

Chemistry of the Transactinide Elements

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The chemistry of the transactinide elements has been a topic of interest since the first reported synthesis of rutherfordium (element 104) in 1964.¹ The main objective of these studies is to determine if the chemical properties of the transactinides are consistent with their expected placement below the *5d* metals in the periodic table.² Empirical aufbau principles suggest that the *6d* orbitals should fill starting with element 104 but, as has been pointed out, there is no firm theoretical basis for the exact order in which orbitals are filled as a function of increasing atomic number.^{3, 4} If the chemical properties of the transactinides do not follow the periodic trends expected by extrapolation of the properties of their lighter congeners, then this result would be evidence that they belong in an isolated series similar to the lanthanides and actinides.

The chemical properties of the transactinides may differ from those of their lighter homologues due to relativistic effects,⁵ which are known to cause non-periodic deviations in the chemical properties of a group.⁶⁻⁸ These effects become more pronounced with increasing atomic number. Classical manifestations of relativistic effects include the inertness of gold, the liquid state of mercury, and the inert-pair effect for sixth-row elements Tl, Pb, and Bi. The transactinides, which have much higher nuclear charges than the aforementioned elements, may exhibit exotic properties due to these effects.

The first chemical studies of the transactinide elements were performed on rutherfordium and dubnium (elements 104 and 105).⁹ Their chemical properties were significantly different from those of the late actinides but similar to those of the lighter group 4 and 5 metals, as expected. Interestingly, however, the chemical properties of these elements did not necessarily follow the expected periodic trends within their groups. For instance, aqueous studies of dubnium indicate that it behaves more like niobium than tantalum.¹⁰

Seaborgium (element 106), on the other hand, not only behaves like a group 6 metal but follows expected trends in volatility for the group.^{9, 11} Studies of SgO_2Cl_2 , which is the analog of the long-known group 6 compounds WO_2Cl_2 and MoO_2Cl_2 , reveal that the volatility of these group 6 oxychlorides decreases down the group ($\text{MoO}_2\text{Cl}_2 > \text{WO}_2\text{Cl}_2 > \text{SgO}_2\text{Cl}_2$).

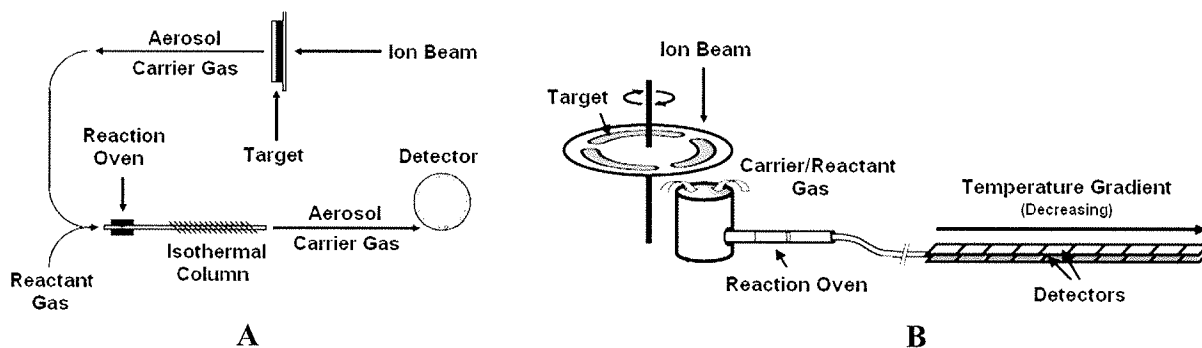


Figure 1. The OLGA and IVO-COLD apparatus for “atom at a time” studies

The longest-lived isotopes of bohrium (element 107), hassium (element 108), and element 112 studied to date have half lives of 17 sec, 9 sec, and 4 sec, respectively, and are generally produced one atom at a time. To study the chemical properties these elements, it is necessary to employ techniques that enable rapid measurements on single molecules, such as the on-line isothermal gas chromatography (OLGA) apparatus (Figure 1A) and the in-situ volatilization and cryo-on-line detection (IVO-COLD) apparatus (Figure 1B).^{2, 12-15} The general approach is as follows: (1) Allow the prepared nuclides to recoil from the back of a bombarded target into a gaseous stream; (2) Introduce gaseous reactants and heat to induce a chemical reaction; (3) Determine the adsorbivity/volatility of the reaction product by gas chromatography or thermochromatography; (4) Measure the decay of the parent isotope and the correlating decays of its daughter nuclides.

The gas-phase studies of bohrium using the OLGA III apparatus reveal that it behaves like its group 7 homologues.^{12, 13} Bohrium reacts with gaseous HCl and O₂ to form BhO₃Cl, which is analogous to the known syntheses of TcO₃Cl and ReO₃Cl. The relative amount of BhO₃Cl that passed through an isothermal column as a function of temperature (gas adsorption chromatography) was used to determine that its enthalpy of adsorption is -75 kJ mol⁻¹. This value is more negative than the adsorption enthalpies of TcO₃Cl and ReO₃Cl (-51 and -61 kJ mol⁻¹, respectively), which suggests that the volatilities of these group 7 compounds decrease down the group as expected based on the periodic trend.

Chemical studies of hassium were designed to exploit the predicted volatility of HsO₄.¹⁴ Hassium is first allowed to react with O₂ to form HsO₄, which is then sublimed so that a carrier gas can sweep it into the COLD detector. The COLD detector is a series of 12 pairs of nuclear decay detectors situated around the adsorption column, which is maintained as a temperature gradient ranging from -20 to -170 °C. The relative volatility of the HsO₄ molecules can be determined by measuring the number of decay events as a function of where (i.e. at what temperature) the decays are detected. The resulting thermochromatogram of seven molecules of HsO₄ showed that they adsorbed at slightly higher temperatures than OsO₄, indicating that HsO₄ is somewhat less volatile than OsO₄. This result is consistent with the periodic trend that the volatilities of the group 8 oxides are in the order RuO₄ > OsO₄ > HsO₄.

A key chemical property of element 112 is its degree of chemical inertness.¹⁵ Element 112 was previously suspected of having chemical properties closer to that of a noble gas rather than its lighter homologue, mercury.¹⁶ The element was studied in a modified IVO-COLD apparatus that used 32 gold-coated detectors instead of the silicon nitride detectors employed in previous experiments. Along with atoms of element 112, atoms of mercury and radon were produced *in situ*, and their respective distributions within the temperature gradient column were determined relative to that of element 112. Two decay events corresponding to element 112 were detected within the temperature range at which mercury adsorbed, but well outside the range measured for radon, indicating that the adsorption properties of element 112 on gold are closer to that of mercury than to radon.

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