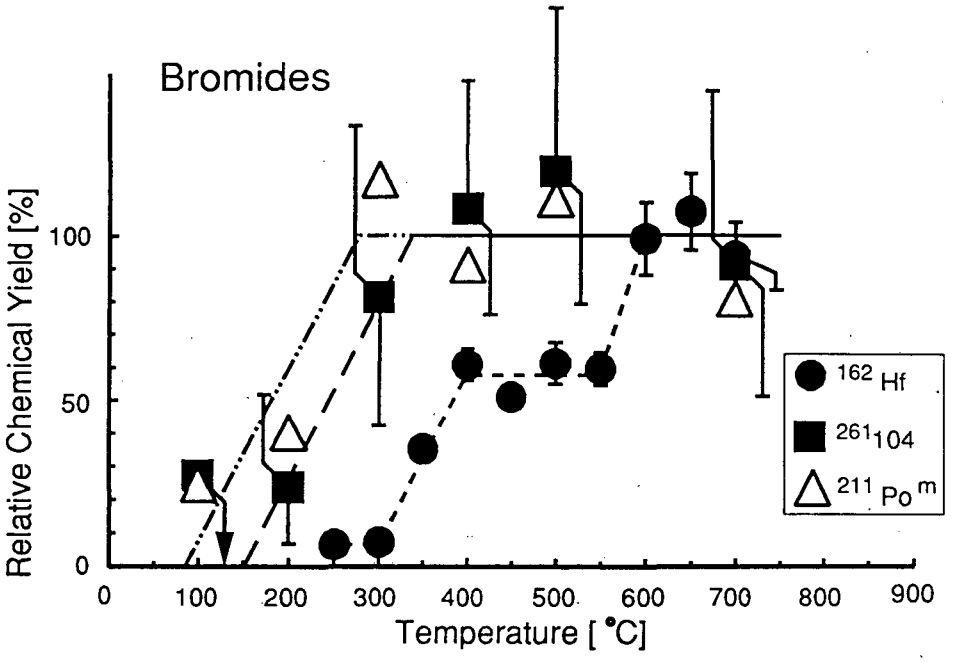

Fig. 3. Relative chemical yields of bromides of 41-s ^{162}Hf (●), 65-s $^{261}104$ (■) and 25.5-s $^{211}Po^{m}$ (Δ) as a function of the temperature in the isothermal part of the oven.

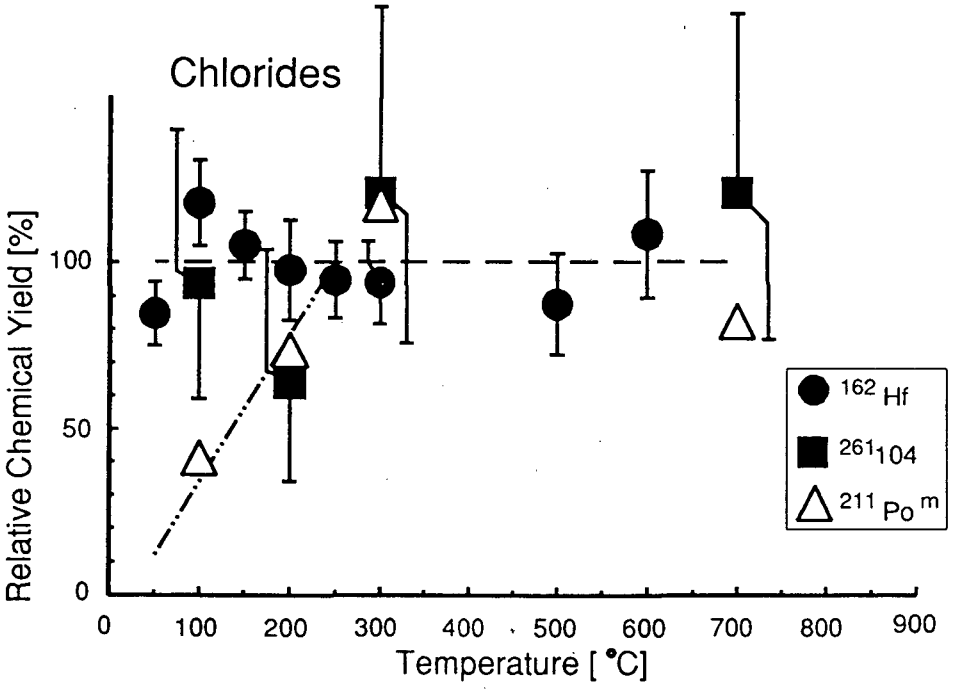

Fig. 4. Relative chemical yields of chlorides of 41-s ^{162}Hf (●), 65-s $^{261}104$ (■) and 25.5-s $^{211}Po^{m}$ (Δ) as a function of the temperature in the isothermal part of the oven.

dropped to a level of a few percent at 300 °C. The presence of two regions of sharply decreasing yield measured for Hf bromides may be due to two different species with different volatilities. A possible explanation might be the formation of oxybromides. In a thermochromatographic study, DOMANOV et al.[26] investigated the influence of O_2 (10^{-8} to 50 vol. %) on the deposition temperature of Hf chlorides. They found deposition positions at 100 °C and 150 °C and concluded that two species were formed, namely $HfCl_4$ and $HfOCl_2$. However, $HfOCl_2$ seemed to be unstable at temperatures above 450 °C. In our experiments we had no way to determine the chemical form of the volatile species. The formation of less volatile $HfOBr_2$, for instance, cannot be excluded.

The yield of 104-bromides was determined with the MG-RAGS system at temperatures of 700 °C, 500 °C, 400 °C, 300 °C, 200 °C, and 100 °C in the isothermal part of the oven. The chemical yield remained stable at temperatures above 300 °C. The yield dropped at 200 °C and at 100 °C no events were detected. The error bars shown on the $^{261}104$ data points reflect only the statistical uncertainties arising from the number of the detected events. Even though the errors associated with the 104-bromide data points are large, it appears that 104-bromides are more volatile by about 100 °C than their Hf-bromide homologs. The alpha-particle spectra revealed that the major activities were due to Fr and Po isotopes originating from traces of Au and Pb impurities in the target. The chromatographic behavior of Po is shown in Figs. 3 and 4. Unfortunately, the isotope $^{211}Po^m$ ($T_{1/2}$= 25.5 s) has a weak alpha-line at 8.305 MeV (0.25%) which interfered with the alpha-lines of $^{261}104$ and its daughter ^{257}No, which were expected in the region from 8.15 to 8.40 MeV. We detected a total of 53 events in this region. Based on the observed count rate for the main group of $^{211}Po^m$ (7.275 MeV, 91.05%), $12.8^{+4.6}_{-3.6}$ events out of 53 were attributed to $^{211}Po^m$. The activity of $^{261}104$ was determined with a two-component decay curve analysis[27] with the components $^{211}Po^m$ ($T_{1/2}$= 25.5 s) and $^{261}104$ ($T_{1/2}$= 65 s). The initial activity of $^{211}Po^m$ was fixed at the value derived from the main alpha-line of this nuclide, whereas the initial activity of $^{261}104$ was allowed to vary. Since ^{257}No, the daughter of $^{261}104$, has a relatively short half-life of 26 s,[28] a number of mother-daughter correlations should be detected. A total of 8 correlated pairs have been observed, compared to an expected number of 9 to 11 correlated pairs. A daughter half-life of 24^{+13}_{-6} s was derived, in agreement with the literature value.[28]

No drop in yield was observed down to temperatures of 50°C in the isothermal column for $HfCl_4$ indicating that the chlorides of Hf are more volatile than the bromides. Higher deposition temperatures for $HfCl_4$ in thermochromatographic experiments have been observed.[26,29] It can be shown that the deposition temperature determined in thermochromatographic experiments[30] should be nearly the same as the temperature where the relative yield drops to 50% in on-line isothermal chromatography.[31] Due to the high temperature in the first section of the column the isothermal length at 50 °C is much shorter than at higher temperatures, which may account for the observed differences.

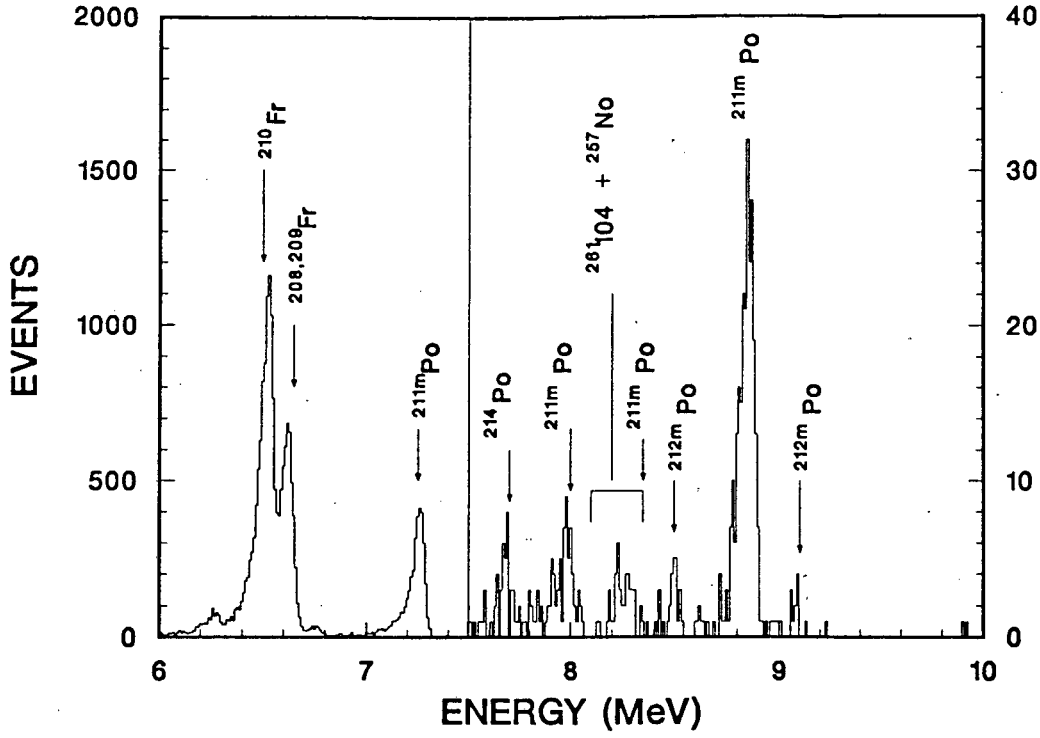

Fig. 5. Sum of the measured alpha spectra from all 104 chloride chemistry runs (100 °C - 700 °C).

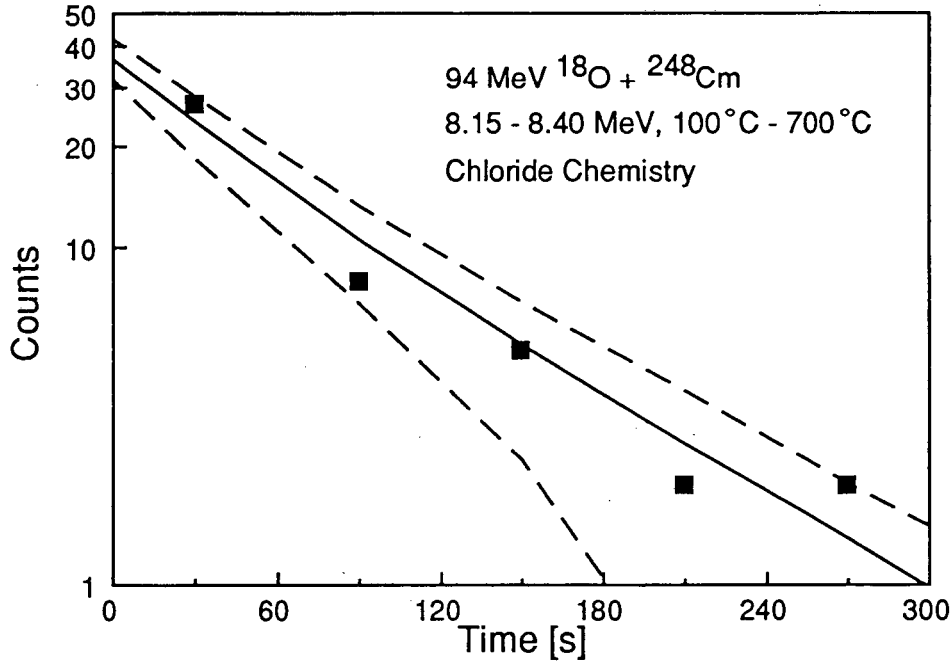

Fig. 6. Decay curve of the alpha events in the region 8.15 - 8.40 MeV. The numbers of events in each detector are indicated by (■). The center curve is the most probable fit to the data assuming a two component decay curve with the components $^{211}Po^{m}$ ($T_{1/2}$ = 25.5 s) and $^{261}104$ ($T_{1/2}$ = 65 s). The initial activity of the $^{211}Po^{m}$ component was fixed at a value derived from the main alpha group of this nuclide at 7.275 MeV, whereas the initial activity of the $^{261}104$ component was allowed to vary. The upper and lower dashed curves encompass 68% of the probability in a Poisson distribution centered on the number of counts in the most probable fit.

The yield of 104-chlorides was measured at temperatures of 700 °C, 300 °C, 200 °C, and 100 °C in the isothermal part of the oven. The yield of 104-chlorides remained high down to a temperature of only 100 °C, which leads to the conclusion that 104-chlorides appear to be more volatile than 104-bromides. The yield of Po-isotopes showed the same behavior as in the bromide experiments. It was, therefore, possible to chemically separate 104-chlorides from Po if the isothermal section was kept at 100 °C. In Fig. 5 the measured alpha spectrum for the sum of all chloride chemistry experiments (sum of top detectors 1 through 5) is shown. The assignments of the main alpha-lines are given. As in the experiments for the bromide system, the major activities were due to Fr and Po isotopes originating from trace Au and Pb impurities in the target. A total of 44 events was detected in the region from 8.15 - 8.40 MeV. Based on the observed count rate for the main group of $^{211}Po^{m}$ (7.275 MeV, 91.05%), $7.7^{+3.8}_{-2.8}$ events out of 44 in the 8.15 - 8.40 MeV region were expected to originate from $^{211}Po^{m}$. The decay curve for the alpha events in the region from 8.15 MeV to 8.40 MeV is shown in Fig. 6. A total of 6 correlated pairs has been observed, compared to an expected number of about 5 correlated pairs. A daughter half-life of 29^{+20}_{-8} s was derived in agreement with the literature value.[28]

ZHUIKOV et al.[2] have performed relativistic SCF-Xα scattering wave Dirac-Slater computations for $104Cl_4$ molecules and their homologs and predict a slight increase in the population of $s_{1/2}$ -orbitals due to their relativistic stabilization in 104 relative to Zr and Hf. This results in a lower effective charge of the 104 atom and a more covalent bonding in the $104Cl_4$ molecules, which may explain the high volatility of this compound.

Volatility Studies of Group 5 Bromides

In Fig. 7 the relative chemical yields of $^{99}Nb^{g}$ (data from Ref. 16), ^{166}Ta, and $^{262,263}105$ bromides are shown as a function of the temperature in the isothermal part of the oven. Initially 100 ml/min of HBr(g) were added as halogenating agent, but contrary to the case of Nb and 105, volatile Ta species were only formed when the $HBr_{(g)}$ was saturated with the stronger brominating agent BBr_3. The average yield of Nb and Ta bromides remained constant down to a temperature of 300 °C. Below 250 °C the yield of Nb and Ta bromides rapidly dropped to a few percent at 100 °C. The volatility of Ta and Nb bromides turned out to be very similar.

In the volatility studies of 105-bromides alpha particles and SF events were detected with the moving tape system (see Fig. 2). Unfortunately, large amounts of Po activities originating from trace Pb impurities in the target were formed. The activities of 45-s $^{212}Po^{m2}$ (8.524 MeV 2.05%) obscured the alpha activities from $^{262}105$ and its daughter ^{258}Lr in the range of 8.40 - 8.65 MeV. However, in direct catch experiments a short-lived SF activity of 26^{+8}_{-6} s was detected,

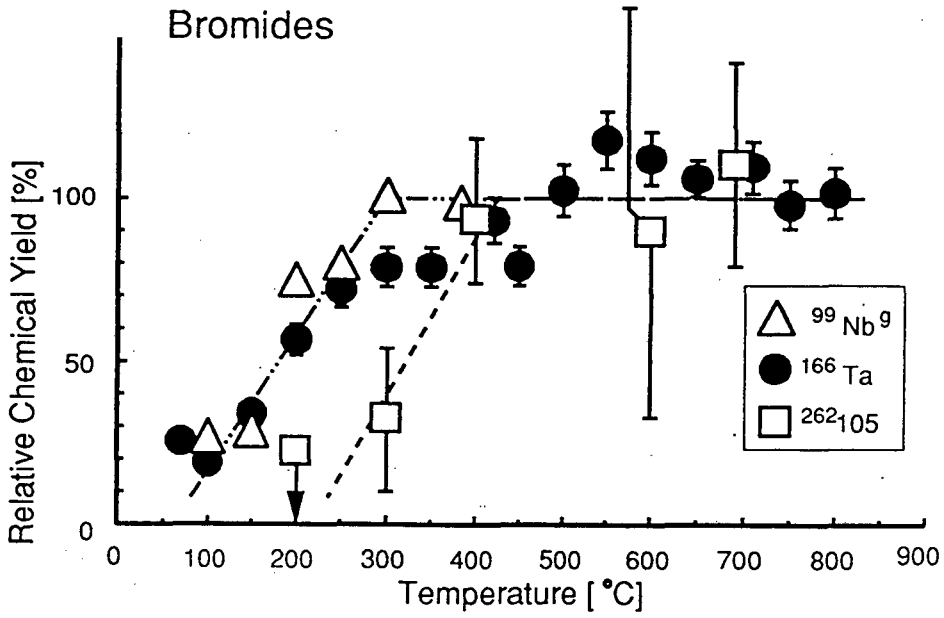

Fig. 7. Relative chemical yields of bromides of 15-s $^{99}Nb^{g}$ (Δ), 32-s ^{166}Ta (●) and 34-s and 27-s $^{262,263}105$ (❑) as a function of the temperature in the isothermal part of the oven.

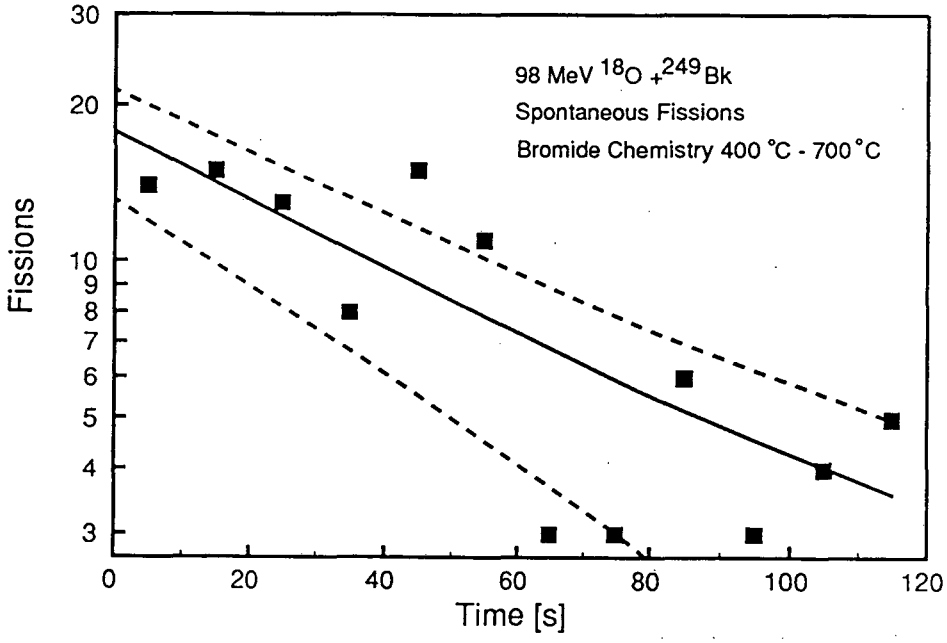

Fig. 8. Decay curve analysis of the SF activity measured with the magnetic tape system in bromide chemistry experiments at 400 °C - 700 °C. The number of decays in intervals of 10 s are indicated by (■). The center curve is the most probable fit to the data assuming a short-lived SF activity and the long-lived contaminant ^{256}Fm (^{256}Md). The initial activities of the short-lived activity, the ^{256}Fm (^{256}Md) component, and the half-life of the short-lived component were allowed to vary. The upper and lower dashed curves are the limits which encompass 68% of the probability in a Poisson distribution centered on the number of counts in the most probable fit.

which was attributed to the SF decay of $^{262}105$ and $^{263}105$. A longer-lived component attributed to the growth of ^{256}Fm from the decay of ^{256}Md was also identified. The yield of the short-lived SF activity was measured at temperatures of 700 °C, 600 °C, 400 °C , 300 °C, and 200 °C in the isothermal part of the chromatography oven. The decay-curve analysis of the sum of the SF's from all the chemistry experiments at temperatures from 400 °C through 700 °C is shown in Fig. 8. A short-lived SF activity with a half-life of 44^{+19}_{-12} s was identified compared to the 26^{+8}_{-6} s half-life of the direct-catch experiment, the 34-s literature value[20] for $^{262}105$ and the 27-s half-life[18] of $^{263}105$.

The relative chemical yields of 105-bromides are shown in Fig. 7. The yield of 105 bromides was determined relative to that of $^{212}Po^{m2}$, which remains constant down to about 300 °C. Fluctuations in the gas-jet transportation yield were thus accounted for. The yield of 105 bromides remains constant down to a temperature of 400 °C and then drops significantly at 300 °C. At 200 °C only an upper limit could be established. The error bars show only statistical errors based on the number of observed events. Even though the errors associated with the 105 bromide data points are large, it is obvious that 105 bromides are less volatile than their Ta and Nb homologs by about 100 °C. The volatility of group 5 bromides increases in the order 105 < Ta ≈ Nb, in contrast to the Group 4 bromides where the volatility is reversed, Hf < 104.

Conclusions

We have positively identified element 104 in a gas phase chemistry experiment by measuring the alpha decay energies and the half-life of $^{261}104$. In our experiments we did not determine the chemical form of the volatile species, but indications are that we observed the species $104Br_4$ and $104Cl_4$. Our gas phase chemistry apparatus was shown to continuously separate volatile chlorides and bromides of elements which are produced only at an atom-at-a-time level in times as short as about 30 s. We determined a higher volatility for 104-bromides than for their lighter Hf homologs and found a surprisingly high volatility for 104-chlorides. These results agree qualitatively with results discussed recently by ZHUIKOV et al..[2] The high volatility of 104-halides is rather surprising and has been interpreted[2] to be due to a relativistic stabilization effect. The high volatility of 104-halides would, therefore, represent an experimental indication of "relativistic chemistry", which has been predicted theoretically for some time. A comparison of our data with the work of ZVARA et al.[2,9,13,14] has to consider the fact that the inside of our quartz columns were covered with visible amounts of KCl after each experiment. It is therefore likely, that our chromatography took place on a KCl surface and not on a pure SiO_2 surface as in ZVARA's work.

105-bromides were identified in gas phase chemistry experiments by detecting SF's and determining the half-life of $^{262,263}105$. The 105-bromides turned out to be less volatile than their

lighter homologs Nb and Ta. This is in contrast to calculations by PERSHINA et al.,[4] which predict that the volatility of pure $105Br_5$ should be higher or close to that of Nb and Ta bromides. Since in our experiments the chemical structure of the molecules passing through the column was not determined, the formation of oxybromides or tribromides, both of which would be expected to have a lower volatility than the pentabromide, cannot be ruled out.

The 104-bromides appear to be volatile at a temperature nearly 100 °C lower than the 105-bromides, in contrast to the Hf-bromides which only become volatile at temperatures some 150 °C higher than do the Ta-bromides. Thus the trend towards higher volatilities for group 5 relative to group 4 elements seems to be reversed.

Because of the poor statistics in the experiments with 104 and 105 halides, the results should be regarded as preliminary. Further experiments must be performed to gain a clear understanding of the volatilities of the various compounds and their chemical compositions.

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