Mineral Oils in Food: Major Sources and Analytical Determination

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Abstract

Mineral oils are complex Mixtures of Saturated (MOSH) and Aromatic Hydrocarbons (MOAH), which can reach the food through different routes (environment, field production, food processing and packaging). Particularly, the use of recycled paper for food contact has raised an increased concern due to the presence of huge amounts of MOSH and MOAH that can migrate into food. Recycled cardboard contains mineral oil from different routes such as newspaper and other printed paper entering the recycling process, adhesives, solvents, waxes and additives used in the production process as well as printing inks and sealants used in the final product. This mini-review deals with the issue of food contamination with mineral oils, focusing on possible sources and analytical methods for their determination in food.

Keywords: Mineral Oils in Food; Sources of Contamination; Sample Preparation; On-Line HPLC-GC; MOAH; MOSH

Introduction

Mineral oils are widespread environmental and processing contaminants of petrogenic origin, comprising a complex Mixture of Saturated (MOSH) and Aromatic Hydrocarbons (MOAH) of different toxicological relevance. MOSH are of concern mainly because of their bioaccumulation potential in human tissues, while MOAH comprise suspected carcinogens and for this reason their presence in food should be avoided or maintained “as low as is reasonably achievable”. At present there is no approved legislation on mineral oils. The legal limit of 50 mg/kg established for Ukrainian sunflower oil in 2008, has been repealed in 2014, once the emergency ended. Since 2011, there have been several attempts to establish legal limits by the BMEL (German Ministry of Food and Agriculture), which published four draft ordinances, without approving any. The third draft ordinance, disclosed by BMEL in 2014, established a maximum limit for MOSH and MOAH in recycled paperboard, specifying that higher levels of contamination can be accepted in the presence of a suitable barrier material that ensures that limits in food are not exceeded. Proposed limits in food (as a consequence of migration from recycled paperboard) are: 2 mg/kg food for MOSH C20-35, and 0.5 mg/kg food for MOAH C16-35 for food. The fourth BMEL draft ordinance (2017) confirmed the MOAH limit, only. In 2011, based on experimental evidence that the MOSH between C10-C16 do not accumulate in the human body, the German Federal Institute for Risk Assessment (BfR) has set a temporary limit of 12 mg/kg, to which a limit of 4 mg/kg for MOSH between C16 and C20, was added in 2012.

Contamination Sources

The routes through which mineral oils can come into contact with food are numerous [1,2], but can be traced back to 3 main routes: migration from packaging, unintentional contamination (environmental contamination, accidental contact with nonfood-grade lubricants, etc.), use of refined mineral oils in food production (admitted uses).

Contamination can occur at different levels of the food supply chain (field production, processing, and packaging). Environmental contamination, mainly due to incomplete combustion of heating oil, diesel, lubricating oils and asphalt debris, is responsible for a background contamination observed in many products (especially edible oils) [3]. Among the possible sources of contamination in the field: the use of mineral oil-based pesticides and mechanized harvesting operations. A carry-over process from the feed to the food may contaminate products of animal origin. During storage and transport of raw materials, the use of jute bags exposes the product to possible contamination with “batching oil”, a crude mineral oil fraction, used to soften the fibers before spinning. Processed foods can be contaminated with food-grade mineral oils: refined oils (treated to remove MOAH), widely used in the food industry as lubricants, release agents, anti-dust agents, protective coatings for fruits and vegetables, cheese, and in some cases as additives and ingredients (e.g. microcrystalline waxes).
Migration from packaging made of recycled fibers represents the most important source of contamination for many foods, even in the case of a secondary packaging not in direct contact with the food [1]. Recycled fibers contain residues of inks from newspapers or other material printed with mineral oil-based inks, which enter the recycling process. In recent years, mineral oil-based printing inks largely used in the food industry up to a few years ago, responsible of contamination in many food, have been gradually replaced with mineral oil free printing inks. Cellulosic packaging may also be contaminated with paraffins to improve water resistance, MOSH from adhesives and solvents used as carriers of binders and additives.

Migration from paper and paperboard packaging can occur from the matrix to the surrounding environment (and vice-versa) and from the fiber matrix into the food (also across different layers or packaging), both by direct contact and by indirect contact (via gas phase). Paperboard material consist in an open and porous structure of fiber and air pores. The mobility of mineral oil and other contaminants through the paper comprises a combination of adsorption and desorption mechanism on the fiber, transfer mechanism across the fibers and diffusion of migrants in the air pores. Migrants can be transferred into food both by the gas phase and by diffusion according to their volatility.

Different strategies have been proposed to limit the migration of MOSH and MOAH from packaging to food: (a) to reduce the percentage of recycled fibers used for paper production; (b) to replace recycled fibers with virgin ones; (c) to select high quality material for the recycling process; (d) to study systems for a better purification of recycled fibers; (e) to use “mineral oil free” printing inks, and (f) to use functional barriers able to reduce migration below the levels required. The use of a functional barrier represents the best choice against the migration problem. Different solutions such as use of internal bags (e.g. PET, PP/EVOH, etc.), modified paperboard packaging material with an integrated barrier layer or incorporating an adsorbent material (such as activated charcoal), have been proposed in the last years.

**Analytical Determination**

The reference method for MOSH and MOAH analysis in food and packaging is the on-line HP(LC)-GC-FID method proposed by Grob and collaborators [4,5], recently approved as the BS EN 16995: 2017 method for vegetable oils and foodstuffs on the basis of vegetable oils. The sample extract is injected into an LC silica column (25 cm x 2 mm id) which has the function to retain polar triglycerides allowing the separation of the MOSH and MOAH fractions which are sent (on-line), separately, to the GC column for quantitative analysis carried out with a Flame Ionization Detector (FID). MOSH and MOAH pre-separation can be also achieved using off-line SPE followed by GC-FID analysis, using large volume injection to compensate for the loss of sensitivity and to avoid discrimination problems [6,7]. On-line LC-GC-FID has the advantages to exploit high separation efficiency, to allow for high sample throughput reducing solvent consumption and sample manipulation and thus enhancing reproducibility of the method. FID is chosen as detector because it provides virtually equal response per unit of mass for all hydrocarbons and because of calibration problems encountered with Mass Spectrometry (MS). Its lack of sensitivity and selectivity must be compensated with suitable pre-separation in order to assure that only the hydrocarbons reach the detector. Correct interpretation of chromatograms presupposes knowledge about the sample and potential interferences. Sometimes auxiliary methods, like enrichment to reach higher sensitivity, removal of biogenic n-alkanes by activated aluminum oxide, and epoxidation to eliminate the interference of olefins (naturally occurring or formed during refining), are needed [4].

The analytical determination must be proceeded by an extraction step, whose importance is often underestimated, and which should guarantee quantitative recovery with minimal solvent consumption. The choice of the extraction method should derive from an in-depth knowledge of the matrix [2]. Ethanol extraction followed by extraction with hexane allows to obtain exhaustive extractions from both dry and wet food. The use of automated extraction techniques that exploit high temperatures and high pressures, such as Pressurized Liquid Extraction (PLE) or Microwave Assisted Extraction (MAE), represent a valid alternative to the classic solvent extraction and allow a considerable reduction in extraction times [8,9]. Microwave Assisted Saponification (MAS) allows for rapid saponification of the sample and simultaneous extraction of unspecifiable matter. It has the advantage that can be applied to all kind of samples and allows to eliminate the fat prior to the LC-GC analysis, enabling to reach high enrichment factors [10].

Although LC-GC-FID analysis furnishes unambiguous results for the large majority of the samples, due to possible presence of interference, some samples requires verification. When there are doubts about the result, or it is important to investigate on the origin of the contamination, it is advisable to carry out a confirmation analysis using GCxGC-MS [11,12]. This technique is very useful to better characterize the MOAH fraction; it provides information on the number of benzene rings and alkylation degree and allows distinguishing mineral oils from hydrocarbons of synthetic origin such as Polyolefin Oligomers (POSH) and Poly-Alpha-Olefins (PAO), the latter mainly derived from hot-melts adhesives.

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