

Green bismuth

Ram Mohan looks at how bismuth — a remarkably harmless element among the toxic heavy metals in the periodic table — has sparked interest in areas varying from medicinal to industrial chemistry.

Bismuth, the 83rd element in the periodic table, has been known since ancient times, but was often confused with lead and tin. In 1753, Claude François Geoffroy from France demonstrated that bismuth is distinct from these elements. The word bismuth itself is derived from the German word 'wismuth' (white mass). Studies showed that it was used as early as the sixteenth century by the Incas, who mixed it with tin to prepare bismuth bronze for knives¹. Bismuth was also the instrument of alchemy fraud in the London Stock Exchange — in the 1860s, a Hungarian refugee named Nicholas Papaffy convinced a large number of investors to support his alleged method to transform bismuth and aluminium into silver. This led to a surge in the price of bismuth on the metal market, and the opening of a new company in Leadenhall Street (home of the London Metal Exchange), but by then Papaffy had absconded with the rather large sum of £40,000 (ref. 2).

Bismuth is mainly found in the ores bismuthinite (bismuth sulfide) and bismite (bismuth oxide), but also occurs in its elemental state, in the form of crystals with an oxide layer of varying width that reflects iridescent colours (pictured). It is commonly obtained as a by-product in copper, lead and tin mining, and is therefore relatively inexpensive for a rare metal.

Frequently referred to as the heaviest stable isotope of any element — and for all practical purposes it is — bismuth-209 is nonetheless slightly radioactive. This was first predicted by theoretical studies, then demonstrated in 2003 by astrophysicists in France³, who showed that bismuth-209 has an incredibly long half-life of 1.9×10^{19} years (the age of the universe is estimated to be about 1.4×10^9 years).

Despite its location amid toxic heavy metals in the periodic table, bismuth and its compounds are remarkably harmless —

many bismuth compounds are even less toxic than table salt (sodium chloride)⁴! This makes bismuth unique among the heavy metals, and has earned it the status of a 'green element'. For this reason, the world of cosmetic and medicinal chemistry has paid it particular attention. Bismuth oxychloride, for example, is used to impart a silvery sheen to cosmetics and personal care products. It is also marketed as BIRON powder, which has found applications in catheters for diagnostic and surgical procedures owing to its radio-opaque nature, and bismuth nitrate oxide is used as an antiseptic during surgery.

Perhaps the most well-known bismuth-based medicine is Peptobismol, now a widely available over-the-counter medicine in the US for stomach disorders. The active ingredient is bismuth oxide salicylate.

It was first concocted by a doctor in his home in the early twentieth century to cure 'cholera infantum', an inflammatory disorder that afflicted infants suddenly, causing diarrhoea, vomiting and sometimes death⁵. Although the exact mechanisms of its action are not well understood, it is believed that it lines the abdominal walls with a protective coating that prevents further irritation.

Bismuth has many interesting properties that have led to several applications in industry, and it is commonly used in solders. It is one of the few substances (water being another) that expands on solidification, and has been used to prepare low-melting typesetting alloys that need to expand to fill printing moulds. Bismuth trioxide is also the main ingredient in fireworks called dragon's eggs — those that produce a visual display before exploding with a sharp crack. Bismuth has become popular as a replacement for the highly toxic metal lead, as it has a comparable density and many countries now prohibit the use of lead shot for hunting water birds. Bismuth

is also, along with graphite, one of the most diamagnetic materials known — it is repelled by a magnetic field — and has found applications in magnetic levitation (Maglev) trains, which can achieve speeds of over 250 mph.

More recently, bismuth and its compounds in the +3 oxidation state have found significant applications as green Lewis acid catalysts in organic synthesis. The low toxicity of bismuth salts, their ease of handling and relatively

low cost make bismuth compounds more attractive than other corrosive Lewis acids⁶. In addition to developing applications of bismuth(III) compounds in organic synthesis,

we have developed some bismuth-salt-catalysed green-chemistry experiments for use in undergraduate laboratories⁷.

Bismuth is a therefore remarkable eco-friendly metal with numerous applications in everyday life. With increasing awareness for the environment, one can expect to see a rise in the use of green metals such as bismuth in applications ranging from organic synthesis to engineering. □

RAM MOHAN is in the Department of Chemistry, Illinois Wesleyan University, Bloomington, Illinois 61701, USA.
e-mail: rmohan@iwu.edu

References

- Gordon, R. B. & Rutledge, J. W. *Science* **223**, 585–586 (1984).
- Brock, W. H. *The Norton History of Chemistry* 1st edn (W. W. Norton, 1993).
- Marcillac, P. D., Coron, N., Dambier, G., Leblanc, G. & Moalic, J.-P. *Nature* **422**, 876–878 (2003).
- Suzuki, H. & Matano, Y. (eds) *Organobismuth Chemistry* (Elsevier, 2001).
- <http://www.pepto-bismol.com/>
- Leonard, N. M., Wieland, L. C. & Mohan, R. S. *Tetrahedron* **58**, 8373–8397 (2002).
- Roesky, H. W. & Kennepohl, D. K. (eds) *Experiments in Green and Sustainable Chemistry* 50–56 (Wiley-VCH, 2009).

