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Two dimensional GC analysis to avoid false positive migration values of mineral oil hydrocarbons

1 Abstract

The European Commission has requested for data regarding the consumers' exposure to mineral oil hydrocarbons (MOH) in food during 2017 and 2018. Due to the complex composition of MOH, it is necessary to have appropriate methods of analysis available. An analytical method based on separation by HPLC followed by GC separation is frequently applied to determine the amount of Mineral Oil Saturated Hydrocarbons (MOSH) and Mineral Oil Aromatic Hydrocarbons (MOAH) in food and packaging materials. However, if a packaging material contains other sources of hydrocarbons, not from Mineral Oils, e.g. resins or rosins used in adhesives, then these hydrocarbons may interfere in the HPLC – GC analysis. An overestimation of the mineral oil content will be the result. A more comprehensive analytical method is required to separate MOSH and MOAH from non-mineral oil-based hydrocarbons present in resins. A method using a pre-separation with HPLC followed by two-dimensional gas chromatography (2D-GC) has been applied by Laboratory Lommatzsch². Analyses of resins that are frequently used in food contact materials were performed. In most cases the determination of MOSH can be performed without interference from resin constituents. Using selective mass spectrometric (MS) detection the distinction between MOSH and resin components is improved.

In the determination of MOAH, the aromatic or unsaturated hydrocarbons present in some resins or rosins are often detected in the same region as MOAH. An overestimation of MOAH is likely. The distinction between MOAH and resin constituents are expected to be feasible using selective MS detection. MS data have been generated and will be inserted in a mass spectrometry reference database like the NIST³ database for use by any interested party. The 2D-GC method is recommended in those cases where the HPLC – GC method has detected the presence of hydrocarbon mixtures, in order to establish the origin of the hydrocarbons and to quantify the MOSH and MOAH.

2 Introduction

Most of our food is packaged to increase hygiene and shelf life and to facilitate its distribution and presentation. However packaging materials may release some of their constituents to the food. The European Regulation (EC) no 1935/2004 requires that food contact materials are safe with respect to human health. This means that transfer of packaging constituents shall be limited. A known category of substances that may migrate are the mineral oil hydrocarbons (MOH), however a proper overview of consumer exposure to MOH is not available and therefore a reliable risk assessment not feasible. Commission recommendation (EU) 2017/84 requests for data of MOH in food and food packaging materials.

Different analytical methods have been published⁴ based on a separation of the MOH from other substances that may be present in packaging materials. It should be born in mind that MOH are very complex substances requiring comprehensive analytical methods. Synthetic resins are authorised in many packaging materials and they have a molecular structure different from MOSH and MOAH. Distinction

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² Laboratory Lommatzsch & Säger. Report HARRPA project tackifier resins

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⁴ Lommatzsch, M. et al. Food additives & contaminants, Part A. 33(3), 473-488.

between MOH and authorized resins is essential to avoid overestimation of MOH in packaging or food. It is obvious that a single analytical method is insufficient to fulfil the request for data on the content of hydrocarbon mixtures in packaging and foods. An additional method that allows separation of MOH from resins is a must.

3 What are Mineral oil hydrocarbons (MOH)?

Hydrocarbons are substances containing only hydrogen and carbon. Mineral oil, also called petroleum or fossil oil is a major source of hydrocarbons. The term MOH covers different types of substances. There are Mineral Oil Saturated Hydrocarbons (MOSH) and Mineral Oil Aromatic Hydrocarbons (MOAH). Refining fossil oil includes a complex procedure of distillation, purification and/or hydrogenation. The distillation product of interest contains hydrocarbons with a chain length ranging from 16 - 50 carbon atoms, mainly branched alkanes and cycloalkanes, but some straight chain alkanes (n-alkanes) will be present as well.

If purification of the mineral oil fraction is limited and not hydrogenated, the product will also contain MOAH. A major source of food contamination with MOSH/MOAH is due to the use of printed paper and board in the production of recycled cardboard for packing dry foods.

Depending on the extent of purification, the MOH are used in many applications, e.g. as a lubricant for machinery, in printing inks, in adhesives or as an additive in plastics food contact materials.

4 What are Resins ?

Hydrocarbon resins and bio-based resins are frequently used in e.g. adhesives to construct cardboard boxes, wax coatings or laminates. These resins are made from bio-based or synthetic ingredients. Usually the resins have a relative low molecular weight compared to polymers like elastomers or plastics. The synthetic resins are made from monomers, which are created in a steam cracker from crude oil or natural gas. The created monomers are separated into different fractions and these are subsequently polymerized to polymers with specific properties. The polymeric resins may be treated with hydrogen to change unsaturated polymers into saturated or partly saturated resins. The resins contain oligomers with physical properties that have a degree of physical similarity with MOSH or MOAH components, although their chemical structure is different.

Bio-based resins, originating from pine tree feedstock, include rosin derivatives, polyterpene resins and terpene-phenol resins. The resins may be chemically modified to achieve specific properties. Although rosin and terpene-phenol resins are excluded from the definition of a hydrocarbon, because they contain oxygen, the resins may contain some terpenes and polyterpenes as a natural constituent of pine trees. Terpenes belong chemically to the hydrocarbons and therefore the bio-based resins have to be included in the list of materials that may interfere in the determination of MOSH and MOAH.

5 Determination of hydrocarbons

5.1 One-dimensional GC

The determination of the migration level regarding hydrocarbons in food starts with a common extraction of the sample with a suitable solvent. The extract contains, besides the hydrocarbons, also food components such as fat. Using a liquid chromatography system (HPLC) these main food components are removed from the extract. At the same time, the hydrocarbons residue is separated in a fraction with (mainly) saturated hydrocarbons (SH) and a fraction with aromatic/unsaturated hydrocarbons (AH). In the next step, the fraction of interest is transferred on-line to a gas chromatograph (GC) where a separation based on chemical structure and volatility of the components is performed. In general, a migration of C₁₆ – C₃₅ hydrocarbons into foods may occur when food is in direct contact with the packaging. The C₁₆ – C₂₄ hydrocarbons can also migrate via the vapour phase into dry foods.

The SH chromatogram shows the MOSH as a broad hump with some sharp peaks on top of the hump. If resin is also present in the analysed fraction, then the saturated oligomers will be detected in the chromatogram in the same interval as the MOSH. Signals for MOSH and resin constituents overlap. It is

not possible to determine which part of the signals is caused by MOSH and which part is caused by resin constituents. This means that the total amount of saturated hydrocarbons can be measured but a distinction between hydrocarbons originating from mineral oil and resins/rosins is not possible. Consequently, the determination of MOSH will be overestimated.

In the AH chromatogram similar interferences are observed. This means that MOAH can be separated and quantified with the GC analysis, but if unsaturated or aromatic resin/rosin constituents are present, they will be included in the total amount of MOAH. Again, an overestimation is the final result.

5.2 Two-dimensional GC

New developments in gas chromatography have provided tools to separate substances by means of two-dimensional gas chromatography (2D-GC). 2D-GC allows separation of complex mixtures using two successive GC columns with different properties. The first column separates substances based on their difference in volatility and polarity, while the second column separates substances mainly based on their polarity and volatility. Prior to a 2D-GC analysis, the food extract shall be pre-separated into SH and AH fractions as described for the HPLC-GC method.

With 2D-GC, the n-alkanes can easily be separated from branched alkanes and cyclic alkanes because they show up at different positions in the two-dimensional contour plot. MOSH tends to form a broad cloud of peaks in the 2D plot, but individual structural subgroups can be detected. The resin constituents present in the SH fraction form clusters of peaks that are properly separated from MOSH. These clusters can be quantified and, if necessary, identified by means of mass spectrometry (MS). Only one resin called non-hydrogenated C₅ resin still shows some significant overlap with the MOSH. Although its peak pattern is different from MOSH, it is not feasible (yet) to determine MOSH in a proper way, i.e. free from interference, if non-hydrogenated C₅ is present in the food. Further research may be needed to distinguish the C₅ oligomers from the MOSH.

The determination of MOAH in the presence of aromatic/unsaturated resin constituents is more demanding. Many aromatic/unsaturated resin constituents are collected in the AH fraction obtained from the HPLC pre-separation. Whereas the MOAH in the 2D-GC form clouds of substances in the 2D plot, the resins form clusters of peaks. In some cases, this separation will be sufficient to determine both the MOAH and the resin hydrocarbons because their signals are free of interference. However, for a number of resins, the separation and the cluster formation can be inadequate for a reliable quantification. Most resin compounds can be identified with MS detection and this may certainly be helpful to determine the contribution of the resin hydrocarbons in the AH fraction. In some cases, 2D-GC preceded with a pre-separation by HPLC will be sufficient to produce a reliable result, but in other cases more research is needed to solve the problem of co-elution of resin constituents with MOAH. It should be kept in mind that the coelution of a resin with MOAH is limited to a certain area of the 2D plot, which means that at least a semi-quantitative approach is generally applicable.

6 Conclusions

Laboratory Lommatzsch & Säger has demonstrated that for all commercially available resin families (rosin esters, polyterpenes, terpene-phenol, AMS, C₉, DCPD and C₅ resins) the interference in the determination of the MOSH, using 2D-GC, is limited - if any. Using additional mass spectrometric detection, the resin oligomers can be distinguished from MOSH using the representative mass fragments of the concerning resin. Only in the case of non-hydrogenated C₅ resin there is a significant overlap, which could result into an overestimation of MOSH. Whether this interference can be neutralised using MS detection requires further validation. The identification of aromatic/unsaturated resin constituents with and without the presence of MOAH is also possible in most cases using proper MS techniques. The determination of aromatic resin constituents and the differentiation to MOAH is limited in some cases. MOAH may coelute with resin hydrocarbons in certain areas of the 2D-GC plot, which leads to a semi-quantitative approach causing an overestimation of MOAH.

The HARRPA project in cooperation with Laboratory Lommatzsch & Säger has generated typical chromatographic properties of the resin oligomers. Clusters of peaks in the 2D-GC plots and typical MS

fragmentation patterns can be linked to the individual type of resin. If the data are inserted in a mass spectrometry reference data base like the NIST database, the information would be available for interested parties like enforcement authorities and would be helpful in the differentiation of resin constituents and MOH.