

# Ambiguous bromine

Many chemical elements behave quite differently depending on the compound they are found in, but **Matt Rattley** argues that bromine does so in a particularly striking manner.

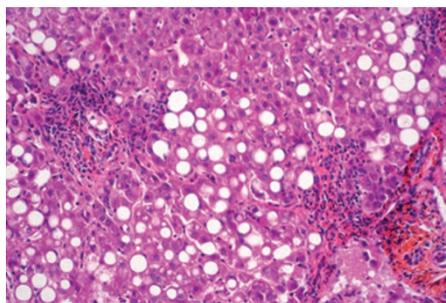
Every element is a little bit schizophrenic in its own way. Carbon's split personality is best exemplified through two well-known allotropes, graphite and diamond; transition metals transform from bland grey blocks to wonderfully colourful salts; and even notoriously inert noble gases, for example xenon, can be coaxed into reacting with other members of the periodic table to produce exotic species including fluorides and oxides. And so it is with bromine too. Sitting quietly in the middle of the *p*-block, it is one of the most deadly elements, yet one with intriguing and useful properties.

It is one of bromine's less pleasant characteristics — a more biting, sour smell than that of chlorine gas — that gave it its name, from the Greek *βρώμος* (*brómos*) meaning 'stench' or 'foul odour'<sup>1</sup>. Despite being a liquid at room temperature, it is highly volatile and produces a thick vapour layer.

The only redeeming feature of the vapour is its distinctive orange colour, which means that you can readily avoid it. And avoid it you should. Bromine is highly toxic, especially in sunlight; radicals generated on ultraviolet irradiation will wreak havoc on anything and everything they encounter, including lung tissue. Bromine atoms are also found in some astonishingly toxic natural products synthesized in some marine sponges and corals, which can exhibit lethal doses more than 1,000 times more potent than aqueous arsenic.

It may sound surprising, therefore, that anyone should want to go near this noxious element. Yet brominated molecules have attracted much attention. The widely used insecticide chlorfenapyr<sup>2</sup>, for example, is an unusual species containing three different halogens (fluorine, chlorine and bromine).

Perhaps nothing shows bromine's equivocal character quite like potassium



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bromide. A not-too-distant cousin of table salt, this deceptively simple compound was used for much of the nineteenth and twentieth centuries as an anticonvulsant and a sedative. It exhibits chronic toxicity — abuse leads to a condition called bromism, characterized by seizures, vomiting, psychosis, skin lesions and delirium — but when suitably administered it works remarkably well by inhibiting the central nervous system. Although for human use it has now been replaced by alternative compounds such as pregabalin<sup>3</sup> that act more rapidly and with fewer side effects, it still fulfils this sedative role today in veterinary medicine.

Other attempts to tame and use brominated compounds have not been so successful. This is no recent trend — and perhaps something the women of ancient Egypt might have preferred to know. They often added small amounts of bromine mannite (a derivative of polyalcohol mannitol found in plants) to a mixture used to colour their lips to obtain a rich red-brown colour. Unfortunately, even the small amount of residual bromine in the mixture was likely to be enough to accidentally kill both women wearing it and men kissing them.

The ambiguous nature of bromine also shines through in uses that were initially intended to keep us safe. A variety of compounds, such as the polybrominated aromatic compound tetrabromobisphenol A, have been incorporated in clothes and other

textiles to prevent, or slow down, the spread of fire should they be placed near an open flame. These compounds may, however, have a harmful effect on human health — the extent of which remains unclear — and some polybrominated diphenyl ethers have recently stopped being used as flame retardants in various countries; whether alternative compounds now in use are harmless is still an open question<sup>4</sup>.

Although a somewhat volatile and unpredictable element, bromine has played an important part in advancing the field of molecular biology in the form of the polybrominated dye eosin, in which this heavy atom ensures efficient absorption of light. Alternative dyes do exist, but in tandem with another small organic compound, haematoxylin, eosin is used almost universally to stain the cytoplasm in a cell and numerous other protein-based structures (although, notably, the nucleus is preferentially stained by haematoxylin). The resulting cell images are rather striking, with rich purple colours arising from eosin (pictured for Hepatitis C cells).

The diverse reactivity that bromine brings goes far beyond simply acting as a relatively sizeable anion to balance charge, taking part in cross-coupling reactions, or forming the basis of a good partner in an  $S_N2$  reaction. We may yet find other ways to make the most of brominated species, owing to, or in spite of, their frequent toxic side effects. □

*This essay was selected as a winning entry in our writing competition, see <http://go.nature.com/oi187X>*

**MATT RATTLEY** is an undergraduate student at the Department of Chemistry, University of Oxford, South Parks Road, Oxford OX1 3QR, UK.  
e-mail: [matt.rattley@some.ox.ac.uk](mailto:matt.rattley@some.ox.ac.uk)

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