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Determination of Mineral Oil Hydrocarbons in Food and Food Packaging using LC-GCxGCMS Technique

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Introduction

Food can get contaminated by mineral oil hydrocarbons (MOH) by paper and cardboard packaging. The source of this contamination are 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.

Figure 1: Fish and chips in a newspaper wrap

According to latest scientific research work , there is not enough toxicological evidence to prove a health risk to humans from saturated mineral oil fractions (MOSH). Mineral oil aromatic hydrocarbons (MOAH), on the other hand, are suspected of having a carcinogenic effect (especially PAH-like compounds 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 amending 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].

Table 1: MOSH/MOAH concentrations in food and packaging [2]

Type of Food sample	Concentration Level Food [mg/kg]
Edible oils	6000
Bread and baked goods	2800
Chocolate and cocoa	1300
Fish	1200

The concentration of MOH in paper products is up to 1000 mg/Kg of which 70% can migrate into the packed product through direct contact or via the gas phase. An overview of MOSH/MOAH 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 (MOSH) and mineral oil aromatic hydrocarbons (MOAH) with on-line HPLC-GC-FID analysis [3].

Figure 2: Shimadzu MOSH/MOAH Analyzer

MOSH/MOAH System Configuration

The system configuration consists of a Shimadzu Nexera system with 1 LC-40BXR pump, CBM-40A LITE system controller, SPD-40A UFLC UV Detector coupled with GC-2030 and 2 FID detectors. For online aluminum oxide purification 1 LC-40D pump is needed. The PAL autosampler and the user-friendly CHRONOS software (AXEL SEMRAU, Sprockhövel) in combination with LabSolutions software platform allow a high level of automation. An automated sample preparation and pre-separation is realized by normal phase HPLC.

MOSH and MOAH fractions are separated from one another and simultaneously from the interfering components like paraffin or wax esters. Unfortunately, some food material like rice or chocolate contain natural occurring (odd numbered) alkanes in the range of C_{23}-C_{33} which can interfere and heavily disturb the analysis of the MOSH fraction. These interferences can be removed by flash chromatography on aluminium oxide columns (Alox-option).

Experimental Setup

The LC is directly connected to two high temperature GC columns with retention gaps which are installed in one GC oven. MOSH and MOAH fractions are separated on a silica gel column using a n-hexane /dichloromethane gradient. The interface between LC and GC is controlled by Axel Semrau LC-GC Chronect interface. After transferring the MOSH fraction on column 1 and MOAH on column 2 the temperature programme is started and both fractions are separated simultaneously and detected by FID. Figure 3 shows a typical LC-Chromatogram with UV-signal in black, pump pressure in green, CH_2Cl_2 concentration in blue and total flow in purple. Figure 2 shows the LC-GC-FID system [5].

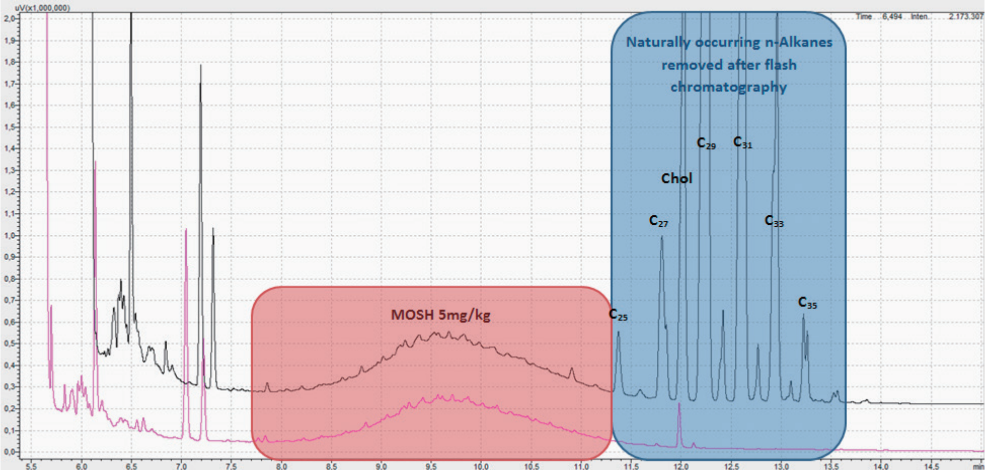

Figure 3: Chromatograms of a Rice sample before and after flash chromatography with Alox

Sample Preparation

Depending on the expected mineral oil concentration 1-10 g of homogenized and finely ground samples were used. The samples were extracted in Hexane, after the addition of an internal standard mixture (Restek MOSH/MOAH 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 (90, basic, 0.063 mm - 0.2 mm, activated for 16h at 500 °C) and 3 g of silica gel (60, 60 µm-200 µm or 70mesh-230mesh respectively, activated for 16h 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 MOSH fraction was eluted with 20 ml of n-Hexane, concentrated in an automated solvent concentrator and transferred into a 2 mL autosampler vial. This was placed in the autosampler rack of the LC-GC system. Aliquots of 50 µl were injected into the LC and 450 µL were transferred directly on the pre-columns for the MOSH fraction only.

Measurement

Figure 4 shows two chromatograms of a MOSH fraction of a rice sample spiked with 5 mg/kg of a mineral oil. Before flash chromatography with Alox n-Alkanes in the range of C_{25}-C_{35} 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 this time. The MOAH value that was measured prior to flash chromatography gives a concentration of 0.64 mg/kg and results in a total MOH recovery of 4.95 mg/kg of the spiked 5 mg/kg.

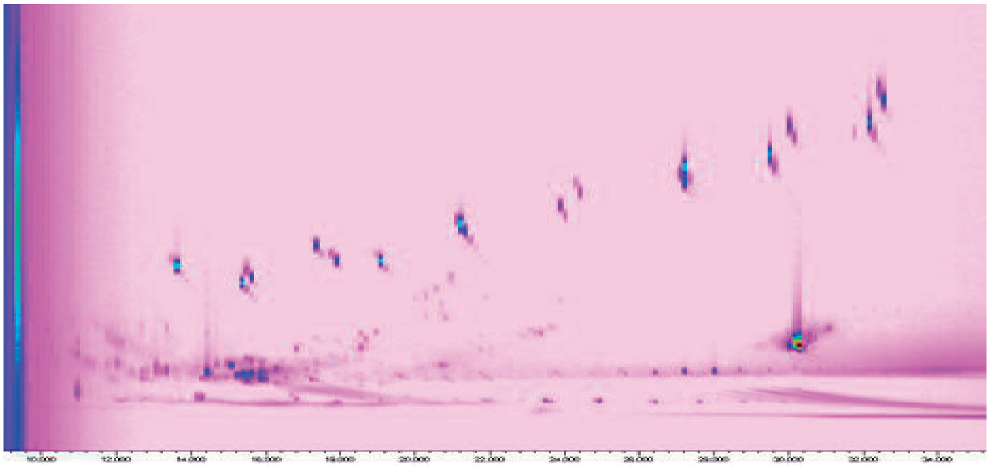

Figure 4: 2-D chromatogram of a standard PAH mix 14 (10 µl /ml, LGC, UK)

Comprehensive GCMS

In case of a detected MOAH concentration in food it is important to understand the origin of the contamination and the toxicity. Also, cross-contamination generated from MOSH, POSH, PAO 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 GC-MS is a powerful technique that provides the two-dimensional chromatography data acquisition, resulting in a significantly improved resolution and sensitivity. Data processing is done via Chromsquare software (Chromaleont srl. Messina),

Conclusion

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

References

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