

Method ring test MOSH/MOAH in edible oils (quantification) P2401-MRT



Summary

The entire report is available to participants only.

The method ring test was designed, realised, evaluated, and authorised on behalf of PROOF-ACS GmbH by

Dr. Birgit Schindler
Managing Director PROOF-ACS GmbH
Project coordinator

The report was approved by

Dr. Birgit Schindler

Participants with any comments or concerns related to this ring test are invited to contact:

PROOF-ACS GmbH
Gottlieb-Daimler-Str. 1
28237 Bremen
Phone: +49 421 388 928 50
E-mail: proof@proof-acs.de
www.proof-acs.de



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PROOF-ACS GmbH does not have any analytical laboratory facilities of its own. Homogeneity testing and stability testing are subcontracted to laboratories, accredited according to DIN EN ISO 17025. The subcontracted laboratory may also participate in the ring tests. If so, the laboratory is treated in the same way as other participants and the same rules of confidentiality apply.

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Method ring tests are a highly valuable instruments to gather deep insight into the real challenges of complex analytical methods like the quantification of low levels of MOSH and MOAH in complex matrices like edible oils.

The method ring test consists of three parts:

- Part 1: Evaluation of the analytical results
The performance of laboratories is evaluated with respect to their ability to quantify MOSH and MOAH in two different samples of edible oils.
- Part 2: The applied analytical methods
Details related to the applied analytical methods are summarised and considered for interpretation of the analytical results.
- Part 3: Chromatograms
The analytical procedure in quantifying MOSH and MOAH is based on the integration of the respective “humps”. The chromatograms of all laboratories are collected and summarised. Conspicuous chromatograms are discussed in the report and are considered for the interpretation of the analytical results.

Olive oil and palm oil are chosen as matrices for the method ring test. An unspiked sample as well as a spiked sample of each oil are provided as blank materials resp. test materials. The oils are spiked with a base oil, a lubricant oil and a technical white oil.

20 laboratories across nine countries (Bulgaria, France, Germany, Indonesia, Italy, Malaysia, Netherlands, Spain, and Vietnam) took part in the test. 20 labs reported results related to the test material palm oil, while 19 labs reported results related to the test material olive oil. The results of all labs are considered for evaluation.

The laboratories were asked to report analytical results related the test materials and the blank materials. Besides the pure analytical data, the laboratories were asked to provide comprehensive data related to the applied analytical methods in a questionnaire and chromatograms related to the test materials and the blank materials and related to reagent blank samples.

Analytical results were reported related to the fractions:

- MOSH \geq n-C10 to \leq n-C16
- MOSH $>$ n-C16 to \leq n-C20
- MOSH $>$ n-C20 to \leq n-C25
- MOSH $>$ n-C25 to \leq n-C35
- MOSH $>$ n-C35 to \leq n-C40
- MOSH $>$ n-C40 to \leq n-C50
- Total MOSH

- MOAH \geq n-C10 to \leq n-C16
- MOAH $>$ n-C16 to \leq n-C25
- MOAH $>$ n-C25 to \leq n-C35
- MOAH $>$ n-C35 to \leq n-C50
- Total MOAH

in accordance with the Guidance of the Joint Research Centre of the EU.

According to the guidance document of the Joint Research Centre of the European Commission, total MOSH and total MOAH should be determined as follows:

„The "total MOSH/MOAH content" (n-C10-C50) is determined by integrating the chromatogram,

- *from the retention time of the beginning of the n-C10 peak;*
- *to the retention time of the end of the n-C50 peak;*
- *after the trimming of the riding peaks [...] above the hump(s); and*
- *after the subtraction of/adjustment for the reagent blank (baseline).*

The obtained "corrected hump" should be an unambiguously identified smooth hump" (page 15).

The results related to total MOSH and total MOAH are considered for evaluation. The results related to the individual fractions of MOSH and MOAH are summarised for information only.

The raw material (= blank material) olive oil contains 5.44 mg/kg of MOSH and 1.04 mg/kg of MOAH. The level of MOSH in the blank material is considered for evaluation of MOSH in the test material.

The raw material (= blank material) palm oil contains 20.0 mg/kg of MOSH, while it is free from MOAH. The raw material was spiked with MOAH only, thus the level of MOSH is identical for the blank material and the test material.

The performance of laboratories in the test is evaluated according to

- the comparability of the results. The evaluation of the comparability is based on the z-score model. The z-score should be at least $\leq |2|$. The comparability criterion is applied to total MOSH and total MOAH related to both oils. The evaluation of the individual fractions of MOSH and MOAH is provided for information purposes only.
- the trueness of the results. The trueness is expressed as the coverage of the spiked level in %. The coverage should be at least between 70 and 120 % of the spiked level. The trueness criterion is applied to total MOSH and total MOAH in olive oil and to total MOAH in palm oil. The levels of MOSH in the blank material olive oil are subtracted from the results of MOSH in the test material olive oil by PROOF-ACS for evaluation.

The statistical evaluation of the results is summarised in the tables below:

Blank material

Matrix	Parameter	Spiked level [mg/kg]	Assigned value [mg/kg]	Total number of results
Olive oil	Total MOSH	unspiked	5.44	18
	Total MOAH	unspiked	1.04	12
Palm oil	Total MOSH	unspiked	20.0	20
	Total MOAH	unspiked	< 1	11

Test material

Matrix	Parameter	Spiked level [mg/kg]	Assigned value [mg/kg]	Total number of results	Comparability: no. of results, which correspond to z-score $\leq 2 $	Trueness: no. of results, which correspond to recoveries of 70 to 120 % of the spiked level
Olive oil	Total MOSH	10	13.6	19	13	11
	Total MOAH	5.2	4.66	19	12	15
Palm oil	Total MOSH	unspiked	20.9	20	13	Not applicable
	Total MOAH	3.3	2.20	20	15	7

Several approaches took place to harmonise the analytical methods, which are applied for quantification of MOSH and MOAH in oils throughout the last years.

Analytical methods were improved to fit to even low levels of MOSH and MOAH of about 1 mg/kg in edible oils. Clean-up procedures were established, and new types of epoxidations were developed.

However, still different approaches and concepts for clean-up are applied by the laboratories. Aluminium oxide, epoxidation, saponification, and/or silica gel are chosen for clean-up depending on the preferences of the labs. Depending on the level of knowledge and the level of experience, the outcome might differ a lot.

If clean-up procedures like aluminium oxide and epoxidation are not applied appropriately, the respective labs over- or underestimate the content of MOSH and MOAH due to misinterpretation of interferences or losses during clean-up.

There is a trend towards harsher conditions during epoxidation. Some labs moved from epoxidation with mCPBA to epoxidation with performic acid according to Nestola or with performic acid and CHCl_3 . Labs should keep an eye on the losses of MOAH during epoxidation to avoid underestimation of MOAH.

In common proficiency tests, the statistical evaluation is limited to the comparability of the results. However, the comparability is just a first step, especially in case of challenging analytical methods. Much deeper insights are possible if the trueness criterion is applied, and if the information related to the applied analytical methods is combined with the provided chromatograms for evaluation.

The summary of the applied analytical methods (part 2 of the report) can support laboratories to improve the quality of the applied analytical method e.g. the choice of the most suitable conditions for epoxidation. Furthermore, the method details can build the basis for further discussion and thus for a standardisation of the analytical methods related to MOSH and MOAH.

The submitted chromatograms of all participants are summarised in part 3 of the report. The provided chromatograms allow for a deep insight in the challenges of quantifying MOSH and MOAH. The chromatograms thus offer a chance to each laboratory to compare the own outcome of the analytical methods to those of other laboratories on the market. Is the chromatography in line with the state-of-the-art or does it need an improvement?

Some of the major challenges by means of the analytical methods and chromatography to be solved are:

- The choice of a suitable method for clean-up (e.g. aluminium oxide, saponification, epoxidation).
- An adequate application of the clean-up and thus a satisfying removal of interfering substances.
- A sufficient sensitivity (e.g. by sufficient pre-concentration).
- An adequate identification and interpretation of interferences.

Analysing MOSH and MOAH is not plug-and-play and requires a high level of experience, especially if low levels of MOSH and MOAH are quantified. Major parts of the analytical procedure are highly automated. However, an adequate clean-up as well as suitable chromatographic conditions are necessary for a reliable quantification. Expert knowledge is indispensable for a correct interpretation of the resulting chromatograms. The laboratories must be able to identify interferences to avoid misinterpretation and thus overestimation of the true values of MOSH and MOAH.

If the labs are experienced and sophisticated analytical methods are correctly applied, a reliable, comparable, and true quantification of MOSH and MOAH in edible oils is possible, even at low levels.