

Selenium stories

Russell Boyd ponders on how selenium — despite close similarities with its neighbours of the chalcogen family, sulfur and tellurium — continues to reveal chemical and biological activities of its own.

Element 34 was discovered in 1817 by Jöns Jacob Berzelius, the ‘father of Swedish chemistry’. While preparing sulfuric acid he noticed a residue, which he first thought was tellurium. Realizing it was a new element, he decided to name it after the Greek word for Moon, *selênè*, in a similar manner to tellurium, named two decades earlier by Martin Heinrich Klaproth after the Latin word for Earth, *tellus*.

In nature, selenium is rarely found in its elemental form and only occurs in a few minerals — for example in sulfide ores such as pyrite, where it partially replaces sulfur. It exists as six naturally occurring isotopes with mass numbers 74, 76, 77, 78, 80 and 82; ^{80}Se and ^{78}Se are the most common, with natural abundances close to 50 and 24%, respectively. Selenium is a semi-metallic element that belongs to the family of chalcogens (group 15). Placed just between sulfur and tellurium in that column of the periodic table, it resembles both elements in some aspects. In particular, it has similar allotropic forms and compounds to those of sulfur — for example, red selenium is a Se_8 macrocycle similar to the sulfur allotrope S_8 .

The recommended daily dietary allowance of selenium can be supplied by a single dried Brazil-nut.

Although standard inorganic chemistry textbooks often seem to imply that the chemistry of selenium is not as well developed as that of sulfur, it certainly presents interesting reactivity. Selenic acid (H_2SeO_4) resembles sulfuric acid (H_2SO_4) as its first proton also fully dissociates in water, yet it is a more powerful oxidant, capable, for example, of releasing Cl_2 from concentrated HCl or of dissolving gold to form gold(III) selenate.



Most of the selenium produced worldwide is isolated from the mud that forms at the anode during the electrolytic refining of copper. Selenium was once an essential material in photocopying, but has largely been replaced by organic photoconductors. Combined with bismuth, it has replaced lead in plumbing brasses since the 1990s to meet lead-free environmental standards. Selenium is now particularly promising for various electronic devices — the grey allotrope, its most stable form, is a semiconductor that conducts electricity better in the light than in the dark, and serves in photovoltaic cells. The grey form also converts electric current from a.c. to d.c., which explains why it is a component in rectifiers. The largest worldwide use of selenium, however, resides in glass manufacturing, where it is used as a dopant to produce vivid red and pink colours.

One hundred and forty years passed between the discovery of selenium and its recognition as essential for cellular function in most mammals. It is incorporated in proteins through the amino acids selenocysteine and selenomethionine — in which it replaces the sulfur atom of cysteine and methionine, respectively. Selenoproteins, in turn incorporated in enzymes, are essential components of several metabolic pathways, including thyroid hormone metabolism, antioxidant defence systems or immune functions. There is evidence¹ that selenoproteins reduce cancer risk by

preventing cellular damage from radicals produced as by-products of oxygen metabolism, and they may also prevent, or slow, tumour growth by enhancing immune-cell activity.

In many countries, meat, seafood, rice, noodles and bread are common sources of dietary selenium, but ingesting too little or too much can have serious consequences. The recommended² dietary allowance (55 μg per day for adults according to the Institute of Medicine of the National Academy of Sciences in the US) can be supplied by a single dried Brazil-nut. Selenium deficiency can cause heart disease or weaken the immune system, whereas excessive ingestion leads to selenosis (selenium poisoning), with symptoms such as discoloration of the skin, a garlic odour to the breath and lack of mental alertness — more than 5 mg per day can be fatal. The tolerable upper intake level set by the Institute of Medicine is 400 μg per day for adults; it thus cautions that many dietary supplements contain 50 to 200 μg per daily dose.

Elemental selenium is usually assumed to be harmless, but many of its compounds, for example hydrogen selenide (H_2Se) are extremely toxic. This is why the general perception is that selenium is toxic, even though modern science has recognized it as an essential micronutrient. Recent advances indicate that selenium has the potential to improve human lives in varied ways, including as part of more efficient solar cells², synthetic antioxidants³ or nanocluster coatings for use in orthopaedic applications⁴. □

References

1. Combs, G. F. Jr *BioFactors* **14**, 153–159 (2001).
2. Mayer, M. A. *Appl. Phys. Lett.* **97**, 022104 (2010).
3. Heverly-Coulson, G. S. J. *Phys. Chem.* **114**, 10706–10711 (2010).
4. Tran, P. A. *Int. J. Nanomed.* **5**, 351–358 (2010).

RUSSELL BOYD is at the Department of Chemistry, Dalhousie University, Halifax, Nova Scotia B3H 4R2, Canada.
e-mail: russell.boyd@dal.ca

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