Simultaneous Determination of MOSH and MOAH Fractions by means of online 2-channel HPLC-LV-GC-FID

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Introduction

Studies of the cantonal laboratory of Zurich showed that significant quantities of mineral oils contained in recycling cartons can migrate into food if these paperboards are used as food packaging. These mineral oils consist of a fraction of saturated hydrocarbons (MOSH: Mineral Oil Saturated Hydrocarbons) and a fraction of predominantly alkylated polycyclic aromatic hydrocarbons (MOAH: Mineral Oil Aromatic hydrocarbons). An example of such a contamination is shown in figure 1. While there have not yet been any conclusive studies on the toxicology, a mineral oil contamination of foodstuffs is basically undesirable.

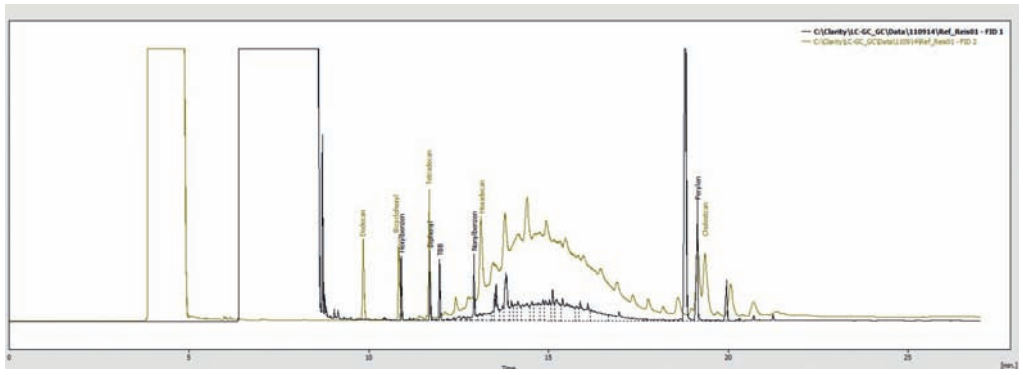

Figure 1: Sample chromatogram of a contaminated rice (black: MOAH, brown: MOSH).

An optimized method for determining mineral oil contamination (MOSH/MOAH) of foodstuffs and packaging materials has been developed and tested. It is based on the original method of M. Biedermann and K. Grob [1], but was further optimized with respect to sample throughput. The optimized method facilitates the determination of MOSH and MOAH in only one HPLC and GC run. At first, interfering lipid and matrix constituents are separated with a normal phase HPLC. By combination of the retention gap technique with an early vapor exit fractions can then be transferred directly to GC – without further concentration – and are detected by means of FID. The original method [1] requires two separate injections on the same sample in order to determine MOSH and MOAH. The methodology presented here uses two channels separate from one another which permits the simultaneous determination of MOSH and MOAH in one HPLC and GC run with the use of a second retention gap/separating column FID combination. The overall duration of the analysis including GC detection, back flushing and subsequent reconditioning amounts to 30 minutes. Using this technique, sample throughput can be doubled and consumption of solvents can be reduced.

Sample preparation

Sample preparation is performed as described in the relevant literature. The essential step is the extraction of the sample with hexane. Depending on sample matrix, desired sensitivity and moisture or fat content the extraction has to be modified.

Principle of operation

After extraction the sample is injected into the apparatus (figure 2) and purified by a normal phase HPLC. MOSH and MOAH fractions are separated from one another as well as from interfering components (paraffins, wax esters). After separation in the HPLC both fractions are transferred to the GC via two large volume injection systems; each can process an injection volume of 450µL. By means of an intelligent software and a valve controller, selecting suitable parameters, it is possible to retain the first eluting fraction (MOSH) without loss until the second fraction (MOAH) enters the GC. Detection takes place by parallel detection in two FIDs; a cumulative parameter is formed for evaluation as described in the literature.

Instrument configuration:

- Binary HPLC pump (Manufacturer Agilent)
- DANI Master GC equipped with 2 FIDs
- CTC CombiPAL Autosampler
- Mastersoftware Chronos Version 3.1
- DataApex Clarity Version 3.0

Figure 2: Device system

Results

Figure 3 shows a UV-chromatogram of a 50 µL injection of the Axel Semrau application standard in the dilution 1:250. The composition of the standard is described in the literature and consists of the substances C12, C14, C16, bicyclohexyl (200 ppm each), tri-tert butyl benzene, biphenyl, hexylbenzene, nonylbenzene 100 ppm) as well as cholestane and perylene (50 ppm each). In addition to tracking of the gradient composition, the detection of LC chromatograms at 230 nm also permit the examination of the perylene peak (5.2 min).

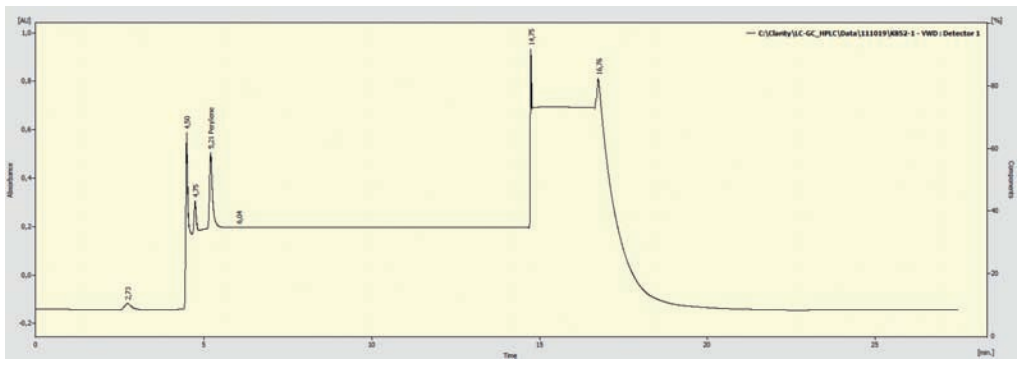

Figure 3: Sample chromatogram of an injection of the AS application standard (UV detection at 230 nm)

With the help of this standard it is possible to verify the correct fraction transfer to the GC (figure 4). Tri-tert butyl benzene, cholestane and perylene denote correct separation of the MOSH- and MOAH-fractions, while bicyclohexyl and biphenyl are used as internal standards. C12 and hexylbenzene are used as marker substances for non-discrimination of highly volatile substances in the early vapor exit.

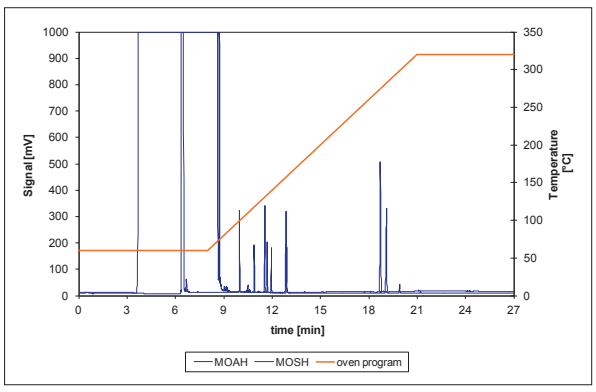

Figure 4: Sample chromatogram of a parallel data acquisition of a standard mixture

Validation

A calibration function was set up with the help of a BAM lubricating oil standard in a concentration range between 4 and 250 µg/mL. This standard contains mainly MOSH (90%) and only about 10% MOAH compounds. The calibration interval was 2 µg/mL in the range of 4 to 12 µg/ml, 10 µg/ml in the range of 10 to 50 µg/ml and 50 µg/ml in the range of 50 to 250 µg/mL, the injection volumes were 50 µL each. Each standard had the AS application standard added in a dilution of 1:250.

Figure 5 shows the calibration curve and highlights the broad dynamic range of an FID, which leads to a good linearity over the whole concentration range. The calibration can be done externally or internally through the AS application standard. Since the FID supplies a substance-independent proportional mass signal and as there are still no suitable commercially available standards the internal calibration is preferred.

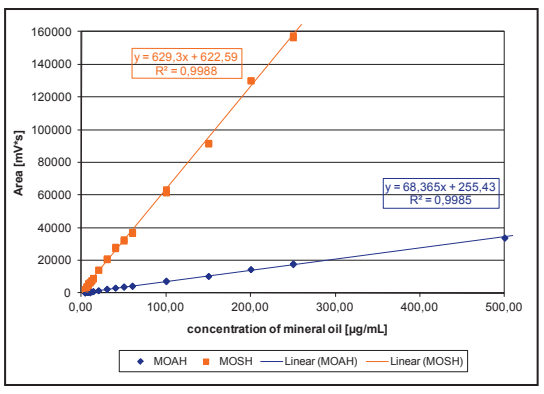

Figure 5: Calibration function for MOSH and MOAH

An overlay of the MOSH fractions of six extractions of one contaminated rice sample is shown in figure 6. Precision and repeatability are very good, with an coefficient of variation of 5.8% at a concentration of 4.3 mg/kg.

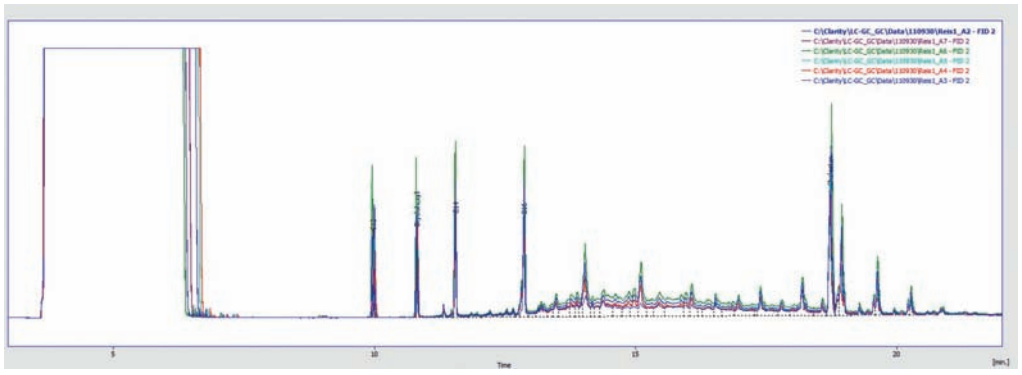

Figure 6: Repeatability of a rice sample (MOSH fraction, overlay of 6 sample preparations)

Summary

The presented solution allows the simultaneous determination of MOSH and MOAH in one run. Analysis time and manual labor at the lab bench are reduced and solvent consumption is lowered. Validation data show good precision and repeatability giving rise to fast and reliable analysis results.

Literature

[1] Biedermann, M., Fiselier, K., and Grob, K., J. Agric. Food Chem. 2009, 57, 8711-8721.

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