OLI MINERALI – STORIA E STATO DELL'ARTE

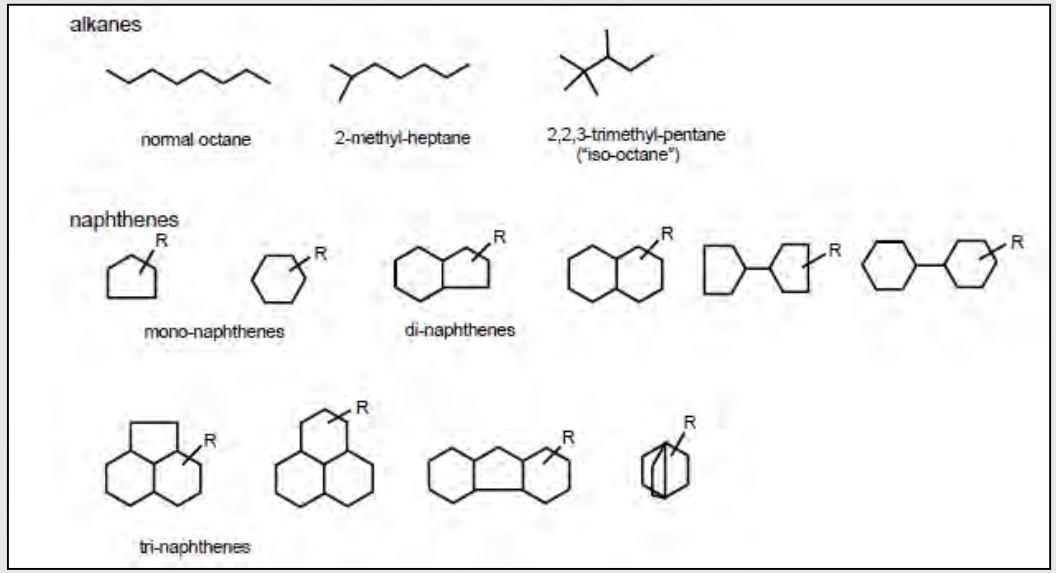
MINERAL OILS - HISTORY AND ART STATE

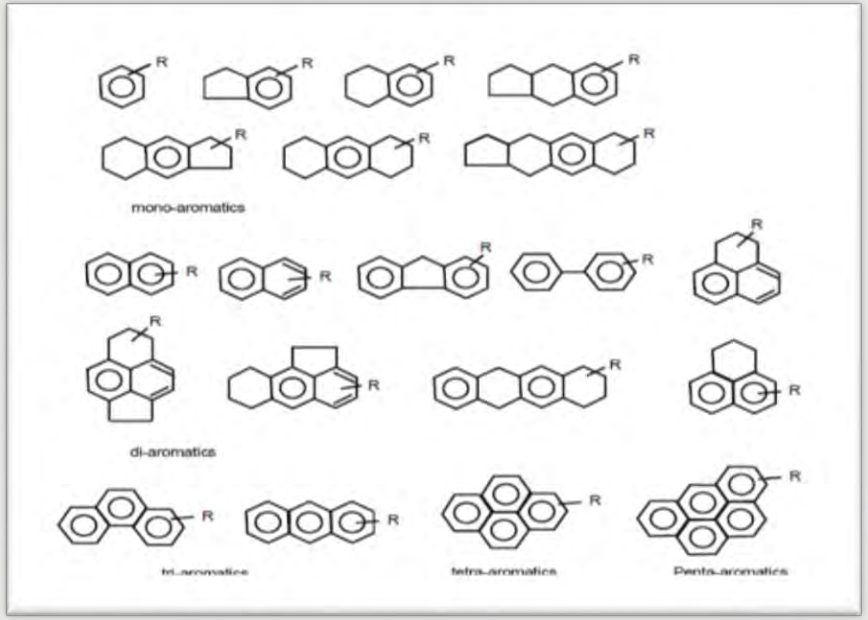
MINERAL OILS (MOH)

- **MOH** comprise complex mixtures, principally of straight and branched open-chain alkanes (paraffins), largely alkylated cycloalkanes (naphthenes), collectively classified as mineral oil saturated hydrocarbons (MOSH), and mineral oil aromatic hydrocarbons (MOAH) *(Biedermann et al., 2009). (EFSA Journal 2012;10(6):2704)*

MOSH

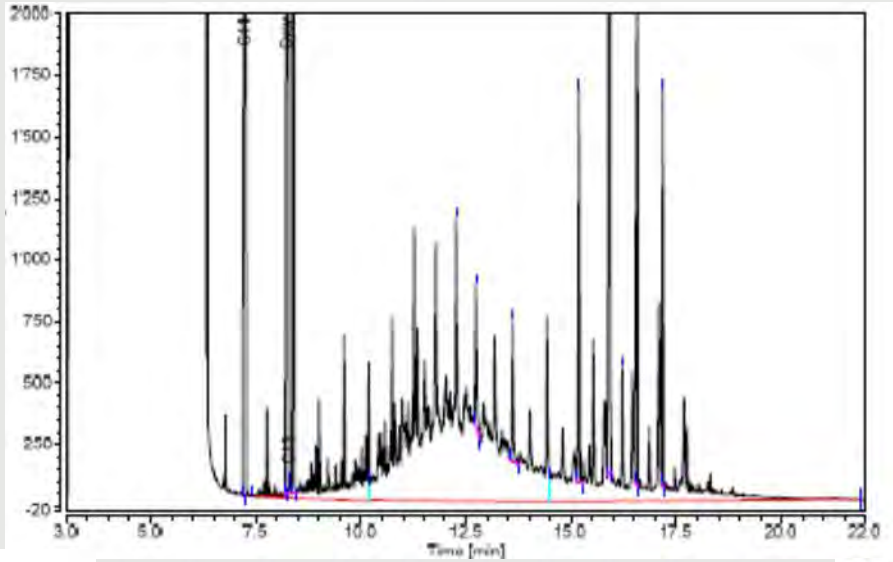
MOAH



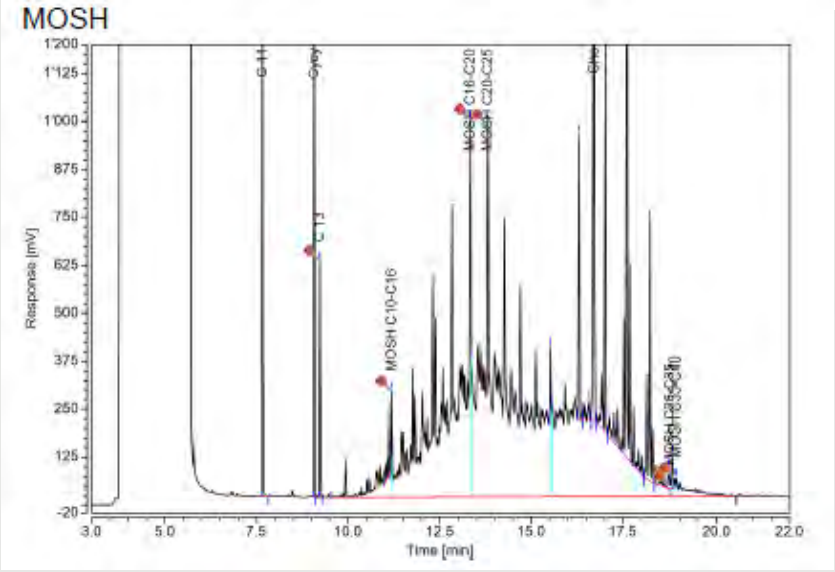


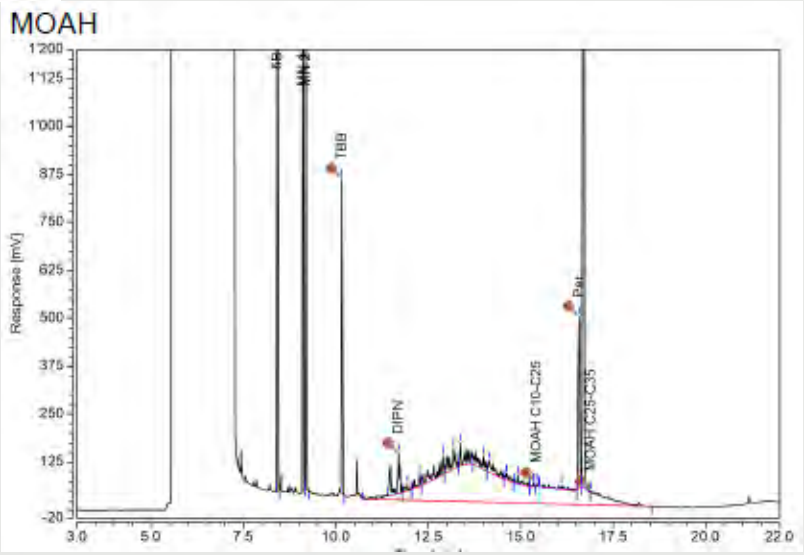
Question: Is possible resolve the MOH with a chromatographic analysis?

Answer: No



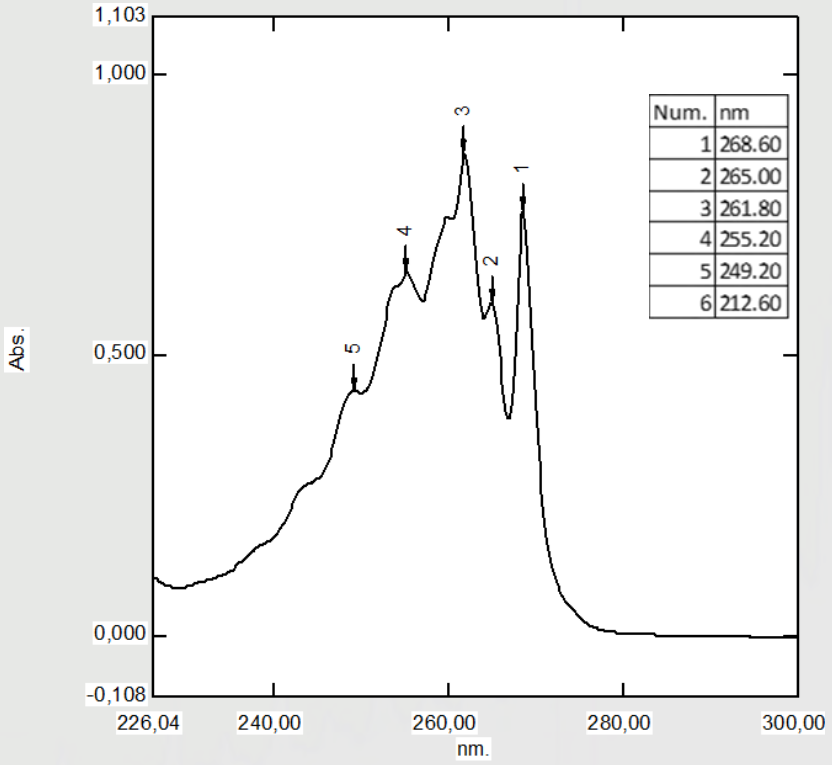
MOH = MOSH + MOAH





The MOH used in a detergent cream for industrial scope

In the list of ingredients of the product is reported: …… mineral oils
After extracion with n-Hexane the residual is a viscous liquid oil.
The chromatogram is a classic hill of unresolved mineral oils.
The UV spectra of the extracted oil is the seguent



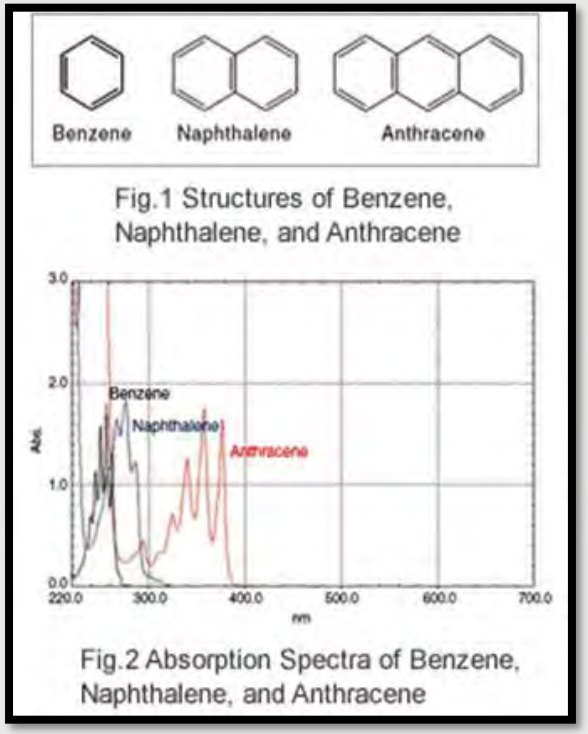


Fig.1 Structures of Benzene, Naphthalene, and Anthracene

Fig.2 Absorption Spectra of Benzene, Naphthalene, and Anthracene

Fortunately the aromatic rings are below three

Historic background of mineral oil food contamination

The Rapid Alert System for Food and Feed (RASFF) was notified on 23 April 2008 that sunflower oil originating from Ukraine was found contaminated with high levels of mineral oil. Several shiploads of such oil had been exported to a number of Member States. *(EFSA Journal 2012;10(6):2704)*

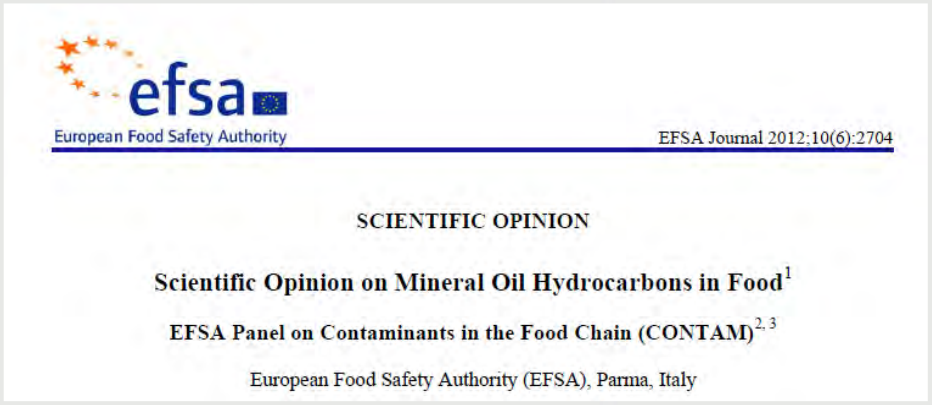
The contamination level of mineral oil was between 100-1000 mg/Kg.
The mineral oil was at high viscosity with an atoms carbon range between C20-C60 .

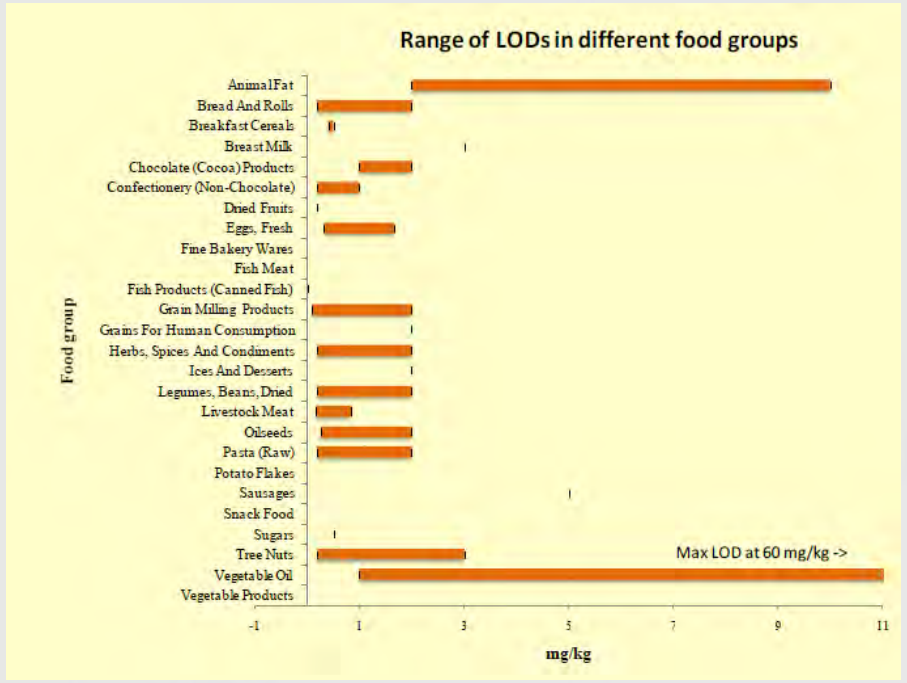
The Italian Healt Ministry requests withdrawal of the products that contain contaminated sunflower oil upper10 %.

In November 2009 the Europen Commision (Reg. 1151/2009) imposing special conditions governing the import of sunflower oil originating in or consigned from Ukraine due to contamination risks by mineral oil and repealing Decision 2008/433/EC.
Article 3
1. Sunflower oil imported into the Community shall not contain more than 50 mg/kg mineral paraffin.

After this RASFF the searches for contamination by mineral oils in vegetable oils and in packaging material began in a systematic way.

EFSA Report





In 2012 EFSA published a scientific opinion regarding the mineral oil contamination.

- Definition of MOH and distinction between MOSH e MOAH
- The food grade MOH products are treated in such a way that the MOAH content is minimized. Technical grades MOH typically contain 15 - 35 % MOAH.

- ***Methods of analysis:*** Currently the most efficient method to analyse MOSH and MOAH in food and feed comprises extraction followed by pre-separation by high performance liquid chromatography (HPLC) on-line coupled to GC with flame ionisation detection (FID). Detection limits depend on the mass distribution, the sample matrix and any prior enrichment, and can be as low as 0.1 mg/kg.

JRC Report

This guidance aims to
1. facilitate harmonised sampling of food and FCM for MOSH and MOAH analysis;
2. facilitate harmonised reporting to EFSA by laboratories that are already familiar with the
analytical approaches and have proven their analytical performance in relevant proficiency
testing (PT) schemes;
3. give the essential performance requirements for the methods to be applied in MOSH/MOAH
analysis;
4. give references to current analytical approaches described in the scientific literature for
laboratories that are not familiar with the analytical methodology

This guidance does ***not*** aim to provide standard operating procedures.

Verification of the 4.5 method performance

GC performance : Column type DB1- lengh 15 mt.
The response ratio of n-C50 to n-C20 should be between 0.8 and 1.2.
Internal standards: For MOSH it can be useful C20 and C40 or C44, and for MOAH Perylene

Guideline - LOQ

MOSH:	MOAH:
total MOSH	Total MOAH
MOSH ≥n-C_{10} to ≤n-C_{16}	MOAH ≥n-C_{10} to ≤n-C_{16}
MOSH >n-C_{16} to ≤n-C_{20}	MOAH >n-C_{16} to ≤n-C_{25}
MOSH >n-C_{20} to ≤n-C_{25}	MOAH >n-C_{25} to ≤n-C_{35}
MOSH >n-C_{25} to ≤n-C_{35}	MOAH >n-C_{35} to ≤n-C_{50}
MOSH >n-C_{35} to ≤n-C_{40}	
MOSH >n-C_{40} to ≤n-C_{50}	

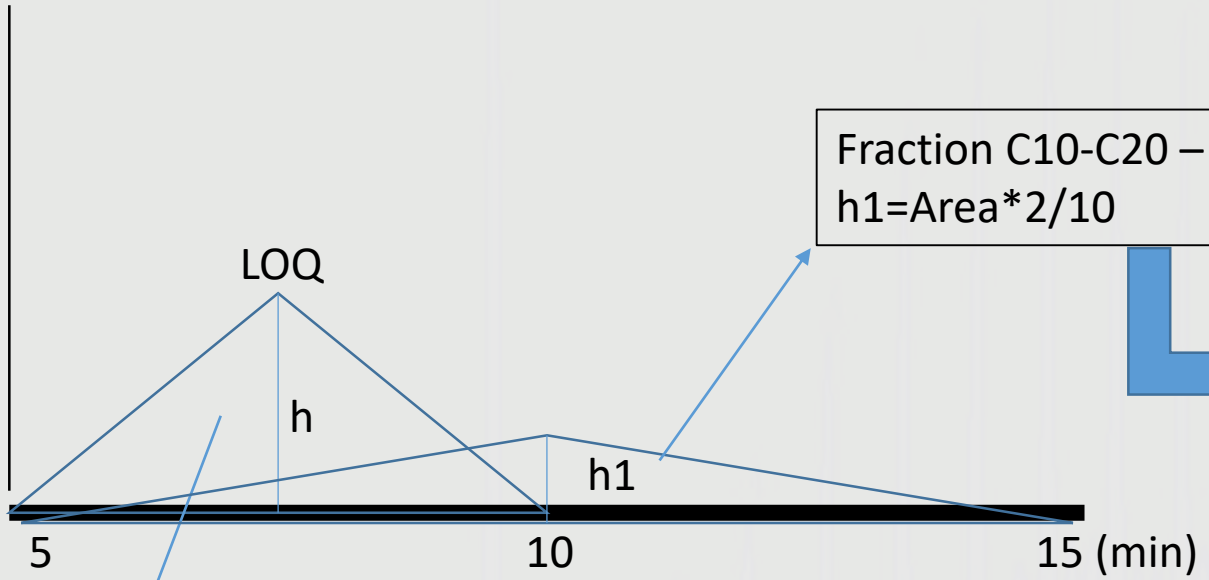
The LOQ for the total MOSH?

If the LOQ is 2 mg/Kg the LOD would be about 0,5 mg/Kg

Table II Performance requirements for MOSH and MOAH analysis: maximum LOQ for each C-fraction (LOQ-max), target LOQ for each C-fraction (LOQ-t), acceptable ranges for recovery (R_{rec}) of mineral oil from samples, and intermediate precision

Categories	Associated foods #	LOQ - max [mg/kg]	LOQ -t [mg/kg]	R_{rec} [%]	interme-diate precision [%]
Dry, low-fat content (< 4% fat/oil)	bread and rolls; breakfast cereals; grains for human consumption; pasta, products derived from cereals	0.5	0.1	80 - 110	15
Higher fat/oil content (> 4% fat/oil)	fine bakery ware; confectionery (incl. chocolate) and cocoa; fish meat, fish products (canned fish); oilseeds; pulses; sausages; tree nuts	1	0.2	70 - 120	20
Fat/oils	animal fat (e.g. butter); vegetable oils	2	0.5	70 - 120	20
Paper and Board	Reporting only up to C_{35} (extraction optimised up to C_{35})	10	5	80 - 110	10

LOQ of single fraction – LOQ of total fraction



Fraction C10-C20 – Area 2 mg/Kg – h1=Area*2/10

h1 = h/2

Fraction C10-C16 – Area 2 mg/Kg – h=Area*2/5

To have the same revelation for the two fractions, the concentration of the fraction C10-C20 must be 4 mg/Kg, so the LOQ of the total fraction will be 4 mg/Kg

Analytical Methods

For the determination of mineral oil in vegetable oils there are two validated official methods:

- **ISO 11780:2015 - Animal and vegetable fats and oils – Determination of aliphatic hydrocarbons in vegetable oils. This method is suitable only for MOSH between 50-1000 mg/Kg.**

- **UNI EN 16995:2017 - Foodstuffs - Vegetable oils and foodstuff on basis of vegetable oils - Determination of mineral oil saturated hydrocarbons (MOSH) and mineral oil aromatic hydrocarbons (MOAH) with on-line HPLC-GC-FID analysis. This method is suitable only for concentrations of MOSH and MOAH above 10 mg/Kg.**

The German Federal Institute for Risk Assessment (BfR) on May 22 2012 has published an off line analytical system to determinate MOSH e MOAH.

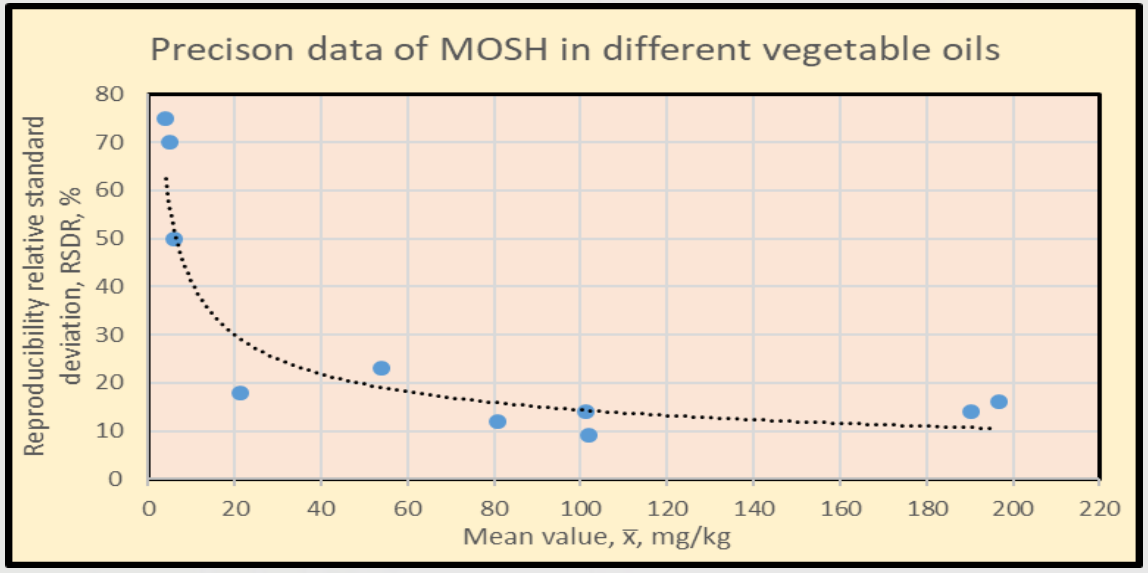
"Determination of hydrocarbons from mineral oil (MOSH &MOAH) or plastics (POSH & PAO) in packaging materials and dry foodstuffs by solid phase extraction and GC-FID"

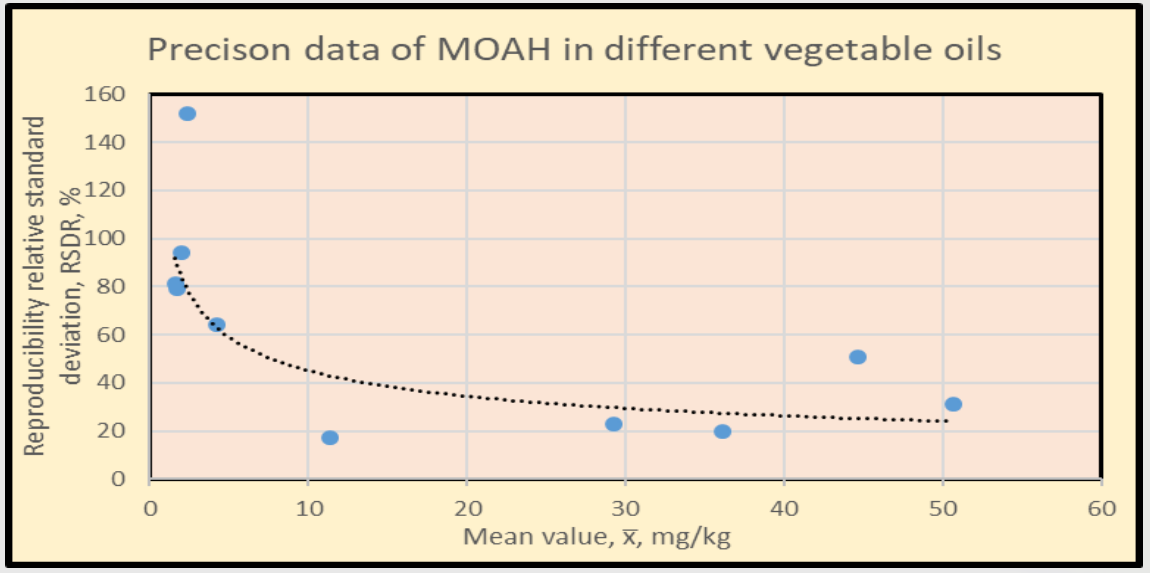
Method - UNI EN 16995:2017

The method use on-line HPLC-GC with optional clean up by epoxidation, when the oil or fat have high contents of squalene and sterenes. For oils that have a high contents of aliphatic hydrocarbons, the method provides a clean up on activated aluminium oxide.

At the point of clean up by epoxidation is reported the possibility of an enrichment eluting 1 gr of oil on silica gel before the epoxidation step. The enrichment is about 5 time.

In the appendix of precision data there isn't reported interlaboratory results after enrichment.

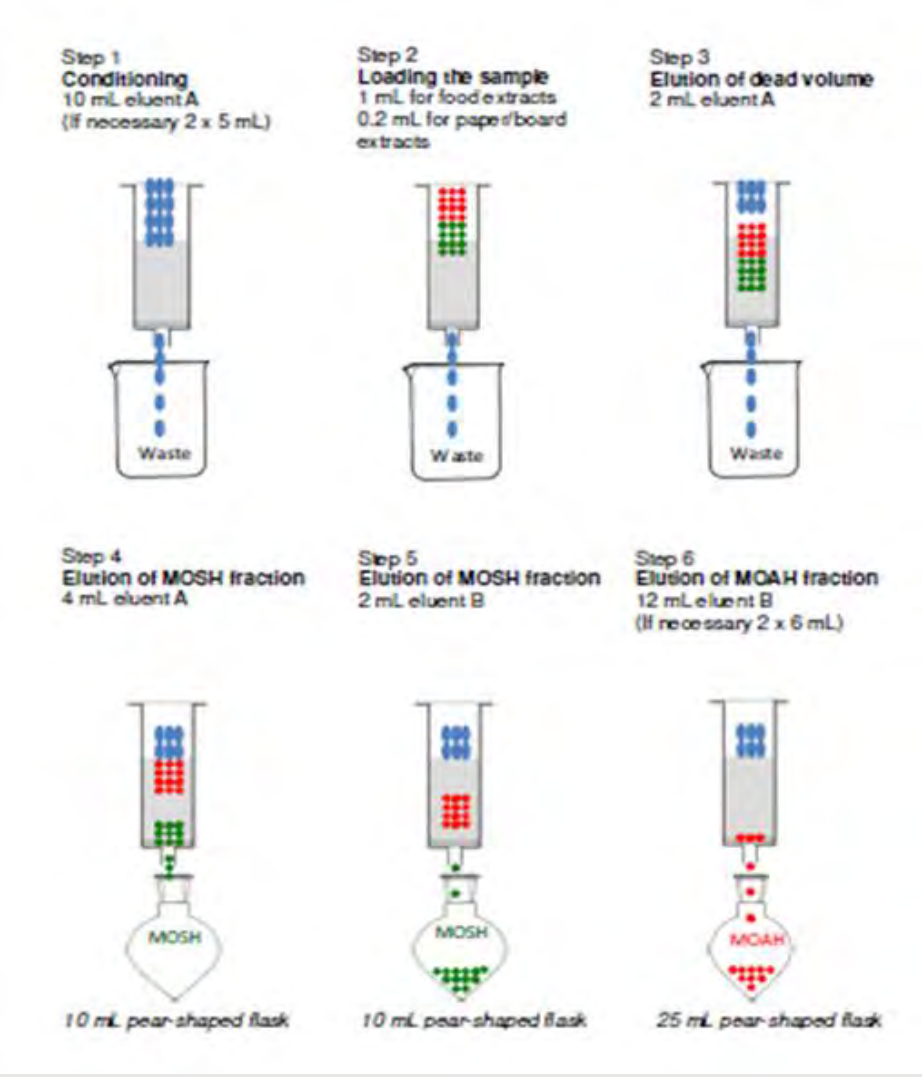




A value of 25 % for the reproducibility relative standard deviation was preferred for the quality assessment of the precision data.

Analytical System – BfR

System off line GC/FID with purification of the sample on silica silvered (0,3%) column



Internal standards

Substance	CAS No.	Abbreviation	Fraction
n-Undecane	1120-21-4	n-C 11	MOSH, POSH, POA
n-Tridecane	629-50-5	n-C 13	
Bicyclohexyl	92-51-3	Cycy	
5α-Cholestane	481-21-0	Cho	
1-Methylnaphthalene	90-12-0	1 MN	MOAH
2-Methylnaphthalene	91-57-6	2 MN	
1,3,5-Tri-tert-butylbenzene	1460-02-2	TBB	
Perylene	198-55-0	PER	
Pentylbenzene	538-68-1	5 B	

To calculate the MOSH the main Internal standards is CyCy.
To calculate the MOAH the main Internal standards are 1MN or 2MN.

In the method there isn't Precision Data and value for LOD & LOQ

International proficiency test (2019)

MOSH				
Value 1	Value 2	Mean (mg/Kg)	Method	Zscore
32	32	32,0	DIN EN 16995	-1,1
32,9	32,5	32,7	MI/C12 r00 2018 (GC FID)	-0,9
37,3	37,8	37,6	DIN EN 16995	0,5
41,1	38,5	39,8	ISO 17780:2015	1,1
54,8	---	54,8	DIN EN 16995	5,4
36,3	38,3	37,3	DIN EN 16995	0,4
35,1	30,9	33,0	--	-0,8
4,8	4,8	4,8	HPLC-GC-FID online	-8,8
30,1	32,3	31,2	--	-1,3
58	62	60,0	--	6,9
37	42	39,5	BfR modified	1,1
76,2	76,7	76,5	DIN EN 16995	11,6
39	39	39,0	--	0,9
Total mean		**35,8**		
Min		**31,2**		
Max		**39,8**		
St.Dev. (Sr)		**3,5**		
R (Sr*2,8)		**9,8**		
R%		**27,4**		

MOAH				
Value 1	Value 2	Mean (mg/Kg)	Method	Zscore
4	4,2	4,1	DIN EN 16995	0,3
3,2	3,1	3,2	MI/C12 r00 2018 (GC FID)	-0,1
6,3	6,2	6,3	DIN EN 16995	1,2
42,6	43	42,8	ISO 17780:2015	16,5
1,9	---	1,9	DIN EN 16995	-0,7
4,8	5	4,9	DIN EN 16995	0,6
1,3	3,5	2,4	--	-0,4
0,3	0,3	0,3	HPLC-GC-FID online (*)	-1,3
2,7	2,5	2,6	--	-0,4
6	10	8,0	BfR modified	1,9
1	1	1,0	DIN EN 16995 (*)	-1,0
14	14	14,0	--	4,4
Total mean		**3,5**	(*) Value=LOQ	
St.Dev. (Sr)		**2,4**		
Min		**0,3**		
Max		**8,0**		
R (Sr*2,8)		**6,7**		
R%		**193,2**		

Our experience

We use a off line system obtained modifying the BfR Method

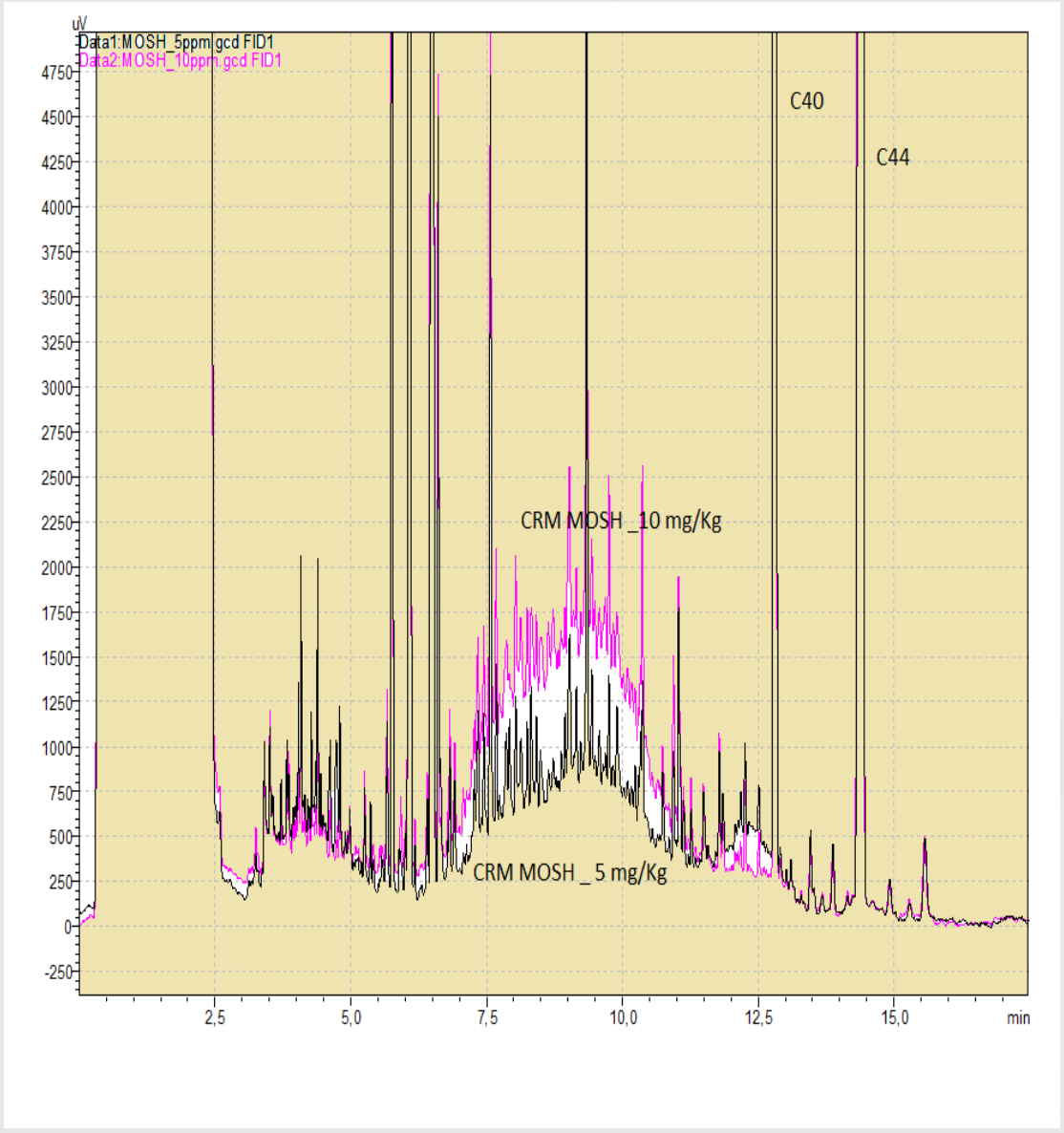
The problem for the BfR system is the small column (3 gr of silvered silica gel) so in the second step often there is co-elution of MOAH and oil.

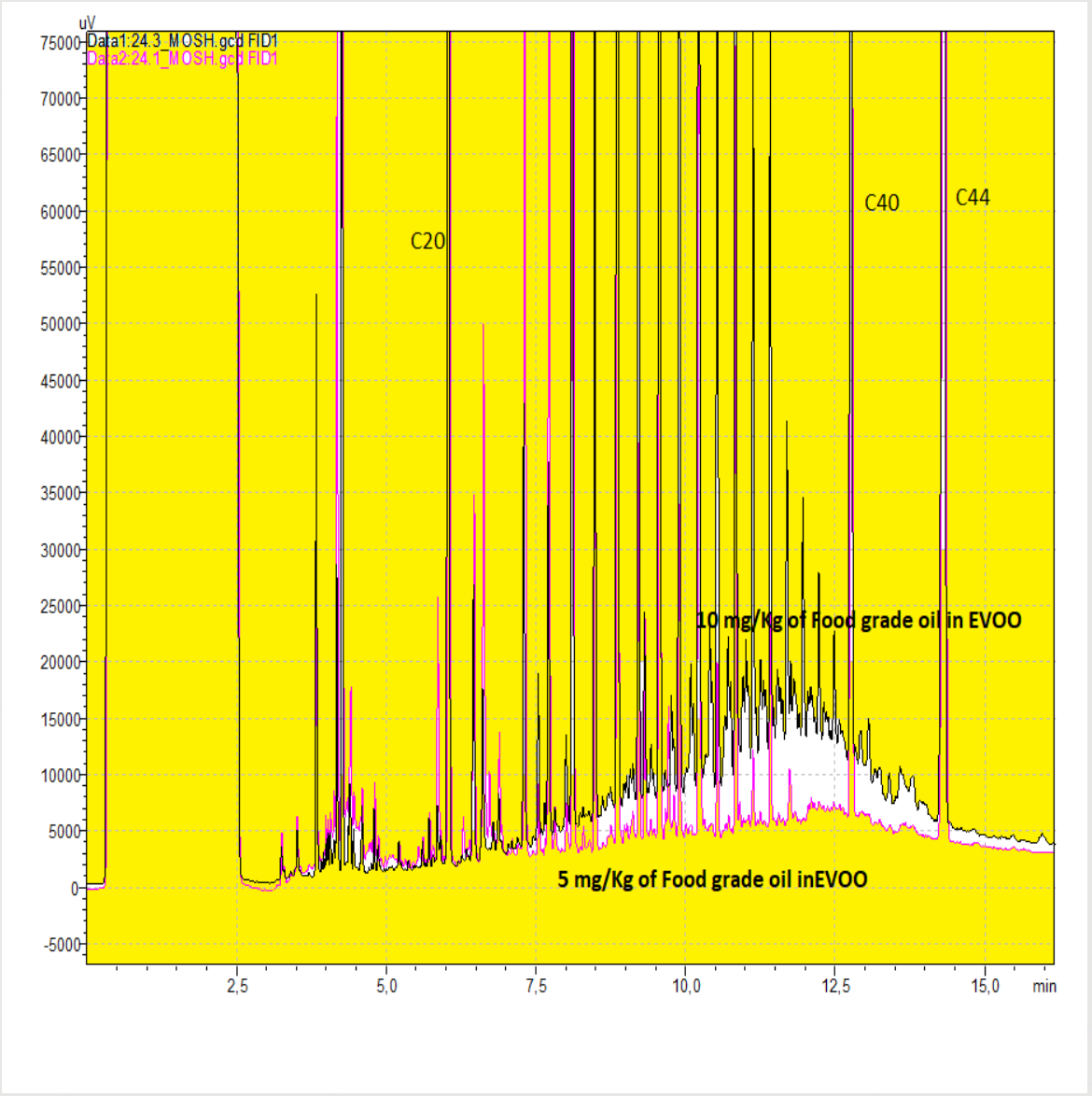
To eliminate this problem with use a pre elution of the oil on silica gel at 2% of water. In this way are retained squalene and triglycerides.

In this way using 2 gr of oil in the first elution we can enrichment until to about 6 time, despite this we haven't an acceptable precision below 10 ppm.

An analytical procedure without official interlaboratory validation cannot call **METHOD** but only **SYSTEM**

Example of chromatogram





THANK FOR YOUR ATTENTION