Who's afraid of bromine?

By Laurence Knight
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Bromine looks sinister - like something you might find on Dr Frankenstein's workbench. But are people sometimes too hard on compounds made from element 35 of the periodic table?

As you read this article, you are probably surrounded by bromine - in the chair or sofa you are sitting on. In the carpet on your floor, the curtains at your window, perhaps even the walls of your house. And in the computer whose screen you are staring at.

All these things are likely to contain unnatural substances such as polybrominated diphenyl ether or hexabromocyclododecane. Bromine-based chemicals have also found their way into food and drinking water - indeed until recently they were added to drinks like Fanta and Gatorade.

Some of these chemicals have been shown to be dangerous to human health, and have been banned or withdrawn. Yet the bromine industry claims it is the victim of "chemophobia" - an irrational public prejudice against chemicals borne out of ignorance and misinformation.

Bromine saves lives, they point out.

There is no denying that pure bromine is extremely unpleasant. It derives its name from the Greek for "stench", and it is a particularly vicious material - just ask Andrea Sella of University College London.

"When I was at school nobody had warned me about how nasty this stuff was,"

the chemistry professor ruefully recalls, as he pours some of the toxic red liquid into a beaker, where it sits under a smog-like haze of heavy brown vapour.

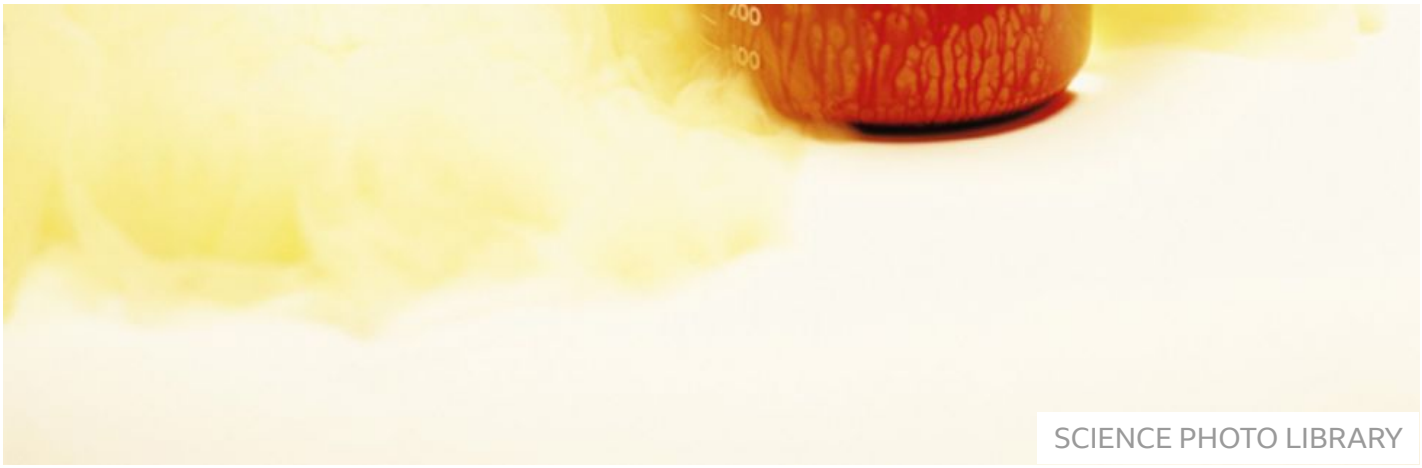
"I managed to spill a bit of bromine liquid on to the back of my hand, and it burned through the skin and left a long scab that took weeks to heal."

Bromine is one of the halogens - the group of elements that occupy the penultimate column of the periodic table. And it is probably the least well known - chlorine we know from swimming pools, iodine from antiseptics, and fluorine from toothpaste.

Being a halogen, bromine atoms are one electron short of a complete outer shell, which makes them highly reactive, readily bonding with other atoms. That is why pure bromine is so dangerous to handle, and also why you never come across it in nature.

Instead, bromine is commonly found in highly un-reactive bromide salts - in much the same way that the poisonous green gas chlorine is commonly found in boring sodium chloride, table salt.

To illustrate the point, Andrea drops some aluminium foil into his beaker of bromine. It bursts into intense flames. When the fire burns out, all that is left is a residue of aluminium and bromide salts.



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It was from naturally occurring salt waters that two chemists independently discovered bromine two centuries ago - the German Carl Jacob Lowig from mineral water in 1825, and the Frenchman Antoine Balard from salt marsh seaweeds in 1826. Both used chlorine gas to displace the bromine atoms from their salt solutions, producing the characteristic acrid fumes of the new element.

Today, bromine is extracted on an industrial scale from salt lakes that are especially rich in the element, above all the Dead Sea.

"The Dead Sea has the highest concentration in the world of bromine," says Ilan Elkan of Israel Chemicals Ltd (ICL) at the company's bromine facility, the world's biggest. "This is the gift of nature. Like Saudi Arabia has the gift of oil,

we have the gift of bromine." He claims it will last thousands of years, far longer than Middle Eastern oil.

ICL draws water down from the Dead Sea into a vast network of evaporation ponds that use the sun's energy to concentrate the minerals. The thickened brines then flow through a series of chemical works that extract potash, magnesium metal and chlorine from the salts - and bromine.

Much of this toxic end-product is then shipped all over the world in gigantic lead-lined tanks - Ilan insists they have never had a spillage. Yet, as hazardous to human health as elemental bromine is, it is actually the products it goes into that have caused the real alarm.

ICL

The earliest use of bromine was in medicines. Some bromide salts, notably potassium bromide, were found to be natural sedatives, and were prescribed in the 19th Century as a remedy for epilepsy.

However, they had a curious side-effect. They dampened the libido, which only reinforced the common misconception at the time that epilepsy was brought on by excessive masturbation. This side-effect also lies behind the urban myth

that bromide was added to the tea of prisoners and World War I soldiers in order to reduce sexual urges.

For most of the 20th Century, the main use of bromine was something now known to have been seriously damaging to public health. When lead first started being added to petrol to improve engine performance, it was found that deposits built up, eventually clogging the engine.

The solution was to add brominated chemicals to the petrol. As the fuel burnt, the bromine combined with the lead, producing lead bromide. This readily passed out through the exhaust, but of course then proceeded to spread the poisonous heavy metal throughout our cities.

Leaded - and brominated - petrol is no more. But the biggest modern use of bromine, accounting for 41% of the market, has also sparked controversy.

"Imagine you're watching your television, and halfway through a soccer game your TV catches fire," says ICL's deputy president Anat Tal at their head office in Beersheva, southern Israel. "You have three minutes of escape time. What do you do? You just run!

"Now imagine the escape time is five-to-10 times more, because inside your TV is a brominated flame retardant. This is the story of flame retardants."

A fire is a self-perpetuating chemical reaction in which the high temperature encourages fuel to combine with oxygen in the air, further raising the temperature in the process. Bromine disrupts this chemical reaction. Because the bromine is itself so hyper-reactive, in effect it queue-jumps the oxygen and re-bonds with the fuel, rendering it inert.

Brominated flame retardants crop up in a surprising number of places. From a bag, Anat produces, Mary Poppins-style, a series of products - white beads that are mixed into the plastic casings and circuit-boards of TVs and computers, fluffy yellow pillow stuffing that refuses to catch fire, and blue polystyrene bricks that are used as cavity wall insulation in homes.

So what's the problem with these products?

Well, take for example, polybrominated diphenyl ethers (PBDEs), which used to be widely used to prevent materials from melting. No longer. "It's pretty dangerous if it gets into the human body," explains chemical industry analyst Laura Syrett of Industrial Minerals. "It can cause cancer, developmental disorders, thyroid problems."

Or how about hexabromocyclododecane (HBCD) - the chemical in Anat's blue cavity wall insulation. It is set to be banned in the EU next year, after an

academic study in Texas in 2012 found that **tiny amounts of the stuff were getting into some supermarket foods**.

The retardants are organic molecules - an entirely different class of chemical from bromide salts - that can take years to decompose. And although they should be tied up inside plastics and other materials, when they do get free they tend to accumulate through the food chain - meaning top predators such as humans face a particular risk of these chemicals slowly building up in our bodies.

This highlights an unavoidable problem for the chemicals industry - much of what they do is still a learning process, and it often takes many years for the long-term risks inherent in a particular product to emerge. Yet it is also important to get these risks in perspective. So far, there are no known cases of brominated fire retardants actually causing anyone major health problems - they are being banned because of the potential hazard they pose. Meanwhile, these chemicals have undoubtedly saved people from the very real risk of burning to death in their own homes, although there is some dispute whether that amounts to the thousands per year claimed by the industry.

But Laura Syrett says the industry also labours under another problem - "chemophobia".

As an example **she cites brominated vegetable oil or BVO**, which was commonly added as an emulsifier in soft drinks such as Fanta and Gatorade. Without BVO or a substitute, the orange colour would gravitate to the bottom of your bottle, leaving the top half clear. Something similar would happen to the flavour.

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Gatorade no longer contains BVO

In 2013 Buzzfeed **published an article** with the title "8 Foods We Eat In The U.S. That Are Banned In Other Countries". The list included BVO - banned in the EU and Japan - which it claimed was "linked to major organ system damage, birth defects, growth problems, schizophrenia, and hearing loss".

Pepsi and Coca Cola insisted BVO was safe. Nonetheless, a petition on Change.org gathered 200,000 signatures, and both companies have since stopped using the chemical.

Was the campaign against BVO rational? The chemistry blogger Derek Lowe points out that the few people known to have suffered health problems (none of which were quite like those listed by Buzzfeed) were drinking a vast amount of BVO-containing drinks - **in the order of two to four litres per day**.

Another controversial case, according to Laura Syrett, is connected with fracking. In 2011, tests of drinking water wells in Pennsylvania found increased levels of bromide salts - the same kind of stuff that supposedly makes people prefer an early night with a hot water bottle - linked to fracking activity at the Marcellus shale deposit.

Bromide salts are widely used in oil and gas drilling. Being near the bottom of the periodic table, bromine atoms are heavy. Dissolve its salts in water and you get an exceptionally heavy brine that can be used to stabilise high pressure wells and stop them collapsing.

In the end, an error was found in the Marcellus tests - in reality only one well showed elevated bromide levels, not seven as originally reported. One case, Syrett suggests, is a long way from proving a causal connection.

At ICL, Anat complains that her company hears via the media and NGOs "almost on a daily basis... all kinds of things that are not scientifically proven". Meanwhile, she points out, tourists are happy to come and bathe in the Dead Sea, with the world's highest concentration of bromide at 0.5%, because of its "healthy" mineral salts.

THINKSTOCK

The criticisms sting for an industry that feels it is actually doing a lot of good for the world. Besides fire retardants, one of the biggest new uses of bromine is in capturing mercury in the coal burned in power stations - in much the same way that it used to capture lead in the petrol burned in your car engine, except that this time it actually helps to stop the emission of a poisonous metal into the air.

As Anat laments: "The bromine industry has not done a very good job in PR, in educating people that there are chemicals there that save your life and keep you safe."

It certainly does not help that so many of the chemicals they produce have such terrifyingly long and alien names… polybrominated diphenyl ether and hexabromocyclododecane, for example.

To put it another way, who would drink coffee if they knew it contained 1,3,7-Trimethylpurine-2,6-dione (caffeine)? Especially if you added a spoonful of ((2R,3R,4S,5S,6R)-2-[(2S,3S,4S,5R)-3,4-dihydroxy-2,5-bis(hydroxymethyl)oxapent-2-yl]oxy-6-(hydroxymethyl)oxahexane-3,4,5-triol) - better known as sugar?

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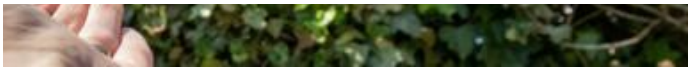

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