INDUSTRY ADVISORY: MITIGATION OF MINERAL OIL HYDROCARBONS

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Mitigation of Mineral Oil Hydrocarbons

Mineral oil hydrocarbons (MOH) are chemically stable molecules that persist in the environment, and which can accumulate in tissues of living organisms, including humans. They originate from fossil fuels, petrochemical processes, and the use of mineral oils. MOH can contaminate the food supply chain in multiple ways. MOH are typically subdivided into saturated (MOSH) and aromatic (MOAH) hydrocarbons. These two broad classes are each composed of a very large number of compounds.

Mineral oil is composed of a mixture of hydrocarbons from crude petroleum oil. Saturated paraffins (alkanes) are linear and branched hydrocarbons that include only single bonds throughout their chemical structures. Saturated naphthenes also include only single bonds within their structure but also include one or multiple rings, which may be substituted with further alkyl groups. These saturated compounds are collectively called mineral oil saturated hydrocarbons (MOSH). Aromatic hydrocarbons are cyclic hydrocarbons that include carbon-carbon double bonds limited to the aromatic ring portions of the structure, and which may also be substituted with alkyl groups. These aromatic hydrocarbons are called mineral oil aromatic hydrocarbons (MOAH).

MOH exposure via the consumption of food is considered of potential concern, in particular for MOAH. MOAH possessing 3 to 7 rings are considered to be potentially mutagenic and carcinogenic. Regulations involving maximum limits in ingredients and retail products are expected to be implemented in the future.

Hydrocarbon compounds are also produced in nature - for example waxes, long chain alkanes and terpenes synthesized by plants, which may confound the interpretation of hydrocarbons derived from petrochemical sources and mineral oils. Other interferences may be generated during the processing of oils. Specific and improved sample preparation approaches can minimize the presence of interfering substance in the GC-FID analysis of MOSH and MOAH. It is estimated from occurrence data provided by GOED members that in approximately 20% of omega-3 oil batches, interferences are present that obstruct the quantification of MOH. MOH contamination detected by GC-FID that exceeds desired maximum levels should be confirmed by GC-MS or GCxGC-MS analysis. These methods allow confirmation if the contamination is indeed due to MOH or due to the presence of interfering substances.

Objective

This document aims to bring together knowledge about potential points of contamination of omega-3 EPA/DHA oils with MOH, how to reduce such contamination, and how to reduce the levels in ingredient EPA/DHA omega-3 oils that are known to contain MOH. Information on such mitigation approaches may be valuable for GOED members to achieve ingredient oils and retail products that have low levels of MOH, and which meet internal specifications and (future) regulations.

At this point of time, much of the below information is based on observations by members of GOED obtained from experience and small-scale studies. Systematic studies around mitigation of MOH in EPA/DHA omega-3 oils are not available to GOED currently. This document can nevertheless be useful to GOED members in identifying point of contact for MOH contamination, and approaches whereby contamination can be avoided or reduced.

Contamination and points of contact:

MOH can theoretically enter the omega-3 supply chain at many different points. Multiple theoretical and known points of contact are listed and explained below.

Source or point-of-contact for MOH contamination	Mitigation	Note
MOH as an environmental pollutant, and already accumulated in fish tissue (or other types of omega-3 biomass).	Measure MOH levels in the biomass you employ. Do not use heavily contaminated biomass, unless a method is available to reduce MOH levels during refining/processing to a level considered acceptable.	From EFSA's Comprehensive Food Consumption Database, the average content of MOSH in fish meat is 21 mg/kg (and for canned fish, 40 mg/kg).
Mineral oil-based greases used in the transport, storage and discharging of biomass. For example, lubrication of machinery on board of fishing vessels, on land processing-sites (e.g. moving belts to transport biomass).	Measure MOH levels at different points along your production process. Replace undesirable lubricants, if possible, with alternative non-mineral oil-based lubricants, or reduce their use.	
Mineral oil-based lubricants used in moving parts of equipment employed in the extraction/refining/processing of omega-3 oils (blending/mixing/stirring, pumping equipment).	Check that suitable lubricants are used. Check if lubricant use can be lowered. Update your lubricant management plan.	
Mineral oil-based greases used in the transport, storage and discharging of crude and refined oils.	Check that suitable lubricants are used where applicable, including by suppliers, transporters and clients.	
Accidental or non-intentional exposure, including leaks and drips of mineral oil used for lubricating equipment not intended to get into contact with biomass or processed oil.	Check equipment overhanging the omega-3 biomass or oil for risk of accidental drips, splatter, of excess or leaking mineral oil.	

Mineral oil-based lubricants used in product formulation (lubricants use in encapsulation is explained below).	When allowed, make sure the correct type of mineral oil is used, i.e. devoid of MOAH. If not allowed, make sure that an alternative lubricant that is not mineral oil-based is used.	
"Lurking" lubricant use, i.e. the use of unsuitable, mineral oil-based, lubricants that are not declared/not controlled but preferred for their known historic suitability by operators.	Update lubricant management plan to control all lubricants used internally.	
Exhaust gases from operations in the vicinity of traffic, trucks and forklifts.	Check air quality in the area where oils are handled.	
Use of pressurized/compressed air and gasses.	Use air/gas of highest possible grade (e.g. 4N, 99.99% pure, less than 0.01% contaminants, incl. hydrocarbons). For compressed air (always produced inhouse) it is necessary to have an oil free type of system (meaning that the air is cleaned/filtered).	
Additives.	- When adding tocopherols to EPA/DHA omega-3 oils, make sure that the carrier oil (typically a vegetable oil, like sunflower oil) is not contaminated with MOH, and that any alternatives are of good quality (also with respect to other contaminants). The added tocopherol-rich oil can constitute up to 1.5% of the final oil volume. - Interference in the GC-FID analysis by high concentrations of tocopherols has been reported, but does not seem to be relevant up to 2%.	

	- The addition of astaxanthin oleoresin has been reported to cause interference in MOH analysis. It is not clear if astaxanthin itself or other substances in the matrix are responsible.	
Contamination of samples for analysis.	Be cautious not to contaminate samples of oil taken for analysis (avoid false positives): - Do not use gloves - Wash hands with soap, do not use disinfectants - Do not touch samples with creamy hands (creams can contain paraffins) - Do not use plastic in direct contact with the samples (e.g. plastic pipette tips) - Ship the samples in glass containers, in MOH-free plastic containers (e.g. PET, polyacrylate, polyacetate, polyamide), or in the original package - Be careful in the choice of sample bottles, as resin hydrocarbons from the cap liner adhesive can migrate into the oil - Ship the samples in glass containers, in MOH-free plastic containers (e.g. PET, polyacrylate, polyacetate, polyamide), or in the original package - Be careful in the choice of sample bottles, as resin hydrocarbons from the cap liner adhesive can migrate into the oil	

	- Do not use parafilm or sticky tape to create a better seal for closing the bottles - Avoid any contact of the product with recycled card-board (e.g. from the transport box or cleaning paper).	
Use of aluminum getting in contact with the oil, or oil sample shipped to a laborato-ry. In the production of food-grade aluminum bottles and foil, aluminum is often rolled/formed using mineral oil, or emulsions containing mineral oil, as lubricants.	Be cautious with the use of aluminum containers to store an omega-3 oil, and to close a container using aluminum foil, until confirmed that the alu-minum is free of MOH. This is also of relevance in the sam-pling and transport of an oil sample to a testing laboratory (avoid false positives).	Hexane can be used to rinse and remove any MOH from a piece of aluminum foil. PET bottles may be a suitable alternative to aluminum bot-tles. Be careful also with other materials used in laborato-ries to create a better seal, for example avoid the use of parafilm for closing sampling containers.
Solvent recovery systems that recover extraction solvents from exhaust air.	Make sure no MOH contam-ination is picked up in the solvent recovery process.	

Possible points of contact for which we have do not have any evidence or confirmation, but about which members have asked:

- the possibility that the gelatin material used for encapsulation of EPA/DHA oils might be a source of contamination

A special note about encapsulation

The encapsulation process requires the use of a lubricant, i.e. a processing aid and food contact material. Because of this, it will get in contact with the encapsulated oil by means of coating the inside of the capsule. In many geographies, such as Europe, mineral oils are not allowed (or not supposed) to be used for encapsulation. It is believed that most encapsulators in Europe use lubricant alternatives to mineral oils, like MCT (medium-chain triglyceride) oil, for encapsulation, but make sure that is the case for your products. In other specific geographies, mineral oils are allowed to be used, for example in the US where the mineral oil is allowed to constitute up to 0.6% of the final volume. In cases where mineral oils are permitted, the mineral oil employed must be sufficiently highly refined to be devoid of MOAH, and can be called pharmaceutical grade, pharmaceutical "white" mineral oil, technical white oil, or a highly-refined base oil. It is believed that in the US >90% of capsules for dietary supplements are produced using mineral oils as encapsulation lubricants.

You should know if and which lubricant your contract manufacturer uses, in accordance with your purpose and applicable regulations. (Note that the term "food-grade lubricant" does not necessarily mean the oil is devoid of MOAH, just that such an oil can be used in an environment where food is handled, but not necessarily allowed to come in contact with a food product).

Mitigation - Reducing the risk of contamination:

If a contamination is identified, one can aim to track down the source of contamination by measuring MOH levels at various points of the process where contamination is suspected. The points of contact will be different for different GOED members and operations.

Choosing alternative lubricants to mineral oil:

The use of lubrication usually comes down to efforts that have been developed for a specific process, enabling consistent utilization in a specific plant and equipment. The willingness to change from established in-house methods can be a bigger challenge than applying the theoretical characteristics of individual alternative lubricants for a specific purpose. For example, in encapsulation, mineral oils are widely used, but when an alternative needs to be identified, it can take time to optimize the same process with a new lubricant. MCT oils are frequently mentioned as a suitable alternative in encapsulation. There are many producers and suppliers of MCT oils, including KLK, Croda, Stepan, Abitec, and Witarix. Alternative lubricants may have a different cost and are typically more expensive than mineral oils.

Mitigation through removal measures:

Limited information is available on the possibilities to remove MOH in different refining and processing steps.

- AOCS has published a summary of the literature on removal of MOH during (vegetable) oil refining (Gibon, 2021). The summary reads, *"Removing MOSH/MOAH during the refining process is mainly possible during deodorization* and is temperature dependent. The relative removal and final content depend on the initial contamination. Under process conditions, the short chains of MOSH (C10-C16 and C16-C20) are generally stripped easily. The medium ones (C20-C25 and C25-C35) can be efficiently stripped, but the heavy ones (C35-C40 and C40-C50) usually remain in the oil. Similarly, the C16-C25 fraction of MOAH is easily distilled, removal of the C25-C35 is possible, but the C36-C50 fraction is more difficult to remove. In industrial practices, mineral oil can best be stripped over a packed column stripper operating at higher temperature and at low pressure with an ice condensing system. The efficient countercurrent stripping and short residence time in the packed column will provide the most efficient mineral oil stripping, with minimal formation of trans fatty acids and glycidyl esters. Mineral oil can also be stripped via molecular or short-path distillation, but use of these technologies will be difficult to justify due to high costs and higher oil losses. Higher stripping efficiency to remove MOH will also lead to more removal of essential components like tocopherols and sterols, which is disadvantageous for oil stability and nutritional quality."*

* Note: Unfortunately, deodorization temperatures have been reduced because of the 3-MCPD topic in many production processes. The main reduction in MOH therefore can only be achieved via distillation, because this applies a much better vacuum. Yield losses by distillation should be similar to

deodorization done at higher temperatures.

- One member (producer) explains, "Our investigation shows that MOSH levels follow those present in crude fish oil, and are not introduced during production. During refinement the MOH content is reduced. But for those chain lengths that match our products' fatty acid chain length, it is not possible to avoid or reduce the content further."

- Anecdotal information from one member (producer) indicates that during washing of a crude fish oil, MOH can increase slightly due to removal of a portion of the weight of the oil (removal of water-soluble substances).

- Specialized companies that have developed mitigation approaches to remove MOH from edible oils:
    - Artisan Industries – Removal of contaminants from edible oils, such as MOSH and MOAH (and others) with up to 99% yield.

Concluding remarks

To date, there is no evidence for a single, predominant, point of contamination with MOH of EPA/DHA omega-3 oils, except during encapsulation in the case that mineral oils are allowed to be used. The sources of MOH contamination are often multi-factorial, such as from raw materials, the production process, storage and transport, and formulation. GOED members employ a wide variety of processing technologies, and each company should assess for themselves the risk of contamination with MOH in their specific processes. In general, having a lubricant management plan in place will aid in improving oversight on which lubricants are in use in your operations. Replace mineral-oil based greases and lubricants with suitable alternatives, when possible.

References

Gibon V *et al*, Mineral oil hydrocarbons: a new challenge for the oils and fats processing industry. AOCS Inform Magazine, Nov-Dec 2021.

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