

Probing bohrium

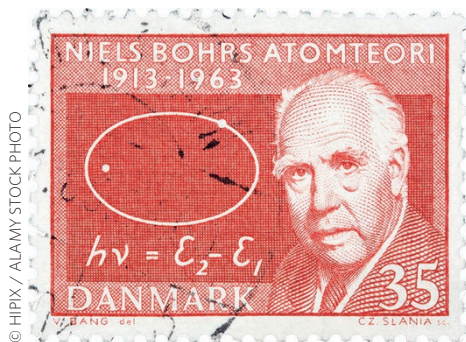
Bohrium behaves just as a group 7 element should — but this is in fact surprising, **Philip Wilk** explains.

The superheavy element bohrium was first identified in 1981 at the GSI Helmholtz Centre for Heavy Ion Research in Darmstadt, Germany¹ and was named after one of the founders of modern atomic and nuclear physics, Niels Bohr. Simply placing bohrium in group 7 of the periodic table would suggest a chemical behaviour similar to its above neighbour rhenium — that is, if periodic trends were to continue at the extreme end of the table. However it is not obvious that they should and, in fact, theory suggests that they must not.

The now ubiquitous periodic table as proposed by Dmitri Mendeleev in 1869 was arranged by increasing atomic weight, this original form was expanded to include the noble gases and the lanthanides. It was then modified in 1913 by Henry Moseley to arrange the elements by their X-ray energy (proportional to the square of the atomic number), which solved the vexing problems of a few elements appearing out of sync with their chemical properties. Tellurium and iodine, for example, swapped position, thus falling into place with the groups they were expected to belong to.

The next — and so far final — change to the table was made in 1944 when Glenn Seaborg postulated the existence of the actinide series analogous to the lanthanide series² instead of a uranium-like group, which was the prevailing wisdom of the time. By this date, the basic chemistries of neptunium and plutonium were fairly well understood, and the initial chemical experiments on as-yet-unnamed elements 95 and 96 were being carried out. Seaborg interpreted the existing evidence as indicating decidedly non-transition-metal-like behaviour, which pointed toward the filling of the 5f orbitals instead of the 6d ones.

With the end of the actinide series comes a transition metal series characterized by filling these previously



discarded 6d orbitals. The behaviour of these 'superheavies' is expected to be greatly influenced by relativistic effects, due to the tight binding of the inner electrons that have velocities not far-removed from the speed of light. These effects should have such a profound effect on chemical bonding that traditional extrapolation of chemical properties down and across the periodic table will be misleading at some point. Chemical studies on the heaviest members of the table are therefore important, to test these theoretical predictions and determine the influence of the relativistic effects. Such investigations have shown that the chemical behaviour of dubnium (element 105), for example, does not rigorously follow trends down the fifth group.

Those chemical studies at the extreme end of the periodic table are challenging to perform, due to the low production rate of these elements. To reach the superheavy elements, heavy elements are bombarded with lighter ones, resulting in (on rare occasions) the complete fusion of target and projectile nuclei with production rates of an atom a day, or less.

Starting in the late 1990s, Robert Eichler, Heinz Gaggler, and a host of international collaborators set upon the task of elucidating the chemistry of bohrium and other superheavy elements. The only chemical or physicochemical method that has the sufficient speed and efficiency to achieve a chemical determination on these ultra-rare elements is gas chromatography³.

Over the course of many years and a few different device iterations, the researchers constructed and tested a purpose-built gas-phase chromatographic separator at the Paul Scherrer Institute in Switzerland.

During seminal investigations in 1999 and 2000, five atoms of ²⁶⁷Bh were identified by observing their distinctive pattern of decay and chemically analysed⁴. Although reaction parameters were selected that favoured the longest-lived isotope, this isotope still decayed with a half-life of only ~17 s. Over two dozen scientists were involved in this scientific marathon to perform a volatility analysis on five individual atoms of bohrium. The volatility was measured as adsorption enthalpy of the oxychloride, and ultimately determined that bohrium does in fact form an oxychloride — like the other group-7 elements technetium and rhenium. These experiments further showed that the bohrium oxychloride is less volatile than rhenium oxychloride, which is in turn less volatile than its technetium analogue.

What is rather surprising is that this result is thoroughly in line with predictions based purely on bohrium's position at the bottom of group 7 in the periodic table — despite the expected breakdown of periodic trends as the relativistic effects dominate the chemical behaviour of the heaviest of elements, supported by the peculiar behaviour of other transactinide elements, such as the previously mentioned dubnium. □

References

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