Non-Intentionally Added Substances in Food and Food Contact Material – Determination of Mineral Oil Hydrocarbons with LC-GC Online Technique

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■ Introduction

Non Intenionally Added Substances (NIAS)

Non-intentionally added substances (NIAS) are chemical compounds that are present in a material but have not been added for a technical reason during the production process. Their presence in food contact materials (FCM) is generally not known by the consumer and often is a challenge for the FCM producer. NIAS originate from break-down products of food contact materials, impurities of starting materials, unwanted side-products and various contaminants from recycling processes.

Mineral Oil Residues

One group of NIAS are mineral oils (MO) in food which raised public concern due to some elevated concentrations up to several thousand milligrams per kilogram food [1]. Due to the chemical structures two groups of MOs can be differentiated. Mineral oil saturated hydrocarbons (MOSH) consist of linear and branched alkanes, and alkyl-substituted cycloalkanes, whilst mineral oil aromatic hydrocarbons (MOAH) include mainly alkyl-substituted polyaromatic hydrocarbons. Technical grades of mineral contain aromatic hydrocarbons in a concentration range from 15-35%. Food grade mineral oils (white oils) can have lower MOAH concentrations. The concentration of mineral oil in food was reported to be even up to the gram per kilogram ranges as given in table 1.

Table 1: MOSH/ MOAH concentrations in Food [1]

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

At the moment there are no legal limit in Europe for MOSH/MOAH, but MOSH concentrations up to 2 mg/kg and MOAH levels below 0.5 mg/kg are considered to be acceptable.

Analytical Challenges

Mineral oil fractions consists of thousands of different substances which can't be chromatographically resolved. In addition the proposed method uses a large volume injection in combination with a rapid temperature program to increase the sensitivity of the method. Figure 1 shows how different substance groups can arranged to possible isomers in the dependence of the carbon chain length.

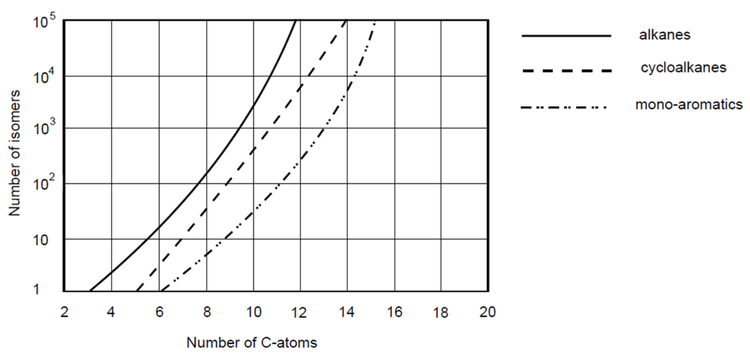

Figure 1: Numbers of isomers

To ensure a proper separation of the MOSH and the MOAH fraction and for quantification several internal standards are used. For detection flame ionization detectors (FID) are used due to their identical response for different hydrocarbon structures. Unfortunately no further structural identification is possible.

■ Why do we need MOSH/ MOAH Analysis?

Due to toxicological concern the MO concentration in food should be as low as possible. So it is of huge importance to identify the different sources of contamination. The use of recycling food contact material was identified as one of the major sources, but can be reduced by the use of functional barriers. In addition there are several other sources for contamination as shown in Figure 2. MOH can be present in food through environmental contamination, lubricants for machinery used during harvesting and food production, processing aids, food additives, printing inks and batching oils. Food grade MOH products are treated in a way that the mineral oil aromatic hydrocarbons (MOAH) content is minimized.

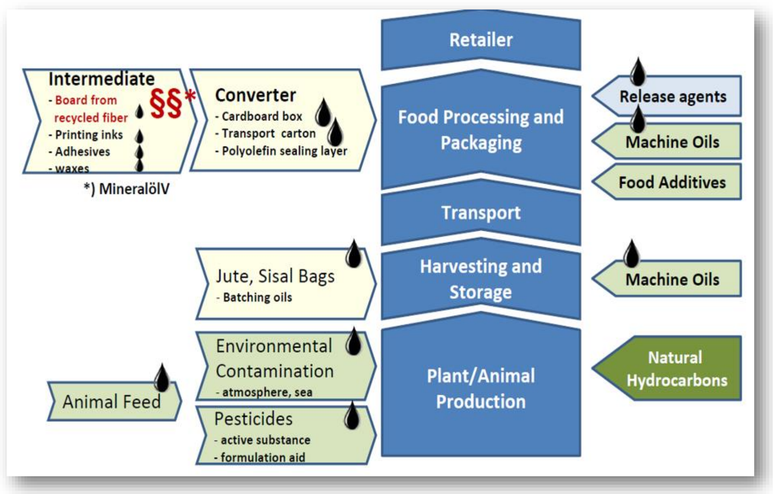

Figure 2: Sources of MOH contamination

Member States of the EC should, with the active involvement of food business operators as well as manufacturers, processors and distributors of food contact materials and other interested parties, monitor the presence of MOH in food during 2017 and 2018. The monitoring should cover animal fat, bread and rolls, fine bakery ware, breakfast cereals, confectionery (including chocolate) and cocoa, fish meat, fish products (canned fish), grains for human consumption, ices and desserts, oilseeds, pasta, products derived from cereals, pulses, sausages, tree nuts, vegetable oils, as well as food contact materials used for those products [2].

In July 2017 the European Norm EN 16995:2017 Foodstuffs – Vegetable oils and foodstuff on basis of vegetable oils – Determination of mineral oil saturated hydrocarbons (MOSH) and mineral oil aromatic hydrocarbons (MOAH) with on-line HPLC-GC-FID analysis; German and English version has been released which give a detailed explanation on the analytical procedure [3].

■ Experimental Setup

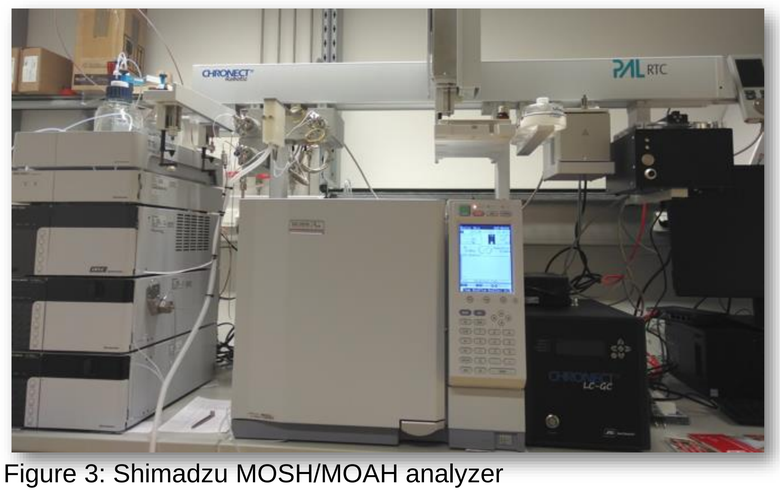

Figure 3: Shimadzu MOSH/MOAH analyzer

The system consists of a Shimadzu Nexera system with 2 LC-20ADXR pumps, CBM-20A LITE system controller, SPD-20A UFLC UV Detector coupled with GC-2010 Plus AF and 2 FID detectors. The PAL autosampler and the user-friendly CHRONOS software 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. Time consuming manual sample preparation by solid phase extraction (SPE) is obsolete.

In routine analysis, simplification and time reduction of sample preparation are the most important requirements. High sample throughput with short analysis cycle times make the use of highly automated systems inevitable. LC-GC can comply with these requirements. Up to now the LC-GC hyphenation technique was thought to be complicated and prone to errors and without no doubt the coupling of two powerful chromatographic techniques is challenging. Consequently, the deficiencies of existing and published LC-GC hardware solutions had to be analyzed and tried to be fixed. As mentioned, the origin of most LC-GC solutions dates back to one common source. By improving the stability and robustness of most system parts such as HPLC, GC, and software, a new LC-GC hardware approach could be designed implementing the following features:

Sensitive determination: for the most effective detection of MOSH and MOAH levels in food and food contact material

High level of reproducibility and accuracy: Great measuring accuracy by a validated method, similar to a normal split/ splitless injection

Routine-capable methods: A proper connection of LC and GC reduces solvent consumption and contamination of the GC system. Additionally, it increases the stability of the system. The sample throughput is therefore higher and facilitated by the control through the user-friendly CHRONOS software.

Additional features which enhance the possibilities of the instrumentation:

Fract & Collect: For further detailed analysis of the MOSH and MOAH fraction by GC-MS, GCxGC-MS or GC-TQMS a sample can fractionated several times for improved sensitivity.

Online Epoxidation: To remove natural occurring byproducts which can cause heavy chromatographic interferences.

■ Sample Preparation and Analysis

Depending on the expected mineral oil concentration 1-10 g of homogenized and finely ground samples were used. The sample was extracted in Hexane/Ethanol 1/1 after the addition of an internal standard mixture (Restek MOSH/MOAH standard Cat.#:31070 containing 9 internal standards) at room temperature for 2 hours under occasionally shaking the flask. After the extraction water was added and centrifuged. The washing step was repeated a second time. Afterwards the organic layer was dried over anhydrous sodium sulphate and the volume was adjusted to 1 mL in an automated solvent concentrator. The extract was transferred into a 2 mL autosampler vial and put 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 and MOAH fraction respectively.

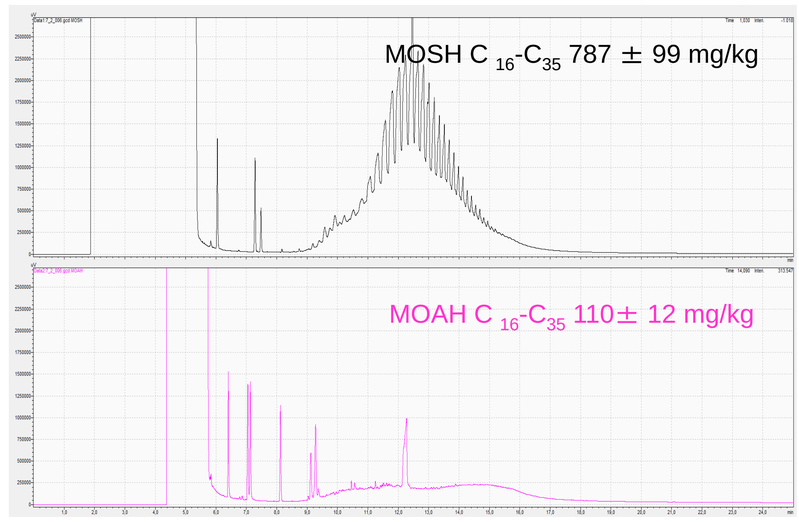

Figure 4: Chromatogram of MOSH/MOAH of a recycled paper grade

■ Conclusion

The Online LC-GC-FID system offers a fast and reliable tool for the determination of MOSH and MOAH residues in food and food contact material. Additional features (fract & collect and online epoxidation) expand the analytical possibilities of the instrument.

■ References

[1] Mineral Oil Hydrocarbons in Food, EFSA Journal 2012;10(6):2704

[2] EU: COMMISSION RECOMMENDATION (EU) 2017/84 of 16 January 2017

[3] EN 16995:2017 Foodstuffs – Vegetable oils and foodstuff on basis of vegetable oils – Determination of mineral oil saturated hydrocarbons (MOSH) and mineral oil aromatic hydrocarbons (MOAH) with on-line HPLC-GC-FID analysis

[4] M. Nestola, T.C. Schmidt, J. Chromatogr. A, 1505 (2017) 69–76

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