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A portrait of Cadmium

Nadezda Tarakina *and* ***Bart Verberck*** *explore the vivid history and assets of element 48.*

In early-19th-century Prussia, quality control of pharmaceuticals was entrusted to government-appointed physicians. In 1817, one such physician, Johann Roloff, became suspicious of a batch of zinc oxide that could be traced back to the factory of Karl Hermann. Roloff's preliminary tests suggested that the samples contained arsenic, and so Hermann — worried about the reputation of his business — investigated further. He and others soon discovered that As had nothing to do with it, but that an unknown metal was involved.

Meanwhile, Friedrich Stromeyer, Inspector-General of the apothecaries in the neighbouring Kingdom of Hanover and professor at the University of Göttingen, was investigating some puzzling zinc carbonate samples that, upon heating, left behind a yellow oxide. He managed to isolate the source of the yellowness down to the oxide of a new metal.

The entangled roles of Roloff, Hermann and Stromeyer — who corresponded and wrote about their findings — make it virtually impossible to give someone sole credit for the identification of the new element [1]. Moreover, others too published reports on the discovery. Different names for the element were suggested, including klaprothium, in memory of chemist (and element-discoverer) Martin Klaproth, and melinum, from the Latin 'melinus', pertaining to quince. However, the name cadmium, originally proposed by Stromeyer, stuck. His proposal came from the root 'cadmia', Latin for calamine, which is an umbrella term referring to various zinc-based minerals.

Cadmium partners vividly with sulfur, CdS being a yellow solid — hence the suggestion of melinum — and is a fixture on painters' and graphical artists' colour palettes under the name 'cadmium yellow'. Solid solutions with selenium, cadmium sulfoselenides, serve as pigments covering orange to red, and mixing CdS with ZnS produces a yellow-green tone. As such, cadmium pigments have been embraced by artists since the 19th century and are known for their outstanding hiding power, light-fastness and stability — qualities that also make them excellent industrial paints. Indeed, thanks to their resistance to temperatures up to 3000 °C, they can be used for painting hot pipes or glass — for example in red traffic lights or the lit stars on the Moscow Kremlin (pictured).

The physical reason for this plethora of colours is that these II-VI Cd compounds are semiconductors with a bandgap in the visible spectrum. CdS has a bandgap of 2.42 eV (512 nm) and therefore absorbs blue, indigo and violet; the spectral complement is thus perceived by the human eye as a yellow.

On account of their bandgap, CdS and CdSe nanoparticles are popular quantum dots. On the nanoscale, due to quantum confinement effects, the absorption threshold of semiconductors becomes size-dependent; the smaller the dot, the higher ('bluer') the energy threshold. The size of such nanoparticles therefore provides a handle for tuning their optical properties, handy for use in display screens— modern pigments, if you like.

The element has no known biological function in higher organisms. In fact, it is highly toxic. As such, regulations on the use of cadmium have become increasingly stringent and cadmium salts are gradually being replaced by azo compounds in commercial paints.

Because of its ability to capture neutrons, cadmium played an instrumental role in the development of the very first nuclear reactor, Cd-coated rods being used to control the nuclear reaction [2]. Other neutron-capturing elements are sensitive to different neutron energies, and so these days control rods consist of mixtures of materials, still including Cd.

From 1907 to 1960, cadmium moonlighted as a metrology standard. During that time, the ångström was defined by fixing the wavelength of a distinct, red spectral line of Cd at 6438.4696 Å — a choice put forward by physicist Albert Michelson [3]. In 1960, the ångström became coupled to the metre, and the latter was redefined in terms of a particular spectral wavelength of ^{86}Kr.

But Cd is perhaps best known for its use in battery technology. The invention of the rechargeable nickel-cadmium battery goes back to 1899, and has played a major role in electrical technology throughout the 20th century. A cell built from Cd and NiO(OH) electrodes delivers a potential of 1.2 volt; Ni–Cd batteries have superb characteristics, including robustness, stability and long life. However, because of Cd's toxicity, the use of Ni–Cd batteries has been increasingly banned in recent years, for example by the European Union's 'Battery Directive' [4], encouraging adoption of less hazardous alternatives such as nickel–metal hydride and lithium-ion batteries.

According to Greek mythology, Cadmus brought the (Phoenician) alphabet to Hellas. Over the past 200 years, cadmium has brought us plenty. Its toxic nature has somewhat caught up with it colourful past, seeing it replaced here and there. But when handled with care, the element's unique merits in chemistry's alphabet can still be put to good use.

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[1] Marco Fontani, Mariagrazia Costa, Mary Virginia Orna, The Lost Elements: The Periodic Table's Shadow Side (Oxford University Press, 2014).

[2] https://www.aps.org/publications/apsnews/201112/physicshistory.cfm

[3] Transactions of the International Union for Cooperation in Solar Research **2**, 17-34 (1908).

[4] Directive 2006/66/EC of the European Parliament and of the Council, http://ec.europa.eu/environment/waste/batteries/

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