

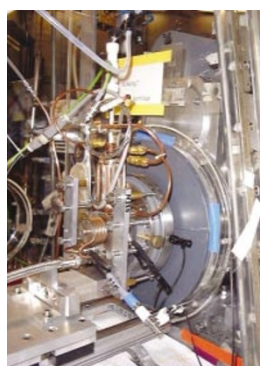
# A very brief encounter

Little is known about the heavy elements that lie at the outer limits of the periodic table. But how do you investigate atoms that decay within seconds? Kendall Powell finds out. Kendall Powell finds out.

Christoph Düllmann cracked open a bottle of vodka when he detected his first hassium atom. Over the next few days, six more atoms registered on detectors at the GSI, a heavy-ion research centre in Darmstadt, Germany. Each one was a relief to Düllmann. He had spent two years developing the experimental game plan, and staked his doctoral thesis on the apparatus being able to study hassium.

Düllmann was not alone in feeling relieved. More than 30 researchers from 10 institutions had helped to plan how to probe the chemistry of hassium, a huge element that weighs in at number 108 in the periodic table and decays seconds after it is formed. They had gambled all on hassium conforming to the patterns of the periodic table — and the results, which appear on page 859 of this issue<sup>1</sup>, show that they were right.

But researchers are finding that other heavy elements defy normal behaviour. The properties of most elements in the periodic table can be predicted by which column — or group — they appear in. But some heavy



Getting heavy: researchers at the GSI (above), and the equipment (inset) they used to detect the volatile tetroxide of the element hassium.

elements in the lower regions of the table buck this trend, throwing chemists' predictions into chaos.

Probing the chemistry of the heavy elements would be difficult even if they did play by the rules. Elements heavier than uranium have to be created artificially, usually by firing a beam of ions into a stationary target. Few collisions result in the creation of the desired element, so the process is very time-consuming. And the heavy elements tend to be unstable — many of them decay into lighter elements in seconds. So although physicists have extended the periodic table by a few new elements every decade since 1940, mapping out the territory as far as element 112, only in the past two decades have advances in target design and beam intensity allowed researchers to study heavy-element chemistry.

The quirky behaviour displayed by heavy elements has its roots in their electronic structure. In all large atoms, electrons orbiting close to the nucleus act as a shield between the attractive forces of the nucleus and the electrons in the outer orbits. But in the heavy elements, the high positive charge on the nucleus causes the electrons in the inner orbits to move at speeds close to that of light which, according to the special theory of relativity, increases their mass. This sends the electrons into even shallower orbits, increasing the shielding effect for those in the outer orbits.

The heightened shielding can change the way in which the outer electrons interact with other atoms and molecules, potentially

putting the element out of step with the other members of its chemical group. "One would expect a major break from periodic trends," says Pekka Pyykkö, a theoretical chemist at the University of Helsinki. "But no one knows when it will happen. In what column, if any, will you see major changes?"

## Risky business

These uncertainties are a major problem for nuclear chemists, who risk spending years designing equipment that, if an element behaves in an unexpected way, may not be able to detect what they were seeking. To succeed, sometime fierce rivals have had to collaborate, and everyone involved has had to rely on a little luck.

In the case of hassium, researchers had to wait 12 years before they could even begin work. The element was discovered in 1984 at the GSI, and takes its name from Hesse, the state in which the institute is based. Researchers there fired a beam of iron ions into a lead target. For a few of these collisions, an iron nucleus overcame the repulsion from a lead nucleus and the two fused to create hassium. But with a half-life of 1.5 milliseconds, the hassium isotopes were too short-lived to be used in experiments.

The breakthrough came in 1996, when GSI researchers were searching for element

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Christoph Düllmann gambled that hassium would behave in line with the rest of its group.

Group theory: the properties of some of the heavier elements deviate from what would be expected from their position in the periodic table.

|          |          |           |           |           |           |           |           |           |          |            |            |          |          |          |          |          |          |          |          |          |          |          |          |          |          |          |          |          |           |           |           |
|----------|----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|----------|------------|------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|-----------|-----------|-----------|
| H<br>1   |          |           |           |           |           |           |           |           |          |            |            |          |          |          |          |          | He<br>2  |          |          |          |          |          |          |          |          |          |          |          |           |           |           |
| Li<br>3  | Be<br>4  |           |           |           |           |           |           |           |          |            |            |          |          |          |          |          |          | B<br>5   | C<br>6   | N<br>7   | O<br>8   | F<br>9   | Ne<br>10 |          |          |          |          |          |           |           |           |
| Na<br>11 | Mg<br>12 |           |           |           |           |           |           |           |          |            |            |          |          |          |          |          |          | Al<br>13 | Si<br>14 | P<br>15  | S<br>16  | Cl<br>17 | Ar<br>18 |          |          |          |          |          |           |           |           |
| K<br>19  | Ca<br>20 | Sc<br>21  | Ti<br>22  | V<br>23   | Cr<br>24  | Mn<br>25  | Fe<br>26  | Co<br>27  | Ni<br>28 | Cu<br>29   | Zn<br>30   | Ga<br>31 | Ge<br>32 | As<br>33 | Se<br>34 | Br<br>35 | Kr<br>36 |          |          |          |          |          |          |          |          |          |          |          |           |           |           |
| Rb<br>37 | Sr<br>38 | Y<br>39   | Zr<br>40  | Nb<br>41  | Mo<br>42  | Tc<br>43  | Ru<br>44  | Rh<br>45  | Pd<br>46 | Ag<br>47   | Cd<br>48   | In<br>49 | Sn<br>50 | Sb<br>51 | Te<br>52 | I<br>53  | Xe<br>54 |          |          |          |          |          |          |          |          |          |          |          |           |           |           |
| Cs<br>55 | Ba<br>56 | Lu<br>71  | Hf<br>72  | Ta<br>73  | W<br>74   | Re<br>75  | Os<br>76  | Ir<br>77  | Pt<br>78 | Au<br>79   | Hg<br>80   | Tl<br>81 | Pb<br>82 | Bi<br>83 | Po<br>84 | At<br>85 | Rn<br>86 |          |          |          |          |          |          |          |          |          |          |          |           |           |           |
| Fr<br>87 | Ra<br>88 | Lr<br>103 | Rf<br>104 | Db<br>105 | Sg<br>106 | Bh<br>107 | Hs<br>108 | Mt<br>109 | H<br>110 | Uuu<br>111 | Uub<br>112 |          |          |          |          |          |          |          |          |          |          |          |          |          |          |          |          |          |           |           |           |
|          |          |           |           |           |           |           |           |           |          |            |            |          |          |          |          |          |          | La<br>57 | Ce<br>58 | Pr<br>59 | Nd<br>60 | Pm<br>61 | Sm<br>62 | Eu<br>63 | Gd<br>64 | Tb<br>65 | Dy<br>66 | Ho<br>67 | Er<br>68  | Tm<br>69  | Yb<br>70  |
|          |          |           |           |           |           |           |           |           |          |            |            |          |          |          |          |          |          | Ac<br>89 | Th<br>90 | Pa<br>91 | U<br>92  | Np<br>93 | Pu<br>94 | Am<br>95 | Cm<br>96 | Bk<br>97 | Cf<br>98 | Es<br>99 | Fm<br>100 | Md<br>101 | No<br>102 |

112. By firing a beam of zinc ions into a lead target, they became one of the first groups to succeed at creating the element, which currently has the temporary name ununbium. Amid the debris of the particles and nuclei that 112 decayed into, a hassium isotope with a half-life of nine seconds was discovered.

This started the ball rolling on the hassium chemistry study. Düllmann and his collaborators focused on the volatility of hassium tetroxide, the gas formed when hassium reacts with oxygen. Elements lower in the group form more volatile tetroxide gases, so hassium tetroxide was expected to be at least as volatile as osmium tetroxide, the gas formed by the element just above it in the group. This was backed up by work from GSI theoretician Valeria Pershina<sup>2</sup>, who suggested that hassium tetroxide would follow the pattern of the other elements in its group, such as osmium and ruthenium.

### In character

Magnesium ions were pounded into a curium target to create atoms of the long-lived hassium isotope, which were then flushed into a thin tube by a stream of helium and oxygen. The mixture was heated to 600 °C, which, if the predictions were right, should have prompted the formation of hassium tetroxide. The gas was then sent over a series of silicon detectors held at different temperatures. Tetroxide gases adsorb on silicon, and the temperature at which they do so can be used to infer the gases' volatility.

Crunch time came last May, as experiments were run to reveal whether the researchers had gambled their time and money on the right kind of experiment. Ten days into the study, the first hassium tetroxide molecule was detected — and it was within the expected temperature range. Düllmann double-checked the equipment and toasted others in the control room with a small drink of vodka. Hassium, it seems, does conform to the behaviour expected of it as a member of its chemical group.

But other heavy elements are less predictable. During the 1980s, experiments on dubnium, element 105, showed that it behaves similarly to niobium, the element two places above it in its group, rather than its nearest upstairs neighbour tantalum<sup>3</sup>. Rutherfordium (104) is also known to break patterns within its group<sup>4,5</sup>, but others including seaborgium (106) follow some normal trends<sup>6</sup>.

### Deviant behaviour

One element, however, looks set to throw the rulebook away completely. A team led by Alexander Yakushev at the Flerov Laboratory of Nuclear Reactions in Dubna, Russia, is currently trying to capture element 112. This element is in group 12, so it ought to behave like a more volatile version of mercury. But relativistic effects are expected to make some of its properties more like those of an inert gas such as radon<sup>7</sup>.

Yakushev and his colleagues decided to hedge their bets by building an experimental set-up to detect both mercury-like and radon-like activity. Unlike the hassium experiment, the group is assessing the chemistry of element 112 in its unbonded state. Calcium ions are smashed into a uranium target, and the atoms of element 112 that are created are flushed onto two different detectors. If the element behaves like mercury, it should bind to the gold-covered surface of one of the detectors. If it doesn't, it will be



All together now: the international team celebrates the end of the hassium experiment.

swept into an ionization chamber where its radioactive decay chain will be detected.

In preliminary, unpublished results, nothing stuck to the gold surface, but eight atoms were detected in the chamber, indicating that 112 may display radon-like properties. Other elements disrupt the trends within their groups, but 112 appears to be acting as if it belongs to another group altogether.

Like other work on the chemistry of heavy elements, the Flerov team relies heavily on techniques and predictions developed by researchers around the world. The hassium study was an equally multinational affair. Teams at Lawrence Berkeley National Laboratory in Berkeley, California, and the Paul Scherrer Institute in Villigen, Switzerland — where Düllmann is based — designed the detectors. Flerov researchers performed preliminary studies of osmium and various German groups made the target, organized the final experiment and provided theoretical calculations. "In principle, it was everyone working in gas-phase chemistry of super-heavy elements in the world," says Yakushev, who is a co-author on the hassium paper.

Such collaborative spirit does not always come easily. The competition between groups to find new elements is intense, partly because the discoverers get to name the element. But the complexity of the chemistry experiments forces the groups to work together. "It requires walking a fine line and tremendous diplomacy," says Heino Nitsche, a nuclear chemist at Lawrence Berkeley.

This delicate balance was damaged earlier this year, when Victor Ninov, a physicist on the Lawrence Berkeley team, was accused of falsifying some of the data behind his lab's claim to have detected elements 116 and 118. Ninov, who denies any wrongdoing, was sacked from his lab and the paper on the results was retracted<sup>8</sup>. Earlier studies in which he was involved at the GSI are also under investigation.

Yakushev calls the incident "a lesson for all of us", and says future results need to be available for others working in the field to check. With funding for basic research shrinking and use of particle beams reserved for high-energy physics, nuclear chemists worry that the scandal will hinder their efforts. With few immediate applications, their field can do without bad publicity, even if they are producing fascinating science. "The international group is too small to be pulling in different directions," says Nitsche. "The field cannot afford it when the fundamentals of the periodic table are in question." ■

**Kendall Powell is an intern with Nature.**

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