Separation of tri- and polyaromatic from mono- and diaromatic compounds of the MOAH fraction in cosmetic raw materials

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Introduction

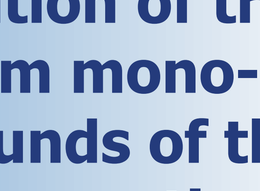
Mineral oil hydrocarbons (MOH) can be subdivided into saturated (MOSH) and aromatic (MOAH) hydrocarbons. Humans are exposed to MOSH and MOAH orally either via food or through cosmetic and pharmaceutical products such as lip balms and laxatives, which can consist almost entirely of MOH [1].
EFSA stated 2012 that "MOAH with three or more, non- or simple-alkylated, aromatic rings may be mutagenic and carcinogenic, and therefore of potential concern" [2]. For that reason a differentiation between the mono- and diaromatic fraction (MDAF) and the tri- and polyaromatic fraction (TPAF) is needed, since the latter is the fraction of toxicological concern [3].

Experimental overview

1 *n-Hexane solution of cosmetic raw material*

1 g sample was dissolved in 20 mL n-Hexane

Addition of MOSH/MOAH internal standards (Undecane (C11), Tridecane (C13), Bicyclohexyl (CyCy), Cholestane (Cho), Tetracontane (C40), pentylbenzene (5B), 1- and 2- methylnaphthalenes (1MN, 2MN), 1,3,5-tri-tert-butylbenzene (TBB) and perylene)



Cosmetic raw material (petrolatum and paraffin oil)

2 *Preparative separation*

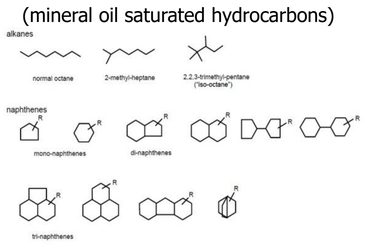
on silver ion loaded silica gel

1 mL of sample solution is used for separation on 6 g Ag^+ (0,3 %) silica gel, elution with n-Hexane/Dichloromethane

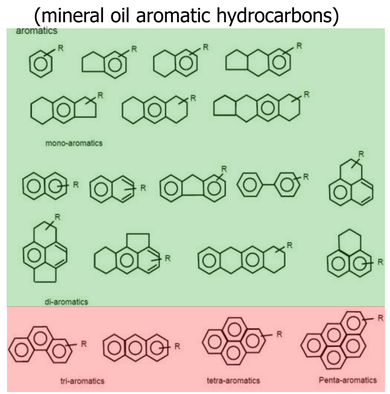
Advantages compared to NP-HPLC separation:

- isolation of larger amount of MOAH
- avoidance of the excessive MOSH tailing into MOAH

MOSH
(mineral oil saturated hydrocarbons)

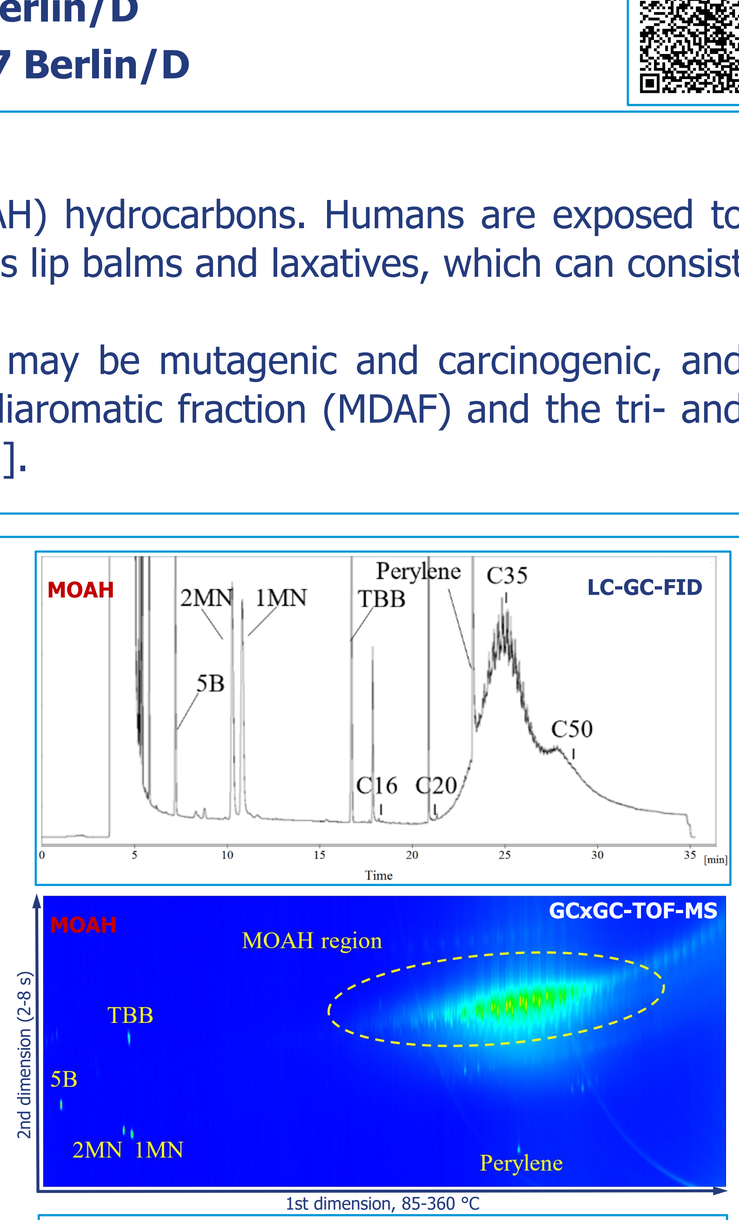


MOAH
(mineral oil aromatic hydrocarbons)



Quantification

Characterization

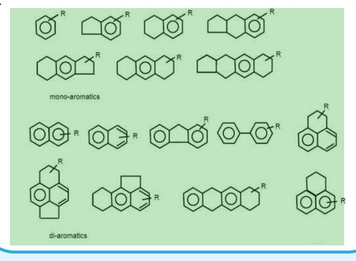


3 *Donor acceptor complex chromatography (DACC)*

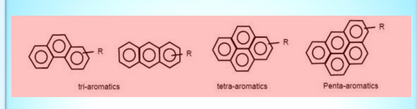
Separation and enrichment of TPAF with ***Octylphenanthrene*** *marking the beginning of the TPAF*

HPLC separation of the isolated MOAH into **MDAF** and **TPAF** with multiple chromatographic runs for TPAF enrichment

MDAF
(**m**ono- and **dia**romatic **f**raction)



TPAF
(**t**ri- and **p**oly**a**romatic **f**raction)



Fraction of toxicological concern

Quantification

Characterization

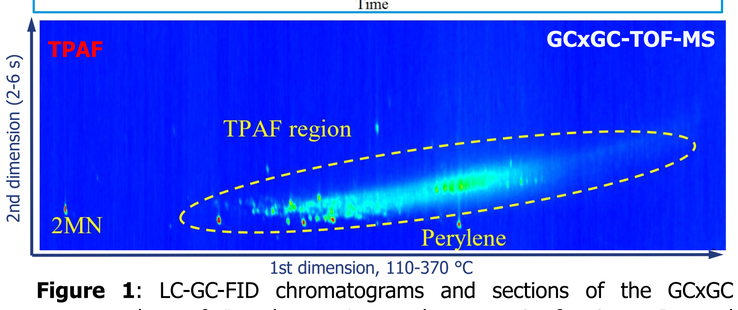


Figure 1: LC-GC-FID chromatograms and sections of the GCxGC contour plots of Petrolatum 1 sample aromatic fractions. Internal standards are marked. C16, C20, C35, C50: retention time marker of respective n-alkanes.

Results

Table 1: Summary of quantification results

Sample	MOAH-amount [%]	MDAF-amount [%]	TPAF-amount [%]	TPAF-amount [mg/kg]
Petrolatum 1	2.0	1.7	0.011	110
Petrolatum 2	2.3	2.3	0.005	50
Paraffin oil 1	0.014	0.013	<0.001	<10
Paraffin oil 2	0.071	0.057	<0.001	<10

- Analyzed samples (two petrolatums and two paraffin oils obtained from a cosmetic manufacturer) contained MOAH.
- TPAF was determined only in the petrolatum samples, the signals in the paraffin oils were below the limit of quantification (**LOQ**) of **10 mg/kg**
- The determined **TPAF** amounts constitute 0,011 and 0,005 % of the sample which corresponds only to **0,6** and **0,2 % of the MOAH** fraction
- Characterization with GCxGC-TOF-MS proved the presence of alkylated triaromatic compounds
- TPAF of one petrolatum sample was found to contain heteroaromatic compounds (dibenzothiophenes). This is a limitation of the used DACC phase and should be taken into account.

Conclusion

- The separation of TPAF from MDAF is fulfilled by the means of donor acceptor complex chromatography (DACC).
- The developed method enables the determination of toxicity-relevant MOAH, as stated by the EFSA [1] and concluded by others [3].
- LC-GC-FID quantification showed that the MOAH of cosmetic raw materials consists of up to >99% out of MDAF, which constitutes lower toxicological concern [3].

Outlook

- Automation of the separation procedures and development of an LC-LC-GC-FID on-line separation method will improve sensitivity and reduce turnaround time for analytical procedures.
- Further determination of TPAF contents for better knowledge of MOAH composition and their toxicological evaluation. Analysis of food and food contact materials.

References:
[1] BfR Aktualisierte Stellungnahme Nr. 008/2018 des BfR vom 27. Februar 2018 DOI 10.17590/20180219-123914 [2] European Food Safety Authority (EFSA) Panel on Contaminants in the Food Chain (CONTAM): EFSA J. 2012; 10(6): 2704. [3] K. Grob J. Agric. Food Chem., 2018, 66 (27), pp 6968–6974, doi:10.1021/acs.jafc.8b02225

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