CHRONECT Workstation MOSH/MOAH

Product information

Introduction

Undesirable mineral oil residues are found in numerous food or food contact materials. These substances can be divided into two classes: Saturated (MOSH - mineral oil saturated hydrocarbons) and aromatic hydrocarbons (MOAH - mineral oil aromatic hydrocarbons). While the first substance class accumulates in the human body, the second compound class is suspected to contain carcinogenic substances. These substances can enter food via numerous contamination pathways. These include gas phase migration or contact with lubricants within the production chain.

Mineral oil residues are complex mixtures of substances with many different individual components. This is noticeable in the typical chromatogram, which shows an unresolved peak cluster, the so-called hump. Within the scope of quantitative MOSH/MOAH analysis, the sum of the individual substances is always determined. This complexity of the analytes as well as the ubiquitous occurrence of hydrocarbons makes the analysis difficult and requires special analytical systems and sample preparation.

Since 2010, Axel Semrau is engaged in the development and support of systems for the analysis of MOSH/MOAH. Many of today's options such as the 2-channel setup, automatic epoxidation, or online aluminum oxide (AlOx) purification have been developed in close cooperation with customers and have been brought to routine suitability.

System configuration

The analysis of MOSH/MOAH is performed with an online LC-GC-FID coupling. In this process, a HPLC is connected to a GC via a special interface. The GC uses FIDs as detectors, because they show a uniform response for hydrocarbons. This is the only way to quantitatively determine the sum of all individual components. Optionally, mass spectrometers can also be used for detection. The aim is usually to be able to make qualitative statements about single substances.

The coupling is done via an interface, which consists of a control unit and a heated valve unit. The temperature of the valve unit can be varied from room temperature to 150 °C. The temperature control effectively prevents condensation of the HPLC solvent in the valve unit and improves the stability of the system. An integrated flushing of the valve unit with carrier gas prevents tailing of the solvent and possible carryover.

Figure 1: Heated valve unit.

HPLC consists of a pump and a UV detector, which is used to check the HPLC chromatogram and to verify the correct fractionation. The gas chromatograph is equipped with two FIDs.

This 2-channel setup, developed by Axel Semrau, allows the simultaneous determination of MOSH and MOAH in one GC run, thus halving the analysis time.

In HPLC, the substance groups MOSH and MOAH are separated. After separation, the fractions are transferred completely to the GC. In this transfer, 450 µL of solvent per fraction are introduced

into the GC and removed by evaporation via the interface before the gas chromatographic separation.

Figure 2: Control unit.

The CHRONECT Workstation MOSH/-MOAH can be configured based on devices by the manufacturers Agilent or Shimadzu.

The control of the entire system is done user-friendly by the software CHRONOS by Axel Semrau. Options such as automatic epoxidation or online aluminum oxide purification can be selected simply by clicking in the sample list for the respective sample.

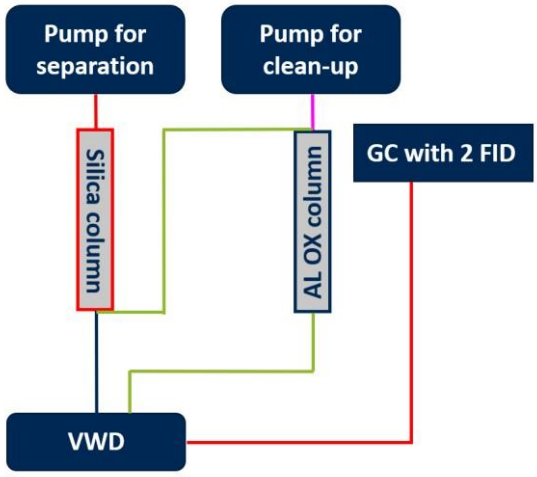
Removal of interferences

Especially when analyzing food, interferences by interfering substances are a problem and have a negative influence on the limit of determination and accuracy of the analysis. Major interfering substances are natural olefins such as squalene or β-carotene. These elute in the MOAH fraction and can lead to false positive results for this parameter.

By reacting these components with a peracid before injection into HPLC, the olefins are converted to polar epoxides and thus separated from the less polar MOAH in HPLC. The process of epoxidation at room temperature in ethanol as solvent was developed by Marco Nestola during his work for Axel Semrau and is now part of the current standards and recommendations of the European Union. This reaction can be carried out manually in the laboratory or automated by the CHRONECT Workstation. A centrifuge integrated into the system ensures reliable phase separation after the reaction has taken place.

Figure 3: Centrifuge as part of automatic epoxidation.

The other major interfering components are biogenic alkanes, which elute in the MOSH fraction. The ISO 20122 and DGF standard method C-VI 22 (20) describe the removal of these interferences by purification of the sample with aluminum oxide.



Since this manual process is very time-consuming and requires re-injection of the sample, Axel Semrau has developed an online purification using an aluminum oxide column. An additional HPLC pump is integrated into the system and the MOSH fraction is purified automatically after separation from the MOAH fraction. This online approach allows the determination of MOSH and MOAH with simultaneous epoxidation and AlOx purification in one run and has found its way into the current ISO method as an alternative to the manual approach.

Figure 4: Schematic structure of online aluminum oxide purification.

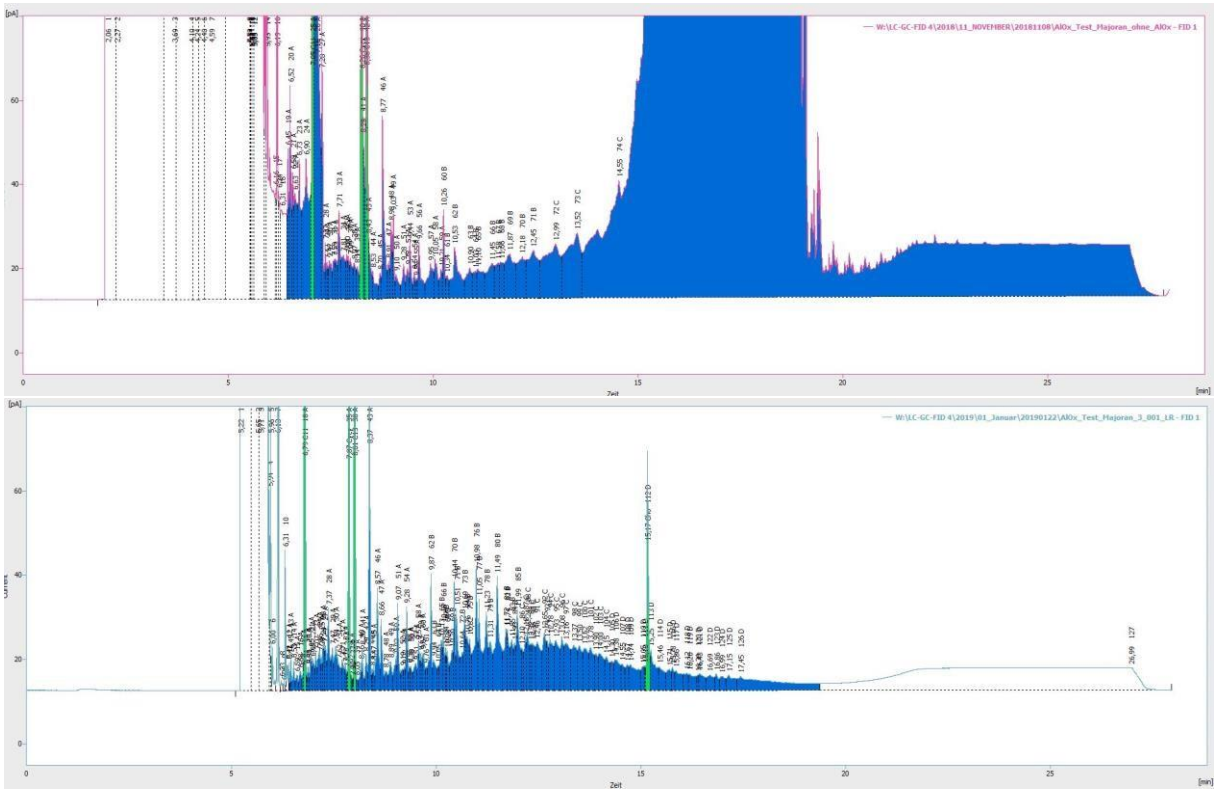


Figure 5: Marjoram sample without and with AlOx purification.

Determination limits and standards

In the analysis of MOSH and MOAH, the limit of determination depends very much on the actual matrix. This is due to interfering substances that cannot be completely removed even with epoxidation and aluminum oxide cleanup. Therefore, no general limit of quantitation can be defined for an LC-GC system. If no interferences by interfering substances occur, the CHRONECT Workstation MOSH/MOAH can be used to achieve a limit of quantification in edible oils of 2 mg/kg and sometimes lower without further sample purification.

There are currently three standards or methods that define the analysis of MOSH and MOAH in edible oils using LC-GC-FID. The DIN EN 16995 of 2017 describes a method that allows a determination limit of 10 mg/kg. This method has been officially retracted in 2024.

Lower limits of quantification, which are desired by many users, are possible, but sometimes require variations and cannot be guaranteed for every matrix. Due to these variations, there may be deviations between the values of individual laboratories.

This problem was addressed by the DGF with the standardized method C-VI 22 (20). The method described there allows robust determination limits of up to 1 mg/kg after sample purification, ethanolic epoxidation according to Nestola and on-line AlOx clean-up and its development was an important milestone in MOSH/MOAH analysis.

This method has been further improved and tested in international round robin tests. This resulted in ISO 20122 of 2024, which uses a double extraction of the sample and describes for the first time the use of performic acid for epoxidation. This process has several advantages over the use of MCPBA as an peroxidizing agent.

Automated Workflow

All actual official methods require manual sample preparation before the sample can be subjected to LC-GC-FID. Additional steps are here:

- Saponification and enrichment for lower limits of quantitation (LOQ)
- Silica gel cleanup for removal of substances that influence the epoxidation

These manual procedures require a lot of work and are always sources of blank values and contaminations.

To overcome this problem, Axel Semrau developed an automated workflow for the analysis of MOSH/MOAH in edible oils and fats. This workflow consists of:

- Saponification using KOH
- Two extraction of the unsaponifiable matter according to ISO 20122:2024
- Evaporation and epoxidation using performic acid
- Enrichment and HPLC injection
- Optional online AlOx cleanup during LC run

Using this workflow, an LOQ of ≤1 mg/kg is achieved for many types of edible oils and fats without manual intervention.

Since multiple samples can be prepared in parallel, up to approximately 30 samples per day can be analyzed.

This automatic workflow is suitable for samples with up to 20% unsaponifiable matter; above this, partial manual sample preparation must also be carried out.

The extension for this automatic workflow contains an evaporation unit for 6 positions, which can be used in parallel. This is the only way to achieve the high sample throughput of 30 samples per day including evaporation steps. Furthermore, this workflow includes the double extraction of the sample, which is prescribed in ISO 20122:2024, as otherwise MOAH sub-samples can occur due to incomplete extraction.

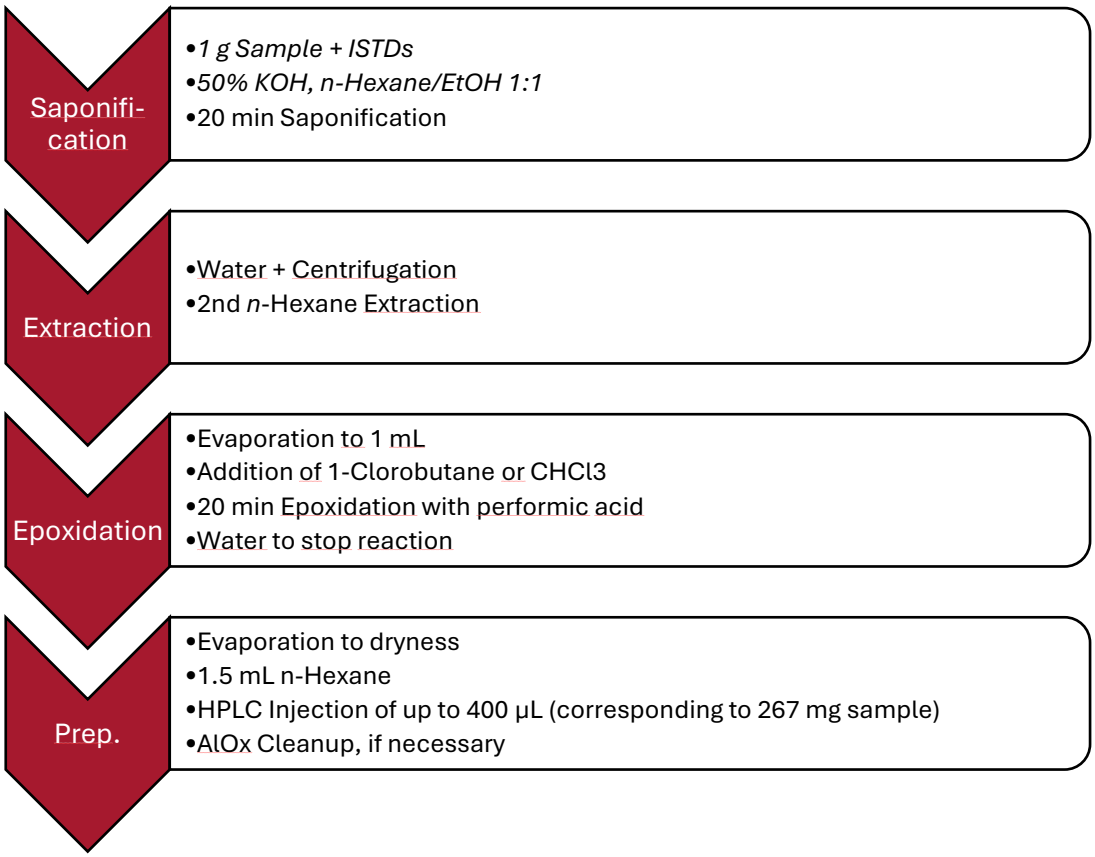


Figure 6: Automated Workflow for the analysis of MOSH/MOAH in edible oils and fats.

Further options

The CHRONECT Workstation MOSH/MOAH can be extended by different options:

High Capacity Extension

This option enables to run up to 60 samples with the AWF. The option includes a 200cm robot and additional modules for the higher capacity

Fract & Collect

This option allows the targeted collection of a fraction for further analysis with other methods. Very often a GCxGC-MS analysis is used. This method should allow the qualitative composition of e.g., the MOAH fraction in case of positive MOAH findings to allow more precise conclusions about the origin and a more in-depth evaluation of the sample.

Figure 7: Fraction collection tool.

MOSH depletion

It allows the determination of MOAH in samples that have a very high percentage of MOSH, such as petrolatum-based cosmetics. Only the depletion of the MOSH content allows the determination of the MOAH content.

Determination of the sterol distribution

The MOSH/MOAH system can be supplemented by sterol analysis. With the CHRONECT Workstation Sterols, the sterol distribution in edible oils can be determined fully automatically.

Determination of further quality parameters

Furthermore, different quality parameters of edible oils, such as alkyl esters and stigmastadiene, can be analyzed.

Evaluation

The evaluation of MOSH/MOAH analyses differs in some points from a classical gas chromatographic evaluation. First, the area of a single peak must not be determined. The entire hump of the mineral oil contamination must be quantified. Secondly, peaks on top of the hump must be subtracted depending on the type of samples, since they are considered to be not originating from the mineral oil and would thus falsify the result. For a more precise evaluation of the sample, it is also necessary to obtain partial results for certain boiling point ranges. A classical chromatography data system often has difficulties in fulfilling these requirements, so a software called Chrolibri was developed for simple, automated MOSH/MOAH evaluation. Hump Inspector software creates specialized mineral oil reference databases to determine the source of contamination

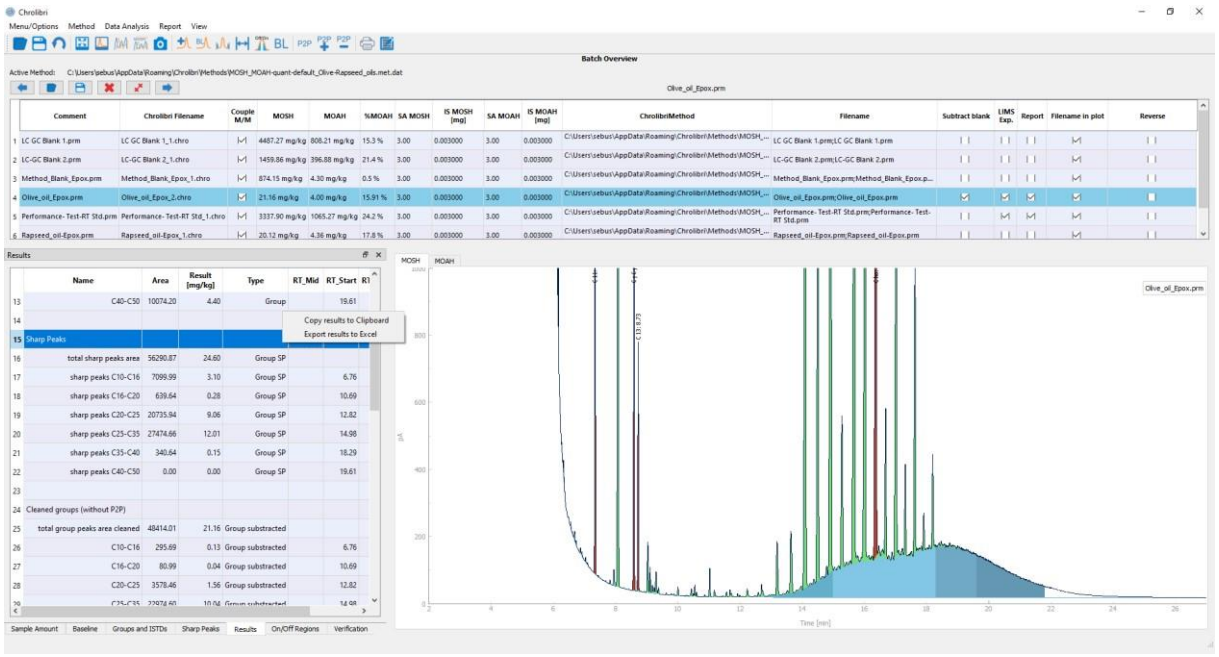


Figure 8: Evaluation of MOSH/MOAH analyses with Chrolibri.

Trainings

Appropriate sample handling, prevention of blank values, use of correct chemicals and sample vessels are pitfalls that influence the result. To support the users in these important points, Axel Semrau works together with Funke Analytic Consult. This enables us to offer a training program specially adapted to MOSH/MOAH analysis.

Commissioning

To ensure that the systems function without any problems, CHRONECT Workstations are put into operation in advance. During a comprehensive Factory Acceptance Test not only the correct technical function but also the analytical performance is checked. After installation, this test run is repeated in a Site Acceptance Test in the customer's laboratory. In this way the analytical accuracy is verified. The system is ready for use immediately after installation.

Summary

The CHRONECT Workstation MOSH/MOAH is based on 15 years of experience with MOSH/MOAH analysis. It is the result of continuous development in close cooperation with 250 customers. The compliance with current norms and standards together with simple, automatic result evaluation offers routine suitability. A support team specially trained in MOSH/MOAH offers users assistance at all times. Thus, the
CHRONECT Workstation MOSH/MOAH is the ideal system for every laboratory that successfully implements this analytics.

Technical data

Specifications	Values
MOSH/MOAH measuring system using LC-GC-FID according to DIN EN 16995, supports DGF C-VI 22 (20), ISO 20122:2024	Includes HPLC with UV detector, GC with 2 FIDs and oven chamber illumination, CHRONECT Robotic Autosampler, LC-GC-Interface, consumables for 6 months, data system for evaluation, Factory Acceptance Test, installation and Site Acceptance Test
Number of LC-GC channels	2 channels, optionally expandable to 3
Temperature valve unit	Room temperature up to 150 °C, typical operating temperature 80 °C
Option: Automatic epoxidation	supports ethanolic epoxidation according to Nestola, compliant with DGF C-VI 22 (20)
Option: Online aluminum oxide cleanup	includes additional pump, valve set and matching columns
Option: Automated workflow for edible oils and fats	Supports performic epoxidation according to Nestola, includes evaporation unit and vacuum pump
Supported Hardware	Agilent 8890 GC, Agilent 1260 Infinity III, Shimadzu GC-2030, Shimadzu LC-40

The CHRONECT Workstation MOSH/MOAH is a development by Axel Semrau.

Subject to technical changes

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