Automated Clean-up of PAH in Sunflower Oil for GC-MS

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PAL SYSTEM Ingenious sample handling

Introduction

- Food samples like sunflower oil need to be analyzed for unwanted compounds.
- Polycyclic aromatic hydrocarbons are cancerogenic compounds from incomplete combustion of organic matter.
- Sample needs to be cleaned-up in a way that enables the injection to a suitable instrument like a gas chromatography mass spectrometer (GC-MS).
- “Clean-up" especially from edible oil and fat samples is complex and labor-intensive.
- For a sample like sunflower oil, all lipids need to be removed before GC-MS injection.
- However, clean-up with established manual methods like SPE is labor intensive and use large amounts of solvents.

The Solution: Automation with µSPE

- Automation is one of the strategies to increase efficiency of the SPE clean-up.
- Automated SPE methods using mini-tubes, so called µSPE have already been successfully implemented for clean-up of QuEChERS extracts used for analysis of pesticides and PCB´s.
- The miniaturization of the clean-up step to a microliter scale solid phase extraction (µSPE).The PAH fraction is eluted only in a small volume of few 100 µL for direct injection into GC-HRMS.
- Extraction with large solvent volumes and evaporation with a potential loss of compounds is avoided.

Objective

The objective was to establish an automated µSPE clean-up procedure for PAH analysis in edible oils, here used sunflower oil. We were using two µSPE cartridges with Florisil™ and C18/Z-Sep™ sorbent materials.

We were using the greater concepts of Green Analytical Chemistry and automation.

Validation with 24 PAH + 16 IS

- Sample: Sunflower oil, 4 µL direct applied
- Analytes: 24 PAH analyte standard
- Internal Standards: 16 compounds ^{13}C labelled PAHs
- 5 replicates were used for precision calculation
- Recovery study at 326 and 3260 µg/kg

Chromatogram and detailed procedure

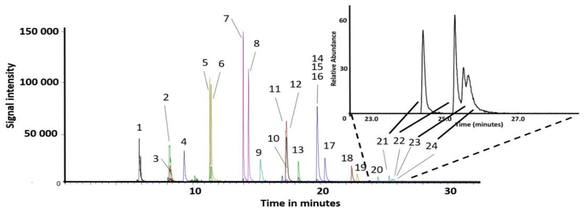

Figure 1 : GC-HRMS ion current (TIC) chromatogram of a sunflower oil eluent after using µSPE clean-up.

Table 1: Results from recovery analysis of sunflower oil spiked at two levels 326 and 3260 µg/kg in five replicates.

#	Analyte	Recovery %	%RSD
1	Naphthalene	97	8
2	Acenaphthylene	101	4
3	Acenapthene	107	8
4	Fluorene	102	5
5, 6	Anthracene + Phenanthrene	99	5
7	Fluoranthene	107	5
8	Pyrene	97	5
9	Benzo[c]fluorene	93	5
10, 11	Benz[a]anthracene + Chrysen	90	6
12	Cyclopenta[cd]pyrene	105	3
13	5-Methylchrysene	98	3
14, 15, 16	Benzo[b+j+k]fluoranthene	115	2
17	Benzo[a]pyrene	104	13
18	Dibenz[a,h]anthracene	96	8
19	Indeno[1,2,3-cd]pyrene	53	14
20	Benzo[g,h,i]perylene	77	22
21	Dibenzo[a,l]pyrene	69	17
22	Dibenzo[a,e]pyrene	72	19

µSPE: The general concept

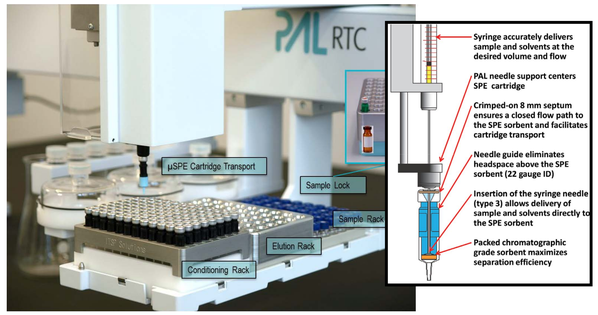

Figure 2: PAL RTC µSPE clean-up configuration

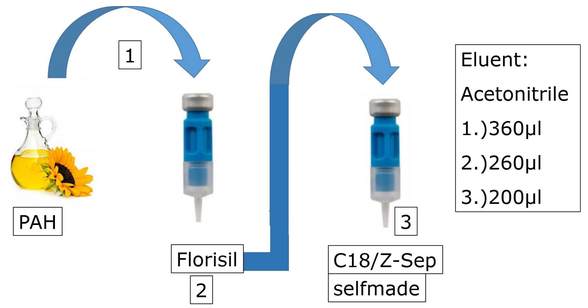

Figure 3: Concept of the automated µSPE clean-up steps

Table 2: The automated µSPE clean-up steps

Sequence	Description	Tool
1	Change Tool to 1ml syringe	1ml syringe
2	Wash syringe two times with 1000 µL acetonitrile	1ml syringe
3	Load 240 µL of acetone to cartridge 1 (florisil) for conditioning	1ml syringe
4	Drying with air, 1000 µL, cartridge 1	1ml syringe
5	Change Tool to 10 µL syringe (Injection Tool)	1ml syringe /Injection
6	Wash syringe two times with 10 µL acetontrile	Injection Tool
7	Load 4 µL of oil sample to the syringe (2 fill strokes prior to avoid bubbles)	Injection Tool
8	Load extracted fat sample to cartridge 1 (florisil)	Injection Tool
9	Wash injection tool two times with 10 µL acetonitrile	Injection Tool
10	Change Tool to 1ml syringe	1ml syringe
11	Wash syringe two times with 1000 µL acetonitrile	1ml syringe
12	Elute cartridge to vial 1 with 360 µL acetonitrile	1ml syringe
13	Wash syringe two times with 1000 µL acetonitrile	1ml syringe
14	Load 240 µL of Acetone Condition of cartridge 2	1ml syringe
15	Drying cartridge 2 with 1000 µL air	1ml syringe
17	Load/Eluate 260 µL of eluate 1 to cartridge 2 above vial 2	1ml syringe
18	Wash syringe two times with 500 µL acetonitrile	1ml syringe

The greater concepts

Automation

Green Analytical Chemistry

Conclusion

- Fully green analytical method.
- New micro-SPE method developed
- Vegetable oil sample could be directly applied and cleaned-up
- Evaporation steps are avoided
- PAH could be analyzed with good recoveries
- Potential for high sensitivity to meet the regulated maximum level (sum of 4 PAH) with10 µg/kg
- Optimize load volume as next step to perform
- Large volume injections allow increased sensitivity

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