Focus on mineral oil residues

MOSH/MOAH food contamination

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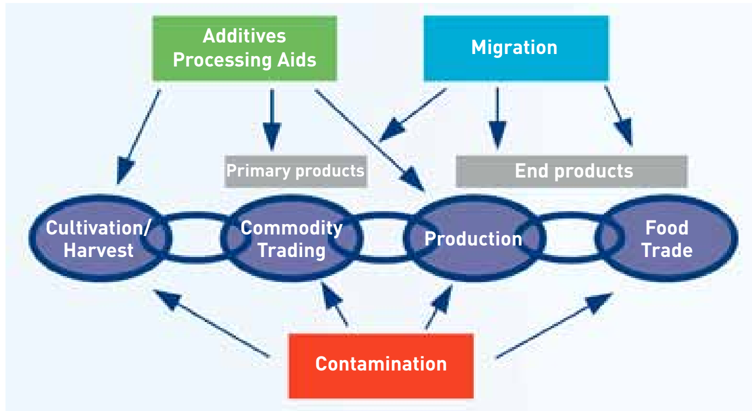


Fig. 1 MOSH/MOAH contamination sources in the food chain.

Mineral oils are almost universally present in our environment. Their constituents can infiltrate foods of both plant and animal origin in many different ways. From the perspective of their chemical structure, the main compounds of interest are mineral oil saturated hydrocarbons (MOSH) and – to a proportionally lesser extent – mineral oil aromatic hydrocarbons (MOAH).

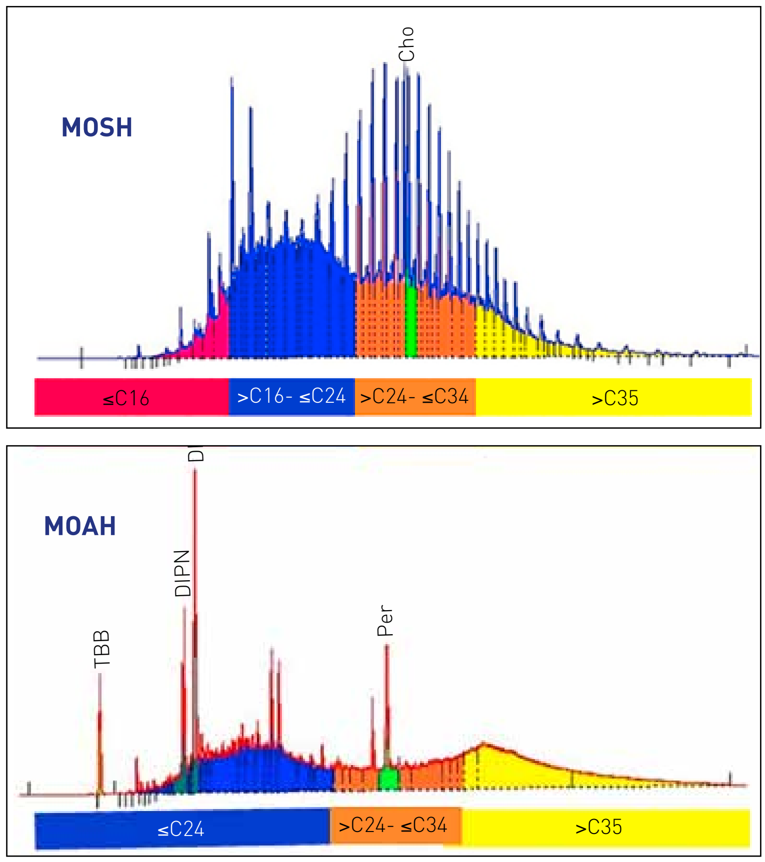


Fig. 2 Diagram illustrating the chromatographic "humps"

Both types are easily absorbed by the human body from food, and can accumulate in body fat and in some organs. As no studies examining the substances' effects on humans are currently available, toxicological assessments are based on animal experiments. According to the Federal Institute for Risk Assessment (Bundesinstitut für Risikobewertung, BfR), ingestion of MOAH should be avoided entirely, since it cannot be ruled out that carcinogenic compounds are also present in this fraction.

The food industry itself is not the primary source of mineral oil contamination in foodstuffs. If we consider the ubiquitous occurrence of mineral oils, the various sources of MOSH/MOAH food contamination, the demanding nature of analysis and the many stakeholders involved, it can be seen that this is a highly complex topic.

What does MOSH/MOAH stand for?

Mineral oils are essentially composed of two chemically and structurally discrete types of fraction. The primary fraction (proportion: 75% to 85%) is made up of MOSH (Mineral Oil Saturated Hydrocarbons), while the secondary fraction (proportion: 15% to 25%) is composed of MOAH (Mineral Oil Aromatic Hydrocarbons). Both fractions consist of carbon chains having generally fewer than 25 carbon atoms (<C25).

MOSH are saturated and paraffin-like – i.e. open-chained, generally branched and naphthenic (cyclic) – hydrocarbons with low to medium viscosity. In contrast, MOAH are a numerous and diverse class of aromatic hydrocarbon compounds, generally composed of one- to four-ring systems and 97% of which are alkylated [1].

How do mineral oil components contaminate food?

Mineral oils are widely present in our environment and there are a number of ways in which their components can find their way into food. Raw food materials are exposed to "background contamination" with mineral oil hydrocarbons from combustion processes (including petrol engine exhaust fumes, emissions from energy production and industrial facilities, forest fires, and so on) and particulate matter from asphalted streets, for example. Contamination from pesticides or harvesting machinery lubricants/hydraulic oils may also occur before or during the harvest. Later handling of the harvest may also involve mineral oil products – e.g. anti-foaming/anti-caking agents, binders (anti-dusting agents) for rice or shine improvers (applied by spraying).

Reinhard Matissek first completed training as a chemical lab technician before studying food technology and food chemistry in Berlin. After obtaining his doctorate at the former Federal Health Office (Bundesgesundheitsamt (BGA), Berlin) in partnership with TU Berlin (TUB) under Professor Werner Baltes, he then completed his habilitation in the discipline of food chemistry. In 1989, he was appointed Director of the prestigious Cologne-based LCI, the BDSI's service centre for the natural sciences. Since 1990, he has also been Adjunct Professor at the Institute for Food Technology and Food Chemistry in the Faculty of Process Sciences at TU Berlin. He holds the Hans F. Dresel Memorial Award from the PMCA (International Association of Confectioners, Pennsylvania/USA) and the FINCKE Prize for Science and Technology from the BDSI (Bonn), and is a member of numerous organisations and committees.

Marion Raters is a state-certified food chemist and studied food chemistry at the Westphalian Wilhelms University in Münster. Joining LCI in 1999, she obtained her doctorate here in 2008 under Professor Matissek on the topic of "Mycotoxins in Cocoa". She is the Institute's Deputy Director, and her work focuses primarily on the application of LS-MS/MS to process contaminant analysis.

Mineral oil components can also leach into raw goods during transportation from transport packaging contaminated with mineral oils. Examples of such packaging include impregnated jute or sisal sacks [2].

In addition, foodstuffs may also be contaminated by mineral oils during production, e.g. from exposure to oiled machine parts or greases that are applied during maintenance or cleaning work [3].

One well-studied exposure route is contamination via cardboard packaging, whereby cartons made from recycled cardboard may contain printer inks from the original cardboard stock. This is why most food packaging is now manufactured from virgin fibre. Yet this does not alter the fact that the secondary packaging used for carriage or packaging – as stored near food in transit, at the retailer or in the household – may also contain mineral oil components capable of migrating into foodstuffs. There are proven cases where food has left the manufacturer's premises with no MOSH/MOAH contamination and where it has subsequently been contaminated with mineral oil components during transportation or while in storage.

Aside from the mineral oils contained in recycled cardboard packaging, mineral oil-based printer inks can also be a source of contamination with mineral oil components when used to print product packaging. At least in the case of food packaging, this source has been largely eliminated, as the food industry has mostly switched to using printer inks with low or zero mineral oil content for product packaging. Packaging production processes using adhesives containing mineral oils could also present a possible route whereby mineral oil components leach into foodstuffs. Figure 1 shows a range of potential contamination routes for foodstuffs as found along the food chain.

For dry goods stored at room temperature, the migration of components into food occurs via evaporation, transport in the gas phase and recondensation within the foodstuff. Accordingly, this is possible only for mineral oil components with a certain vapour pressure (e.g. hydrocarbons <C25). Interior packaging made from paper, polyethylene (PE) or polypropylene (PP) retards migration but cannot prevent it entirely. For example packaging containing aluminium or polyethylene terephthalate (PET) has been shown to act as a "functional barrier" and thus block migration [5, 6]. This introduces other problems, however: The process of manufacturing aluminium foil for inner pouches or cardboard liners not only requires a lot of energy but is problematic in terms of its recycling process and impact on the environment. Moreover, the use of foils impermeable to water vapour can also promote the growth of microbes within the foodstuff [5]. While innovative specialist foils have now been developed, they are likely to be of use only in specific packaging systems.

MOSH/MOAH analysis: complex and still non-standardised

The determination of mineral oil content in foodstuffs is a particularly demanding analytical procedure, not least because it involves a complex mixture that must be quantified as the sum of all of its components. An analysis of individual components is impossible, due to the sheer number of compounds involved. For this reason, the analysis of complex mineral oil mixtures using gas chromatography yields very broad signals instead of sharply-defined peaks. A result of this kind is described as a chromatographic "hump" (or "Unresolved Complex Mixture" (UCM); see fig. 2) by analytical chemists.

Using the most advanced technology available, the simplest approach to MOSH/MOAH analysis is to use on-line coupled

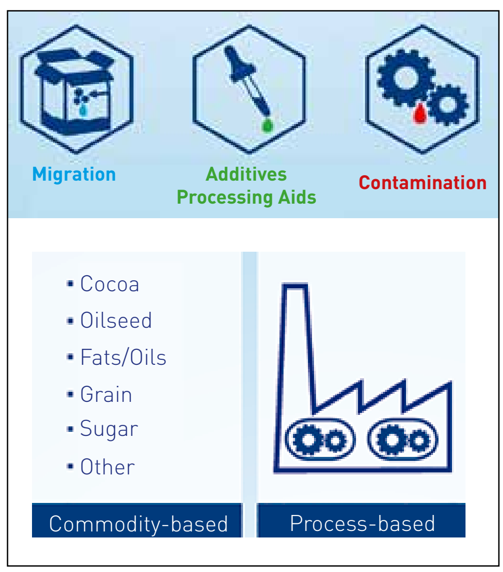


Fig. 3 Schematic diagram of the toolbox for MOSH/MOAH minimization/prevention

liquid chromatography-gas chromatography-flame ionization detection (LC-GC-FID). Until now, no standardised reference procedure verified with a proficiency test is available for the analysis of mineral oil components. Analysis is also made considerably more difficult by the presence of polyolefin oligomeric saturated hydrocarbons (POSH) that can migrate into foodstuffs from polyethylene (PE) or polypropylene (PP) foils, as the analysis procedure cannot distinguish these substances from MOSH/MOAH compounds.

LCI research as part of the BDSI Minimization Plan

Potential contamination of food by mineral oil components is not an issue specific to the confectionery sector but affects the food industry as a whole. Acting in accordance with preventive consumer health protection, the Association of the German Confectionery Industry (Bundesverband der Deutschen Süßwarenindustrie, BDSI) launched a three-year research project on July 1 2013 to investigate the topics of analysis, contamination sources and prevention strategies. The LCI's research aims are to prevent MOAH contamination in confectionery and savory products, and to reduce MOSH contamination to the greatest extent possible. Equipped with state-of-the-art apparatus for on-line coupled liquid chromatography-gas chromatography-flame ionization detection (LC-GC-FID) and comprehensive gas chromatography-mass spectrometry (GCxGC-TOF), the LCI is addressing the following tasks in particular:

- Development and establishment of analysis methods.
- Investigation of samples from raw materials, packaging materials and foodstuffs at all stages within processing and storage, for the targeted discovery of MOSH/MOAH contamination sources.
- Development of a toolbox for minimization MOSH/MOAH contamination by employing a research approach focusing on raw materials and processes (fig. 3). The structure of this toolbox is oriented on the various contamination

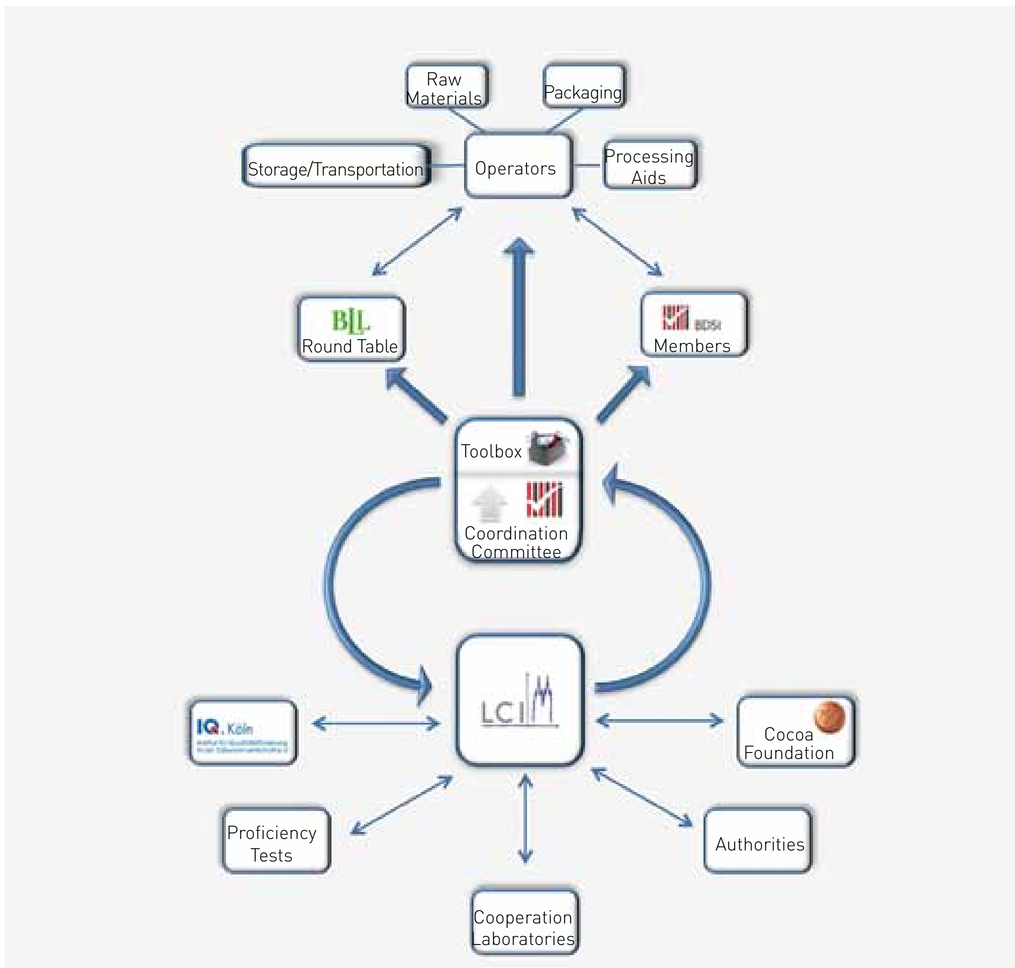
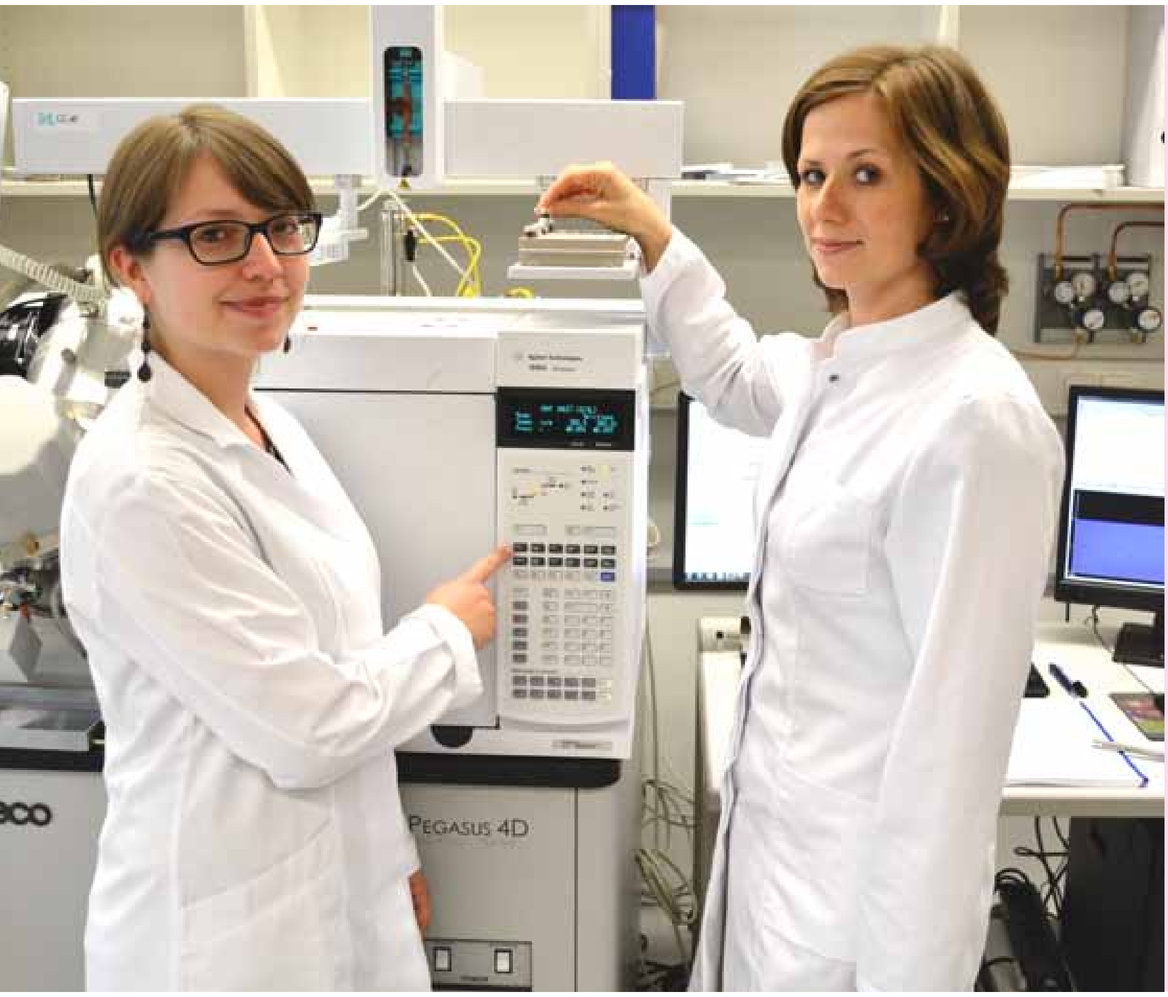


Fig. 4 Flowchart from the LCI/BDSI project for MOSH/MOAH minimization/prevention



Julia Schnapka (left) is a state-certified food chemist. She studied food chemistry at the University of Wuppertal, completing the practical part of her professional training in 2013. Following this, she then commenced her research work at LCI, focusing on the analysis of MOSH/MOAH in confectionery and savory products using methods such as GCxGC-TOF.

Anna Dingel (right) is a state-certified food chemist. After studying food chemistry at the University of Bonn, she was appointed lead researcher for gas chromatography at LCI in 2010. Here, she is responsible for managing research activities within the BDSI research project "Minimization/Prevention of MOSH/MOAH in Confectionery and Savory Products".

routes themselves: migration, additives/processing aids, contamination.

- Creation of a database that can be used to trace both contamination with mineral oil components and the sources of contamination.
- Identification of various factors influencing the migration of mineral oil components into foodstuffs.

Coordination Committee/ Stakeholder Cooperation

To accompany the project, a BDSI-internal coordination committee has been set up, staffed with experts from member companies.

As these issues (potentially) affect any type of foodstuff, the BDSI and LCI are supplementing their coordination committee activities by maintaining close contact with all stakeholders in the food chain. In establishing suitable analysis methods for quantifying MOSH/MOAH, the LCI is also participating in proficiency tests and cooperating with other labs (see fig. 4).

Summary

Together with its own research laboratory LCI and its member companies, the BDSI is conducting a wide-ranging project for MOSH/MOAH minimization and/or prevention that has made a highly successful start. The project focuses in particular on analysis and sources of contamination (and thus to extending the knowledge base) and on promising and practical prevention strategies for industry. Results obtained by the confectionery sector will also be used as input for discussions held with stakeholders throughout the food chain [7, 8].

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