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# Mineral Paraffins in Vegetable Oils and Refinery By-Products for Animal Feeds

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#### Introduction

Mineral paraffins are saturated alkanes obtained from mineral oil. In the context of foodstuffs, they may be used as such ("white oils"), but more often they are the main components of materials also containing other types of substances. As these materials cannot be analyzed in their entirety, the mineral paraffins serve as markers.

Mineral paraffins were detected in many foodstuffs, most commonly at concentrations in the range of 1–100 mg/kg (1). Frequent sources were lubricating oils (2, 3), release agents, anti-dust agents, printing inks (4), and components of packaging materials (5–8). Edible oils and fats were among the frequently affected foods (9). Cocoa butter and edible oils from seeds transported and stored in jute or sisal bags were contaminated with batching oils used for the manufacturing of these bags (10, 11). Some palm oils contained diesel oil. Oils were also contaminated in containers or ships previously used for the transport of technical products or during drying of oil seeds by direct firing. Animal feeds were contaminated with wastes, which also affected the resulting meat and eggs (12).

Occasional high concentrations of mineral paraffins in vegetable oils (500– 3500 mg/kg) could often be explained by the use of technical oils during pression. Primarily small volume products (often cold pressed oils) were concerned, maybe because of the use of special machinery. However, as will be shown below, in the majority of the cases the sources of the contamination are still unknown.

# Toxicological evaluation

In the EU, the Scientific Committee on Food (SCF) summarized the toxicological data on saturated mineral hydrocarbons (white paraffin oils) by concluding that the effects observed on rats strongly depend on the type of mineral oil fraction orally administered (13). Adverse effects were always observed at a concentration of 20 g/kg in the diet, often at 200 mg/kg and still sometimes at 20 mg/kg. The SCF concluded on the opinion that human exposure of up to 4 mg mineral paraffin oil per kilogram body weight (b.w.) and day can be tolerated provided the content of hydrocarbons with less than 25 carbon atoms does not exceed 50 g/kg and the average molecular weight is not below 480 Dalton (480 D approximately corresponds to the alkane C32). This opinion became the Directive 99/91/CE and in the mean time national legislation in the EU. The mineral paraffins usually encountered in foods are, however, still of substantially lower molecular weight. Recently the SCF also evaluated hydrogenated poly-1-decene, a synthetic substitute also called polyalpha-olefines with 1.5% of components with less than 30 carbon atoms (14). The material is poorly absorbed from the gastrointestinal tract and an ADI of 0-6 mg/kg b.w. was established.

The US-FDA tolerates up to 800 mg/kg of white oils in rice (600 mg/kg in grain) for dust control (15), the oils being specified by viscosity.

Toxicity was tested for oils exclusively consisting of saturated hydrocarbons. Food contaminants, however, usually also contain other materials, and these are likely to determine toxicity. This renders toxicological evaluation difficult: either the contaminant is analyzed comprehensively (which is technically highly demanding), or the source of the mineral paraffins is determined in order to predict the probable accompanying components.

# Edible oil refining

For the better understanding of the background, the two procedures for refining edible oils should shortly be described. "Chemical" raffination is the older procedure, but is still important in Switzerland. It implies the extraction of the free fatty acids from the raw oil by alkali as the first step of the raffination. The resulting soap is acidified, which separates the fatty acids from the aqueous phase. These acids are then used for stripping the organic material from the effluent steam leaving the deodorizer (deodorization being the last step of oil raffination). They are sprayed into the vapor and recovered, circulating for days or weeks. During this time they accumulate the volatile materials from many batches of oil, usually also from several types of oil. Often some valuable components, such as tocopherols and sterols, are extracted from this by-product (16) and the remaining material used as fat substitute for mixed animal feeds. In Switzerland, however, these acids are no longer fed to animals because of the high contents of mineral paraffins (see below).

The more modern raffination, called "physical refining", reorganized the procedure: the free fatty acids are removed by distillation during the deodorization step. The raw oil is degummed, bleached, and then subjected to steam treatment at a temperature sufficiently high  $(240-260^{\circ}C)$  to evaporate the free fatty acids. The condensate, consisting of the acids and the other evaporated oil components, is circulated over some time to strip the organic material from the effluent steam. The surplus is (or was) again used for the preparation of mixed animal feeds.

# Aim of this work

Control of the oils used for the production of mixed animal feeds revealed that the by-product from edible oil refining was nearly always contaminated with high concentrations of mineral paraffins: 1000 mg/kg were exceeded rather frequently. It was then determined that this contamination consists of material stripped from raw vegetable oils. The removal of the higher molecular weight mineral paraffins from the refined oils is only partial, however, leaving a substantial amount in the oils used for human consumption. This paper describes the composition and the concentration of the mineral paraffins in various products, as well as the connection between the contamination of the oils for human and animal consumption.

## Experimental

In Zurich, oils were analyzed by on-line LC-LC-GC-FID, applying the method described as method 2 in ref. (12). On a first silica gel HPLC column, the hydrocarbons were separated from the usually 20 mg oil injected (0.5–2 mg for strongly contaminated samples). Then this column was backflushed, while the paraffins were isolated from the unsaturated hydrocarbons on the second silica gel column and transferred into GC in a 300  $\mu$ l fraction through the on-column interface, using partially concurrent eluent evaporation. GC involved a 7 m×0.53 mm i.d. uncoated precolumn, an early vapor exit, and a 5 m×0.25 mm i.d. separation column coated in the laboratory with the methylpolysiloxane PS-255 (Fluka, Buchs, Switzerland). LC-GC transfer occurred at 46°C and was followed by a temperature program of 15°/min to 340°C.

At Udine, a similar LC-GC-FID method was applied, involving a single LC column and transfer by concurrent eluent evaporation through the in-line vaporizer/overflow interface (17).

An alternative method was developed for laboratories without on-line LC-GC equipment. It is based on the isolation of the paraffins with the help of a small aluminium oxide column and large volume on-column injection into GC-FID. It was ring-tested and produces results equivalent to on-line LC-GC-FID (18). Preseparation on highly active aluminium oxide may be helpful also for the LC-GC method, since it enables to remove the straight chain hydrocarbons with more than about 24 carbon atoms, i.e. the interference by the bulk of the natural paraffins.

The mineral paraffins have to be distinguished from those of plant origin. The material quantitated as mineral paraffins primarily consisted of highly isomerized isoalkanes forming unresolved humps in the gas chromatograms. n-Alkanes on top

of the hump were considered to be of mineral origin only when the even and odd numbered homologues were present at balanced concentrations. Natural n-alkanes are characterized by a strong predominance of the odd numbered species.

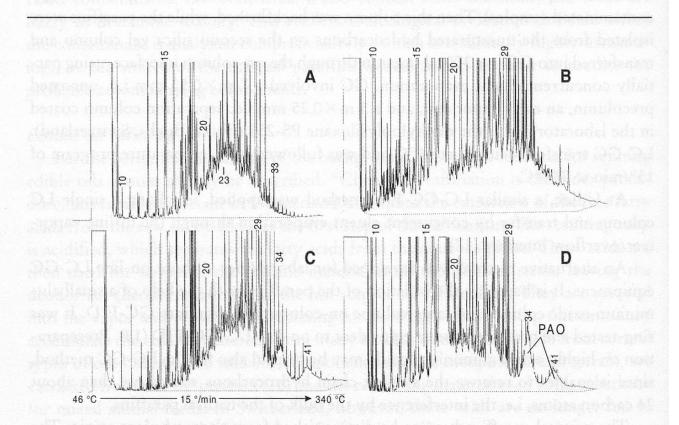
As described previously (12), the identity of the material comprised in the hump was checked in two ways. Firstly, the sample was brominated, which removed the olefins (the more polar bromo derivatives were retained by HPLC). Secondly, samples were analyzed by GC-MS on the ions m/z 57 and 71, quantitating with a response factor determined for gas oils of similar composition.

# **Results and discussion**

## Refinery by-products

Figure 1 shows GC-FID chromatograms of the paraffins from four examples of by-products of edible oil refining, i.e. free acids with the condensate from deodorization, from Swiss refineries. The chromatograms contain saturated hydrocarbons ranging about from the C10 to the C45 n-alkanes.

Sample A contained a fairly symmetric hump of unresolved isomeric paraffins situated between the n-alkanes C16 and C33, with a maximum corresponding to the elution of the n-alkane C23. The n-alkanes C13–16 (C15 being marked) were added as internal standards. The bunch of peaks in the region of C17–C19 are natural



# Figure 1 Examples of paraffins in the by-products from edible oil refining. PAO, poly alpha olefines

components frequently encountered in plant material. Most of the later eluted n-alkanes are odd numbered (C29 being the largest) and are also of plant origin. The hump corresponded to a concentration of 1200 mg/kg in the matrix.

Chromatogram B shows a more complex mixture of paraffins. The n-alkanes C9 to C12 are of balanced size, i.e. are of mineral origin. The smaller peaks between them correspond to isoalkanes as encountered in mineral oil products like diesel or heating oil and kerosene. The large peak eluted just before n-C10 is probably from a monoterpene of plant origin. All important signals beyond C15 are also of plant origin, including the group between C16 and C19. The hump representing the bulk of the mineral paraffins is broad (reaching up to about C40) and centered around the C29 n-alkane. Quantitation of the mineral paraffins is difficult because the upper contour line of the hump, separating the latter from the peaks on its top, can only be approximated (12). The estimated concentration was 230 mg/kg.

Samples C (ca. 350 mg/kg mineral paraffins) and D (ca. 250 mg/kg) contain similar mineral paraffins as A and B, but also two more narrow humps centered at the C34 and C41 n-alkanes. They are typical for poly-alpha-olefins, synthetic base oils commonly used for high grade motor oils or as food-compatible technical oils.

Among the 28 samples of refinery by-products analyzed, two from Germany and 26 from Switzerland, none contained less than 120 mg/kg mineral paraffins. The average concentration was 650 mg/kg, with a maximum at 6800 mg/kg. In the rather small amounts of condensate recovered in a second condensation step just before the vapors leave the deodorizer, as much as 10 g/kg of mineral paraffins were found.

# Raw edible oils

The mineral paraffins in the refinery by-products originate, primarily at least, from the raw edible oils. Figure 2 shows a selection of results from a variety of oils and fats from the Swiss market. The wheat germ oil contained 40 mg/kg of mineral paraffins centered at the C28 n-alkane – beside massive amounts of natural paraffins. To verify the presence of mineral isoalkanes, the natural n-alkanes were removed by clean up over highly active aluminium oxide prior to LC-GC. The oil was gently deodorated, i.e. components more volatile than about C23 were largely removed. All six wheat germ oils analyzed contained a similar mixture of hydrocarbons at concentrations of 20–180 mg/kg. In the laboratory, oil was extracted from wheat germs using hexane at 60°C. It contained the same mineral paraffins at 200 mg/kg, but included more volatile material (in the refined oils removed during deodorization). This indicates that the contamination may occur before the germs reach the oil mill.

The raw cocos fat (chromatogram below) contained 80 mg/kg mineral paraffins of a composition similar to that in the wheat germ oil, centered at the C28/C29 n-alkanes and with an almost Gaussian distribution. The n-alkanes C17–C24 correspond to those found in, e.g., diesel or heating oil.

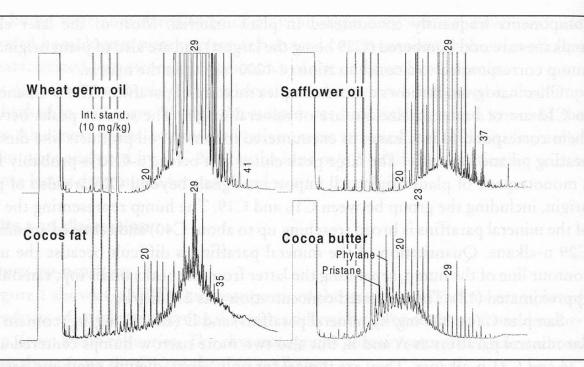
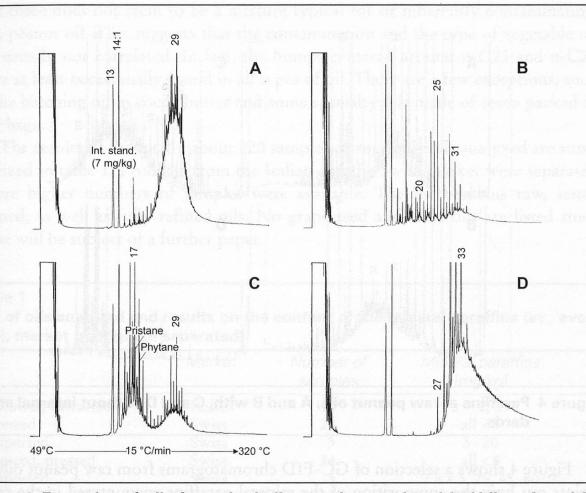


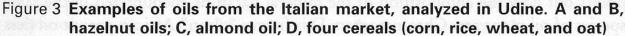
Figure 2 Mineral paraffins from selected edible oils and fats

The raw safflower oil was contaminated with 35 mg/kg paraffins centered at the C27 n-alkane. In this case, the source turned out to be a paraffin oil used during pression – in fact, part of the batch was contaminated at far higher concentration. The hope that this could also explain the contamination of many other oils was futile, however: where the oil seeds were available, the contamination was already found on the seeds. It was concluded that the contamination of this safflower oil was an exceptional case.

The raw cocoa butter contained a mixture of hydrocarbons situated between C15-C28 (70 mg/kg). The n-C23 is the predominant natural hydrocarbon in cocoa butter, but the n-alkanes eluted earlier are of mineral origin, as confirmed by the presence of pristane (tetramethyl pentadecane) and phytane (tetramethyl hexadecane). The contamination probably originated from the jute bags used for the transport and storage of cocoa beans (19, 20) – although in 1998 the International Jute Organisation (IJO) set standards on the production of jute bags ruling out the use of mineral batching oil (21).

Figure 3 shows four examples of vegetable oils from the Italian market analyzed in Udine. Chromatogram A is from a French hazelnut oil containing 150 mg/kg of a narrow fraction of isoparaffins ranging from C21 to C35, centered at the n-alkanes C28/C29. In Switzerland a hazelnut oil labeled as being of Swiss origin contained 120 mg/kg of a mixture of similar composition, centered at C27. The symmetric shape and the width of the hump correspond to a gas oil from mineral oil refining, the molecular weight to the gas oils used for lubricating and hydraulic oils. Two other hazelnut oils were free of mineral paraffins (<5 mg/kg), as was an oil extracted from hazelnuts grown in the area of Zurich.





Chromatogram B is from a Turkish hazelnut oil and shows a pattern of paraffins suggesting the presence of oligomers from a synthetic oil rather than of a raffination product from mineral oil. Chromatogram C was obtained from a French almond oil. The totally 75 mg/kg of mineral paraffins are probably from two sources. The hump between C14 and C21 (center at the C16/17 n-alkanes) is topped by n-alkanes, i.e. the contaminant was not deparaffinated. Pristane and phytane confirm the mineral origin. The mixture resembles that found in many products transported in jute bags, although it is restricted to lower boiling material than that in the cocoa butter shown in figure 2. The hump eluted around n-C28 virtually only carries n-alkanes of natural origin, i.e. the mineral oil product was deparaffinated. It resembles that found in most of the contaminated vegetable oils.

Chromatogram D is from an oil labeled "four cereals" (corn, rice, wheat, and oat). It contained 250 mg/kg of mineral paraffins centered at n-C33 and reaching beyond the end of the temperature program (beyond n-C43). The mixture differs from those observed in most other contaminated samples in that it is of such a high boiling point that it could hardly be obtained by distillation. It bears some similarity to synthetic oils commonly added to gasoline for two-stroke engines.

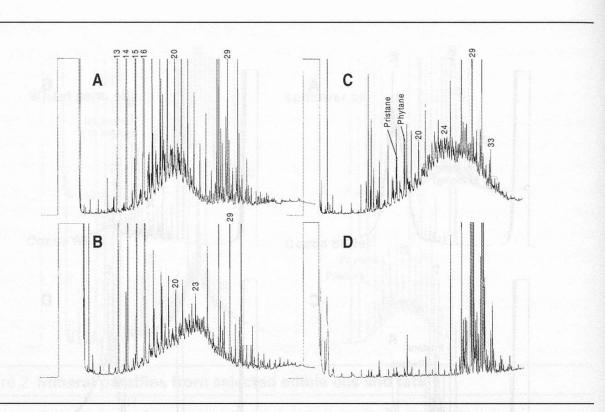


Figure 4 Paraffins of raw peanut oils; A and B with, C and D without internal standards

Figure 4 shows a selection of GC-FID chromatograms from raw peanut oils. It points out how the composition of the mineral paraffins encountered in the same species of oil may vary. Chromatogram D is from a "clean" African peanut oil (less than 5 mg/kg). Most African oils (11 out of 14 samples analyzed) contained less than 5 mg/kg mineral paraffins, whereas all 52 raw Argentinean oils (some shown in chromatograms A–C) contained more than 5 mg/kg, with an average of about 35 mg/kg. The difference between the two varieties is visible also in the natural hydrocarbons: African oils contain substantially more of them and the mixture shows a particular, rather complex pattern.

Chromatogram A shows a hump of paraffins similar to that found in the cocoa butter in figure 2, ranging from the C15 to the C25 n-alkanes (50 mg/kg). There are n-alkanes and distinct peaks of isoalkanes on it, which is typical for non-deparaffinated mineral oil fractions of intermediate boiling point (such as batching oil used for jute or sisal bags, although it is doubtful that peanuts for oil production are packed in such bags). In chromatogram B, the mineral paraffins form an asymmetric hump between the C14 and the C30 n-alkane, with a maximum at n-C23 (60 mg/kg). There are some n-alkanes of mineral origin, but they do not seem to be part of the material forming the main hump. In C, the hump extends from n-C15 to n-C37, perhaps with two maxima around the C24 and C28 n-alkanes (the most frequently observed maxima). The concentration in the oil was 50 mg/kg.

The comparison of the four peanut oils illustrates the general finding that in a given species of oil the composition of the mineral paraffins may strongly vary, i.e.

that there does not seem to be a mixture typical for or inherently contaminating, e.g., peanut oil. This suggests that the contamination and the type of vegetable oil are usually not correlated. In fact, the humps centered around n-C23 and n-C28 were at least occasionally found in all types of oil. There are a few exceptions, such as the batching oil in cocoa butter and some specialty oils made of seeds packed in jute bags.

The results of the totally about 220 samples of vegetable oils analyzed are summarized in table 1. Products from the Italian and the Swiss market were separated where higher numbers of samples were available. The list contains raw, semirefined, as well as fully refined oils. No grape seed and olive oils are listed since these will be subject of a further paper.

# Table 1 List of oils analyzed and results on the content of the mineral paraffins (av., average); market of origin (if separated)

Oil	Market	Number of samples	Mineral paraffins (mg/kg)		
Sunflower, extracted	Italian	10	5-10, 53		
pressed	Swiss	20	all <5		
imported	Swiss	5	5-20		
Rapeseed, pressed	Swiss	24	all <5		
imported	Swiss	5	2×<5, 25, 45, 80		
Soybean, pressed	Italian	2	12, 20		
extracted	Italian	2	<3		
	Swiss	5	5-15		
Safflower		11	7×<5, 5–20		
Peanut oil, Argentinian	Swiss	52	av.: 35, 5–85		
African	Swiss	14	11×<5, 10, 15, 50		
	Italian	6	av.: 11		
Corn	Italian	9	4×<3, 8–35		
	Swiss	5	5-25		
Palm		7	2×<3, 10-35		
Palmkernel		5	20-40		
Cocos		6	30-105		
Rice bran oil		2	14, 260		
Hazelnut		8	2×<5, 5–120		
Walnut	Swiss	4	2×<5, 30, 60		
Almond		4	1×<5, 15, 40, 75		
Wheat germ	Swiss	6	20–180		
Sesame		7	2×<5, 5-95		
Linseed		3	1×<5, 5–20		
Pumpkin		5	4×<5,5		

All sunflower and rapeseed oils produced in Switzerland contained less than 5 mg/kg of mineral paraffins (44 samples analyzed), but all the imported sunflower oils 5–20 mg/kg, as did the 10 oils from the Italian market. Two imported rapeseed

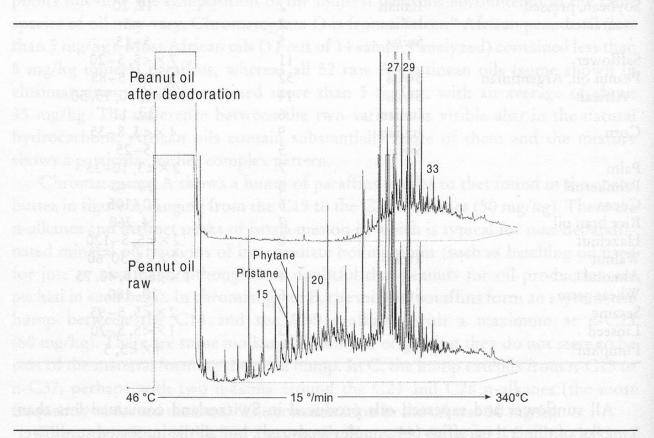
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oils were clean (<5 mg/kg), while the three others contained up to 80 mg/kg mineral paraffins. All the oils produced in Switzerland were obtained by pression, whereas those imported probably consisted of or contained solvent-extracted oil. The influence of the extraction step was confirmed by the four soybean oils, the two obtained by pression again being clean. On the other hand, the two pressed sunflower oils analyzed in Italy contained 5 and 10 mg/kg paraffins, respectively. It is not clear how the contamination with mineral paraffins is related to solvent-extraction. The two samples of fresh hexane for solvent extraction analyzed did not contain the paraffins encountered in the oils. It seems more likely that the solvent has a stronger extraction power for paraffins than the oil (as well known for other components of the oil seeds).

# Effect of deodorization

Figure 5 shows chromatograms of a peanut oil before and after deodorization at approximately 240°C (chemical raffination process). The oil contained at least two types of mineral paraffins, one centered at n-C22, the other reaching from C28 to beyond C40. Deodorization completely removed the hydrocarbons up to C23 and still about 50% of C25 alkanes. Harder conditions (particularly physical refining) also remove higher boiling products, as concluded from the observation that the condensates (fig. 1) often contain substantial amounts of hydrocarbons beyond C30.





The content of mineral paraffins was monitored for the chemical raffination of a peanut oil at Florin AG, Muttenz, Switzerland. The composition of the mineral paraffins in the raw oil resembled that shown in chromatogram B of figure 4 and had a maximum at n-C24; the concentration amounted to 55 mg/kg (table 2). The acids, extracted by alkali and subsequently acidified, contained 40 mg/kg of mineral paraffins. Bleaching with earth had no effect on the hydrocarbons. Deodorization at approximately 235 °C completely removed the paraffins up to about C24 and reduced the content to 14 mg/kg of a mixture similar to that shown in figure 5. At the same time, the concentration of mineral paraffins in the acids used to wash the effluent steam of the deodorizer increased from 3000 to 3400 mg/kg.

Table 2

Concentration	(mg/kg) of	f mineral	paraffins	in a	peanut	oil	during	raffination	
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nd helor on hadligd gan 68.46 aland	Mineral paraffins (mg/kg)
Raw oil	- Charles and 55 and a charle of States and and
Neutralized soap	40
After bleaching	
After deodorization	14

#### Table 3

Concentrations (mg/kg) of mineral paraffins accumulated in the fatty acids circulating in the washer of the deodorizer after fresh acids had been filled in on day 1

Day	Mineral paraffins (mg/kg)	akadan
1 Card and series	in all cloub her own was 7 because of a result in the cloub	C. C. C. C. L.
2	170	
3	140	
4	1800	
5	2800	
6	3000	
7	3400	nsaetako n.C
the second s		100 - 12 - 10 - 10 - 10 - 10 - 10 - 10 -

Table 3 shows the accumulation of mineral paraffins in the condensate of the deodorizer for a real example. Concentrations are listed for the seven working days ending with the raffination of the peanut oil mentioned above. On day 1, fresh acids from the alkali treatment were filled into the system. During the first days, sunflower, soybean, and rapeseed oil was deodorized, typically containing little mineral paraffins and transferring correspondingly little into the condensate. The strong increase in the concentration was observed after treatment of peanut oils on the following days.

The deodorizer had a capacity of 30 t. During the observation period, four batches of peanut oil were refined (besides other oils contributing small amounts of mineral paraffins). Since these 120 t of raw peanut oil were deodorized into about 1.5 t of acids, the 3400 mg/kg in the condensate translate to an average of 43 mg of

mineral paraffins extracted from a kilogram of oil. In fact, on day seven, 41 mg/kg were extracted (table 2, difference between the bleached and the deodorated oil).

The 3400 mg/kg of mineral paraffins observed in the acids on day seven corresponded to an amount of 5.1 kg. Considering this substantial quantity, it seems that the source should be detectable rather easily: for instance, a loss of lubricating or hydraulic oil at a corresponding rate should attract attention – but we did not find a person who constantly refilled machinery.

## Conclusions

# Acids for animal feed

The by-products of edible oil refining, consisting of the free fatty acids and the condensate from the deodorization process, contained between 120 and 6800 mg/kg of mineral paraffins. This by far exceeds the Swiss limit of 30 mg/kg for fats used in animal feeds (22).

The contamination is present already in the raw vegetable oils. Chemical refining produces soap with a mineral paraffin content which is lower than that of the raw oil and would usually comply with the 30 mg/kg limit. Even if it exceeded this limit (as, e.g., the sample in table 2), it seems questionable to tax a contamination excessive for animal feeds when it is (at least so far) tolerated for human consumption. The main contamination occurs when the fatty acids are used in the deodorizer to strip the organic material from the effluent, because this also reconcentrates the mineral paraffins (and maybe other contaminants) from a large amount of oil. With physical raffination, the free fatty acids are removed from the oil during deodorization, hence together with the mineral contaminants, and there is no way to obtain relatively clean acids.

# Edible oils

Probably more than half of all raw vegetable oils and fats produced worldwide contain more than 10 mg/kg mineral paraffins and still a substantial proportion exceeds 50 mg/kg. Deodorization removes the hydrocarbons up to C25–C30, depending on the conditions. Usually this corresponds to about two thirds of the contamination (depending on the composition of the paraffins and the conditions of deodorization). However, many refined oils on the market still contained 20– 80 mg/kg mineral paraffins. Some exceptional samples reached concentrations up to 3000 mg/kg.

# Origin of the contamination

The origin of the mineral paraffins could be determined only in a few cases (technical oils used in the oil mill, explaining the extremely high concentrations). For many samples it was confirmed that already the raw oil was contaminated. The finding that many samples of oil seeds contained the mineral paraffins in question suggests that at least an important part of the contamination occurs before the seeds reach the oil mill. This leaves a wide variety of possible explanations, such as a contamination associated with plant protection, treatment of the seeds (e.g. during the drying process), transport in contaminated containers, or environmental pollution. The data presented suggests following rather general diagnostics:

- 1. There are several sources contaminating vegetable oils with mineral paraffins. Many oils contain more than one contaminant.
- 2. Particularly the mixture centered at the C27–C29 n-alkanes finds its way into almost all types of edible oils.
- 3. There is no type of oil for which no contaminated sample has been found. Nearly all of the pressed oils were clean, but this might be the result of the extraction procedure (such as pression rather than solvent extraction) and not necessarily means that the seeds were clean.
- 4. Of nearly all types of oil also samples free of mineral paraffins were found. With a detection limit of 3–5 mg/kg, the differences between clean and contaminated samples amounted to a factor often exceeding 20.

# Toxicity

The tolerance towards food contamination by mineral paraffins is a subject of debate, but probably not the relevant point when evaluating the possible toxicity of the contaminants considered here. It is crucial to know whether the materials of which the paraffins have been analyzed are purified white oils (pure paraffins), soot from environmental pollution, used motor oils, or other materials bringing along additional components (such as aromatics, additives, or degradation products). The paraffins might well turn out to be the least toxic components.

As the concentrations of the paraffins often approach 100 mg/kg in the vegetable oil or fat, other materials representing 10% of the contaminant equally frequently approach 10 mg/kg and even a minor component easily exceeds 1 mg/kg. This is a high concentration for an unknown material and calls for further investigation.

Comprehensive analysis of the contamination (including the accompanying other constituents) in the oil is difficult. It seems more promising to identify the sources of the contamination by other means and to assess the toxicity of these materials.

The other aspect of food contamination concerns the feelings of the consumers, in particular their disgust for technical products in foods. This aspect is often underestimated, perhaps following an unwritten rule that food contamination must be accepted closely up to the limit of the toxicological safety.

# Summary

Raw vegetable oils often contain mineral paraffins with 10-40 carbon atoms at concentrations of 30-150 mg/kg, of which around a third remains in the oil after deodorization. The presence, concentrations, and compositions of the contami-

nant(s) seem to be irregular, suggesting several (largely unknown) sources. Toxicity of the contamination cannot be assessed as long as the material, of which the mineral paraffins analyzed are part, is unknown.

Raffination of edible oils yields by-products consisting of free fatty acids and the condensate of the deodorization process. These were usually used for the production of mixed animal feed (possibly after extraction of some valuable components), but they commonly contain 200–3000 mg/kg of mineral paraffins, which by far exceeds the Swiss limit of 30 mg/kg. These paraffins are stripped from the raw vegetable oils for human consumption during deodorization and are enriched in the fatty acids used for washing the effluent stream.

# Zusammenfassung

Rohe Pflanzenöle enthalten oft 30–150 mg/kg mineralische Paraffine mit 10–40 Kohlenstoffatomen, wovon etwa ein Drittel nach der Ausdämpfung im Speiseöl verbleibt. Das Auftreten der Verschmutzung, die Konzentrationen sowie die Zusammensetzungen der Paraffine sind unregelmässig, was auf eine Mehrzahl von (weitgehend unbekannten) Quellen deutet. Die Toxizität dieser Verunreinigung kann nicht abgeschätzt werden, solange die Materialien, welche die gefundenen Paraffine enthalten, nicht identifiziert sind.

Bei der Raffination von Speiseöl fallen sogenannte Spaltfette an, die aus freien Fettsäuren und dem Kondensat aus der Ausdämpfung bestehen. Sie wurden bisher oft für die Herstellung von Tierfutter verwendet (evtl. nach der Extraktion wertvoller Komponenten). Sie enthalten jedoch normalerweise 200–3000 mg/kg mineralische Paraffine, was den Schweizer Höchstwert von 30 mg/kg bei weitem überschreitet. Die Paraffine werden bei der Ausdämpfung aus den rohen Speiseölen ins Spaltfett übertragen, das im Dampfwäscher zirkuliert.

#### Résumé

Les huiles végétales brutes contiennent souvent entre 30 et 150 mg/kg de paraffines minérales avec 10-40 atomes de carbone, dont environ un tiers reste dans l'huile après le processus de désodorisation. La présence, les concentrations et les compositions de ces paraffines paraient être irrégulières, ce qui suggère plusieurs sources (la plupart du temps inconnues) de contamination. La toxicité ne peut pas être évaluée tant que les matériaux, qui contiennent les paraffines analysées, ne sont pas identifiés.

Pendant la raffination des huiles alimentaires on obtient un sous-produit contenant des acides gras libres et le condensat de la désodorisation. Il était souvent utilisé pour la production d'aliments pour animaux (ev. après l'extraction d'autres constituants nutritifs). Il contient normalement entre 200 et 3000 mg/kg de paraffines minérales, ce qui dépasse largement la limite suisse de 30 mg/kg. Ces paraffines sont extraites pendant la désodorisation et enrichies par les acides utilisées pour laver les vapeurs qui quittent le désodorisateur.

# Key words

Mineral paraffins in edible oils, Deodorization of edible oils, Fatty acids for animal feeds, Raffination of edible oil

## References

- 1 Grob, K., Artho, A., Biedermann, M. Egli, J., Lanfranchi, M., Caramaschi, A., Etter, R. und Romann, E.: Wieviel Mineralöl ist in den Lebensmitteln tolerierbar? Mitt. Gebiete Lebensm. Hyg. 83, 40-54 (1992).
- 2 Grob, K., Artho, A., Biedermann, M. and Egli, J.: Food contamination by hydrocarbons from lubricating oils and release agents; determination by coupled LC-GC. Food Addit. Contam. 8, 437-446 (1991).
- 3 Standard DIN V 10517
- 4 Droz, Ch. and Grob, K.: Determination of food contamination by mineral oil material from printed cardboard using on-line coupled LC-GC-FID. Z. Lebensm.-Unters.-Forsch. 205, 239-241 (1997).
- 5 Grob, K., Biedermann, M., Artho, A. and Egli, J.: Food contamination by hydrocarbons from packaging materials determined by coupled LC-GC. Z. Lebensm.-Unters.-Forsch. 193, 213-219 (1991).
- 6 Grob, K., Huber, M., Boderius, U. and Bronz, M.: Mineral oil material in canned foods. Food Addit. Contam. 14, 83-88 (1997).
- 7 Castle, L., Mitchell, K. and Gilbert, J.: Migration of mineral oil hydrocarbons into foods. 1. Polystyrene containers for hot and cold beverages. Food Addit. Contam. 8, 693-700 (1991).
- *S.M., Nichol, J.* and *Castle, L.:* Migration of mineral oil hydrocarbons into foods.
  Miscellaneous applications of mineral oil hydrocarbons in food contact materials. Food Addit. Contam. 11, 333-342 (1994).
- 9 Grob, K., Biedermann, M. und Bronz, M.: Resultate einer Kontrolle von Speiseölen: Fälschungen durch Zumischungen, Verunreinigungen. Mitt. Gebiete Lebensm. Hyg. 85, 351–365 (1994).
- 10 Grob, K., Lanfranchi, M., Egli, J. and Artho, A.: Determination of food contamination by mineral oil from jute bags using coupled LC-GC. J. Assoc. Off. Anal. Chem. 74, 506-512 (1991).
- 11 Grob, K., Artho, A., Biedermann, M., Caramaschi, A. and Mikle H.: Batching oils on sisal bags used for packaging foods: analysis by coupled LC-GC. J. Assoc. Off. Anal. Chem. 75, 283-287 (1992).
- 12 Grob, K., Vass, M., Biedermann, M. and Neukom, H.P.: Contamination of animal feed and food from animal origin with mineral oil hydrocarbons. Food Addit. Contam. 18, 1–10 (2001).
- 13 European Union, Scientific Committee on Food, Opinion on mineral and synthetic hydrocarbons, expressed on 22 September 1995.
- 14 European Union, Scientific Committee on Food, Opinion on hydrogenated poly-1-decene, expressed on 12 July 2001.
- 15 Wilson, E.: Mineral oil considered an effective option to control grain dust. World Grain, May 2000, 18.
- 16 Verleyen, T., Verhe, R., Garcia, L., Dewettinck, K., Huyghebaert, A. and De Greyt, W.: GC characterization of vegetable oil deodorization distillate. J. Chromatogr. 921, 277-285 (2001).
- 17 Moret, S., Grob, K. and Conte, L.S.: On-line HPLC (LC)-solvent evaporation (SE)-LC-capillary GC-FID for the analysis of mineral oil polyaromatic hydrocarbons in fatty foods. J. Chromatogr. 750, 361-368 (1996).
- 18 Wagner, Ch., Neukom, H.-P., Galetti, V. and Grob, K.: Determination of mineral paraffins in feeds and foodstuffs by bromination and preseparation on aluminium oxide: method and results of a ring test. Mitt. Lebensm. Hyg. 92, 231–249 (2001).

- 19 Grob, K., Lanfranchi, M., Egli, J. and Artho, A.: Determination of food contamination by mineral oil from jute bags using coupled LC-GC. J. Assoc. Off. Anal. Chem. 74, 506-512 (1991).
- 20 Moret, S., Grob, K. and Conte, L.S.: Mineral oil polyaromatic hydrocarbons in foods, e.g. from jute bags, by on-line LC-solvent evaporation (SE)-LC-GC-FID. Z. Lebensm.-Unters.-Forsch. 204, 241-246 (1997).
- 21 International Jute Organisation, Standard 98/01 (February 1998)
- 22 Swiss Federal Research Station for Animal Production, RAP Posieux, Letter from 26 November 1999.

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