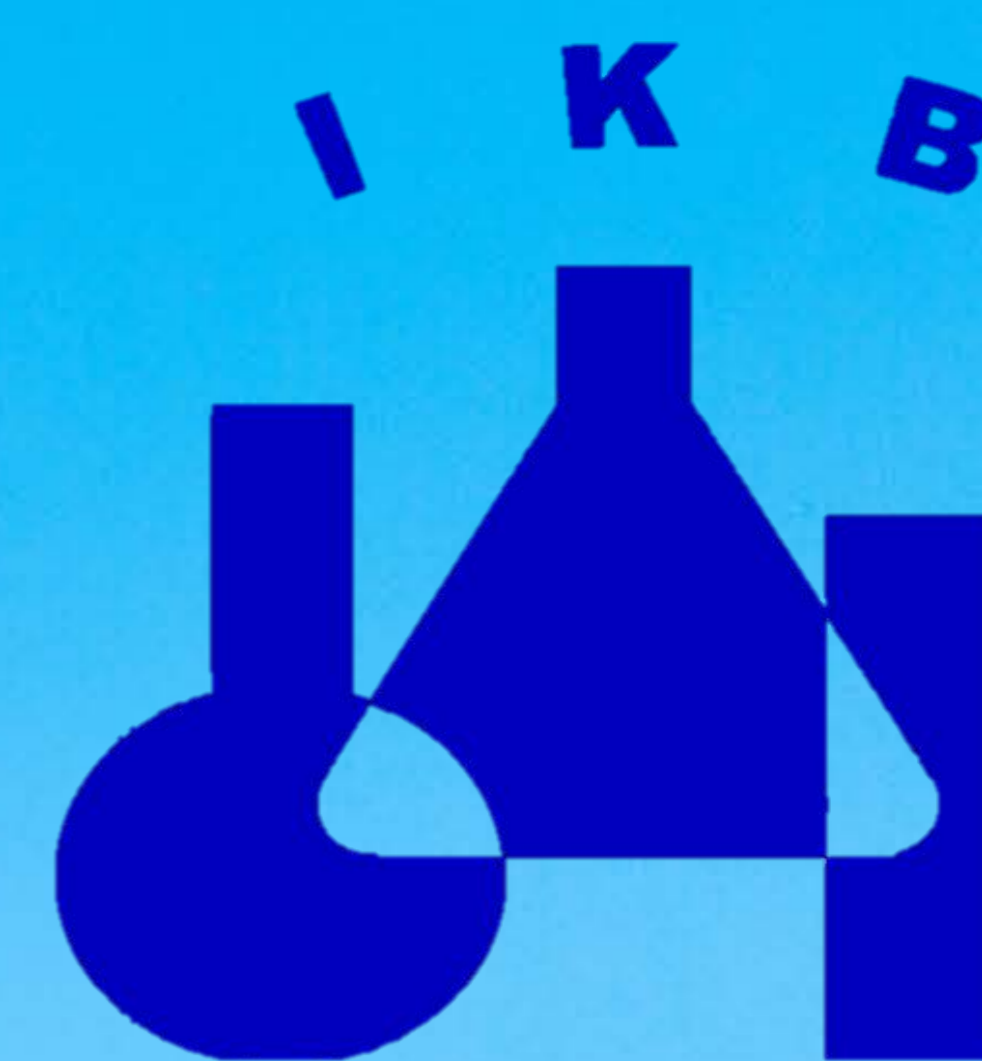


„Unconventional“ contaminants in grain and grain-based products

- modern analytics, „new“ compounds -



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Introduction

Mineral oil, tropane alkaloids, pyrrolizidine alkaloids - these contaminants have probably occurred for a long time in cereals and cereal products, but have never been analyzed. Institut Kirchhoff Berlin GmbH (IKB) has established modern analytics which can uncover even traces of these contaminants.

Which are the sources of these food contaminations? What can be said about the toxicological relevance and legal aspects. How do we analyze these contaminants?

Mineral oil

Pyrrolizidine alkaloids

Tropane alkaloids

Origin

In many foods mineral oil hydrocarbons (MOSH=mineral oil saturated hydrocarbons; MOAH= mineral oil aromatic hydrocarbons) are detectable, often the food is already contaminated before packaging. There are a number of possible sources for an entry of mineral oil hydrocarbons. Raw materials can be contaminated for example by lubricating oils of harvesting machines, pollution or exhaust gases of diesel engines. Another important aspect is the transport packaging of the raw materials. Among other mineral oil containing recycling packaging or plastic packaging can contribute to contamination. In the manufacturing process contamination can be carried out by oiling machine components. Furthermore packaging of the food and printing plays an important role.

Pyrrolizidine alkaloids (PA) are substances that are formed by many plant species for protection from predators. Over 500 compounds are among the pyrrolizidine alkaloids, which occur in more than 6000 plant species, especially in Compositae, Leguminosae and Boraginaceae. PA are often entered in food via weeds, for example in herbal teas, cereals, salads and leafy vegetables. Also contamination from animal foods such as honey (entry via nectar from PA-producing plants) and milk (entry via feed) are known.

Tropane alkaloids (TA) are natural ingredients of certain plant species such as hyoscyamus, datura and atropa. More than 200 different TA have been identified in plants so far. Due to the contamination of grain (for example known in buckwheat and millet) with seeds of hyoscyamus or datura tropane alkaloids may also occur in grain-based foods.

Toxicological risks and legal limitations

Actually there are no legal limits for mineral oil hydrocarbons. Due to the carcinogenic potential of compounds of the MOAH fraction those are undesirable. According to the Federal Institute for Risk Assessment (BfR) the intake of MOAH should be completely avoided. The ALARA principle is applied here.

Acute health damage caused by PA is unlikely, but PA are chronically toxic. They have partially proved to cause cancer in animal studies; but most of all they are toxic on the liver. With the exception of pharmaceutical drugs, there are no general worldwide legal limits for PA in food and feed. A limit of 1 µg PA per day for oral intake and 100 µg PA per day for external application is applied for herbal medicinal products. These products may be used up to 6 weeks a year. With prolonged use a lower limit of 0.1 µg PA respectively 10 µg PA per day will apply. These drugs should not be used for pregnant women and breast-feeding women. The European Food Safety Authority (EFSA) sees no possibility of establishing a tolerable daily intake (TDI).

According to the Federal Institute for Risk Assessment (BfR) TA can affect the heart rate and the central nervous system even at low doses. Dizziness, headache and nausea are typical symptoms. For risk assessment the European Food Safety Authority (EFSA) derived an acute reference dose (ARfD) as health based guidance value of 0.016 µg/kg body weight (bw), based on the sum of (-) - hyoscyamine and (-) - scopolamine (group ARfD). No legal limit exists.

Analytics

Mineral oil hydrocarbons are determined using an on-line-HPLC-GC. The normal phase HPLC retains interfering lipids, wax esters and separates the MOSH fraction from the MOAH fraction. The respective fraction (MOSH/MOAH) is then detected by FID. The limit of quantification is 0.5 mg/kg.

To determine the pyrrolizidine the IKB established an analysis method originally published by the German Federal Institute for Risk Assessment (BfR) and made further developments. Diluted sulfuric acid is used as extraction solvent. The extract is purified by Online-SPE. A total of 28 compounds with quantitation limits of 1 to 5 µg/kg are analyzed.

The Tropane alkaloids atropine (racemic mixture of (-) - hyoscyamine and (+) - hyoscyamine) and scopolamine are determined by HPLC-MS/MS using isotope-labeled internal standards after extraction and purification of the extracts by dispersive SPE. The analysis method established in the IKB achieves a detection limit of 1 µg/kg.

Conclusion

Because of the toxicological relevance of these contaminants an analysis in terms of consumer protection is quite reasonable. The IKB has already analyzed many samples on mineral oil hydrocarbons, tropane alkaloids and pyrrolizidine alkaloids.