„Poison in textiles“

Quantitative determination of organotin

Analysis of organotin compounds in the eco-Umweltinstitut in Cologne, Germany (Dr. Hans-Ulrich Krieg, Managing Director)

In January 2000, the German *plusminus* TV programme started a media frenzy with a report called 'Poison in textiles' featuring the presence of organotin compounds in, among others, soccer shirts. Although the concentration of organotin compounds found in textiles was quite low, interest in this class of compounds was awakened, particularly for the highly toxic compound tributyltin (TBT).

The *Öko-Test* ("eco test") magazine included the organotin compounds in its evaluations. A discussion began which went further than the contamination of textiles. Concerns regarding the intake through food consumption and the pollution of ecosystems by organtin compounds were raised. The internationally recognized *eco-Umweltinstitut* (Eco Environmental Institute) in Cologne, Germany, took up the challenge to react rapidly to these developments and included the determination of organotin compounds in the wide range of analyses carried out by the Institute. The range of analytical services that the Institute provides includes testing of consumer goods and furnishing materials with respect to prohibited or hazardous substances.

Use and toxicity of organotin compounds

In general, all organotin compounds are considered to be toxic. The most notorious compound is tributyltin (TBT), a very persistent and highly toxic cell poison that is difficult to degrade. TBT is one of the most poisonous compounds released into the environment, and in humans it causes damage to the hormonal, immune and central nervous systems as well as to the liver and kidneys.

The greater part of the worldwide production of organotin compounds is used as heat and ageing stabilizers in plastics, for example, PVC. These compounds are also employed as antifouling paints for ships, as pesticides, as preservatives in water-miscible and antifungal paints and as fungicides in textiles, leather, paper and wood. Synthetic fibres in particular were frequently treated with TBT, monobutyl- and dibutyltin. The organotin compounds prevent the development of an unpleasant smell in textiles during heavy sweating.

Recommended values for organotin compounds

The investigation of textiles for organotin compounds is, at present, an important part of the quality control of these products. Since there are no legally prescribed threshold values, recommended values are used for private labels and quality brands.

The *Öko-Test* magazine, for example, recommends a TBT value of 0.025 mg/kg textile, and for other organotin compounds a value of 0.25 mg/kg. The Öko-Tex Standard 100 differentiated between the categories Baby (TBT: 0.5 mg/kg; DBT: 1 mg/kg) and other categories (TBT: 1 mg/kg; DBT: not specified). The ‘Association of Environment-compatible Latex Mattresses’ (QUL, Qualitätsverband Umweltverträgliche Latexmatrazen) uses the following orientation values: TBT: 0.05 mg/kg and DBT: 0.25 mg/kg textile. The analytical methods described

compounds using the GCMS-QP2010

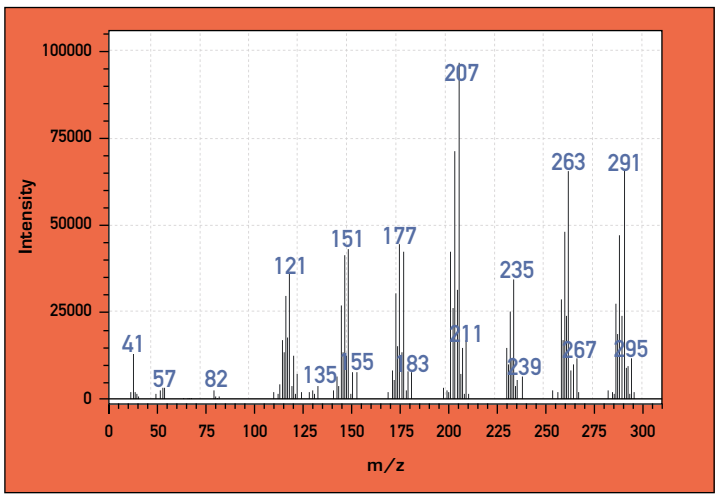

Figure 1: Mass spectrum of TBT after ethylation

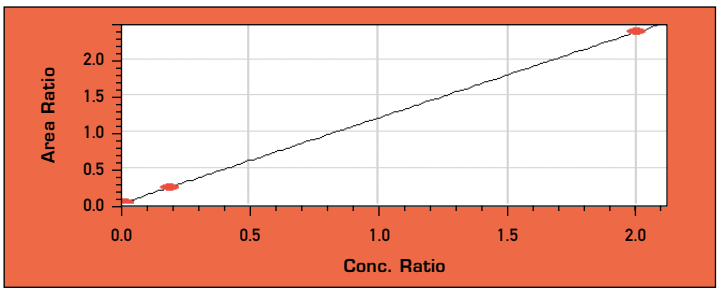

Figure 2: Calibration of TBT using the internal standard method (concentration TBT: 0.1; 1.0; 10 ng/µl)

below are based on the QUL values.

Analysis of organotin compounds in textiles

Extraction: 2 g of the substance to be investigated are boiled in acidified methanol (0.1 %) under reflux conditions for 30 minutes. During sampling, close attention should be paid to the homogeneity of the sample. If the textile consists of several different fabrics or different colours, an aliquot from each fabric or coloured part should be prepared.

Derivatization: Ethylation of the organotin compounds is performed using sodium tetraethylborate at pH 4.5 in n-hexane and takes approx. 3 - 4 hours.

Purification: After derivatization, the sample is purified over silicagel (EN DIN 38407-13D) using hexane as solvent. The final volume of the purified sample is 200 µL in n-decane.

GCMS-Methode: The analysis is carried out using a Shimadzu GCMS-QP2010 quadrupole mass spectrometer. Separation is carried out on a capillary column DB-5, 30 m, 0.25 mm ID, 0.25 µm. Injector temperature: 260 °C, splitless injection, high-pressure injection 100 kPa, 2 min. temperature program 60 °C for 2 min, at 8 °C/min to 160 °C, at 20 °C/min, holding for 2 min. Parallel to the temperature program, a pressure program is performed (linear velocity mode). Ion source temperature: 250 °C, interface temperature 320 °C, SIM mode.

For each degree of alkylation, organotin chlorides (for example, monoheptotin trichloride) are used as internal standards.

Summary

Tin has many naturally occurring isotopes and TBT exhibits strong fragmentation. TBT was therefore considered not to be suitable for mass spectrometric detection. TBT can, however, be determined on a QP2010 at high sensitivity in textiles using the above-described analytical method. The detection limit for the routine analysis of TBT is 0.5 ng/L absolute - if the instrument is in good operating condition, a detection limit of 0.1 ng/L can be obtained. In textiles, this corresponds to a concentration of 0.05 mg/kg.

This value exactly coincides with the recommended value of the QUL for TBT. The orientation values of the Öko-Tex Standard 100 are also within the range of the detection limit of this analytical method.