

Simultaneous Observation of Volatility of Zr, Hf, and Rf Chlorides

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⁸⁵Zr, ¹⁶⁹Hf, and ²⁶¹Rf were produced simultaneously from ^{nat}Ge(¹⁸O, xn), ^{nat}Gd(¹⁸O, xn), and ²⁴⁸Cm(¹⁸O, 5n) reactions, respectively, and the volatility of their chlorides was examined using an isothermal gas chromatographic system. The observed gas chromatogram indicated that ZrCl₄, HfCl₄, and RfCl₄ had almost similar volatility.

1. Introduction

The group 4 elements zirconium (Zr) and hafnium (Hf) have quite similar chemical properties and the chlorides of these two elements in a macro amount have almost equal volatility.¹ The first transactinide rutherfordium (Rf) is a group 4 element of the periodic table and is expected to have the chemical property similar to those of Zr and Hf. The modern relativistic molecular orbital calculation²⁻⁴ predicts that RfCl₄ is slightly more volatile than ZrCl₄ and HfCl₄, whereas the simple extrapolation of classic periodic trend predicts a less volatile property for RfCl₄.⁵

An isothermal gas chromatograph is a widely used tool to inspect the relative volatility of the chloride of the group 4 elements and used frequently to compare the volatility of transactinide elements with their homologues. Türler et al.⁶ reported that the chlorides of Hf and Rf had quite similar volatility. On the other hand, Kadkhodayan et al.⁷ reported that ZrCl₄ and RfCl₄ had almost equal volatility and HfCl₄ was less volatile than ZrCl₄ and RfCl₄. These two experiments were carried out by using tracer scale samples. Thus, the observed trend needs not coincide with that shown in Reference 1. However, the two research groups claimed obviously the different trend of the volatility of Zr, Hf, and Rf. These two previous findings were obtained by observing separately the volatility of each element. Therefore, there is a doubt whether each experiment was carried out exactly in the identical condition. Türler et al.⁸ re-investigated the volatility of HfCl₄ and RfCl₄ by observing simultaneously their isothermal chromatograms and reported that RfCl₄ was more volatile than HfCl₄. But they did not observe the volatility of ZrCl₄.

As described above, the volatility of the chlorides of the group 4 elements including Rf is a still challenging research target in modern chemistry. The objective of this work is to examine the trend of the volatility of ZrCl₄, HfCl₄, and RfCl₄ by inspecting simultaneously recorded their isothermal gas chromatograms.

2. Experimental

An experimental set-up used in the present work is schematically shown in Figure 1. It consists of a target and recoil chamber arrangement with a He/KCl gas-jet system, an isothermal gas

chromatographic apparatus, and an α -particle detection system. In order to study the isothermal gas chromatographic behavior of Zr, Hf, and Rf chlorides under a strictly identical experimental condition, the isotopes of these elements, ⁸⁵Zr, ¹⁶⁹Hf, and ²⁶¹Rf, were simultaneously produced and their volatility was inspected simultaneously. For the production of these isotopes, we used two targets; one is a ²⁴⁸Cm target and the other is a Ge and Gd mixed target. The ²⁴⁸Cm target of 490 $\mu\text{g cm}^{-2}$ in thickness and 5 mm in diameter was prepared by electrodeposition of Cm(NO₃)₃ from isopropyl alcohol onto a 2.2 mg cm⁻² thick beryllium backing foil. The mixed target was prepared as follows. Initially ^{nat}Gd of 180 $\mu\text{g cm}^{-2}$ in thickness and 5 mm in diameter was electrodeposited on a 2.07 mg cm⁻² thick beryllium foil. Then ^{nat}Ge of 210 $\mu\text{g cm}^{-2}$ in thickness was deposited on the surface of Gd by vacuum evaporation. The two targets were mounted in a target chamber as shown in Figure 1.

The irradiation was performed at the JAERI tandem accelerator. The isotope ²⁶¹Rf ($T_{1/2} = 78$ s) was produced in the ²⁴⁸Cm(¹⁸O, 5n) reaction, while ⁸⁵Zr ($T_{1/2} = 7.86$ min) and ¹⁶⁹Hf ($T_{1/2} = 3.24$ min) were produced in ^{nat}Ge(¹⁸O, xn) and ^{nat}Gd(¹⁸O, xn) reactions, respectively. The ¹⁸O⁶⁺ beam energy was 94 MeV at the middle of the ²⁴⁸Cm target. The average beam intensity was about 200 particle nA. The nuclear reaction products recoiling out of the targets were transported to the gas chromatographic system via the He/KCl gas-jet transport system through a 2.2 mm inner diameter stainless steel capillary. The stainless steel capillary was employed in order to

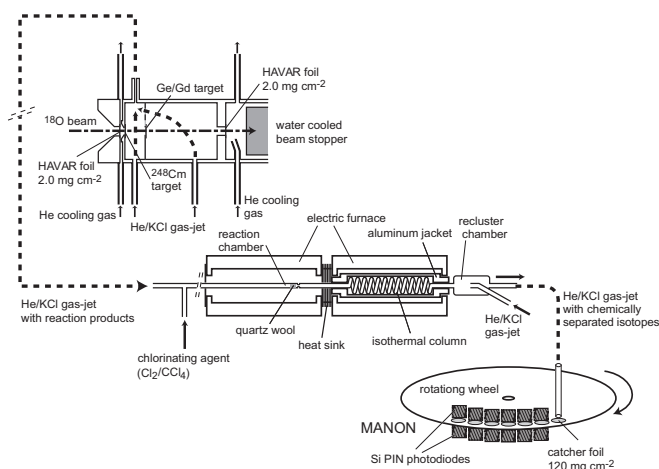


Figure 1. Schematic diagram of experimental set-up.

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avoid oxygen entering through a capillary wall. The concentration of oxygen impurity in He gas was monitored with an oxygen monitor and was kept to be less than 30 ppm. Domanov et al.⁹ reported that in gas chromatographic experiments chlorination of Zr and Hf is not affected by oxygen in this order of concentration. The flow rate of the He carrier gas was 1.2 L min⁻¹.

The isothermal gas chromatographic apparatus consists of a reaction chamber, an isothermal column, and a re-clustering chamber. Each section is made of quartz and connected in a series. The isothermal column is a spiral tube of 2000 mm long and inner diameter of 3 mm. The reaction chamber and the isothermal column can be independently heated by electric furnaces up to a maximum temperature of 1200 °C and 500 °C, respectively.

The transported nuclear reaction products were stopped at quartz wool in the reaction chamber and a mixture of chlorine (Cl₂) gas and carbon tetrachloride (CCl₄) vapor was introduced for chlorination. Volatile tetrachlorides of Zr, Hf, and Rf were formed in the reaction chamber at 1000 °C and passed through the isothermal column. The volatile species, after leaving the column, entered the re-clustering chamber, where they were caught by new KCl aerosols in He gas, and were transported to the detection system. An HPGe γ -ray spectrometer system was employed for the detection of characteristic γ -rays of ⁸⁵Zr and ¹⁶⁹Hf, and α -particles were measured with MANON (Measurement system for Alpha-particle and spontaneous fission events ON-line),^{10,11} having a rotating wheel detection system with an 80 cm diameter wheel. The activity-laden aerosols were deposited on polyethylene terephthalate foils of 120 $\mu\text{g cm}^{-2}$ in thickness and 20 mm in diameter at the periphery of an 80-position stainless steel wheel. The wheel was periodically rotated to set each foil at the center of one of the six pairs of Si PIN photodiodes. Each sample was collected for 30 s and the spectrum was acquired for 30 s with one detector pair, that is, 180 s in all. Each detector has an active area of 18 \times 18 mm² and the detection efficiency was approximately 40% for α particles. The energy resolution (FWHM) was about 30 keV for the top detectors and 100 keV for the bottom ones.

3. Results and Discussion

Volatile chlorides of Zr and Hf were efficiently formed in the reaction chamber at the temperature of above 800 °C and the chlorination yields for Zr and Hf were evaluated to be about 80% at 1000 °C. After passing through the isothermal column, about 25% of the volatile chlorides was transported to the detection position. Lanthanides that were produced as nuclear reaction by-products did not pass through the column. As the chlorides of lanthanides are non-volatile under the examined condition, only volatile species passed through the column.

Figure 2 shows an α spectrum taken at the temperature of the isothermal column of 400 °C and the total beam dose of 2.5×10^{16} particles. The α -particle group in the energy range of 8.00–8.40 MeV was assigned to ²⁶¹Rf and its daughter ²⁵⁷No ($T_{1/2} = 26$ s). The spectrum is contaminated by α -particles from ^{211m,212m}Po which were produced by nucleon-transfer reaction on a Pb impurity in the target and formed volatile compounds. Due to much effort to remove the Pb impurity from the ²⁴⁸Cm target, the background was greatly reduced compared with that by Kadkhodayan et al.⁷

In Figure 3 the measured relative yields of ²⁶¹Rf together with those of ⁸⁵Zr and of ¹⁶⁹Hf are shown as a function of the temperature of the isothermal column. The yields at 400 °C are normalized to 100%. Above the temperature of 300 °C, Zr, Hf, and Rf chlorides start to pass through the isothermal column. The passing yields of those chlorides increase steeply with the increase of the temperature, and reach the maximum around 350 °C. This steep increase of the yield with the temperature

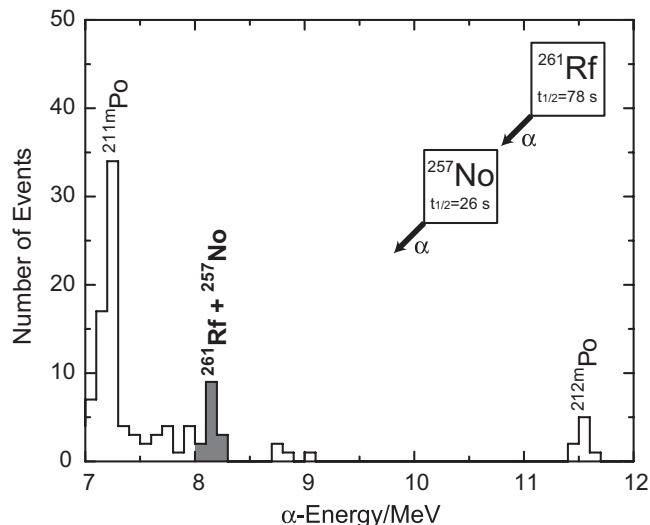


Figure 2. α Spectrum after chemical separation.

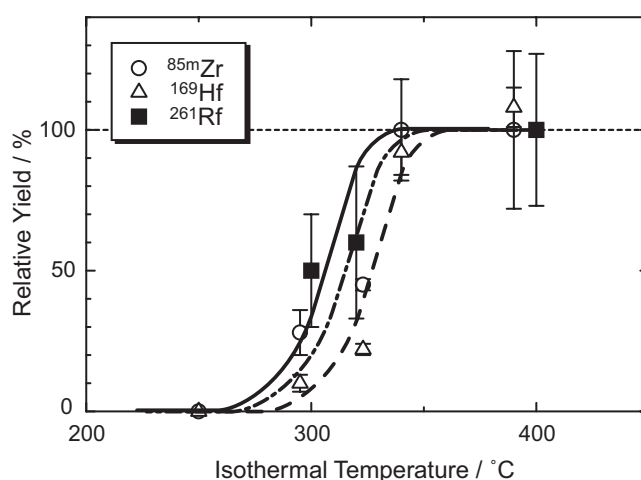


Figure 3. Relative yields for ⁸⁵Zr, ¹⁶⁹Hf, and ²⁶¹Rf chlorides. The curves are the calculated results based on a Monte Carlo simulation.¹³ Zr: dot-dashed line, Hf: dashed line, Rf: solid line.

is characteristic of a simple adsorption-desorption transport mechanism¹² and oxychlorides were not involved in chromatographic transportation because of low oxygen concentration in the system.⁹ The lines in Figure 3 are the calculated results of a Monte Carlo simulation based on the Zvára's model.¹³

In the present work, KCl aerosol was used for the transportation of nuclear reaction products, thus the surface of the chromatographic column would be partially coated with a thin layer of KCl. In such a case, the temperature at which the volatile species pass through the column tends to be higher compared with those for pure quartz surface.^{14,15} However, it may be reasonable to consider that the order of relative volatility for the elements of interest is not affected by materials of a column surface.

It was clearly shown that the volatility of Zr, Hf, and Rf chlorides closely resemble each other under the identical experimental conditions. From this result, we may conclude that the volatility of Zr and Hf chlorides is quite similar to each other as expected from the standard sublimation enthalpy of Zr and Hf chlorides in macro scale and that the volatility of Rf chloride is nearly the same as those of Zr and Hf. The latter conclusion is qualitatively consistent with the prediction by the relativistic calculations.²⁻⁴

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