

Californium gleaming

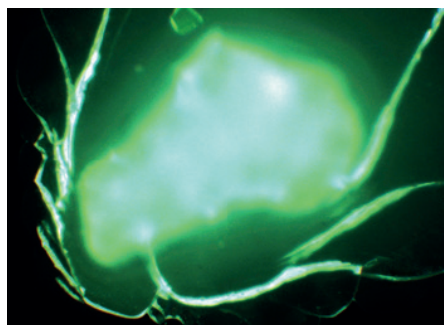
Thomas Albrecht-Schmitt explains the origin of element 98's striking green glow, and why the future for californium chemistry is just as bright.

A late actinide with twenty known isotopes, californium is a man-made transuranic element that does not occur naturally. It was first identified by Glenn Seaborg and co-workers in February 1950 in an experiment that used a 60-inch cyclotron to bombard curium-242 targets with helium ions. Although named primarily for the State of California, it also recognizes the University of California at Berkeley where many elements beyond uranium in the periodic table were first discovered. We now know that this was not the first observation of californium; late actinide elements up to fermium had been previously identified in debris from the first nuclear detonations in the 1940s, but this information was classified for many years.

Isotopes of elements beyond californium have half-lives much shorter than one year, meaning that it is the last element in the periodic table that macroscopic chemistry can be reasonably conducted on. Even einsteinium, its immediate neighbour in the periodic table, has only been made in microgram quantities. The majority of californium synthesized today is ^{252}Cf , although the hazards associated with this isotope makes chemistry — beyond tracer levels — essentially impossible. Owing to an unusually high rate of spontaneous fission, one microgram of ^{252}Cf releases 2.3 million neutrons every second.

Fortunately, ^{249}Bk is also generated during the production of ^{252}Cf and can be separated with high chemical and radiochemical purity from the other neutron-capture products. ^{249}Bk is short-lived, with a half-life of 320 days, and it undergoes β decay to ^{249}Cf , which has a much more chemically useful half-life of 351 years. Nearly all of the chemical studies on californium have been conducted with this isotope, but the truly desirable isotope — with a half-life of nearly 900 years — is ^{251}Cf . Unfortunately, ^{251}Cf is difficult to synthesize.

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Although the first californium compounds (containing mixtures of Cf isotopes) were prepared on microgram scales in the 1960s¹, it was not until the High Flux Isotope Reactor located at Oak Ridge National Laboratory started to produce meaningful quantities of isotopically pure ^{249}Cf that single-crystal X-ray diffraction studies and detailed physical property measurements could take place². This work really came to fruition in the early 1970s with the work of John Burns and Richard Haire, both unsung heroes of actinide chemistry.

Burns established that Cf(III) had an ionic radius similar to that of Gd(III). This is notable because it results in fluxional behaviour in solution whereby eight- and nine-coordinate aqua complexes rapidly equilibrate, a property exploited when using Gd(III) as an MRI contrast agent. As a result of this, Cf(III) is similar to Gd(III) in its ability to adopt both hexagonal and orthorhombic structures for trichloride compounds². Some californium compounds are also self-luminescent — they emit green light as the consequence of their intense radioactive emission causing the excitation of *f*-electrons. The green glow (pictured being emitted by $^{249}\text{Cf}[\text{B}_6\text{O}_8(\text{OH})_5]$) is beautiful to behold and harmless — it is the invisible emissions that you have to be extremely cautious of. ^{249}Cf emits γ -rays (388 keV) that have sufficiently high energies that they are detectable through more than 2 cm of lead. Holding a 5 mg sample of ^{249}Cf in your hand would result in exceeding your yearly radiation threshold

in less than 10 minutes. Hence, californium chemistry can only be conducted in purpose-built radiological facilities, and experiments have to be carefully choreographed to minimize exposure times.

Today, the chemistry of californium and the related actinides, curium and americium, is undergoing a renaissance³ because of the increased use of commercial nuclear reactors to generate electricity. Most nations are determined to develop ways to recycle used nuclear fuel, a complex mixture of elements and isotopes that includes curium, americium and californium, and this requires the development of sophisticated chemistry to separate these elements from each other on an industrial scale.

The Manhattan Project in the 1940s produced data to suggest that valence orbitals of actinides might be involved in covalent bonding, in contrast to the ionic nature that would be expected for late actinides. Recently, a combination of theory and experiment has provided strong evidence that the *6d* and *5f* orbitals of mid-to-late actinides can be deliberately utilized to form covalent bonds, and that such bonding can differ substantially between neighbouring actinides, even if they are in the same oxidation state^{4,5}. This ability to control bonding is the key to designing selective extractants and materials for trapping and differentiating radionuclides from nuclear waste, and shows that californium chemistry has a glowing future. □

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