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Application News

No. SCA_100_003

Food – MOSH/MOAH

Mineral Oil Residues in Food Sample Preparation Part 3 Fract and Collect

Introduction

Mineral oil residues in food gain a lot of public concern in the recent years. No matter if talking about rice, noodles, olive oil or chocolate, there are numerous examples of mineral oil contaminations in food. At the moment the challenges we face are the ubiquitous presence of mineral oils from raw material to the finished product and the big lack of information concerning composition, health effects, analysis and regulatory limits. Mineral oil hydrocarbons (MOH) are divided into the two groups mineral oil saturated hydrocarbons (MOSH) and mineral oil aromatic hydrocarbons (MOAH).

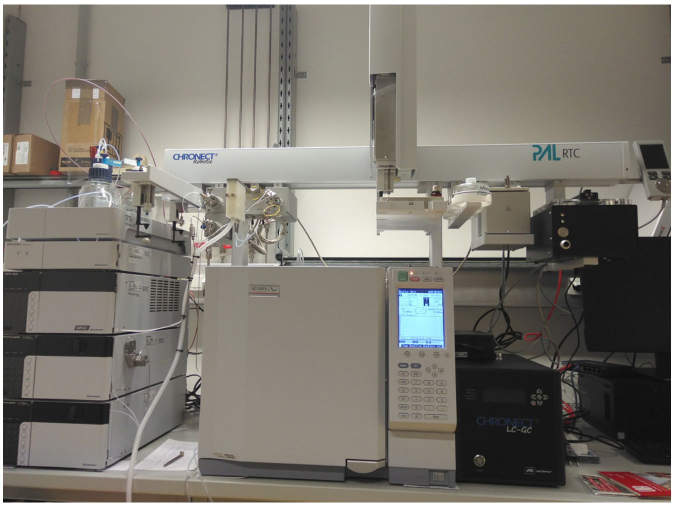

Figure 1: LC-GC-FID System with automated epoxidation unit

The MOSH consist of branched and unbranched open chain hydrocarbons called paraffines and cyclic hydrocarbons with at least one saturated ring called naphthenes. They can accumulate in the human body and cause granulomas. The MOAH consist of aromatic substance classes, that can be highly alkylated and have 1-4 rings. They make up 15-30% of the whole mineral oil fraction and contain potential mutagenic and carcinogenic substances. [1]

The determination of MOs in food can be done by an automated LC-GC-FID system for routine analysis which is shown in Figure 1. However, using this method with flame ionisation detection gives only information about the total concentration of MOH, without any further information about the constituents.

The Fract & Collect-tool gives the opportunity to collect MOSH and MOAH fractions after the HPLC fractionation and to use them for further analysis on GC-MS or 2D-Comprehensive GCxGC-MS.

System Setup

For determination of whole mineral oil concentration 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.

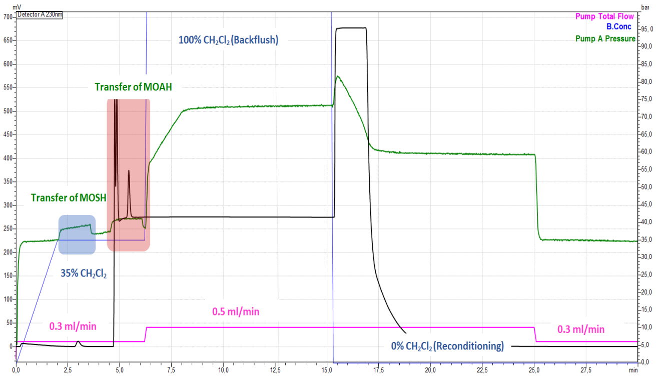

Figure 2: LC Chromatogram

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 2 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.

- **LC Parameters**

Instrument:	Shimadzu LC 20AD
Column:	Allure Silica 5 µm (250 × 2.1 mm)
Gradient:	Start with 100% n-Hexane (flow 0,3 ml/min), raised to 35% CH_2Cl_2 within 2 min (hold for 4.20 min), column was backflushed 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

- **GC Parameters**

Instrument:	Shimadzu GC 2010 dual FID
Columns:	Restek MXT ®-1 (15m × 0.25 mm id × 0.1 µm df)
Carrier gas:	Hydrogen (150 kPa analysis pressure; evaporation pressure: 75 kPA MOSH, 80 kPA MOAH
Temperature program:	60 °C (6 min) @20 °C/min to 120 °C (0 min) and followed by 40 °C/min to 400 °C (9 min)

- **GCMS Parameters**

Instrument:	Shimadzu GCMS-TQ8050, Q3 scan, 50-400 amu, 5 scans/s
Column:	30 m Restek RXi5MS 0.25*0.25 60 ºC (1 min) @5 ºC/min to 340 ºC (5 min)

■ Fract and Collect

For Fract & Collect only the LC is used. The samples are injected as usual (50 µL on LC) and the two fractions separated on the normal phase column. A switching valve is responsible for the separated transfer of MOSH and MOAH. It can either transfer the two fractions on the GC-Columns or redirect it to the Fract & Collect Tool. The tool, which consists of a transfer line and a needle, collects the fractions in prepared autosampler vials in the rack.

- **Experimental Work**

The following chromatogram shows the MOAH fraction of a recycled paper sample. Five fractions were collected as described above, combined and brought to a final volume of 500 µL in an automated solvent concentrator. Aliquots of 1 µL were injected in the GCMS- TQ8050 system.

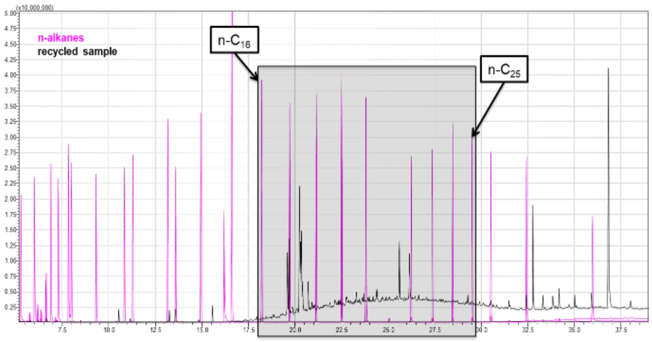

Figure 3: TIC of MOAH extract (black) and standards (purple)

Using extracted ions a more detailed information of the composition of the fractions can be generated.

Figure 4 shows the Total Ion Chromatogram (TIC) and five different ions (m/z 218, 232, 246, 260, 274 & 288). These ions are the molecular peaks of alkylated benzenes with a chain length from C_{10}-C_{15}.

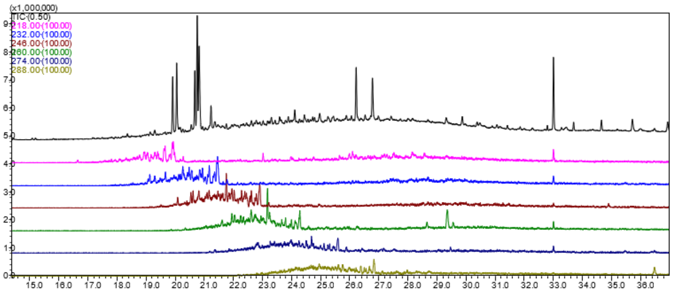

Figure 4: TIC of MOAH and extracted ions for alkylated benzenes

Rice	1.8-160 mg/kg
Fish (related to fat content)	10-1200 mg/kg
Cocoa and chocolate	5-1300 mg/kg
Baby food (packed in paperboard)	up to 33 mg/kg
Products stored in jute bag (rice, coffee, cocoa)	up to 500 mg/kg
Bakery products	up to 2800 mg/kg
Edible oil	up to 6000 mg/kg

Table 1: Found levels of MOHs in food [2]

▪ Conclusion

The new LC-GC-FID with automated MOH analysis and the possibility of collecting pre-separated fractions gives the opportunity for additional analysis of complex sample mixtures using GC-MS or GCxGC-MS.

▪ References

[1] Bundesinstitut für Risikobewertung (BFR), Stellungnahme Nr. 008/2010, 09.12.2010.

[2] EFSA Panel on Contaminants in the Food Chain (CONTAM), EFSA Journal, 2012 10(6), 2704-2889.

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