Analytical Methods for Determining MOSH and MOAH – FID vs. MS

Mineral oils are composed of a complex mixture of hydrocarbons. These vary in chain length and can be structurally classified into two types: MOSH (Mineral Oil Saturated Hydrocarbons) make up the majority of mineral oils (75-85%). MOAH (Mineral Oil Aromatic Hydrocarbons) form the minor fraction (15-25%) and are composed of highly alkylated aromatic mineral oil hydrocarbons with one or more benzene rings.

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The analytical challenge

Due to the multitude of possible carbon hydrogen compounds in mineral oils, analysing MOSH and MOAH represents quite a challenge. Given the complexity of MOSH/MOAH structures, a chromatographic separation into individual components is not possible. Instead one gets a broad unresolved signal which one has to quantify as an aggregate amount. In technical terms this signal is known as a "hump". Under toxicologically relevant aspects, mineral oil samples are fractionated into MOSH and MOAH and then analysed separately. Analysis is additionally complicated by the presence of structurally similar compounds, such as biogenic or synthetic hydrocarbons.

How is analysis conducted?

Currently routine analysis of MOSH and MOAH is performed using on-line coupled liquid chromatography-gas chromatography-flame ionisation detection (HPLC-GC-FID).

This method, which ring trials have proven to be suitable, is recommended by the European Food Safety Authority (EFSA) and is currently used in compliance with the convention by many laboratories. What is more, the method is defined in EN 16995:2017 on the analysis of vegetable fats and oils and foodstuffs on the basis of vegetable oils. Currently under discussion is an additional and alternative method, published by Spack et al. (2017), in which a gas chromatography-mass spectrometer (GC-MS) is used to determine MOSH/MOAH.

LC-GC-FID vs. GC-MS

The flame ionisation detector is a mass-flow-dependent detector and produces an almost identical response to all hydrocarbons. Hence only one internal standard is used for the MOSH/MOAH fraction, hence simplifying quantification. The downsides of this method are, on the one hand, the low sensitivity level and, on the other, possible false positives generated by the presence of biogenic hydrocarbons, such as carotenoids.

The alternative method, using a MS as a detector, can avoid such false positives by means of verifying the spectra. Quantification is conducted via a total ion current (TIC) chromatogram, enabling determination of all mass fragments from m/z 30 to 700. By way of validation, a measurement is additionally made in Selected Ion Modus (SIM), where particular mass fragments characteristic of MOSH and MOAH are selected (e.g. m/z 43, 57, 71, 85 for MOSH). A comparison of TIC and SIM chromatograms can determine whether the TIC chromatogram contains any interference of biogenic hydrocarbons. However, this method is also unable to quantify the proportions of biogenic and mineral oil hydrocarbons. Nor can it be excluded that biogenic hydrocarbons and mineral hydrocarbons are similarly fragmented, hence making differentiation impossible.

The higher sensitivity level of the GC-MS is a strength of this system, enabling the possible determination of MOSH and MOAH in low concentrations. However, the downside is that the column bleed, and the corresponding raising of the baseline, makes quantification more inaccurate.

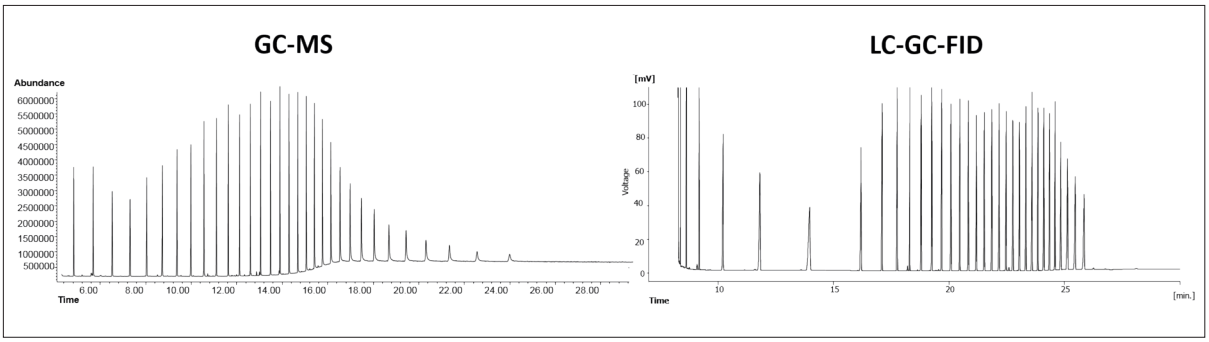

Figure 1. Comparison of GC-MS (total ion current) and LC-GC-FID chromatogram obtained from an alkane mixture (C10-C40)

A further disadvantage of the GC-MS method is the detector's dependency on the molecular mass, the molecular structure, and the scan range. Hence TIC measurements cannot achieve a uniform response (e.g. figure 1). In consequence, quantification of one standard may be tainted with an error factor. To achieve a more accurate quantification, a larger number of standard substances would have to be examined, thereby increasing the level of analytical work involved.

In conclusion it can be said that, for the very complex task of determining MOSH and MOAH, the analytical method LC-GC-FID (currently well-established in many laboratories) and the GC-MS method each have their respective shortcomings; hence the evaluation of corresponding measurement values quite generally requires a comprehensive level of analytical expertise. SV