Determination of mineral oil contaminations in foodstuff, cosmetics and packaging

with the CHRONECT® Workstation MOSH/MOAH

Introduction

Mineral oil contaminants are found in numerous products. These substances can be divided into two classes: saturated (MOSH – mineral oil saturated hydrocarbons) and aromatic hydrocarbons (MOAH – mineral oil aromatic hydrocarbons). While the first class accumulates in the human body, the second class is suspected to contain carcinogenic compounds. There are several ways by which the substances can contaminate foodstuff for instance:

- Recycled packaging, which is manufactured from newspapers or magazines. The use of inks containing mineral oils is responsible for the gas phase migration into the foodstuff.
- Damage during the manufacturing of a foodstuff
- Mineral oil-based lubricants within the production chain
- etc.

If contamination due do migration is suspected, especially hydrocarbons occurring in the boiling range between C_{16} and C_{25} are observed. This is due to their compatible volatility range.

Additionally, mineral oil hydrocarbons may enter the human body when using cosmetics. Highly refined mineral oils which are applied in the cosmetic industry might also contain MOAH.

Device setup

For determination of MOSH/MOAH contaminations from packaging, cosmetics or foodstuffs a sample preparation involving a pre-separation by normal-phase HPLC has been developed and used as the preferred method [1]. The samples are first extracted by hexane according to their origin and kind [2].

The HPLC step is required to separate disturbing matrix compounds from the MOSH and MOAH fractions. Using a non-modified silica gel column, high amounts of fat and polar substances are retained and therefore efficiently separated from MOSH and MOAH. This kind of purification is also the basis of DIN EN 16995:2017-08, which is entirely accomplished through the system described here [3].

After pre-separation both fractions are transferred to the GC dimension, as a large volume injection and without losses. They are then separated by their boiling point and detected via FID. Quantification is performed as sum parameter. One chromatographic run, i.e. the parallel determination of MOSH and MOAH by a single injection, requires approximately 30 minutes.

Basic system components:

- CHRONECT LC-GC Interface
- Agilent Infinity II 1260 HPLC system
- Agilent 7890B GC with two FIDs
- PAL3 Autosampler
- Integrated software
  - CHRONOS for control
  - Clarity for data acquisition and evaluation

Optional add-on for epoxidation:

- FastWash station
- Agitator
- Centrifuge
- Implementation of the epoxidation protocol [4]

Optional add-on for aluminum oxide purification:

- additional Agilent Infinity II 1260 HPLC pump
- HPLC valve
- Aluminum oxide HPLC column

The device configuration is subject to modifications.

Results

HPLC separation

Figure 1 shows a HPLC-UV chromatogram of an injection of a standard mixture. The mixture consists of the substances C_{11}, C_{13}, cyclohexylcyclohexane (Cycy), cholestane (Cho) as well as pentylbenzene (5B), 1- and 2-methylnaphthalene (MN), tri-*tert*-butylbenzene (TBB) and perylene (Per).

The HPLC separation is performed through a *n*-hexane/dichloromethane gradient. The previously enumerated single standards serve the quantification and control for a successful MOSH/MOAH separation. Here, perylene is especially well visible within the UV signal.

After 6 minutes, the LC column is backflushed with dichloromethane. This backflush method assures a fast and efficient removal of retained matrix compounds. After 9 minutes, the column in regularly conditioned with *n*-hexane until ready for the next injection.

Figure 2 reveals the MOSH and MOAH GC chromatograms derived from the HPLC measurement. The absence of aromatic hydrocarbons within the MOSH fraction as well as saturated hydrocarbons within the MOAH fraction can be seen as an indicator for a successful MOSH/MOAH separation.

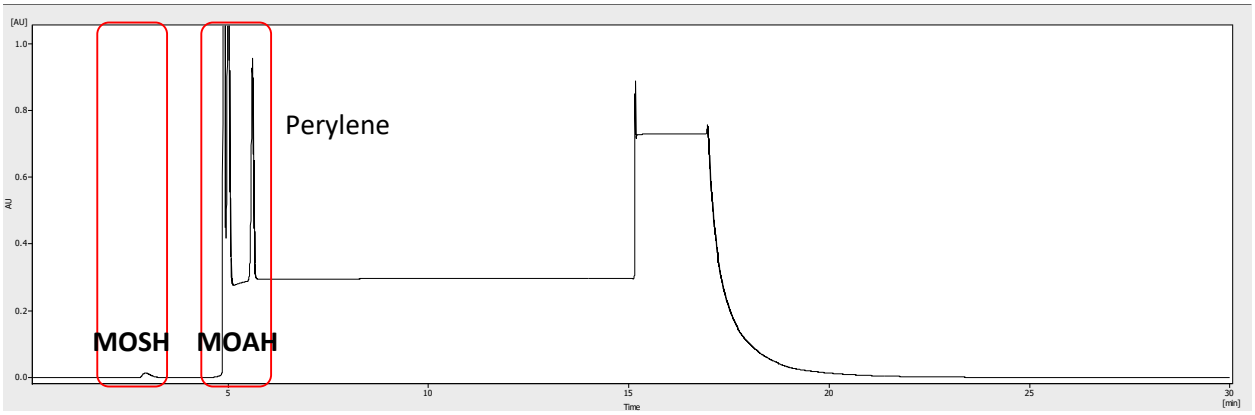

Figure 1: HPLC-UV chromatogram of a standard injection (wavelength: 230 nm). The indicated fractions (each 450 µL) are transferred to the gas chromatograph, large-scale and loss-free.

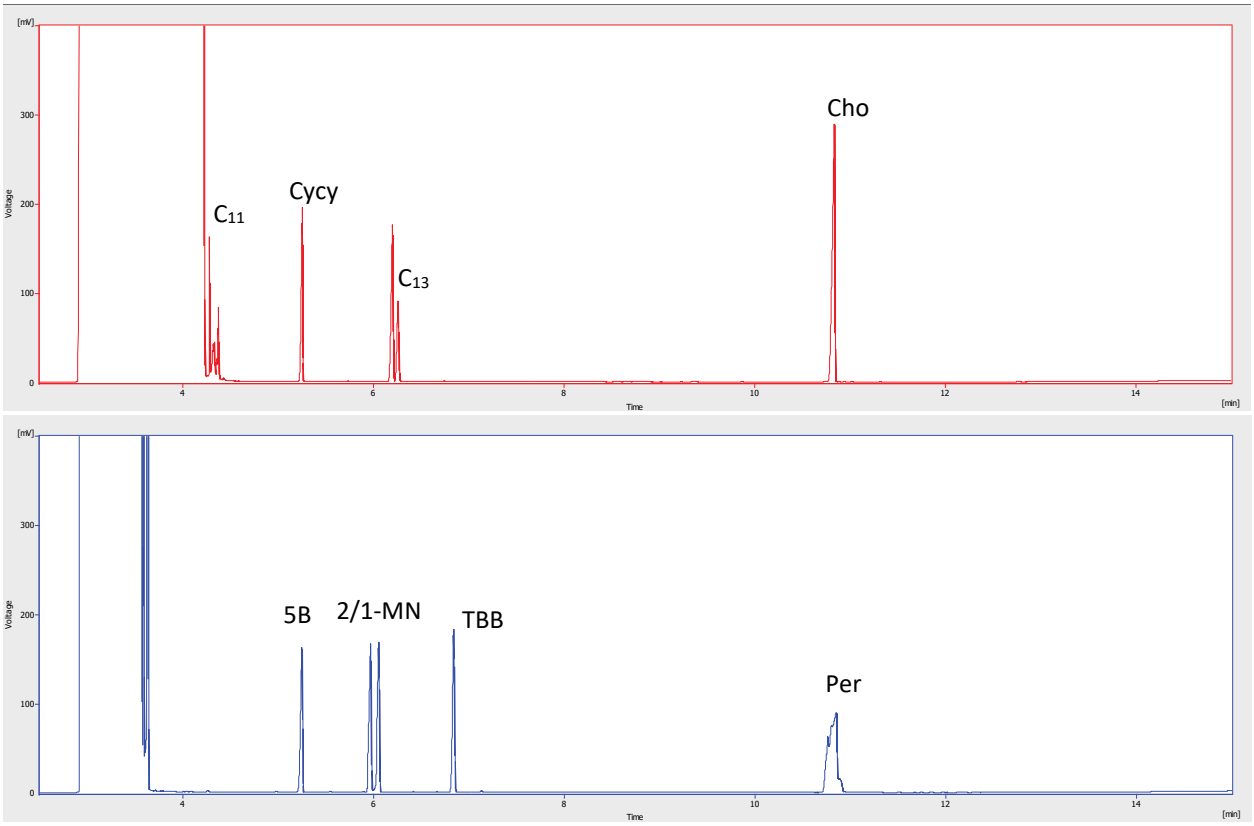

Figure 2: MOSH and MOAH GC-FID chromatograms of the injection from Fig. 1. Both fractions are measured in parallel. C_{11} and 5B are recovered quantitatively.

Following DIN EN 16995:2017-08, spiked sunflower oil is diluted by *n*-hexane and directly measured. Figure 3 is a typical MOSH/MOAH chromatogram. The indicated signal humps are quantified using the internal standard. Peaks on top are usually subtracted and not included.

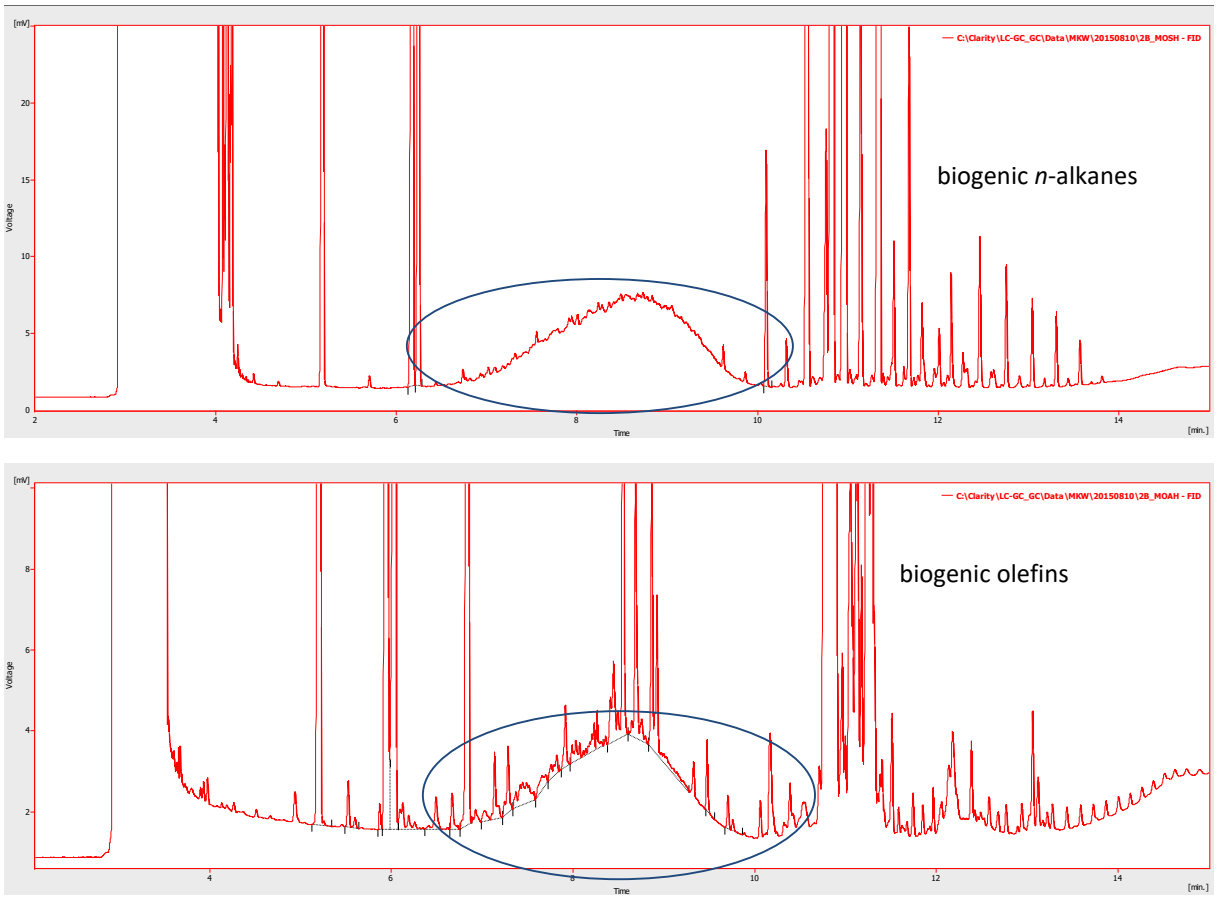

Figure 3: MOSH (top) and MOAH (below) GC-FID chromatograms of a doted sunflower oil. The contamination (integral of the indicated area) is 40 and 14 mg/kg, respectively.

As Figure 3 reveals, there are several additional single peaks and humps besides the obvious MOSH/MOAH humps. These are of a natural origin and therefore carefully need to be differentiated from MOSH/MOAH.

For that reason, there are additional purification techniques which remove those biogenic compounds from the sample. On the one hand, the MOSH fraction contains natural *n*-alkanes, which may overlap with MOSH. On the other hand, there are olefins which primarily impair the quantification of MOAH.

Axel Semrau has automated the available purification techniques (aluminum oxide chromatography and epoxidation) and adapted them to the system presented here. Figure 4 shows a sunflower oil which was purified through aluminum oxide and epoxidation prior to measurement.

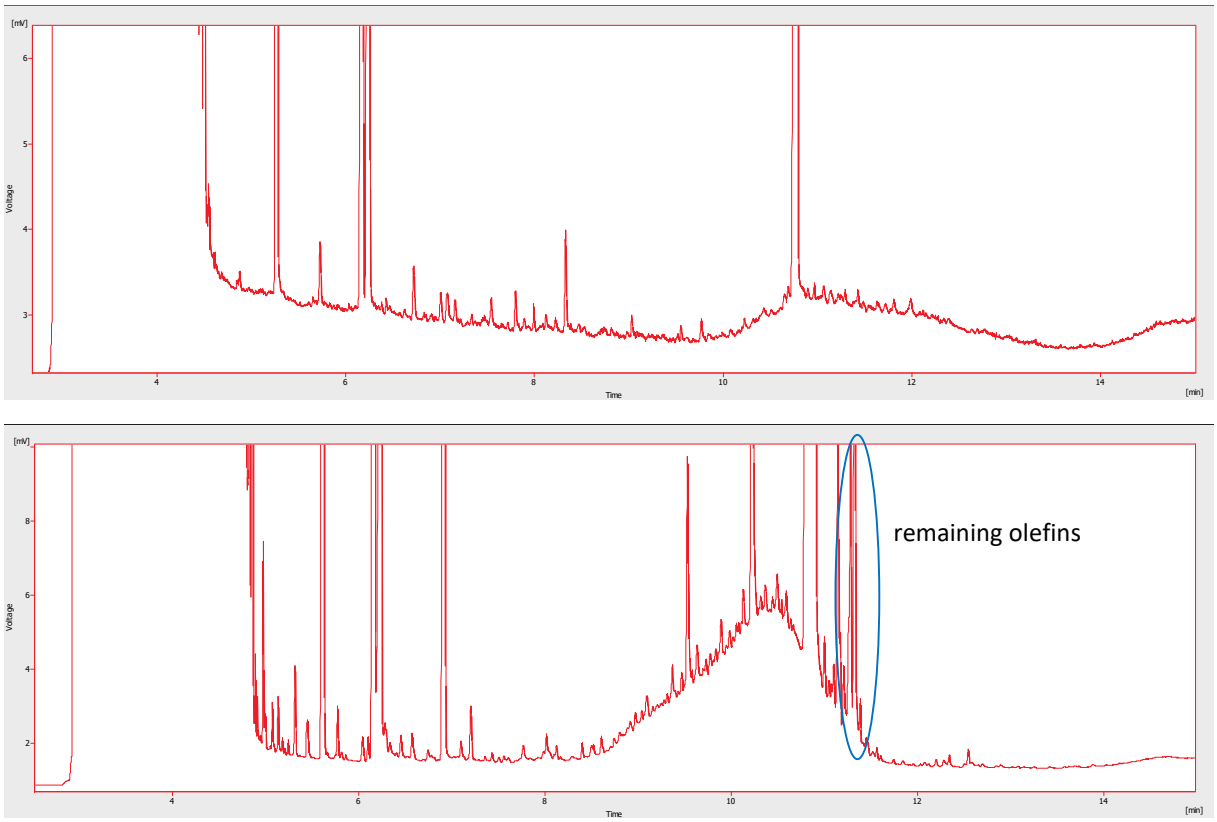

Figure 4: MOSH and MOAH GC-FID chromatograms of a spiked sunflower oil after aluminum oxide and epoxidation purification. The contaminations are 3 and 25 mg/kg, respectively (For visualization, MOAH was specifically spiked). Depending on the matrix, the conditions for epoxidation may be adjusted.

The MOSH fraction is entirely free from biogenic *n*-alkanes. Thus, even small MOSH contaminations can be quantified. The same applies for the MOAH fraction, which is free from olefins to a large extent.

Both purification techniques are an obligation for a successful und safe detection of MOSH and MOAH.

Summary

Hyphenation of normal-phase HPLC and GC-FID allows for a safe quantification of mineral oil residues in foodstuff, cosmetics and packaging.

The utilization of highly porous silica gel columns enables direct injection of fatty samples. Therefore, manual fat separation is avoided. Additional purification techniques such as aluminum oxide chromatography and epoxidation lower the limit of determination and increase the safety of quantification.

The limits of 10 mg/kg which are given by DIN EN 16995:2017-08 are definitely and safely reached by this system. Using additional pre-concentration methods, as known from BfR and other authors, even lower limits down to 1 mg/kg are achievable [2, 5-6].

Literature

[1] European Food Safety Authority, Scientific opinion on mineral oil hydrocarbons in food, EFSA J. *10(6)* (**2012**) 2704.

[2] Messung von Mineralöl-Kohlenwasserstoffen in Lebensmitteln und Verpackungsmaterialien, BfR und Kantonales Labor Zürich, http://www.bfr.bund.de/cm/343/messung-von-mineraloel-kohlenwasserstoffen-in-lebensmitteln-und-verpackungsmaterialien.pdf.

[3] ISO 16995:2017-08: Lebensmittel - Pflanzliche Öle und Lebensmittel auf Basis pflanzlicher Öle - Bestimmung von gesättigten Mineralöl-Kohlenwasserstoffen (MOSH) und aromatischen Mineralöl-Kohlenwasserstoffen (MOAH) mit on-line HPLC-GC-FID.

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

[5] M. Biedermann, K. Grob, J. Chromatogr. A. *1216* (**2009**) 8652–8658.

[6] M. Zurfluh, M. Biedermann, K. Grob, J. Verbrauch. Lebensm. *9(1)* (**2014**) 61-69.

AS Application Note 1801

MOSH-MOAH

The CHRONECT® Workstation MOSH/MOAH is a development by Axel Semrau®.

Subject to technical changes

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