1. Introduction

Food can get contaminated by mineral oil hydrocarbons (MOH) by paper and cardboard packaging. The source of this contamination is printing inks, which are either directly applied onto the packaging or introduced via the recycling process. The risk of contamination is not only through direct contact with packaging material, but also along the entire production and commercial chain.

According to latest scientific research work, there is not enough toxicological evidence to prove a health risk to humans from saturated mineral oil fractions (MOH). Mineral oil aromatic hydrocarbons (MOAH), on the other hand, are suspected of having a carcinogenic effect. Especially PAH with three to seven ring systems, therefore their levels in foodstuffs should be kept to a minimum as per the ALARA principle (as low as reasonably achievable). Currently there are no specific legal regulations or maximum allowable concentration levels for mineral oil residues in foodstuffs. In February 2017 the fourth draft of the 22nd Ordinance on determining the German Consumer Goods Ordinance (Mineral oil ordinance) was published. This stipulated, that functional barriers should be used to ensure that MOAHs from materials containing recycled paper in contact with foodstuffs are not transferred to the foodstuff in detectable levels. The applicable detection limit is 0.5 mg/kg foodstuff.

The draft is currently in consultation at the Federal Ministry and is due to be notified by the European Commission (1).

2. MOOH/MAOH System Configuration

The system configuration consists of a Shimadzu Nexera system with 1 LC-400FMR pump, CPU-40A-LITE system controller, SPD-40A UFC UV Detector coupled with GC-2030 and 2 FID detectors. For online aluminium oxide purification 1 LC-40D pump is needed. The PAL autosampler and the user-friendly CHRONOS software (AXEL SEMPRAU, Sprockhövel) in combination with LabSolutions software platform allows a high level of automation. An automated sample preparation and purif.

3. Experimental Setup

The LC is directly connected to two high temperature GC columns with retention times suitable for analysis of the MOH and MOAH fractions. An overview of MOH/MAOH concentrations in food and food packaging reported by EFSA are listed in table 1 (2).

The analytical procedure is described in the European Norm EN 16995:2017 Determination of mineral oil saturated hydrocarbons (MOOH) and mineral oil aromatic hydrocarbons (MOAH) on an on-line HPLC-GC-FID analysis (3).

![Figure 1: Shimadzu MSH/HIDAC analyzer](image)

The concentration of MOH in paper products is up to 1000 mg/kg of which 70% can migrate into the food product through direct contact via the gas phase. An overview of MOH/MAOH concentrations in food and food packaging reported by EFSA are listed in table 1 (2).

4. Sample Preparation

Depending on the expected mineral oil concentration 1-10 g of homogenized samples were used. The samples were extracted in Hexane, after adding an internal standard mixture (Festek MOSH/MAOH standard Cat.#31070 containing 9 internal standards) at room temperature for 2 hours or overnight under occasionally shaking the flask. The glass columns with inserted filters were filled with 10 g of aluminium oxide (99, 0.063 mm - 0.2 mm, activated for 10h at 500 °C) and 3 g of silica gel (60, 60 µm - 200 µm) per 70mL. Hexane-MOSH respectively, activated for 10h at 40 °C. The columns were washed with 20 ml of n-Hexane prior to loading the sample. The extracts were centrifuged if necessary, concentrated to a volume of about 1 ml under a stream of nitrogen. About 100 µl were taken and filled into an autosampler vial with micro insert for analysis of MOAH, the remaining samples was loaded onto the column. The MOAH fraction was eluted with 20 ml of n-Hexane, concentrated in an evaporation concentrator and transferred into a 2 ml autosampler vial. This placed in the autosampler rack of the GC-system. Aliquots of 50 µl were injected into the LC and 400 µl were transferred directly on the pre-columns for the MOAH fraction only.

5. Measurement

Figure 3 shows two chromatograms of a MOSH fraction of a rice sample spiked with 5 mg/kg of a mineral oil. Before flash chromatography with Alu n-Alkanes in the range of C20-C24 are present. “False positive” integration would give a MOSH value of 10.8 mg/kg. After flash chromatography the n-alkanes were completely removed and data evaluation is possible without any interferences. The result for the MOSH value is 4.31 mg/kg oil. The sample that was injected is a foodstuff with MOSH concentration gives a concentration of 0.44 mg/kg and results in a total MOH recovery of 4.95 mg/kg of the spiked 5 mg/kg.

6. Comprehensive GCMS

In case of a detected MOSH concentration in food it is important to understand the origin of the contamination and the totality. Also, cross-contamination generated from MOH, POSH, PAH and others should be excluded. That is why according to EU norm 16995:2017 GCMS is required. More effective is GC x GCMS technique or comprehensive GCMS. Comprehensive GCMS is a powerful technique that provides a two-dimensional chromatography data acquisition, resulting in a significantly improved resolution and sensitivity. Data processing is done via Chromsphere software (Chromatool, Graz).

7. Conclusion

LC-GCMS is a perfect solution for the analysis of MOSH and MOAH contaminations in food samples according to EU norm 16995:2017. The Shimadzu LC-GC online setup is designed for running fullautomatische analysis sequences and verification of complex samples in combination with comprehensive GCMS.

8. References


Table 1: MOSH/MAOH concentrations in food and packaging (2)

<table>
<thead>
<tr>
<th>Type of Food sample</th>
<th>Concentration Level Food [mg/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Editable oils</td>
<td>6000</td>
</tr>
<tr>
<td>Bread and baked goods</td>
<td>2000</td>
</tr>
<tr>
<td>Chocolate and cocoa</td>
<td>1300</td>
</tr>
<tr>
<td>Pulp</td>
<td>1000</td>
</tr>
</tbody>
</table>

Figure 1: Chromatograms of a Rice sample before and after flash chromatography with Alu.