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Method ring test
MOSH/MOAH in tea and spices (quantification)
P2403-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

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The report was approved by

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DAkkS Deutsche Akkreditierungsstelle D-EP-22211-01-00

PROOF-ACS is a DAkkS accredited proficiency testing provider according to DIN EN ISO 17043:2010 (D-EP-22211-01-00). This method ring test is covered by the scope of accreditation.

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.

Method ring tests are a highly valuable instruments to gather deep insight into the real challenges of complex analytical methods like the quantification of MOSH and MOAH in teas and spices.

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 green tea and in paprika powder (spice).

- 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.

Green tea and paprika powder (spice) are chosen as matrices for the method ring test. The green tea was contaminated with MOSH and MOAH during the production process, while the paprika powder was spiked with MOSH and MOAH by means of a process oil and a base oil. An unspiked sample of each matrix is provided as blank material. The unspiked and the spiked sample of the green tea are identical, as the test material is not further spiked with MOSH and MOAH due to the high level of contamination.

15 laboratories across four countries (France, Germany, Netherlands, and Vietnam) took part in the test. All labs reported results and 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 ≥ n-C10 to ≤ n-C16
- MOAH > n-C16 to ≤ n-C25
- MOAH > n-C25 to ≤ n-C35
- MOAH > n-C35 to ≤ n-C50
- Total MOAH

in accordance with the “Guidance on sampling, analysis and data reporting for the monitoring of mineral oil hydrocarbons in food and food contact materials”, published by the Joint Research Centre of the European Commission.

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 parameters "total MOSH/MOAH" should be determined by integration of the whole signal interval in the chromatogram, starting at the retention time of the peak start of n-C10 and ending at the retention time of the peak end of n-C50 after the elimination of the identified sharp peaks above the hump and if possible, elimination of POH and/or POA signals.“ (page 16).*

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 results related to the blank materials are evaluated with respect to the comparability criterion for information only.

The raw material (= blank material) paprika contains 7.42 mg/kg of MOSH and trace levels of MOAH of about 1 mg/kg or lower. The level of MOSH in the blank material paprika is considered for evaluation of the results related to the test material with respect to the trueness criterion.

The raw material (= blank material) green tea is identical to the test material green tea. The materials are used to test the repeatability of the analysis in the labs for identical samples, the trust of the labs in their own results, and the analytical performance.

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 absolute values of z-score should be at least ≤ 2. The comparability criterion is applied to total MOSH and total MOAH related to both matrices.
- 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 paprika. Levels of MOSH in the blank material paprika are considered for evaluation. The trueness criterion is not applicable to the matrix green tea.

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
Green tea	Total MOSH	unspiked	114	15
	Total MOAH	unspiked	19.7	15
Paprika	Total MOSH	unspiked	7.42	15
	Total MOAH	unspiked	< 1	15

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 ≤ |2|	**Trueness:** no. of results, which correspond to recoveries of 70 to 120 % of the spiked level
Green tea	Total MOSH	unspiked	115	15	10	Not applicable
	Total MOAH	unspiked	19.6	15	12	Not applicable
Paprika	Total MOSH	14	21.5	15	14	14*
	Total MOAH	6.2	6.62	15	14	15

* The levels of MOSH in the blank material are considered for evaluation.

Several approaches took place to harmonise the analytical methods, which are applied for quantification of MOSH and MOAH throughout the last years. However, there is still a need to extend the scope of matrices, which are covered by the standardised methods.

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 in 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.

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 is possible, even for complex matrices like teas and spices.