Tin can

Tin has been ubiquitous throughout the course of human history, from Bronze Age tools to lithium-ion battery components, yet **Michael A. Tarselli** warns it should not be deemed pedestrian. Its tendency to linger in human tissues presents a dangerous side that steers researchers towards greener chemistries.

Tin hides everywhere in our culture, often in plain sight. Consider movie relics: from *The Wizard of Oz*'s Tin Man to the tin-can radio often spotted in treehouses. Element 50, whose symbol 'Sn' comes from the Latin *stannum*, has been mined all over the world for centuries. Its tendency to alloy with other metals such as copper or antimony gave the Bronze Age weapons and pewter tableware. Today, tin compounds live inside antifouling paint, PVC pipes and probably even in your bones, where tin compounds often accumulate in the human body. The lustrous silvery metal has a role to play, for good or ill, in the oncoming rush of battery science and electronics.

Metallic tin mainly occurs in two phases. The 'tin pest' — conversion of the strong, crystalline β form into a brittle α form at low temperatures — is recounted[1] as the apocryphal cause of disaster of the Russian campaign, through failure of Napoleon's buttons in the cold winter of 1812. Two other allotropes exist under high temperatures and pressures. Anyone observing a printed circuit board has seen solder: a tin–lead alloy extremely facile to melt and used to join contacts in a complex electronic circuit. Mass-produced tin cans have held a great variety of products — from food to oil to shoe polish — since the late nineteenth century, though today they often comprise the less costly, more malleable aluminium instead.

In its elemental form, tin poses no threat to human health. Organotin toxicity, on the other hand, has been epidemiologically linked to several markers of impaired health and growth in animal models. If there were a poster-child molecule for these studies, it's tributyltin chloride ($(C_4H_9)_3SnCl$, TBTC). A former antifouling compound for naval vessels and a PVC additive, TBTC has been shown to have multiple endocrine-disrupting effects. Chief among these: triggering apoptosis, interrupting metabolism, and

CIRCUIT BOARD: JULIAN JAMES WARD / MOMENT / GETTY
TIN CUP: STEVEN SANDERS / ALAMY STOCK PHOTO

'obesogen' interactivity — rendering TBTC capable of influencing fat storage in animal models and increasing the likelihood of weight gain in later life[2].

Given their tendency to bioaccumulate and to affect multiple enzymatic pathways, are tin compounds worth the risk in any application? From organometallic and synthetic organic chemists' viewpoints over the past century, yes! Organotin has long been used to trigger radical additions, form polymers and serve as cross-coupling partners for palladium catalysis. This latter technology has recently been expanded to aniline-derived quaternary ammonium salts as coupling partners under nickel catalysis, using trimethyltin aryl species, through Ni–F–Sn complexes[3] The coupling proceeds in high yields despite the presence of functional groups — silyl ethers, nitriles, esters and ketones — that might have interfered with its Pd-catalysed cousin.

Yet many synthetic practitioners now also see tin compounds as a potential liability — a troublesome impurity, and former of potentially toxic byproducts. Efforts are underway to develop a mild, tin-free generation of radical precursors[4] from xanthates and organic peroxides. In the green-chemistry movement, element 50 has also slowly waned in popularity relative to organometallic precursors such as boron or copper. To limit tin byproducts, especially in late-stage synthesis where ppm levels must be explicitly controlled, a variety of polymer- and solid-support-immobilized reagents have also been proposed[5]. These reusable precursors can serve as catalytic generators of organotins or radical precursors.

Yet tin has hardly become obsolete. Its unique conductivity, electronic structure and tendency to readily form alloys have landed it a new role in solar energy and next-generation electronic devices. Traditional alloys such as nitinol (nickel titanium) have given way to Ni–Sn–Sr and tin oxides, which harvest a wider range of available wavelengths of light and are often more highly conductive. Tin-based nanoparticles hold promise as next-generation anodic materials for lithium-ion batteries, spurring interest in their formation and characterization. A three-layered $Sn/SnO/SnO_2$ core-shell nanoparticle, for example, was recently probed through a combination of spectral techniques[6].

Time will tell whether synthetic and solar services can outweigh tin's involvement in toxins and endocrine disruptors. For now, governments and environmental agencies are looking into ways to limit it in manufacturing processes and monitor organotins in potable water (http://go.nature.com/2meRuOq) — so as to keep the Tin Man firmly in the realms of fantasy. ❐

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