MODERN TRENDS IN FOOD CONTAMINATION ANALYSIS - AN INDICATIVE RESEARCH PROPOSAL ON MINERAL OIL HYDROCARBONS (MOH) MIGRATION POTENTIAL FROM FOOD CONTACT MATERIAL INTO FOOD PRODUCTS

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Abstract

Consumers may be exposed to mineral oil hydrocarbon (MOH) contamination via packaged foods, but data on the occurrence of MOH are currently available only for a limited number of foods.

In this work, we have carried out an indicative research proposal on the contamination with MOH migrated into milk via food contact material (FCM). Mineral oil saturated hydrocarbons (MOSH) and mineral oil aromatic hydrocarbons (MOAH) were extracted by LC-GC-FID from three sample categories: food contact material (4 samples), milk in directly contact with FCM (4 samples) and milk with no contact with FCM (4 samples). Our results revealed an important contamination given by the contact materials, especially for the MOSH fraction, supported by a common contamination profile, confirmed in the analyzed milk samples. Quantitatively, the MOH contents were variable, with higher values in milk samples in direct contact with FCM, the increase in MOH concentrations being closely related to the important contamination values of FCM (105.4–116.6 mg/g MOSH; 4.3–4.9 mg/kg MOAH).

Key words: *contamination, milk, food contact materials*

INTRODUCTION

Mineral oils hydrocarbons (MOH) are modern groups of contaminants ubiquitous in the environment, with important implications on food chain.

The occurrence of MOH in food chain is a persistent problem for more than a decade and raises serious concerns because of their potential negative effects on health [1-3]. Although the toxicity and effects of MOH have not been fleshed out to date, the recent findings, based of various contamination episodes, have urged the public to manage more deeply the issues related to the incidence of MOH in the environment [4].

Structurally, MOH are petrogenic contaminants consisting of complex mixtures of saturated hydrocarbons (MOSH –Mineral Oil Saturated Hydrocarbons) or aromatic hydrocarbons (MOAH–Mineral Oil Aromatic Hydrocarbons).

MOH may be present in various matrices as a result of environmental contamination [5], or may be released from production cycle. Improper manufacturing practices may include contamination through agricultural machinery lubricants, release agents, mineral oils, inks or similar products. Food contact materials (FCM) containing mineral oils (e.g. cardboard, recycled paper, inks) are also important sources for MOH contamination [6, 7], through direct contact with food [8-12], or through migration in the gas phase [13].

Technological process of raw materials can be particularly relevant for MOSH and MOAH contamination because of composition of packaging and transport

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materials or packaging printing inks composition [14-17].

Toxicologically, the effects and toxicity of MOH on living organisms still remain uncertain, but is topical in the field [4, 13].

Constant discoveries focused on MOH influence on living organisms highlight the high capacity of MOSH to accumulate in human organs and tissues [6, 10, 18], in while MOAH, due to structural similarities with polycyclic aromatic hydrocarbons (PAH), are susceptible to having carcinogenic effects [4, 17].

Because of their lipophilic nature and widespread use in various processes, MOH can contaminate animal productions and vegetables productions, according numerous researches shown over time [6, 10, 19-27].

Although the appearance of MOH and the first studies related have been known since about 30 years ago [28], MOH presence in food chain really became a problem more than a decade [4, 29]. In 2008, a critical case of MOH contamination was reported in Ukraine, for numerous batches of sunflower oil with MOSH and MOAH concentrations up to 3100 mg/kg [30, 31].

MOSH and MOAH topics focus primarily on food and consumer safety [29]. Consumers are exposed to MOH contamination via food [5].

Milk play an important role in providing nutrients for humans, especially for sensitive categories of consumers.

The safety of milk is a particularly important issue in terms of food safety. Although studies have evolved over time, data on the occurrence of MOSH/MOAH are currently available only for a limited number of matrices and only in few countries.

Mineral oil milk contamination has gained attention so far only through potential risks induced by packaging, recent articles reporting the mineral oil presence in infant formula [32, 33].

This paper represents a preliminary research proposal regarding the evaluation of food contamination with MOH via food contact material. The aim of this indicative study is to carry out an analysis of MOH migrated into a food product (milk) from a packaging material, to show the possibility of food contamination via packaging.

Mineral oil saturated hydrocarbons (MOSH) and mineral oil aromatic hydrocarbons (MOAH) extracted from FCM, from milk samples in direct contact with FCM and milk samples with no contact with FCM, were analyzed by LC-GC-FID.

Common contamination profiles between samples in direct contact with FCM and FCM itself, independent of non-contact milk samples contamination, suggest MOH migration potential from packaging materials into food.

Data available in literature so far and the results of this preliminary study can be used to establish future models for confirming food contamination when using similar packaging with the aim of improving public health and reducing the risk of consumer exposure to contamination.

MATERIAL AND METHOD

Samples

MOSH/MOAH content analysis was performed based on 4 samples of cow's milk taken directly from 3 dairy farms in NE Romania. No processing or packaging processes was applied to milk samples before the analysis; before starting the experiment, the crude fat content of each sample was determined.

The 4 samples were divided in categories:
- (MxA) – liquid milk samples, no contact with food contact material (control samples);
- (MxB) – milk samples for testing MOSH/MOAH migration from packaging material (test samples): liquid milk samples covered with waxed food paper; for testing migration potential of MOSH/MOAH from FCM, the samples were subjected to a lyophilizated at -30 ...- 70 ºC, because under the temperature influence, mineral oils can be able to volatilize.

Packaging material tested alongside the milk samples was a classic white waxed food paper purchased from a supermarket.

Samples characteristics are presented in Table 1 and Table 2.

Table 1 Characteristics of milk samples

[1] Code & sample no.	Product type	Fat (%[2]DM)	Sample weight (g)	Contact type
M1A	Cow milk	37.3	5.133	No contact
M1B			4.022	Directly
M2A	Cow milk	35.4	5.103	No contact
M2B			4.032	Directly
M3A	Cow milk	29.6	5.078	No contact
M3B			4.003	Directly
M4A	Cow milk	29.6	5.076	No contact
M4B			4.026	Directly

[1]M1A, M2A, M3A, M4A = control samples/ M1B, M2B, M3B, M4B = test samples; [2]DM = dry matter.

Table 2 Characteristics of food contact material

[1]Code & sample no.	Product type	FCM colour	Sample weight (g)	Product weight (g)	Contact type
FCM1	Waxed food paper (baking paper)	Bleached	1.091	31.421	Directly
FCM2			1.017	31.214	
FCM3			1.038	31.756	
FCM4			1.053	31.603	

[1]FCM1, FCM, FCM, FCM = food contact material.

Principle, standards and reagents

MOH analysis was performed using the coupled LC-GC-FID technique. The method for determining mineral oils was described by Biederman et al. [31]; Bierdemann & Grob [34] regarding the extraction, separation and quantification of MOH. The work protocol was adapted and modified over the years by Moret et al. [35], the method being subsequently applied with good results in numerous papers, such as those developed by Menegoz Ursol et al. [27], Srbinovska et al. [7, 36] and meets the analytical performance criteria mentioned in the JRC Guideline [5].

Numerous solvents and reagents were used for MOH analysis of milk and FCM samples: n-hexane (≥ 95 %; CAS: 110-54-3), methanol (≥ 99.9 %; CAS: 67-56-1); saturated KOH, aluminum oxide (CAS: 1344-28-1) and sodium sulfate (CAS: 7757-82-6). Reagents were purchased from Merck Millipore (Massachusetts, USA), Sigma-Aldrich, Supelco or Milli-Q (pure water), excepting mCBPA, purchased from Acros Organics (Thermo Fisher Scientific). Checking LC-GC performance, for MOSH and MOAH separation, but also for the integration and quantification of results, was used internal standard (IS) #31070 (150-600 µg/ml in 99 % toluene) from Restek (Bellefonte, PA, USA).

MOH analysis was carried out based on a LC-GC 9000 Brechbuhler (Zurich, Switzerland) consisting of an HPLC Phoenix 9000 coupled to an 1310 GC model Trace, Thermo Fisher Scientific (Waltham, Massachusetts, USA), configured with a dual channel, so that MOSH and MOAH fractions can be analyzed at the same time [31, 37]; a 25 cm×2.1 mm i.d. HPLC column, Lichrospher Si 60.5 µm particle size was used (DGB, Germany).

Data were collected and processed by Chromeleon software (Thermo Fisher Scientific, Waltham, Massachusetts, USA). Quantification was carried out based on internal standards n-C_{13} for MOSH and 5B (pentylbenzene) for MOAH. Areas of

MOSH/MOAH fractions were determined by column integration, after removal of interferences. Baseline position was assessed by blind samples procedure [38] running each batch of 6–8 samples obtained on the same day.

MOSH/MOAH analysis for milk samples

MOH analysis protocol for milk samples, include a specific step of organic phase separation. Saponification technique was carried out using MARS 5 microwave system (CEM Corporation, USA), with 14 teflon vials (one cycle of vials purification was required previously using 10 mL of hexane and 10 mL of KOH saturated in methanol). Five grams of control sample (A, liquid milk) and 4 g of test sample (B, freeze-dried milk) were introduced in each vial, added 10 mL of KOH (40 %), 10 mL of n-hexane and 20 µL of internal standard (IS). The mixture was microwave for 20 minutes at 120°C.

After extraction, 40 mL of Milli-Q ultrapure water and 2 mL of methanol were added; the resulting mixture was kept resting until complete phase separation. In the next step, the extract was concentrated under vacuum until 4 mL, using the Uniequip vacuum centrifuge, UNIVAPO-100H model, coupled with the V-700 vacuum pump and the V-850 controller (Buchi).

An auxiliary purification by epoxidation was also performed according to the method described by Nestola & Schmidt [39], modified.

During epoxidation, 500 µL mCBPA (ethanolic solution, 20 %) was added to the extract and then was kept 15 minutes at room temperature under magnetic stirring (500 rpm); 2 mL of sodium thiosulfate solution (aqueous solution, 10 %) and 500 µL of ethanol were added over the previously formed mixture, followed by magnetic stirring for another 30 seconds. From this step, 500 µL of extract was transferred to an autosampler for injection into LC-GC-FID system; in LC-GC-FID system, the injected volumes were calculated proportional to DM content of each sample and based on the amount of analyzed sample.

MOSH/MOAH analysis for food contact material

For MOH analysis of FCM, 10 mL hexane, 10 mL toluene and 20 µL IS were added over the sample (1 g). The resulting mixture was kept under stirring for 5 minutes, then resting 90 minutes, followed again by 5 minutes of stirring. On top of mixture, 20 mL of ultrapure water (MilliQ) was added, and the newly formed mixture was kept at freezing temperatures for 20 minutes. The extract was separated in the next step and loaded into injection vial for LC-GC-FID analysis.

RESULTS

This preliminary work explored research ideas regarding potential migration of MOSH/MOAH from contact materials into food. The results were structured according the followed steps, presenting the preliminary data collected, in order to establish the hypotheses of future research, expected results and possible limitations of the research.

Preliminary data collection and analysis for MOSH/MOAH in milk

MOH contamination has been reported, over time, for numerous animal source foods [13, 20, 36]. Based on research to date and the Commission's Recommendation (EU) 2017/84 [40], the monitoring is important especially for animal fats, meat, dairy, fish, bakery (bread, cereals, pasta), oilseeds and vegetable oils [5].

Milk is a product easily affected by exogenous contamination. Tables 3 and 4 show the MOSH and MOAH distribution following the analysis of liquid milk (MxA, control samples) and lyophilized milk (MxB, test samples).

Table 3 Distribution of MOSH in milk samples

Sample[1]	MOSH (mg/kg)						
n-C fractions	n-C_{10-16}	n-C_{16-20}	n-C_{20-25}	n-C_{25-35}	n-C_{35-40}	n-C_{40-50}	n-C_{10-50}
M1A	1.0	1.4	0.3	0.4	0.1	0.0	**3.2**
M1B	0.5	4.4	2.1	1.4	0.2	0.1	**8.7**
M2A	0.3	1.0	2.2	4.3	0.6	0.3	**8.7**
M2B	0.7	6.4	3.0	2.1	0.5	0.4	**13.1**
M3A	0.9	0.7	0.2	0.3	0.1	0.0	**2.2**
M3B	0.3	2.1	1.4	0.5	0.1	0.1	**4.5**
M4A	0.1	0.2	0.1	0.2	0.1	0.1	**0.8**
M4B	0.6	4.2	2.2	1.4	0.4	0.2	**9.0**

[1]*M1A, M2A, M3A, M4A = control samples/ M1B, M2B, M3B, M4B = test samples*

MOSH concentrations measured in control milk samples (MxA) ranged from 0.8-8.7 mg/kg, with important differences between samples. More or less, all milk samples exceeded the recommended limit by the Standing Committee for Plants, Animals, Food and Feed, Section for Novel Foods and Toxicological Safety of the Food Chain, European Commission [41], of 0.5 mg/kg for products < 4 % fat (M3A; M4A), respectively 1.0 mg/kg for products > 4 % fat. The main concentration of MOSH was revealed in the n-C_{10-25} range for most of milk samples, except for M2A milk sample, where MOSH was found especially in the n-C_{25-35} fraction.

Most important amount of MOSH corresponds to M2A milk samples, with 8.7 mg/kg. The values obtained were similar to those reported by Grob et al. [42] for eggs (9.0 mg/kg), but higher than the values reported by Zhang et al. [33] for bread (1.5–5.0 mg/kg), different types of cereals (1.9–2.4 mg/kg) or vegetable oils (2.9–6.4 mg/kg). Instead, some small amounts of MOSH were revealed for M4A milk samples (0.8 mg/kg minimum values).

Data obtained from sampling sheets shows that the analyzed samples were not subjected to any technological processing; also, no sources or substances that could have contributed to the contamination of the samples were reported. According to Matei [43], it could be considered that this contamination could be a result of a certain background pollution in the geographical area of sample collection, especially modern pollution [44].

Before second stage of analysis, milk samples were lyophilized to obtain the test samples. After 7 days, MOSH content was analyzed and higher values than for control milk samples were obtained. MOSH concentrations measured in test samples (MxB) ranged from 4.5–13.1 mg/kg, being 1.5-11.0 times higher than control samples. Instead, similar to control samples, the presence of MOSH was predominant in the n-C_{10-25} molecular range, but also with important values in the n-C_{25-35} range for M1B, M2B and M4B samples.

The highest content of MOSH for test samples was highlighted for M2B samples (13.1 mg/kg). With highest amount of MOSH, M2B samples did not have a critical increase of contamination level, because an important content of MOSH was revealed even from control samples analysis.

The lowest amount of MOSH was found in M3B samples (4.5 mg/kg), double compared to control sample.

Important levels of total MOSH fraction was found in M1B and M4B samples, with similar values (8.7 mg/kg; 9.0 mg/kg). If for M1B samples, the increase in MOSH concentration was, on average, up to 3 times, for M4B samples, a particularly important increase was revealed; in this case, test milk samples had up to 10 times more MOSH than control samples.

Table 4 Distribution of MOAH in milk samples

Sample[1]	MOAH (mg/kg)				
n-C fractions	n-C_{10-16}	n-C_{16-25}	n-C_{25-35}	n-C_{35-50}	n-C_{10-50}
M1A	nd.	nd.	nd.	nd.	**nd.**
M1B	0.0	2.1	1.1	0.0	**3.2**
M2A	0.6	1.7	0.5	0.0	**2.8**
M2B	0.0	3.95	1.4	0.0	**5.35**
M3A	nd.	nd.	nd.	nd.	**nd.**
M3B	0.0	2.60	1.4	0.0	**4.0**
M4A	nd.	nd.	nd.	nd.	**nd.**
M4B	0.0	3.2	1.2	0.05	**4.45**

[1]M1A, M2A, M3A, M4A = control samples/ M1B, M2B, M3B, M4B = test samples, nd. = not detected.

The results obtained for MOAH showed that for 3 of the 4 analyzed samples no concentrations were detected in milk (LOQ < 0.5 mg/kg); the exception was M2A samples. Table 4 present the molecular intervals obtained for the M2A samples for the MOAH fraction, which shows a total n-C_{10-50} content of 2.8 mg/kg.

The potential sources of contamination of M2A milk samples were evaluated. Based on this, we could consider that the contamination could come during the transport of milk from collection site to processing facility without any special precautions.

For freeze-dried milk, the amounts of MOAH obtained were alarming. If the initial values reported the absence of MOAH in three samples (M1A, M3A, M4A), after freeze-drying, the MOAH content of these samples increased to 3.2–4.45 mg/kg, which indicates an important sign of contamination.

A common contamination was revealed for all four milk samples after lyophilization, with main presence of MOAH in the n-C_{16-35} range. Highest values were obtained for M2B samples, respectively 5.35 mg/kg, but they did not show the most important increase taking into account the initial MOAH content.

With small differences between samples, the total content of MOAH n-C_{10-50} exceeded the limits recommended by the Standing Committee on Plants, Animals, Food and Feed, Section for Novel Foods and Toxicological Safety of the Food Chain of European Commission [41], for all MxB samples. Given the lack of contamination of initial samples, it could be considered that the contamination could have occurred during the lyophilization of milk, following volatilization of mineral oils under temperature influence, as Biedermann and Grob [37] reported in a similar research.

MOSH/MOAH in food contact material

Permitted use of mineral oils as components of some packaging products [16, 47] can causes major concerns regarding MOH contamination. To evaluate the migration capacity of MOH, amount of MOSH and MOAH in waxed paper was quantified.

Tables 5 and 6 shows average values obtained after 2 repetitions/sample (FCMx), expressed in carbon fractions and related to total mass of packaging used to cover the samples (≈ 1.3 g).

MOH fractions identified in waxed paper were separated into six MOSH volatility ranges (n-C_{10-16}; n-C_{16-20}; n-C_{20-25}; n-C_{25-35}; n-C_{35-40}; n-C_{40-50}) and four MOAH volatility ranges (n-C_{10-16}; n-C_{16-25}; n-C_{25-35}; n-C_{35-50}).

For MOSH fraction, total n-C_{10-50} measured in bleached waxed paper were between 105.4–116.6 mg/g. Important proportions were also measured for MOAH fraction, with mean values of n-C_{10-50} of 4.5 mg/kg in all analyzed FCM.

Table 5 Distribution of MOSH in FCM

Sample[1]	MOSH (mg/kg)						
n-C fractions	n-C_{10-16}	n-C_{16-20}	n-C_{20-25}	n-C_{25-35}	n-C_{35-40}	n-C_{40-50}	n-C_{10-50}
FCM1	1.8	40.0	31.1	26.5	4.15	1.85	**105.4**
FCM2	1.6	46.7	31.8	29.9	3.9	1.8	**115.7**
FCM3	3.9	41.5	46.4	20.1	1.5	0.8	**114.2**
FCM4	1.7	36.6	45.2	27.7	5.1	0.3	**116.6**

[1]*FCM1, FCM, FCM, FCM = food contact material*

Table 6 Distribution of MOAH in FCM

Sample[1]	MOAH (mg/kg)				
n-C fractions	n-C_{10-16}	n-C_{16-25}	n-C_{25-35}	n-C_{35-50}	n-C_{10-50}
FCM1	0.15	3.0	0.65	0.5	**4.3**
FCM2	0.5	3.25	1.0	0.0	**4.75**
FCM3	0.1	3.4	0.8	0.6	**4.9**
FCM4	0.0	4.1	0.1	0.3	**4.5**

[1]*FCM1, FCM, FCM, FCM = food contact material*

Regardless analyzed sample (FCM1-4), predominant distribution of MOSH (> 90 %) was in the n-C_{16-35} range (97.6–114.5 mg/kg), and predominant distribution of MOAH (~ 70 %) was in n-C_{16-25} range (3.0–4.1 mg/kg).

Characterization of FCM following the results shows that FCM1 had the lowest content of MOSH and MOAH (105.4 mg/kg; 4.3 mg/kg). The highest MOSH content was found in FCM4 samples (116.6 mg/kg), and the highest MOAH content was found in FCM3 samples (4.9 mg/kg).

MOH migration potential from food contact material

The analysis of migration potential of contaminants from packaging to product is necessary because different components of FCM can be transferred to food [45, 46].

In MxA samples, MOSH fraction was predominant, except M2A samples, where MOSH represented about 75 %. The concentration of MOSH was approximately twice the concentration of MOAH for MxB samples of freeze-dried milk. For FCM, the concentration was predominant (> 95 %) for all analyzed samples. The results thus indicated that there are large differences in terms of proportion of MOSH and MOAH between control samples, test samples and waxed paper (figure 1).

To establish the migration potential of MOH, the chromatographic profile for FCM was analyzed in relation to chromatographic profiles of milk samples.

Figure 2 shows the LC-GC-FID chromatograms for a selection of control (A) and test (B) milk samples comprising MOSH fraction in relation to waxed paper MOSH distribution (MOAH fraction was slightly highlighted).

From chromatograms shown, no humps are observed for control samples (MxA), while MOAH fraction chromatograms for test samples (MxB) indicated hydrocarbon humps ranging from n-C_{16} to n-C_{35}.

Corresponding to information presented by Vollmer et al. [48] regarding the fact that mineral oil can be transferred from waxed paper to food, the chromatographic profile obtained for test samples shows a MOSH distribution similar to waxed paper (red symbol highlights potential MOSH migration from waxed paper to milk).

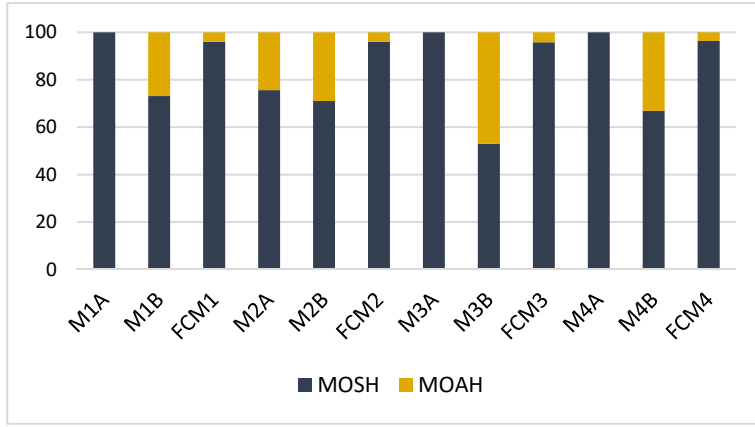

Fig. 1 The proportion of MOSH and MOAH in milk and waxed food paper (FCM)

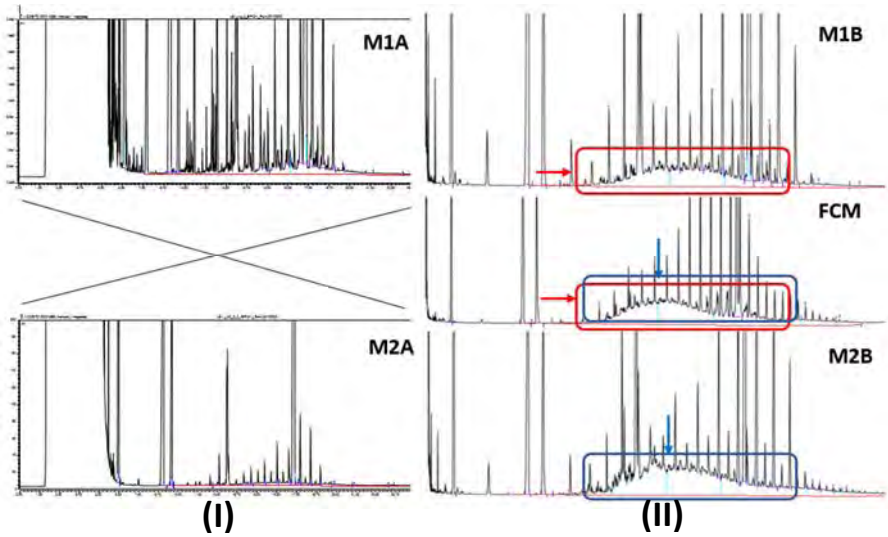

Fig. 2 LC–GC–FID chromatograms of MOSH fractions for control sample (I, left) and for test samples (II, right) in relation to MOSH distribution in FCM; red and blue symbols shows MOSH fraction migrated from the waxed paper into milk samples (MOAH transfer not visible); retention time (x): 0–28,5 min; detector signal (y): 0_200 pA MOSH

The same retentions of MOSH fraction, between n-C_{16} and n-C_{35}, which form a common hydrocarbon hump, demonstrate that migration of contaminants from FCM into food appears to be realistic and may be due to volatilization of paraffin wax compounds used in papermaking [3].

DISCUSSIONS AND EXPECTATIONS

Waxed paper is an FCM based on cellulose and silicone. The chemical composition, mechanical processes (grinding, pulp digestion by alkaline or acid hydrolysis) and chemical processes applied to wood pulp (bleaching with sulfuric acid/zinc chloride/calcium hypochlorite) increase the risk of this material having potential effects on food contamination [49].

Based on the general regulations of European Commission [50, 51, 52], mineral oils have a number of approved uses. Some classes of mineral oils can be used in food, as

additives and processing aids, such as is the microcrystalline wax or additive coded E905 (approved for use as a surface treatment agent for some confectionery products).

In Commission Regulation (EU) 10/2011 [53], mineral oils were also authorized as additives for polymer packaging. Furthermore, some mineral oils derived from petroleum or from synthetic raw materials have been included in the European Union List of additives approved for use as food contact materials, such as paraffinic mineral oils (FCM 95), refined wax with high viscosity (FCM 94) and low viscosity refined paraffinic wax (FCM 93), all with distinct migration capabilities [52].

There are various papers highlighting the transfer of MOH from packaging to food [54-57]. Because the legislation has not yet provided concrete scientific guidelines, the possibility and risk of MOH contamination of food through packaging is still debatable.

In our study, the probability of contaminant transfer was considered between milk samples and waxed paper used in the lyophilization step, which can be an important warning signal if paper-like materials waxed are used for packaging various food products.

As a result of lack of a concrete protocol to assess the quantitative transfer of MOH, quantification of hydrocarbons that migrated from FCM into food was difficult, as reported also by Bierdermann et al. [58] for foods analyzed in their study.

Regarding the overall results, developed study was similar to a previous study [59] which found that MOH can migrate in a large proportion from FCM into food during processing. The fact that MOH migration to food can be caused during food processing prior to packaging or even during the packaging process is an important technological aspect when considering consumer safety.

CONCLUSIONS

In this paper we have carried out a preliminary research on the contamination of food with MOH through packaging materials.

Mineral oil saturated hydrocarbons (MOSH) and mineral oil aromatic hydrocarbons (MOAH) were extracted from three categories of samples: packaging material, milk in contact with packaging material, and milk without contact with any packaging material.

The study was considered relevant from a technological and food safety point of view. MOH migration from FCM into food proved to be dependent on the structure of food matrix, with differences given by technological processing of food, but also with differences given by specifics of packaging. Practical use of packaging considered optimal to reduce absorption or migration of mineral oil quantities to food is not sufficient to prevent MOH contamination given that mineral oils still have a number of approved uses as food contact materials.

Similar to analyzed samples, important contents of MOSH and MOAH were reported in several types of packaged foods, which may indicate that foods with less processing may have less mineral oil contamination. However, the lack of a concrete legislative framework makes MOH contamination of food through packaging still debatable.

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