3–1 What is the Chemical Behavior of the Heaviest Element?

—A Small Breach of the Periodic Law Found in the Volatility of Element 105, Dubnium—

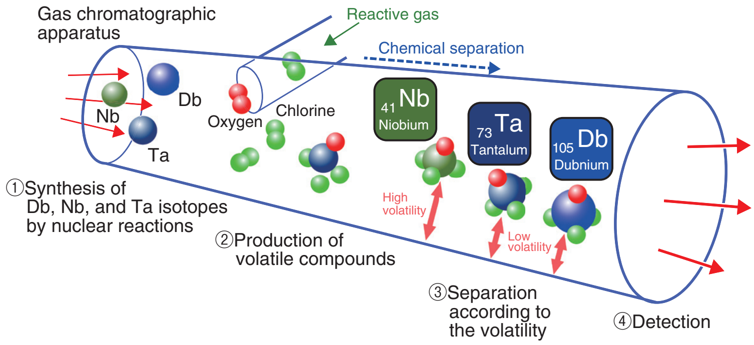

Fig.3-2 Schematic diagram of the experiment
Short-lived niobium (Nb), tantalum (Ta), and dubnium (Db) isotopes synthesized in nuclear reactions are quickly introduced into the experimental apparatus to synthesize their volatile oxychlorides. They are passed through a quartz separation column that is maintained at a fixed temperature by a gas stream. The transparent efficiency changes depending on the volatility. The volatility of the molecule can be determined from the correlation between the column temperature and yield.

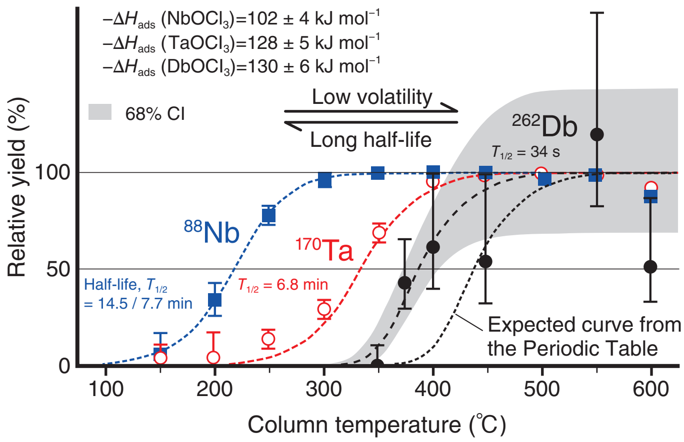

Fig.3-3 Changes of relative yields with the column temperature for the oxychlorides of Nb, Ta, and Db
The values of the adsorption enthalpy, $-\Delta H_{ads}$, as a measure of the adsorption strength, for the compounds on the separation column surface (quartz) can be obtained from the column temperature–yield curves. The curve shifts to higher temperatures for lower volatility and to lower temperatures for longer half-lives. Since the strength of adsorption on a solid surface should be correlated with volatility in the case of physisorption, the ease of each compound to transform into a gas can be estimated.

Heavy elements (atomic number Z > 103) are called superheavy elements (SHEs). SHEs do not exist naturally on the Earth and are artificially synthesized in nuclear reactions. In such heavy elements, the velocity of the inner electrons moving around the nucleus approaches the speed of light, thereby eventually affecting the outermost electron orbits that characterize their chemical properties (relativistic effects). It has been pointed out that the chemical properties of the SHEs may be different from those expected according to the Periodic Table.

Dubnium (Db, Z = 105) is an SHE that belongs to Group 5 elements and is a homolog of niobium (Nb) and tantalum (Ta) in the Periodic Table. The production rate of Db is extremely low (about 1 atom per 5 min), and its half-life is quite short (34 s for ^{262}Db). Hence, only one atom can be used at a time. The chemical properties of Db have not been investigated sufficiently due to the experimental difficulties.

In this work, we synthesized a Db isotope by using the JAEA tandem accelerator and performed a chemical analysis of its volatile compound using an on-line gas chromatographic apparatus. The volatility of the Db compound was compared with the values for the Nb and Ta compounds (Fig.3-2).

We successfully produced and separated dubnium oxychloride ($DbOCl_3$) and clarified that its volatility was comparable to that of the Ta compound, though it was expected to be lower than that of the Ta compound from the simple extrapolation of the Periodic Table (Fig.3-3). This unexpected volatility of Db is explained by considering the strong relativistic effect.

The results of this research were featured on the back cover of the “Angewandte Chemie”. This achievement is expected not only to lead to an understanding of the Periodic Table, but also to contribute to the improvement of the accuracy of theoretical chemical calculations, which are increasingly being used in molecular design and material science in recent years.

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Reference

Chiera, N. M., Sato, T. K. et al., Chemical Characterization of a Volatile Dubnium Compound, $DbOCl_3$, Angewandte Chemie International Edition, vol.60, issue 33, 2021, p.17871–17874.