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

Philipp Eyring*, Thomi Preiswerkˣ, Hans-Joachim Hübschmann|, Henrik Lauritz Frandsen*, Lene Duedahl-Olesen*
* Danish Technical University, Lyngby, Denmark; ˣ CTC Analytics AG, Zwingen, Schweiz, |CTC Analytics Asia Pte Ltd, Singapore
Contact: Thomi Preiswerk at: TPreiswerk@ctc.ch

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 suiting 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 methods is labor intensive

PAH in oil sampes?

The greater concepts

Automation

Green Chemistry

The Solution: Automation with µ-SPE

- Automation is one of the strategies to increase efficiency of the SPE clean-up
- Automated SPE methods using mini-tubes, so called µ-SPE have already been successfully implemented for clean-up of QuEChERS extracts used for analysis of PAH and other analyte classes such as 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-MS
- Extraction and evaporation with a potential loss of compounds is avoided

Objective

The objective was to establish a µ-SPE clean-up procedure for PAH analysis in sunflower oil. We were using two µ-SPE cartridges with Florisil and C18/Z-Sep. We were using the greater concepts of Green Chemistry and Automation.

µ-SPE: The general concept

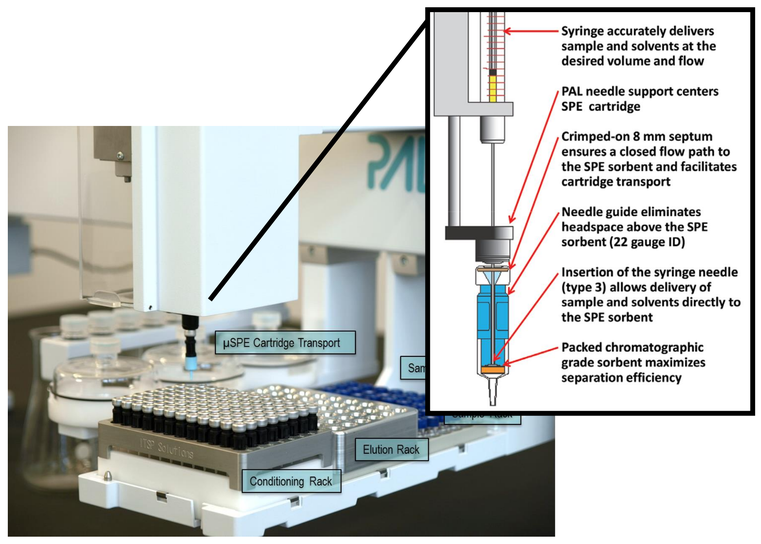

Figure 1: PAL RTC µSPE Clean-up Configuration

µ-SPE: The developed concept

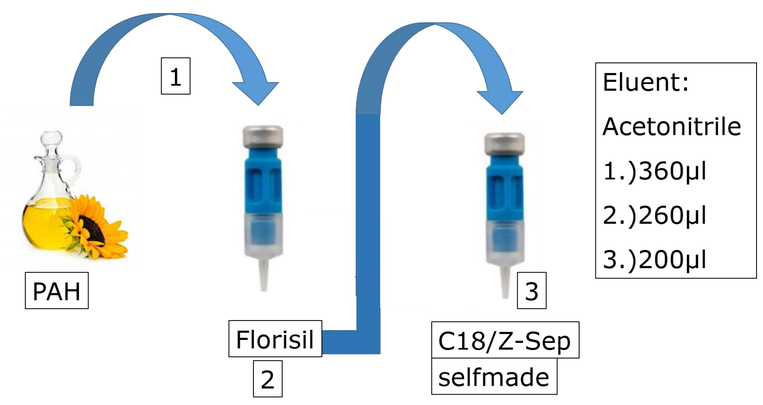

Figure 2: Concept of the Automated µSPE Clean-up Steps

Chromatogram and detailed procedure

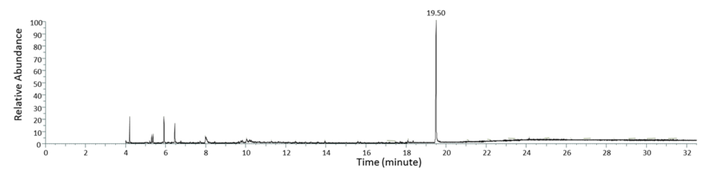

Figure 3 : GC-MS total ion current (TIC) chromatogram of a sunflower oil eluent after using µSPE clean-up.

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 Tc
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

Figure 4: The Automated µSPE Clean-up Steps

Validation with 24 PAH + 22 IS

- Analytes: 24 PAH analytes
- Internal Standards: 22 PAH
- 5 replicates were used
- Sample: Sunflower oil
- Our LOQ: 1090 µg/kg
- Maximum level (sum of 4 PAH): 10 µg/kg

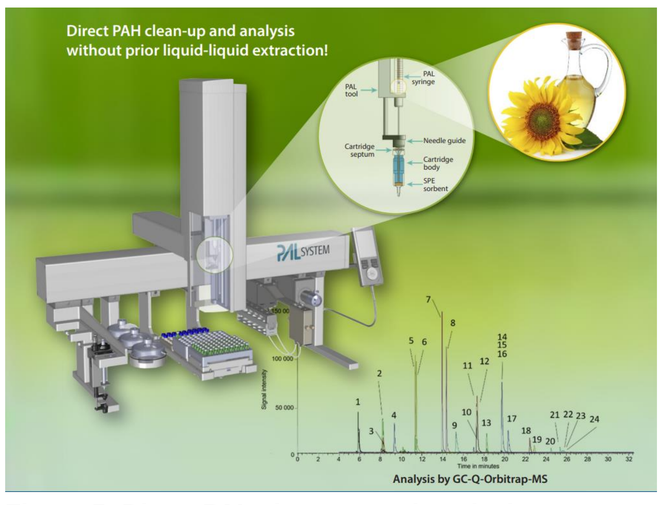

Figure 5: Direct PAL clean-up and analysis
https://onlinelibrary.wiley.com/doi/10.1002/jssc.202000720

Total ion chromatogram after clean-up with µSPE

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

Analyte	Recovery (RSD)
5-Methylchrysene	98(3)
Acenaphthylene	101(4)
Acenapthene	107(8)
Anthracene + Phenanthrene	99(5)
Benz[a]anthracene + Chrysene	90(6)
Benzo[a]pyrene	104(13)
Benzo[c]fluorene	93(5)
Benzo[g,h,i]perylene	73(22)
Benzo[b+j+k]fluoranthene	115(2)
Cyclopenta[cd]pyrene	105(3)
Dibenz[a,h]anthracene	96(8)
Dibenzo[a,e]pyrene	72(19)
Dibenzo[a,L]pyrene	69(17)
Fluoranthene	107(5)
Fluorene	102(5)
Indeno[1,2,3-cd]pyrene	53(14)
Naphthalene	97(8)
Pyrene	97(5)

Conclusion

- New micro-SPE method developed
- Vegetable oil sample could be directly cleaned up
- PAH could be analyzed with good recoveries
- Improvements on sensitivity can be used for decreasing LOQ
- Larger volume injections can be applied for increased sensitivity
- Fully green analytical method, evaporation steps avoided

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