

Application Note 192

Extraction & Analysis of PAHs in Olive Oil Using SupelMIP™ SPE – PAHs and GC-MS

Introduction

Polyaromatic hydrocarbons (PAHs) consist of fused aromatic rings and are formed as a by-product during the combustion of fuels. Seven PAHs in particular are known for their carcinogenic properties: benz[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, dibenz[a,h]anthracene, and indeno[1,2,3-cd]pyrene. As such, they are monitored in both the environment and food (1,2).

Benzo[a]pyrene is found in a number of edible oils (olive, grapeseed, pomace, etc.) due to the production process of such oils. For example, the exposure of oil mash to gasoline exhaust can result in PAH contamination. In addition, the use of contaminated solvent during olive mash extraction and extensive heat during solvent evaporation have also been attributed to PAH contamination (1,2,3).

On February 4 2005, the European Union Commission Regulation (EC) No 2008/2005 set maximum limits of PAHs in food. For oils and fats intended for direct human consumption, the maximum residue limit for PAHs in food, as benzo(a)pyrene on wet weight is 2 µg/kg (4).

In this report, we discuss the use of the molecularly imprinted polymers (SupelMIP SPE- PAHs) for the extraction and analysis of PAHs in olive oil for subsequent GC-MS analysis.

Molecularly Imprinted Polymers

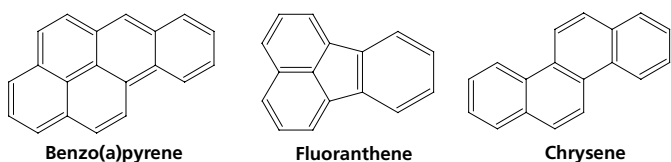
Molecularly imprinted polymers (MIPs) are a class of highly cross linked polymer-based molecular recognition elements engineered to bind one specific target compound or a class of structurally related compounds with high selectivity. The MIP material is designed with cavities that are sterically and chemically complementary to the target analyte(s). As a result, multiple interactions (e.g., hydrogen bonding, ionic, Van der Waals, hydrophobic) can take place between the MIP cavity and the analyte.

Extraction & Analysis

A PAH standard test mix comprising of fluoranthene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenzo(ah)anthracene, and benzo(ghi)perylene (Figure 1) was prepared in methylene chloride.

Store purchased olive oil was spiked with PAHs in duplicate at the level of 2 ng/g. Chrysene-d₁₂ was spiked as the internal standard at the level of 20 ng/g.

Figure 1. Representative Structures of PAHs



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0.5 g of spiked and blank oil sample was mixed with 0.5 mL cyclohexane and was extracted using the SupelMIP SPE procedure described in Table 1 and analyzed via GC-MS under conditions detailed in Table 2.

Table 1. SupelMIP SPE – PAHs Procedure

SPE Cartridge: SupelMIP SPE – PAHs, 50 mg/3 mL (Cat. No. 52773-U)

1. Condition with 1 mL cyclohexane
2. Load diluted oil sample
3. Wash with 1 mL cyclohexane
4. Elute with 3 x 1 mL ethyl acetate
5. Evaporate SPE eluate under nitrogen at 40 °C and reconstitute in 0.2 mL ethyl acetate for analysis

Table 2. GC-MS Conditions for PAH Analysis

column: SLB™-5ms, 30 m x 0.25 mm I.D., 0.25 µm (Cat. No. 28471-U)
 instrument: Agilent GC-MS
 oven: 60 °C, 25 °C/min. to 275 °C (5 min.), 10 °C/min. to 300 °C (1 min.)
 flow rate: helium, 2 mL/min., constant
 injector temp.: 300 °C
 MS detection: Autotune + EM offset of 300
 scan range: SIM
 injection: 1 µL, splitless

High Recoveries of PAHs

The recovery of PAHs was evaluated. The blank sample of oil was analyzed for the presence of background contamination. The overall recovery values were corrected for background levels found in the blank sample. The results are shown in Table 3.

Table 3. Recovery Analysis of Blank and Spiked Olive Oil

Compound	Blank (µg/kg)	Spiked (2 µg/mL) Recovery
Fluoranthene	39.6	48%
Benzo(a)anthracene	3.4	65%
Chrysene	9.4	70%
Benzo(b)fluoranthene	2.2	82%
Benzo(k)fluoranthene	1.4	84%
Benzo(a)pyrene	3	87%
Indeno(1,2,3-cd)pyrene	2.4	95%
Dibenzo(ah)anthracene	1.8	82%
Benzo(ghi)perylene	3.4	87%

Using the SupelMIP SPE approach, an average recovery of 78% was observed. Note that PAH background contamination was found in the blank olive oil sample. This is consistent with previous studies reported (1,2,3). The extraction procedure is very simple (5 steps); and is amenable for larger PAH molecules. Extraction of smaller PAH molecules (2-3 rings) may be possible; however, low recovery may occur.

References

1. Bogusz M.J., El Hajj S.A., Ehaideb Z, Hassan H, Al-Tufail M, J.Chromat. A, 1026 (2004) 1-7.
2. Ballesteros E., Sanchez, A.G., Matos, N.R. J.Chromat. A 1111 (2006) 89-96.
3. Moret S., Conte, L.S. J.Chromat. A 882 (2000) 245-253.
4. EU sets maximum levels of PAHs in food: http://www.ihta.org/word_documents/EU_sets_maximum_levels_of_PAHs_in_food.doc

Ordering Information:

Description	Cat. No.
SupelMIP SPE-PAHs, 50 mg/3 mL, pk. of 50	52773-U

Trademarks

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