

Media communiqué

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Empa and ETH chemists lay the foundation stone for the risk evaluation of brominated flame retardants

Brominated for eternity

Chemically-based flame retardants have paved the way for many plastics to become ubiquitous materials in our daily life. However, what protects plastics and similar substances from fire on the one hand represents a potential risk to the environment, the animal kingdom and humankind on the other. Empa chemists have now taken a close look at hexabromocyclododecane (HBCD), a widely used bromine-containing fire retarding agent. The investigation revealed that HBCD occurs in several different forms, or so called stereoisomers. In cooperation with the ETH Zurich, the Empa researchers have developed an analytical technique which allowed them for the first time ever to identify eight different HBCD stereoisomers and determine their structure. The complicated molecular geometry of the substance has important implications – only two isomers accumulate in fish tissue. How the HBCD types otherwise differ must be investigated further, for only then can a comprehensive risk evaluation of HBCD be made, according to the Empa scientists.

Flame retardants are to be found everywhere. Easily identified examples from office life are the computer, table, chairs and telephone. A little less obvious are cable sheathing and insulating foams. Many plastics contain a dose of flame retarding chemicals, and without these additives a spark would be enough to start the material burning like tinder. Our daily life would be much more dangerous without them. Flame retardants act as built-in fire extinguishers, and they ensure that a moment of carelessness does not turn into a catastrophe.

But this resistance to fire comes at a price. Some flame retardants are suspected of being toxic to humans and to our environment. One example is the frequently encountered range of brominated (bromine containing) chemicals which mix well into the plastic material but cause problems in various ecosystems. In 2004, for example, brominated diphenylethers (with a single exception) were banned internationally for being POPs – Persistent Organic Pollutants, organic environmental pollutants which degrade very slowly, accumulate in the food chain and disrupt the endocrine balance in humans and animals. “But this is only the tip of the iceberg,” says Empa chemist Martin Kohler. “There are many chemical in use today whose effects on the hormonal balance of humans and animals are completely unknown.”

Brominated flame retardants accumulate in the environment

Empa's Analytical Chemistry Laboratory is internationally recognized as being at the head of the field in terms of identifying such environmentally active substances. As long ago as in 2003 Heinz Vonmont and his team drew attention to a possible new danger, hexabromocyclododecane, abbreviated to HBCD.

Researchers discovered that it was accumulating in fish in the Greifensee, a shallow lake in Canton Zurich. It was also accumulating in the lake bed, and from studying the sediment layers it was possible to infer that the concentration of HBCD in the environment has steadily risen over the past twenty years.

This is not a coincidence. HBCD has been available commercially as a flame retardant since 1984, but the chemical composition of the substance has not previously been given much attention. However, recently Empa analytical chemist Norbert Heeb and his colleague Bernd Schweizer of the ETH Zurich made a surprising discovery – HBCD is actually a mixture of at least eight “stereoisomers”. Although all the isomers contain the same ring of 12 carbon atoms and have the same chemical formula and composition, they have different spatial structures.

One name – many different forms

Memories of lindane come flooding back. Sold in the 1960's as an agent for preserving and treating wood, it was later discovered to be a toxic mixture of isomers. Only one form killed insects, the others were ineffective against pests but accumulated in the environment due to their slow rate of degradation and were suspected of being carcinogenic. In the commercially available HBCD mixtures also, two forms dominate – the gamma isomers, as Heeb confirms. “We still don't know if they are toxic or harmless.” All eight isomers do, however, act as flame retardants, since this common property is based on bromine radicals being released as soon as the plastic becomes sufficiently warm.

To date, no one knows much about the long term effects of HBCD in the environment. One thing is however clear – the more complex the mixture of substances to be investigated, the more difficult the risk evaluation. The Empa scientists, for example, found only the two alpha forms of HBCD in fish. They are therefore suspected of being particularly long lasting in the environment. “Alpha HBCD looks like a doughnut,” explains Heeb, referring to its three dimensional structure. “It is the most symmetric of all the isomers.” This has possibly fatal consequences, for there are studies which show that HBCD may act as an endocrine disruptor and so could affect the metabolism of living creatures. Damage to nerve cells has also been observed. Mice which were fed HBCD shortly after birth were poorer at learning to orient themselves and forgot what they had learnt more quickly than those which were not so treated. However, which form of HBCD was responsible for these effects is not yet known.

Selective effects necessary for risk evaluation

In order to determine this, the isomers must be individually tested. “The HBCD effects observed so far could also be caused by the delta and epsilon forms – that is by two isomers which make up less than one percent of the industrial product,” says Heeb. If it turns out that certain isomers are toxic or do accumulate in the environment, then the harmless HBCD isomers could be manufactured using stereoselective synthesis techniques.

The Swedish chemical regulatory authority, «KemI», which is currently working on a European risk evaluation project on behalf of the EU, literally tore the Empa researchers' results out of their hands. That

HBCD actually consists of a mixture of eight different forms of the chemical was not known to them, and now thanks to the Empa results the Swedish authorities can begin the evaluation process more selectively.

Brominated flame retardants are also being studied in Switzerland, in the National Research Program NFP50 «Endocrine Disruptors», in which Empa is playing an active role. Its researchers are focusing on investigating the level at which these kinds of chemicals are being introduced into the environment, and the influence they have on humankind, the animal world and ecosystems. It is expected that sometime this year, based on these scientific results, a consensus will be established between researchers, regulatory authorities and industry on the effects of brominated flame retardants and the legislative measures to be recommended. This consensus will form the basis for a new evaluation regarding which flame retardants can be taken to be harmless in the light of current knowledge, and which belong on the list suspect substances.

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Builder's rubble which includes façade insulating material can contain flame retardants.



Whitefish prepared for the measurement of concentrations of flame retardant HBCD. Two of the eight different forms of HBCD accumulate in the fatty tissue of the fish.