Aromatic mineral oil hydrocarbons

Second Technical Paper Agrifood Commission, UNI GL18 Oils, vegetable and animal fats and their by-products, seeds and oleaginous fruits

INTRODUCTION

The mineral oil, identified with the acronym of MOH may be divided in two main compound types, mineral oil saturated hydrocarbons (MOSH) and mineral oil aromatic hydrocarbons (MOAH). They are present in sub-classes, typically ranges from C10 to C50 globally considered. They consist of three principal classes of compounds: paraffins (linear and branched alkanes), naphthenes (alkyl-substituted cyclo-alkanes) and aromatic (including polyaromatic hydrocarbons generally alkyl-substituted), moreover minor amounts of heteroatom may be present. They are derived by physical separations (distillation, extraction) and chemical conversion processes (cracking, hydrogenation, alkylation, isomerisation) from crude oils and or synthetic products derived from liquefaction of coal, raw petrol, but also synthesized by carbon, natural gas or biomass. Products with the same specification may considerably vary in their composition, depending on the source of the oil and the processes used.

This technical paper represents an updated review respect to the 2018 previous one, focused to aromatic mineral oil hydrocarbons (MOAH). It is well known that they are organic chemical compounds that contain at least one aromatic ring: they include polyaromatic compounds (PAH) which are formed at high temperatures, but most of MOAH are alkylated to more than 98%, consisting of large numbers of compounds and forming broad chromatographic signals (hump) with peaks signal on top that cause difficult in analytical integration. MOAH are considered in different fractions not only as total, because of their different biological effects (C10-C16, C16-C25, C25-C35, C35-C50). Technical grade mineral oil contains up to about 50% MOAH while approved food grade (white oils) contain less than 1% MOAH. From the last UNI technical report in 2018 there have been significant advancements regarding the MOH as contaminants in foods addressing the attention to MOAH fraction because of their higher risk to human health. Nowadays numerous gaps remain in analytical methods, assessment exposure and risk evaluation. The same conclusions were found in the recent bibliography here also reported. About toxicity, when compared with MOSH there are important differences regarding negative biological effects: they could cause cancer, are mutagenic and genotoxic and could cause maternal toxicity and fetal toxicity. From EFSA opinion on risk assessment of MOAH published in 2012 and 2019 the conclusions were that there was a lack of toxicological data to identify and characterize any hazard relevant to human health associated with the presence of MOAH. EFSA opinion did not conclude that all MOAH are of concern and that more information are required to identify and characterize these substances. About MOAH present in infant formula and follow-on formula, and more in general in food, EFSA arrived at the conclusion that contamination, can originate from different sources either via the environment, during industrial food manufacturing and processing, or via packaging food contact transfer. The MOAH with 3-7 ring cyclic aromatic mojety are of main concern for their genotoxic and carcinogenic nature. In absence of relevant dose-response data it is not possible define the hazards so it is really important to get additional information on the MOAH content in food. According to the data collected until 2019, MOAH content in infant formula ranged from 0.2 to 3 mg/kg. The UE recommendation was to apply routinely analytical methods to detect MOAH content in food. From the last 3 reports of FoodWatch was reported the discovery of many products sold on the market contaminated.

The source of the contamination not always is clear, but the recycled packaging material seems be the principal source and most of the producers are trying to use effective barriers in their recycled packaging and working following particular HACCP rules.

LEGISLATION AND REGULATIONS

About legislation, the regulation base is the general food law EC 178/2002 Art. 14 on food safety which states "food shall not be placed on the market if it is unsafe". Recommendation 84/2017 suggest a monitoring of mineral oil hydrocarbons in food products and in materials and objects intended to come into contact with food products. During 2017-2018 the Member States were invited to do monitoring activity on this problem. In 2019 the European Joint Center made available a technical report "Guidance on sampling, analysis and data reporting for the monitoring of mineral oil hydrocarbons in food and food contact materials". In the same guide the analytical performance requirements were included. Nowadays EFSA is working on a new draft expected by the end of 2022. At this moment a regulatory framework yet to be established, no EU limits have been set in food products pending EFSA assessment, only national benchmark levels, exist in some Member States, they are not safety levels but indicate that need to further investigation, to conduct a correct risk analysis. In 2021, the leading association of the German food industry (in agreement with consumer associations and control authorities of the federal states), established benchmark levels based on background levels in different food categories. For vegetable oils, excluding those of tropical origin, the MOSH level was set at 13 mg/kg, while the MOAH should be lower than the LOQ (according to JRC guideline: LOQmax = 2 mg/kg for each C-fraction). In the JRC technical report, was reported that an analytical method «must be sufficiently sensible to ensure that no contamination of food with potentially carcinogenic MOAH is detectable using the most advanced methods of laboratory analysis, such as on-line LC-GC-FID and GC×GC-TOF, but any other detection technique is acceptable, if provides equivalent results to the on-line LC-GC-FID.

JRC also suggest for this type of analysis to use the Eurachem guide for method performance evaluation and fixed LOQ maximum and target as important established requirement. In Italy from many years scientific experts are working about this topic, in particular during the UNI standardization body GL18 "Oils and Fats animals and vegetables and their products, seeds and oleagineaus fruits" meetings, there was always discussion about this problem. In 2018 the same Italian UNI experts wrote a technical report with the conclusion that: "*on the base of the background material analyzed and by all experimental working groups developed around this topic, the LOQs of the official methods tested and available for the laboratories that mean perform the evaluation of MOSH and MOAH, are higher than the North European limit proposed or desirable in vegetable oils*". The document was also distributed by Italian Society of Fats and Oils to all vegetable oils national industries and associations on indication of Assitol association.

COLLABORATIVE STUDIES

Different pre-collaborative trials, aimed at implementing method EN 16995 with a pre-enrichment step (saponification) to improve method sensitivity and inter-laboratory reproducibility at low concentrations, have been organized in the last years by ITERG (Canejan, France) in collaboration with the Max Rubner Institute (Detmold, Germany). In short time it is expected the final report concerning the analysis of 16 test samples including palm olein, coconut oil, sunflower oil, rapeseed oil, olive oil and grapeseed oil.
The European Union Reference Laboratory for Food Contact Materials (EURL-FCM) will organise shortly a proficiency test round, under ISO 17043 accreditation for the determination of MOSH/MOAH in edible oil. The final report is expected for September 2022.

UNI GL18 group organized always in 2018 a first collaborative study, 10 laboratories were interested, the method to be used was freely chosen by laboratories and the test regarded 6 extra virgin olive oils spiked with motor oil and lubricant paste. The coordinator was COTECA (a private laboratory) joined to SALOV (an important Italian olive oil industry). The scope was to compare different methods and observe the influence of sterens and squalene isomers deriving from refining process. It was not possible demonstrate required accuracy and reproducibility coefficient variation was in the range 70.5% - 27.0% for a content between 2-11 mg/kg of MOAH content. It was very high the dispersion of the results suffered for dispersion.

A second collaborative study was organized in 2018 by the GL18 expert group, and as in the first study the method was free, that used for routine analysis, the samples in this case were MOAH in solvent present in different concentration, to verify if the matrix effect was the problem and not the analytical techniques. As the first study the relative reproducibility coefficient RSD % was very high, until 173%, for the blank sample, were found values among 0-10 mg/kg, only for the sample with a content of 5 mg/kg of MOAH the RSD % va-

lue was near to the statistical conformity required (25%). Moreover, the UNI experts shared the following conclusions: there was the need to develop an alternative method to on-line LC-GC-FID (ISO 16995) and the missing of certified material was a big problem. They also suggested to develop a method off-line, available for all laboratories, without the need to have an instrumentation of high level and the engagement of highly specialized technicians. The characteristics of the method must be: capability to distinguish MOSH from MOAH whatever their ratio, sustainability, easy to use and no time consuming. INNOVHUB SSI S.r.l created a collaboration with Milan University and a thesis for this purpose was organized. The thesis was discussed in the academic year 2018-2019 at the Milan University with the support of Chemical and Toxicological Sciences and Safety of Environment Department and a draft of the off-line analytical method was presented in UNI and actually the experts are trying to conforming it to the ISO 16995 for standards and analytical requirements. However the experts did the following observations: the internal standards chosen for MOSH/MOAH separation do not assure a separation comparable to that of the reference method, difficulties to obtain an adequate blank sample, need of a dedicated and separated laboratory glassware, evaporative process could cause problem of lack in low carbon compounds, integration difficulties in respective C ranges, lack of guidelines for gaussian integration, a pre purification of the matrix was always needed to eliminate interference due to refining process, difficulties were met and the applicability of the off-line method was showed superior than 10 mg/kg, not appropriate for market demand. In the course of the year 2021 the UNI GL18 group coordinated by INNOVHUB SSI S.r.l did another collaborative study: 20 national and international laboratories participated. The method to be used was free, that used during routine analysis. Six samples spiked with mineral oil, pre analyzed for MOAH content, in the range from 0.5-20 mg/kg of MOAH were mailed. The scope was to evaluate if different analytical approaches gave similar results. The results have been discussed in the UNI meeting on 8 February 2022. The data collected were discussed by experts and showed that there were again analytical problems for this determination, because of their dispersion no statistical elaboration was performed. Problems were evidenced on refined sunflower oil (blank sample) not only on refined sunflower oil (spiked samples).

CONCLUSIONS

In conclusions, in light of the above, for some fat matrices the analytical result is influenced by the presence of endogenous interferents (e.g. terpenes, carotenoids). The result is an inaccurate and overestimated analytical evaluation. The experts have shared that:

- there is the need of a fully validated analytical method with specificity and reproducibility satisfying;
- the results are affected by high uncertainty with low MOAH concentration and complex matrices;
- a confirmatory method with GCxGC FID-MS validation is missing and the analysis is characterized by a difficult integration and guidelines for chromatogram interpretation are needed;
- new standard of mineral oils commercially available need to obtain a widen range of certified reference contaminated foods at different concentration level;
- actually the method EN16995 used for MOH determination in vegetable oils and fats is not reliable below 10 mg/kg. This value is not considered LOQ value but the value under the which the interlaboratory reproducibility has not acceptable values. There is also a need of a confirmatory methods that provide a detailed characterization of the unresolved complex mixture observed from one-dimensional chromatographic methods;
- the exposure estimation is impossible due to the limited knowledge of the real content of MOAH in food;
- further informations are needed to clarify the complex distribution of MOH in the human body and to establish a relationship between the levels of external exposure and absorption in the organism;
- a clear definition on how report the results and indicate LOQs is required.

The chemical experts GL18 group are always open to be involved in future collaborative study to improve analytical aspects about this important topic.

The UNI GL18 experts

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