

# Determination of Mineral Oil Hydrocarbons in Rice and Noodles using LC-GC Online Technique

Uwe Oppermann<sup>1</sup> and Erich Leitner<sup>2</sup>

<sup>1</sup>Shimadzu Europa, Albert-Hahn-Str. 6-10, 47269 Duisburg, Germany; <sup>2</sup>TU Graz, Institute of Analytical Chemistry and Food Chemistry, Graz, Austria

## 1. Introduction

Food can get contaminated not only through direct contact with its packaging, but also along the entire production and commercial chain. So far, legislation on the migration of substances from plastic packaging into food particularly has covered the starting materials used in the plastics manufacturing. Regarding health risks related to the transfer of substances, the so-called NIAS (non-intentionally added substances) should be focused stronger; these substances are non-intentionally added during manufacturing of plastic packaging materials. These can include impurities originating from raw materials, reaction and degradation products in manufacturing as well as impurities arising from transport and production.

Fatty components in cosmetics, food and transport packaging materials, and printing colors for packagings – mineral oil components such as MOSH/MOAH can almost everywhere be identified in the environment. They can infiltrate food of both plant and livestock origin in different ways, e.g. through migration. Both compounds, the mineral oil saturated hydrocarbons (MOSH) and also the mineral oil aromatic hydrocarbons (MOAH) are easily absorbed by the human body from food, and can accumulate in body fat and in the organs. Yet, it cannot be excluded that MOAH fractions may contain carcinogenic compounds. National governments, particularly ministries of food and agriculture, are pushing the European Community (EC) for fixing analytical determination limits of MOSH/MOAH in food and food packaging.

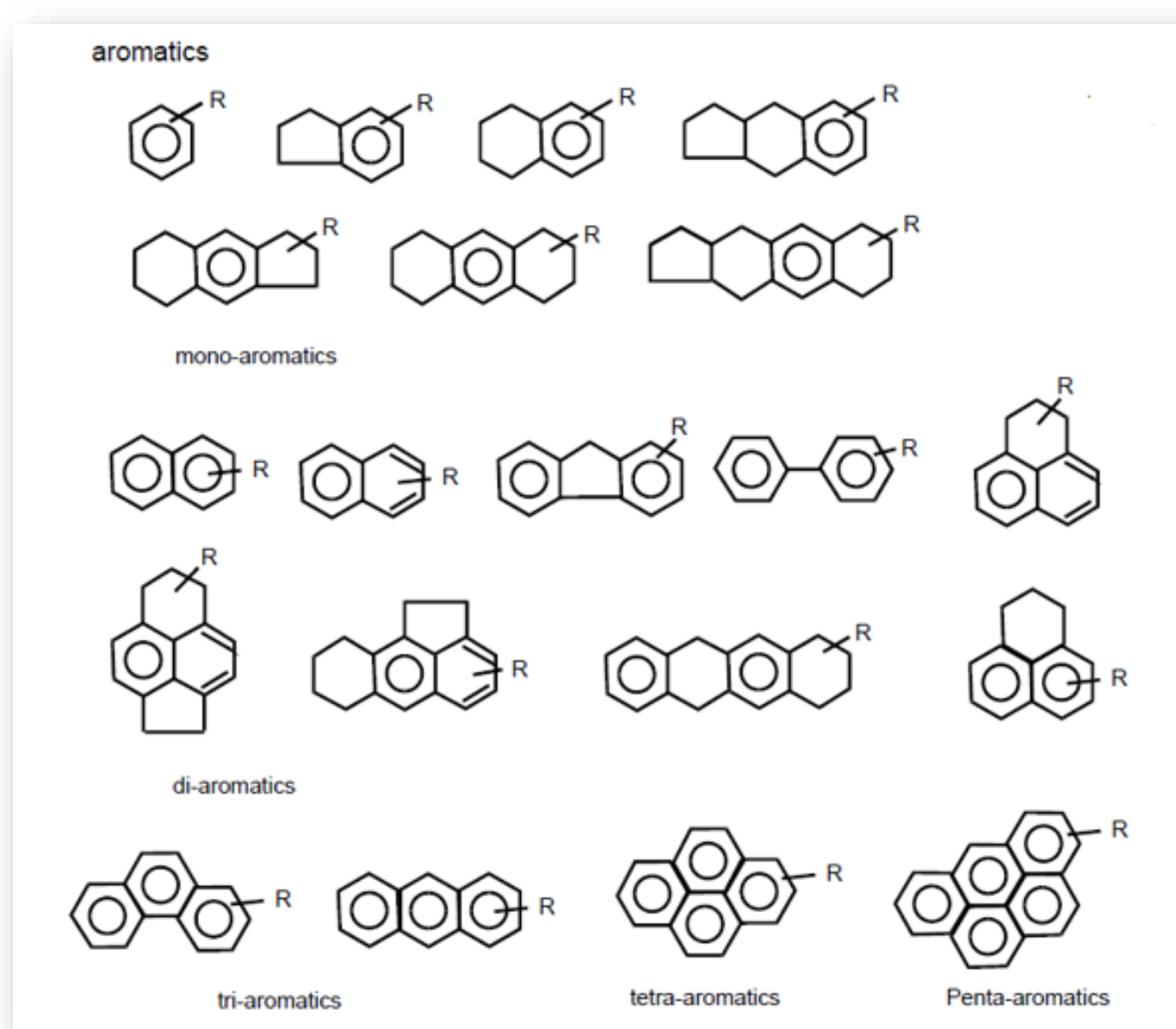


Figure 1: Possible structures

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

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

MOSH and MOAH are bi-products of crude oil and often present in packaging inks. They represent a potential health risk as they easily migrate into the food. The situation is even more serious in recycled material. Industrials in the EU have recently started to test different food products, including bread, pasta, fish, and chocolate, to measure the levels of MOAH and MOSH components (see Table 1).

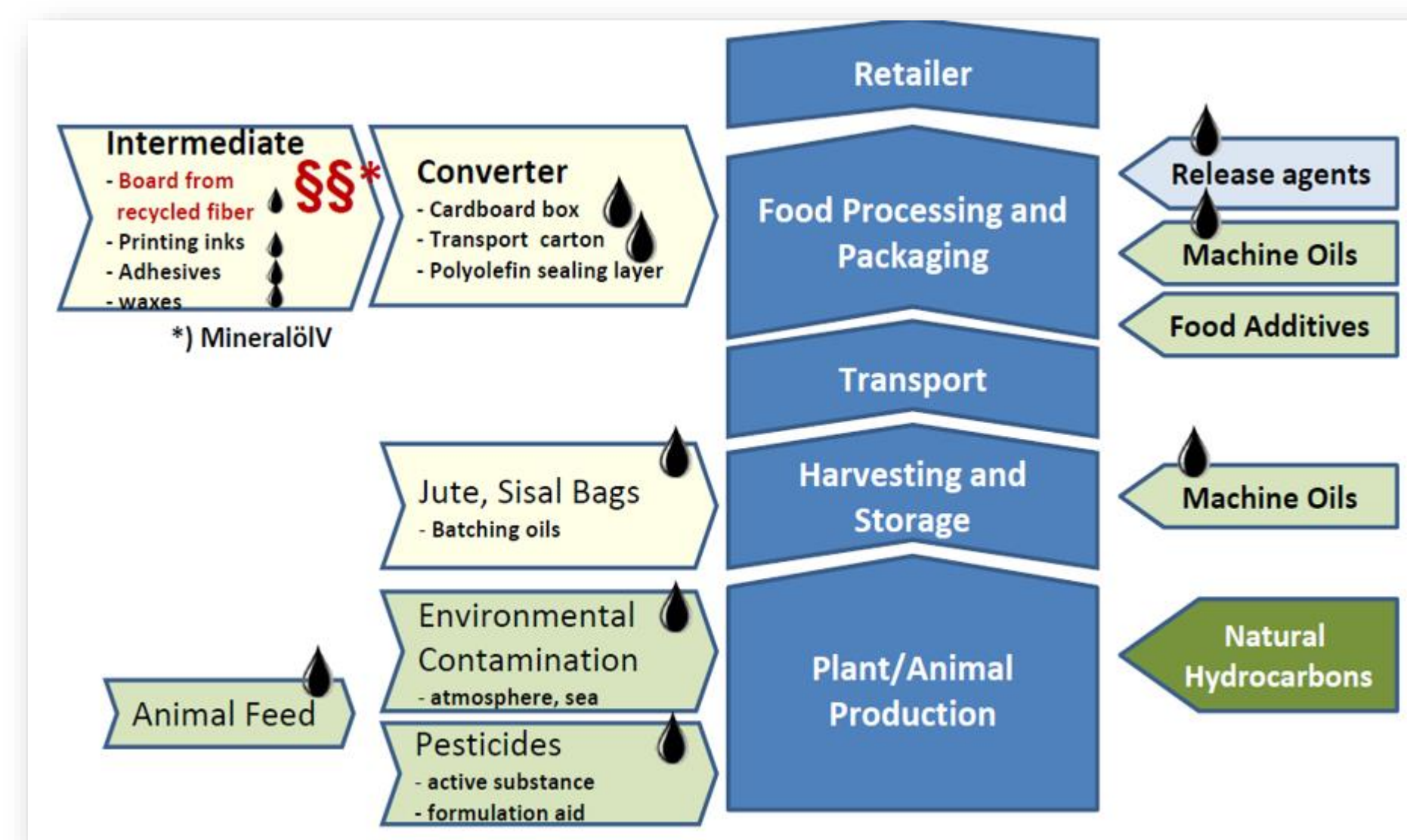


Figure 2: Sources of MOH contamination

## 2. Why do we need MOSH/ MOAH Analysis?

Mineral oil hydrocarbons (MOH) are chemical compounds derived mainly from crude oil, but also produced synthetically from coal, natural gas and biomass. MOH can be present in food through environmental contamination, lubricants for machinery used during harvesting and food production, processing aids, food additives and food contact materials. Food grade MOH products are treated in a way that the mineral oil aromatic hydrocarbons (MOAH) content is minimized.

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].

## 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-2030 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 like paraffin or wax esters. Standard sample preparation steps as solid phase extraction or manual purification are no longer required.

In routine analysis, simplification of sample preparation is the most important requirement. 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 packaging

### 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.

## 4. Quantitative Analysis

According to a proposed method published by the German Bundesinstitut für Risikobewertung (BfR) quantification is done by integration of the hump for different molecular weight regions. They propose for food contact materials three ranges for the MOSH fraction (C<sub>10</sub>-C<sub>16</sub>, C<sub>16</sub>-C<sub>25</sub> and C<sub>25</sub>-C<sub>35</sub>) and two ranges for the MOAH fraction (C<sub>10</sub>-C<sub>25</sub>, C<sub>25</sub>-C<sub>35</sub>). For dry food only the ranges up to C<sub>25</sub> are used [4]. Figure 4a shows the MOSH (black trace) and MOAH (purple trace) of a spaghetti sample with a MOSH concentration of 12.7 mg/kg from C<sub>16</sub>-C<sub>35</sub> and the marked regions of C<sub>16</sub>-C<sub>25</sub> (blue) and C<sub>25</sub>-C<sub>35</sub> (red). The internal standards are marked with symbols (black squares internal standards MOSH: C<sub>11</sub>, Bicyclohexyl, C<sub>13</sub> and Cholestane eluting with the MOSH hump, purple stars internal standards MOAH: Pentybenzene, 1 & 2-Methylnaphthalene, Tri-tert-butylbenzene and Perylene). The rice sample (Figure 4b) shows also additional peak in the rear part of the chromatogram. These are naturally occurring odd-numbered alkanes with a chain length of C<sub>21</sub> to C<sub>35</sub>.

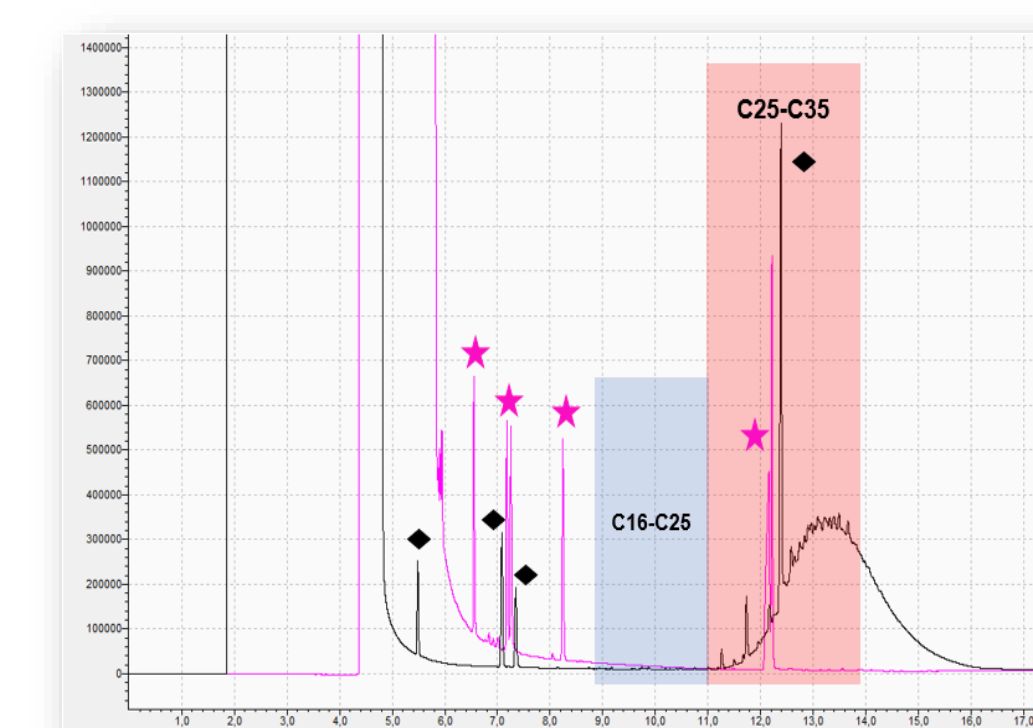


Figure 4a: Chromatogram of a spaghetti sample

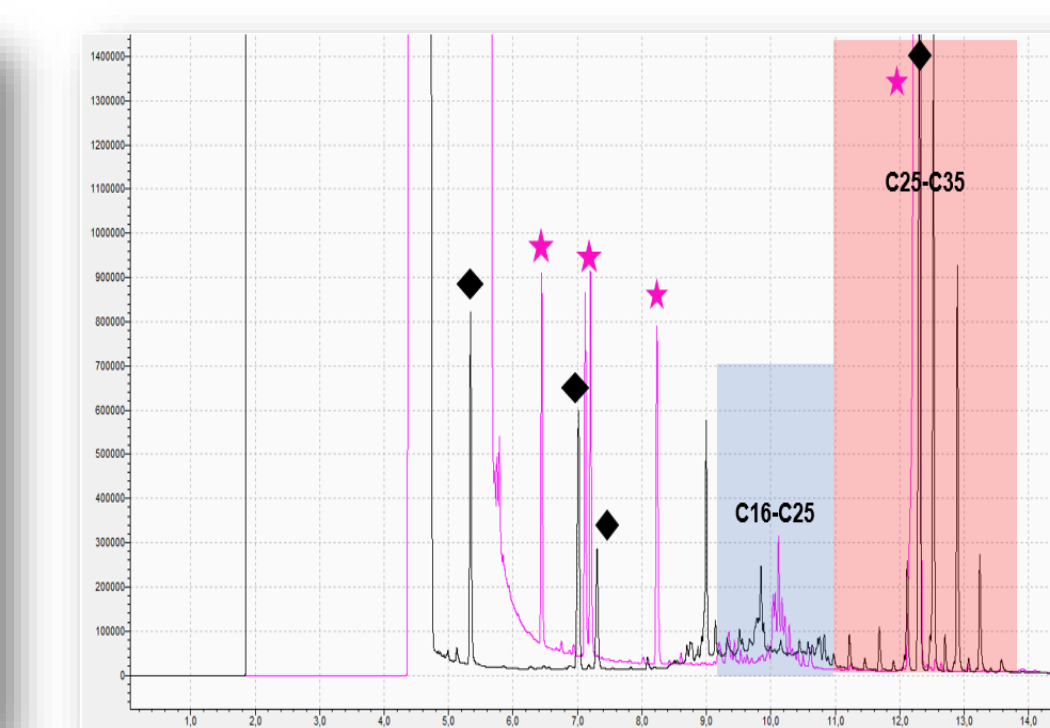


Figure 4b: Chromatogram of a rice sample

## 5. Conclusion

The new LC-GC-FID provides a tool for fast and reliable routine analysis of MOSH and MOAH in dry non fatty food such as rice, noodles and flour. After the extraction step the samples are analysed fully automated with a high sample throughput.

## 6. 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] <http://www.bfr.bund.de/cm/343/bestimmung-von-kohlenwasserstoffen-aus-mineraloel-oder-kunststoffen.pdf>