Simple and fast method for PAHs quantification in oil & oil-rich food using Molecularly Imprinted Polymers extraction

Gisèle USANASE[1], Aurélie CORTEJADE[1], Cecile VINCENT[1], Roxane CHENE[1], Sami BAYOUDH[2], Michel AROTCARENA[2], Kaynoush NARAGHI[2], Mickaël NICOLAS[1]

[1]CARSO-LSEHL, Vénissieux, France (acortejade@groupecarso.com)
[2]Affinisep, Le Houlme, France (contact@affinisep.com)

Overview

- Development of a method for PAHs analysis in oil and rich-oil food
- Comparison of QuEChERS vs. Molecularly Imprinted Polymers (MIPs) extraction
- MIPs offer better selectivity, 4 to 20 times lower detection limits than QuEChERS.
- Method validation: LOQs of 0.5-1 µg/kg for 18 to 25 PAHs, relative standard deviations 5 % - 25 %.

Introduction

This study addresses the growing concern about Polycyclic Aromatic Hydrocarbons (PAHs), carcinogenic organic compounds found in food, especially in oils due to their lipophilic nature. With the implementation of EU Commission Regulation 2023/915, which sets maximum PAH levels in edible oils at 2 µg/kg for benzo[a]pyrene and 10 µg/kg for a combination of four PAHs, developing a reliable and sensitive analytical method became essential. Therefore, the objective of this study was to develop such a method, and to achieve this, two PAH extraction techniques in oils and oil-rich foods QuEChERS and Molecularly Imprinted Polymers (MIPs) were tested to determine the most effective method in compliance with the regulatory standards.

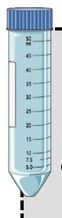
Sample preparation

Sample type :

Oil

Oil-rich food

✓QuEChERs Extraction



Extraction from 10 g of sample by QuEChERs and clean up by dSPE.

Extraction
10 g of sample
10 mL acetonitrile + 4 g $MgSO_4$

Centrifugation & freezing
10 min at 3900 rpm & freeze for 3 h at -20°C

Clean up
~10 mL of extract with dSPE

Centrifugation
10 min at 3900 rpm

Evaporation, concentration

✓AFFINIMIP® SPE PAHs Extraction

Solid sample

Liquid sample

3 g sample + 3 mL cyclohexane

Centrifugation

Supernatant + 2 mL cyclohexane: Loading solution

Conditioning
3 mL cyclohexane/ethyl acetate (50/50; v/v)
3 mL cyclohexane

Loading
6 mL of the loading solution

Washing
5 mL cyclohexane

Elution
3 mL ethyl acetate

Evaporation, concentration

Analysis Method

- **Samples were analysed by GC-MSMS-TSQ-8050-NX (Shimadzu)**

GC separation

MS/MS detection (QqQ)

- **Column:**

Column Rxi-PAH (Restek)
L 30 m, DI 0.25 mm, 0.10 µm

- **Gradient**

Rate (°C/min)	T (°C)	Duration (min)
-	50	1
30	260	0
15	325	20

Compounds	Transition 1	Transition 2	RT (min)
Naphthalene	128.00>102.10	128.00>78.10	6.1
Acenaphthylene	152.00>150.70	152.00>126.10	7.6
Acenaphthene	153.60>152.80	153.60>152.00	7.7
Fluorene	165.00>165.00	165.00>115.10	8.2
Phenanthrene	178.00>176.00	178.00>152.10	9.2
Anthracene	178.00>176.00	178.00>152.10	9.3
Fluoranthene	202.00>200.00	202.00>199.10	10.5
Pyrene	202.00>200.00	202.00>199.10	10.9
Benzo (c) fluorene	215.10>213.10	216.10>213.00	11.3
Benz(a)anthracene	228.00>226.15	226.00>224.10	12.5
Cyclopenta[c,d]pyrene	226.10>223.90	224.10>221.80	12.6
Chrysene	228.00>226.15	226.00>224.10	12.6
5-MethylChrysene	241.10>239.00	242.10>239.00	13.2
Benzo(b)fluoranthene	252.00>250.10	252.00>248.90	14.4
Benzo(k)fluoranthene	252.00>250.10	252.00>248.90	14.4
Benzo(j)fluoranthene	252.00>250.10	252.00>248.90	14.5
Benzo(e)pyrene	252.00>249.10	250.00>248.00	15.2
Benzo(a)pyrene	252.10>249.90	250.10>248.00	15.3
Dibenz(a,h)anthracene	278.10>275.80	278.10>273.90	18.4
Indeno(1,2,3-cd)pyrene	276.00>274.00	138.00>125.10	18.5
Benzo(g,h,i)perylene	276.00>273.10	138.00>124.90	19.7
Dibenzo (a,l) Pyrene	302.10>300.00	-	25.4
Dibenzo (a,e) Pyrene	302.10>299.70	302.10>297.80	27.9
Dibenzo (a,i) Pyrene	302.10>299.80	302.10>297.80	29.3
Dibenzo (a,h) Pyrene	302.10>299.70	302.10>297.80	30.1

Extraction method comparison: QuEChERs Vs MIP

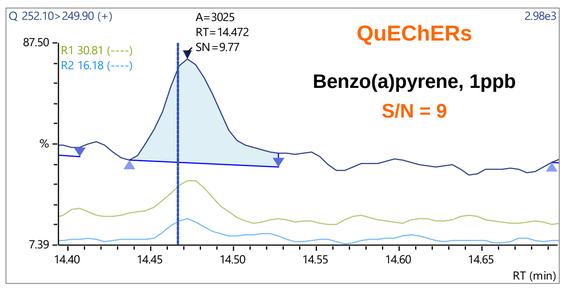
✓ **PAH Extraction in Sunflower oil**

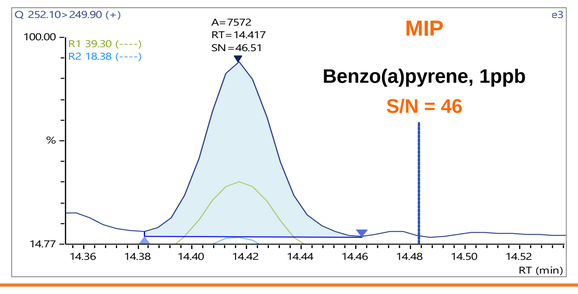
Less noise on the MIP chromatogram

Signal/noise ratio improvement

MIP cartridges are more selective

Better results with MIP extraction





✓ **Lower LOQs for MIP**

✓ **4 to 20 times lower LOQs with MIP**

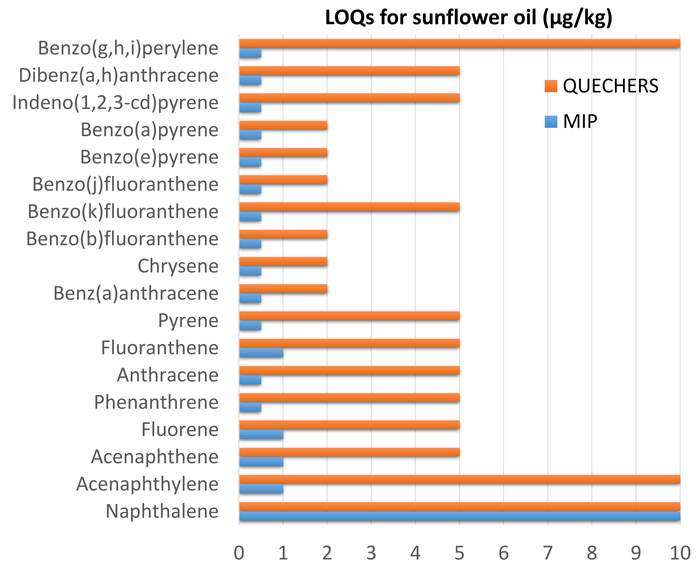
- Benzo(a)pyrene

LOQ → MIP = 0.5 µg/kg QuEChERs = 2 µg/kg

- Benzo(g,h,i)perylene

LOQ → MIP = 0.5 µg/kg QuEChERs = 10 µg/kg

✓ **Naphthalene same LOQs for QuEChERs & MIP**



Method validation

Method validated in accordance with EU COMMISSION REGULATION 2023/915 of 25/04/2023 on maximum levels for certain contaminants in food.

Regulated PAHs :
Benzo(a) pyrene at 2 µg/kg
Σ4PAH* at 10 µg/kg
4PAH : benzo(a)pyrene, benzo(a)anthracene, benzo(b)fluoranthene et chrysene

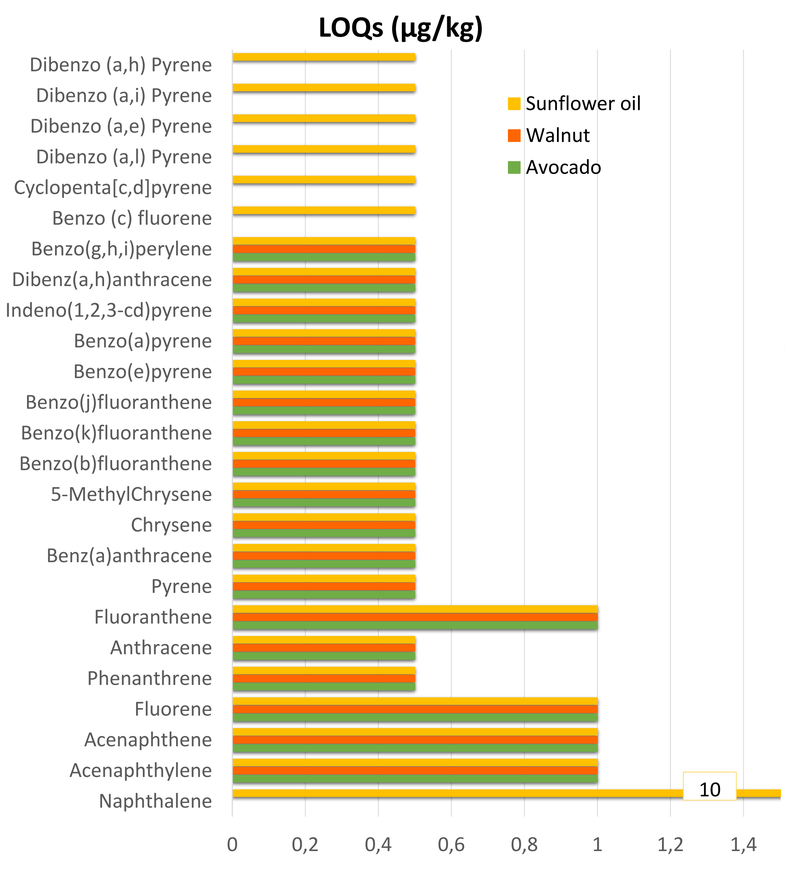
✓ ***Validated matrices***
Sunflower oil, avocado, and walnut

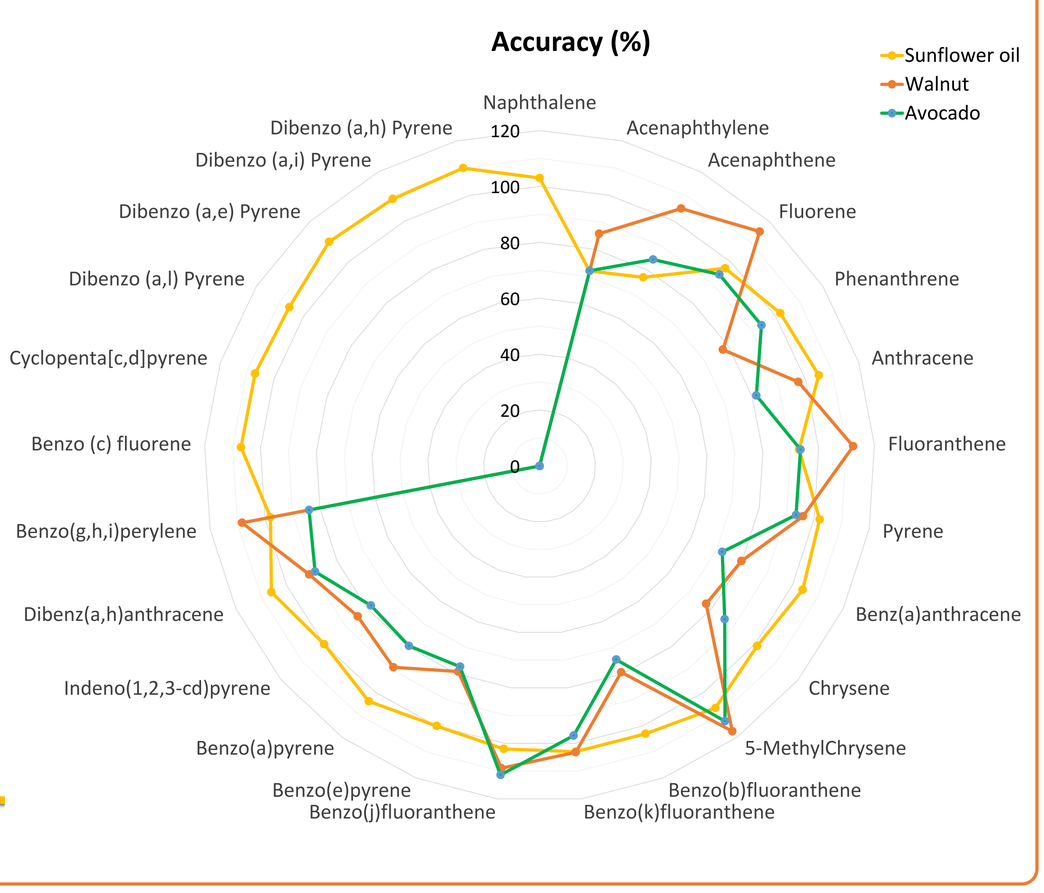
✓ ***LOQs***
Very low LOQs were validated: 0.5 to 1 µg/kg
Except for Naphthalene: 10 µg/kg

✓ ***Accuracy: 72-110 %***

✓ ***Repeatability: 5-25 %***

✓ ***Validated compound:***
25 PAHs for oils (sunflower oil)
18 PAHs for oil-rich food (avocado and walnuts)





Conclusions

MIP cartridges for PAHs have demonstrated good performance in the extraction and analysis of oil and oil-rich foods. Specifically, 25 PAHs were validated in sunflower oil, and 18 PAHs were validated in both avocado and walnut. The method exhibited excellent accuracy ranging from 72% to 110%, with repeatability varying between 5 % and 25 %. Additionally, excellent LOQs were achieved ranging from 0.5 to 1 µg/Kg (except for naphthalene at 10 µg/Kg) , further highlighting the high efficiency and reliability of the MIP cartridges for the extraction of PAHs in complex oil-based matrices. The next step would be to use this method with even more complex matrix such as meat, fish…