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## THERMOCHROMATOGRAPHY OF BROMIDES

### A PROPOSED TECHNIQUE FOR THE STUDY OF TRANSACTINIDE ELEMENT CHEMISTRY

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#### SUMMARY

Our interest in elements 105, eka-tantalum, and 104, eka-hafnium, led us to study the thermal chromatographic behavior of gamma-emitting isotopes of Hf, Nb and Ta produced by bombarding suitable targets with heavy ions at the Oak Ridge Isochronous Cyclotron. Atoms recoiling from the target were collected, chemically processed, and separated on-line with gaseous bromide systems. A mixture of bromine and boron tribromide was shown to be effective as the brominating agent. The separation of the metallic bromides produced was carried out in open tubular columns made of nickel or glass. A possible technique is outlined for the detection of alpha-emitting isotopes, which are of great importance in the transactinide region. Nickel was found to be sufficiently chemically resistant to the brominating atmosphere to be useful as the material for the chamber and target backing.

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#### INTRODUCTION

Workers at Dubna, including one of us (I.Z.), have developed chromatographic and thermochromatographic methods for separating short-lived transactinide nuclides using volatile chlorides<sup>1-4</sup>. The isotopes employed, whose half-lives were of the order of seconds, were detected by their decay through spontaneous fission. The activities were produced using thin targets in a heavy-ion cyclotron. The atoms recoiling from the target were collected in a flowing gas and then mixed with a chlorinating agent downstream. In this system, passage of the elemental activities through a thermochromatographic column produced distinct adsorption zones that could be correlated with metallic chloride volatilities. This correlation makes it possible to estimate the properties of chlorides of new elements from their adsorption peak positions.

Recent physico-chemical data on bromides of heavy transition elements suggests that bromides of transition elements might behave suitably for one-atom-at-a-time investigations. Furthermore, a bromide system might give higher chemical

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yields and might be more easily adaptable to the detection of alpha-emitting isotopes than the more corrosive chloride systems. Our principal aim was to develop a technique for the separation and study of element 105, eka-tantalum<sup>5</sup>.

## EXPERIMENTAL

### *Bromination and thermochromatography of Zr, Nb and Ta tracers*

Preliminary experiments using Zr, Nb and Ta tracers were carried out first in the laboratory in an attempt to gain experience for cyclotron runs. Carrier-free <sup>95</sup>Zr + <sup>95</sup>Nb tracer was employed as the oxalate solution. The tracer was adsorbed onto activated charcoal and heated to 350° in air. The sample was then heated to 800° and helium gas (20 ml/min) carrying bromine at a partial pressure of about 200 mm of Hg was passed over it and then into a thermochromatographic column having a gradient from 500° to ambient. The results (Fig. 1) show a clear separation of Nb and Zr with the former peak below 300°. The column could be either glass or nickel.

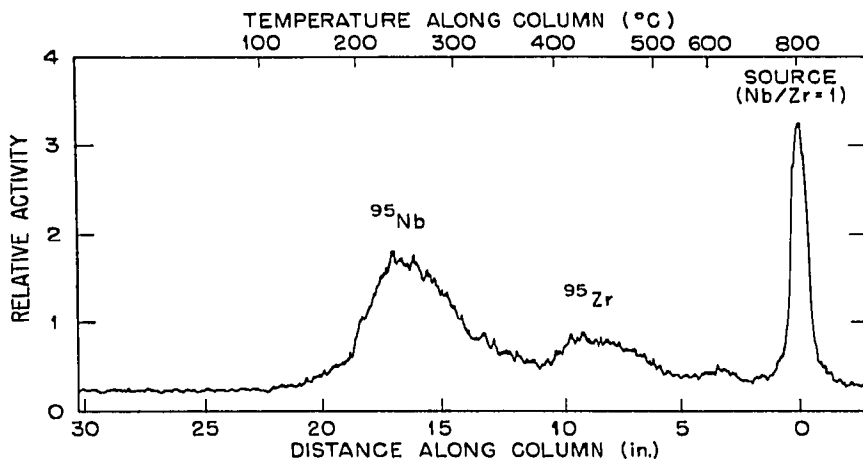


Fig. 1. Distribution of <sup>95</sup>Nb and <sup>95</sup>Zr activity along a 1/8 in. I.D. quartz thermochromatographic column. Initial sample contained equal activity levels of these isotopes.

The high reaction temperature of 800° is apparently specific for the bromination of oxides in the presence of charcoal. It is known, for example, that the reaction of Nb and Ta metals with bromine<sup>6</sup> is rapid at temperatures as low as 250°. For this reason, we believed that recoils stopped in bromine vapors might be brominated at comparable temperatures. We found that the corrosion resistivity of nickel towards flowing bromine vapors at a partial pressure of 200 mm of Hg is good up to 350°; the corrosion rate is 0.25 mg/cm<sup>2</sup>·h at 400° and increases rapidly with still higher temperatures. From these data, we hoped that, with the target chamber made of nickel, it might be possible to introduce bromine vapors below 350° directly into the volume behind the target. This is, in principle, a very good way to achieve high chemical yields, for, when the reactive species are introduced downstream as with the

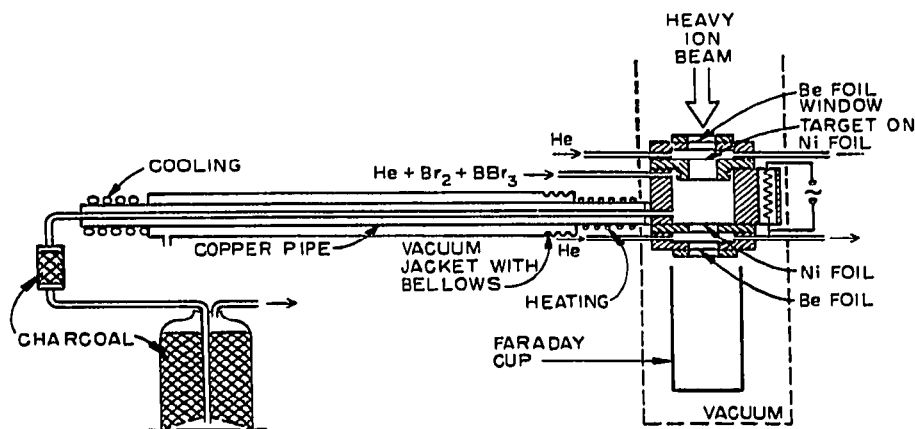


Fig. 2. Schematic diagram of the apparatus for continuous bromide processing of recoils from the cyclotron bombarded target.

chloride system, a large fraction of thermalized recoil atoms are lost when they strike the walls of the target chamber and are irreversibly adsorbed.

#### *Apparatus for on-line experiments*

Targets were made by electroplating about  $0.5 \text{ mg/cm}^2$  of various rare earth oxides onto  $0.00035\text{-in.}$  nickel foils. The energy of the heavy-ion beam was adjusted to the necessary value by passing it through a beryllium window (Fig. 2) and through the nickel backing of the target. Through the small space between the two foils, helium gas was flowed in order to remove heat from the beam. The target material,  $1/4 \text{ in.}$  in diameter, faced a small chamber ( $3/4 \times 3/4 \text{ in. I.D.}$ ) in which the recoil atoms were stopped. The chamber was made of nickel and was heated electrically by an independent nichrome wire. At the other end of the reaction chamber, there was another nickel and beryllium foil, to let the beam pass into a Faraday cup. The recoils stopped in the chamber were swept by the gas into a  $1/8 \text{ in. I.D.}$  open tubular column made of Pyrex, quartz or nickel. A linear temperature gradient was established over the column through heating and cooling the opposite ends of a vacuum jacketed copper pipe.

Helium gas was passed through a bed of Drierite and divided into two separate streams. Each of the streams was equipped with a metering valve and flowmeter. The total flow-rate was maintained at  $500 \text{ ml/min}$  (standard temperature and pressure). One fraction of the gas was bubbled at  $20^\circ$  through a liquid mixture of bromine and boron tribromide. The relative concentrations were adjusted so as to ensure the required ratio of partial pressures in the outgoing gas. The second was dried with anhydrous and used to dilute the first stream when a bromine vapor pressure well below  $200 \text{ mm Hg}$  was needed.

At the exit of the column, the carrier gas was passed through a  $30\text{-ml}$  charcoal-filled trap. This efficiently removed the most volatile carrier-free bromides from the gas even after having been saturated with bromine. The brominating agents were finally trapped in another larger charcoal filter. Both charcoal beds were ambient temperature. The flow-rate of the clean exit gas was continuously measured to check the material balance through the system.

### Bombardments and measurements

Bombardments with  $^{12}\text{C}$  and  $^{11}\text{B}$  beams were performed at the Oak Ridge Isochronous Cyclotron. The beam current was typically 0.5 electrical  $\mu\text{A}$  of fully stripped ions. The Se, As, Ge and Zn activities detected in our experiments originated from the nickel backing of the target. The isotope  $^{90}\text{Nb}$  was produced through the interaction of  $^{12}\text{C}$  ions with bromine vapors in the target chamber. Targets of  $^{162}\text{Dy}$  (enriched) + Ho and Ho +  $^{170}\text{Er}$  (enriched) bombarded with  $^{12}\text{C}$  and  $^{11}\text{B}$ , respectively, were utilized to produce simultaneously isotopes of Hf and Ta. After terminating a (2- to 10-h) run, the distribution of activities over the thermochromatographic column was measured with a 30-cm<sup>3</sup> Ge(Li) gamma-ray detector coupled to a 2000-channel analyzer. Successive sections of the tube were measured through a 2-in. wide slit in the 2-in. thick lead shield of the detector. The walls of the target chamber were thoroughly washed with methanol to look for the percentage of activity retained in the chamber.

### RESULTS AND DISCUSSION

The first experiments with the on-line equipment were performed using pure helium as the carrier gas and a quartz column. There was no rare-earth target. The temperature of the target chamber was 300° and the hot end of the column was 350°.

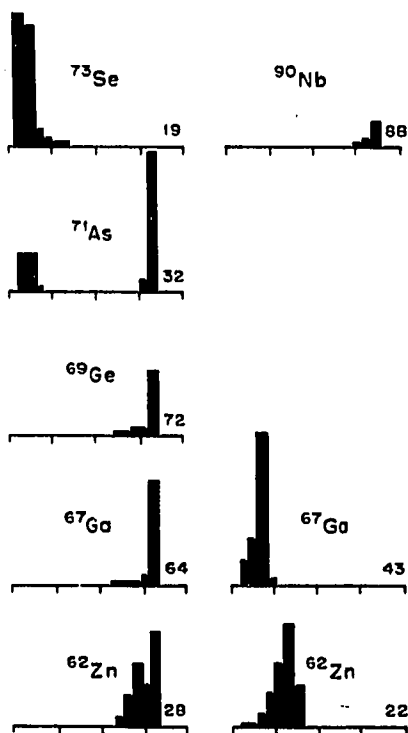


Fig. 3. Distribution of various cyclotron-produced activities processed with pure helium (left) and with helium-bromine (200 mm Hg) mixture (right). The percentage of the activity found in the target chamber is indicated by figures.

Fig. 3 shows the distribution of various activities along the column. It will be seen that about 90% of the  $^{73}\text{Se}$  is deposited on the column below  $150^\circ$ . About 10% of this activity was found in the target chamber; these atoms were probably entrained and trapped in a very thin layer of impurities that could be seen on the walls. A small fraction of  $^{71}\text{As}$  was found in the same position as was most of the  $^{73}\text{Se}$ . We believe that this portion of the  $^{71}\text{As}$  came from the decay of the volatile parent  $^{71}\text{Se}$ , rather than from some volatile arsenic species. The rest of the arsenic was found in the target chamber or within the first few inches of the hot end of the column. This behavior is typical for activities that do not form volatile compounds under the conditions of the experiment (*cf.* the distribution of Ge and Ga in Fig. 3).

Zinc seems to be moderately volatile at  $350^\circ$ . The comparison of its distribution with those of Ga, Ge, As and Se shows that the behavior of zinc does not reflect the volatility properties of any of the possible higher-Z parents.

From the above experiment, the order of the 4th period elements studied, according to their "microscopic" volatility, is  $\text{Se} > \text{Zn} > \text{As}, \text{Ga}, \text{Ge}$ . This is in accord with the sequence  $\text{Te} > \text{Zn} > \text{As} > \text{Ga} > \text{Ge}$  observed by Eichler<sup>7</sup> in thermochromatographic separations using a reducing atmosphere of hydrogen as the carrier gas. This order correlates with the values of enthalpy of sublimation for monoatomic elements.

Next we used bromine as the carrier gas. The partial pressure was about 200 mm Hg. The elements from Zn to Se formed volatile bromides under these conditions. Ge, As and Se went to the cold end of the column and into the trap at the end. Ga and Zn positioned themselves within the column (Fig. 3). The ordering of the adsorption positions ( $\text{Ge} > \text{As}, \text{Se} > \text{Ga} > \text{Zn}$ ) is consistent with the volatilities of the bromides (Table I). The same results were obtained when the chamber temperature was reduced to  $200^\circ$ . Nickel and Pyrex tubing gave the same results as quartz for the column.

Unfortunately, Nb was non-volatile only under the conditions of bromine as the carrier gas (Fig. 3). This is probably due to the formation of oxycompounds, which are preferred thermochemically over bromides<sup>9</sup>. Recently, Lapport *et al.*<sup>10,11</sup> investigated the reactions of  $\text{BBr}_3$  with a number of oxides, including most of the elements involved in our work, and showed that bromides are easily obtained in all

TABLE I  
BOILING POINTS OF THE BROMIDES STUDIED

Compound	Boiling point ( $^\circ\text{C}$ )	Melting point ( $^\circ\text{C}$ )
$\text{YBr}_3$	1470	
$\text{ZnBr}_2$	702	
$\text{Ga}_2\text{Br}_6$	280	
$\text{NbBr}_5$	356	
$\text{TaBr}_5$	344	
$\text{ZrBr}_4$	360 subl.	450
$\text{HfBr}_4$	323 subl.	425
$\text{Se}_2\text{Br}_2$	227	
$\text{AsBr}_3$	221	
$\text{GeBr}_4$	186	

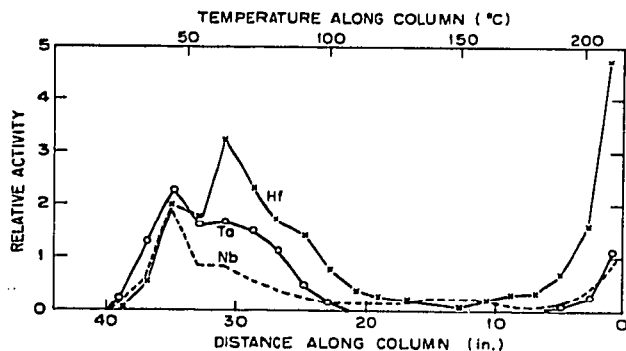


Fig. 4. Distribution of various activities processed with He + Br<sub>2</sub> + BBr<sub>3</sub> as the carrier gas. Gamma energies: <sup>90</sup>Nb, 141.5 keV; <sup>173</sup>Ta, 172.1 keV; <sup>170</sup>Hf, 164.7 keV.

cases. We found that addition of BBr<sub>3</sub> to the Br<sub>2</sub> carrier gas was effective in brominating recoil atoms of Nb, Hf and Ta activities as well (Fig. 4). The bromine was at a partial pressure of 40 mm Hg and the BBr<sub>3</sub> at 1 mm Hg and the target chamber at 200° for these experiments.

There are two features of this picture that are worth noting. First, the order of volatilities, Ta = Nb > Hf, can be compared with Nb > Zr in Fig. 1. There is little doubt that hafnium and zirconium are present in the gas phase as tetrabromides as no lower bromides are known to be volatile and all possible oxybromides are expected to be non-volatile. Tantalum and niobium are most probably in the form of pentabromides as the oxytribromide of tantalum is unstable<sup>12</sup> and the volatility of NbOBr<sub>3</sub> seems<sup>13</sup> to be much lower than that of both NbBr<sub>5</sub> and HfBr<sub>4</sub> within the temperature range of interest here. The observed order of the peaks of Nb, Ta and Hf cannot be deduced straightforwardly from the volatility of their bromides as characterized by the boiling or sublimation points given in the Table I. The enthalpy of sublimation may be a better parameter to correlate microscopic and macroscopic volatilities. Unfortunately, the existing data are not sufficiently accurate for such a comparison.

The second interesting feature of Fig. 4 is the low deposition temperatures of Nb, Ta and Hf bromides compared with the data of Fig. 2. A possible explanation might be that BBr<sub>3</sub> vapors modify the adsorption properties of the column surface both by chemical "polishing" (reaction with active sites) and, as was suggested in Dubna work with chlorides<sup>14</sup>, by physical adsorption.

It might also be mentioned that the small hafnium peak appearing under the Ta and Nb peaks is undoubtedly <sup>173</sup>Hf from the electron-capture decay of <sup>173</sup>Ta (*t*<sub>1/2</sub> = 3.7 h). The main hafnium peak is due to <sup>170</sup>Hf detected by its 164.7-keV gamma. The <sup>173</sup>Hf gamma detected was at 162.1 keV. Thus, the low-temperature Hf peak reflects the chemical behavior of tantalum rather than hafnium.

## CONCLUSION

In the Dubna experiments with chlorides, only transactinide nuclides decaying by spontaneous fission were measured. Mica sheets, which are stable in the hot and

corrosive environment, were spaced along the tubular column for detecting fission fragments. They were etched after finishing each run to look for tracks. With the much less corrosive bromides and lower temperatures, both fission fragments and  $\alpha$ -particles can probably be detected with more ease. One possible technique, which looked promising in our preliminary experiments, would be to shield the cooled alpha detector with a thin-nickel-foil window. Another possible technique might consist in having the cold end of the thermochromatographic column maintained at a temperature slightly above the deposition temperature of the bromide under study, while the exit gas would strike upon a somewhat colder catcher to collect the element. The catcher could be periodically (according to the half-life of the activity) positioned next to the solid-state particle detectors.

Poor separation of Hf and Ta probably will not be a serious disadvantage of the bromide technique when studying the chemistry of element 105. In most heavy ion reactions for the production of 105, the yield of the simultaneously produced 104 is expected to be low.

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