SHIMADZU

Application News

No. SCA-100-001

Food – MOSH/MOAH

Mineral Oil Residues in Food
Part 1- Dry Food (Flour, Noodles and Rice)

■ Introduction

Mineral oil (MO) residues in food 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 cyclo-alkanes, whilst mineral oil aromatic hydrocarbons (MOAH) include mainly alkyl-substituted polyaromatic hydrocarbons. Technical grades of mineral oil contain aromatic hydrocarbons in a concentration range from 15-35%. Food grade mineral oils (white oils) can have lower MOAH concentrations. Rice and pasta and other grain based food products including flour from different grain varieties are consumed in high amounts all over the world. The annual rice consumption per capita is over 54 kg per capita [2]. The annual pasta consumption in Italy is 26 kg and approximately 8 kg in Germany [3].

At the moment there are no legal limits 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.

■ System Setup

For the determination of the two mineral oil fractions an online LC-GC –FID system was used. The LC is directly connected to two high temperature GC columns with retention gaps which are installed in one GC oven. MOSH and MOAH fractions are separated on a silica gel column using a n-hexane /dichloromethane gradient. The interface between LC and GC is controlled by Axel Semrau LC-GC Chronect interface. After transferring the MOSH fraction on column 1 and MOAH on column 2 the temperature programme is started and both fractions are separated simultaneously and detected by FID. Figure 1 shows a typical LC-Chromatogram with UV-signal in black, pump pressure in green, CH_2Cl_2 concentration in blue and total flow in purple. Figure 2 shows the LC-GC-FID system.

LC Parameters:
Shimadzu LC-20AD solvent delivery pump
Column: Allure Silica 5 µm (250 × 2.1 mm)
Gradient: Start with 100 % n-Hexane (flow 0.3 ml/min), CH_2Cl_2 raised to 35 % within 2 min (hold for 4.20 min), column was flushed at 6.30 min with 100 % CH_2Cl_2 (flow 0.5 ml/min; hold for 9 min) and reconditioned to 100 % n-Hexane (flow 0.5 ml/min; hold for 10 min). Flow was decreased afterwards to 0.3 ml/min until next injection.
UV-Detector: D_2-lamp; 230 nm, 40 °C cell temperature

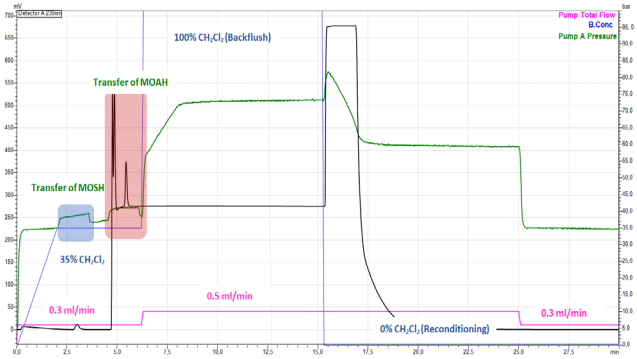

Fig. 1: LC-Chromatogram

GC Parameters:
Shimadzu GC-2010 Plus dual FID
Guard Columns: Restek MXT Siltek (10 m × 0.53 mm id)
Columns: Restek MTX ®-1 (15 m × 0.25 mm id × 0.1 µm df)
Carrier gas: Hydrogen (150 kPa analysis pressure; evaporation pressure: 87 kPA MOSH, 85 kPA MOAH
Temperature program:
60 °C (6 min) @ 20 °C/min to 100 °C (0 min) and followed by 35 °C/min to 370 °C (9.29 min)

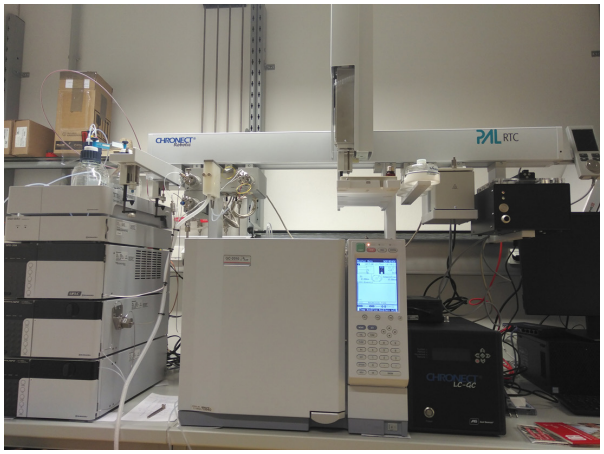

Fig. 2: LC-GC-FID System

■ Experimental Work

Sample preparation
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. Here the separation into the MOSH- and MOAH fraction is performed. Each fraction has a size of 450 µL and is transferred to the respective channel of the GC for parallel MOSH/MOAH determination.

Quantification

For the quantification of the MOSH fraction the internal standard Bicyclohexyl (CyCy) is used. For the MOAH fraction 2-Methyl-naphtahlene (2-MN) is used. All other internal standards are used to ensure no losses of analytes and a good separation between the MOSH and MOAH fraction.
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_{10}-C_{16}, C_{16}-C_{25} and C_{25}-C_{35}) and two ranges for the MOAH fraction (C_{10}-C_{25}, C_{25}-C_{35}). For dry food only the ranges up to C_{25} are used [4]. Figure 3 shows the MOSH (black trace) and MOAH (purple trace) of a spaghetti sample with a MOSH concentration of 12.7 mg/kg from C_{16}-C_{35} and the marked regions of C_{16}-C_{25} (blue) and C_{25}-C_{35} (red). The internal standards are marked with symbols (black squares internal standards MOSH: C_{11}, Bicyclohexyl, C_{13} and Cholestane eluting with the MOSH hump, purple stars internal standards MOAH: Pentylbenzene, 1 & 2-Methylnaphthalene, Tri-tert-butylbenzene and Perylene) .The rice sample (Figure 3) shows also additional peak in the rear part of the chromatogram. These are naturally occurring odd-numbered alkanes with a chain length of C_{21} to C_{35}.

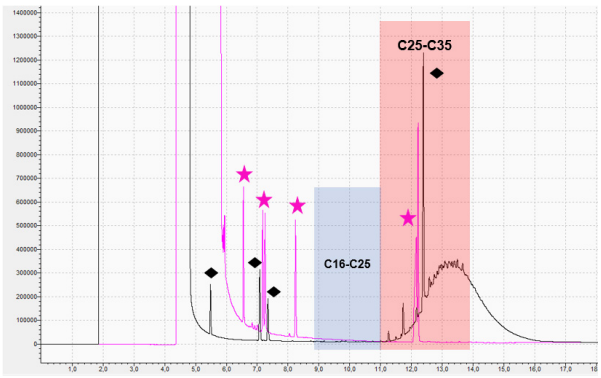

Fig. 3: Spaghetti sample

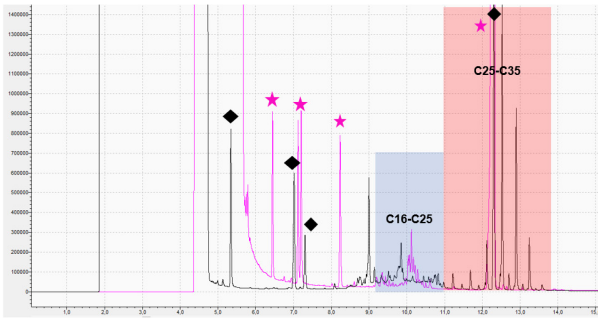

Fig. 4: Rice sample

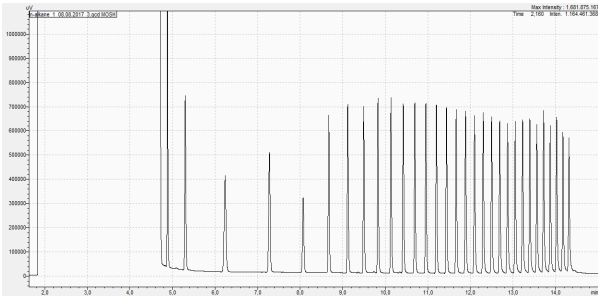

Fig. 5: n-Alkane standard C10-C40 as retention time marker

■ Conclusion

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

■ References

1) EFSA Panel on Contaminants in the Food Chain (CONTAM) Scientific Opinion on Mineral Oil Hydrocarbons in Food DOI: 10.2903/j.efsa.2012.2704

2) Link: https://www.statista.com/statistics/256002/global-per-capita-rice-use-since-2000/

3) Link: http://www.internationalpasta.org/index.aspx?idsub=118

4) Link: http://www.bfr.bund.de/cm/343/bestimmung-von-kohlenwasserstoffen-aus-mineraloel-oder-kunststoffen.pdf