Determination of Trace levels of PAHs in Food Grade Oils using Heart-cutting 2D-GC and Triple Quadrupole MS

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INTRODUCTION

Polycyclic Aromatic Hydrocarbons (PAH) can potentially be present in food grade oils (white mineral oil), that are used in food production. Quality control of these oils at ppm level can be done by spectroscopic techniques (UV), but for speciation and for accurate determination of the most toxic high molecular weight PAHs, a combination of chromatographic and spectroscopic techniques is needed.
For the determination of 4-5 ring PAHs at ppb levels, labor intensive sample preparation, often including column chromatography, is needed. Hereby the aromatics are isolated from the bulk of the apolar alkanes. Column chromatography has the advantage of high sample capacity, but solvent consumption and process time are high.

Can ppb levels of PAHs in mineral oil be detected if direct injection is used?

In this work, a comparison was made between GC-MS using a single quadrupole system, GC-MS/MS using a triple quadrupole system and GC-GC-MS/MS using heart-cutting two-dimensional GC.

SAMPLES

Two food grade oils with different boiling point/MW range were selected. The oils were diluted at 10% in iso-octane (1 g in 10 mL). For each oil, two samples spiked with PAHs at respectively 100 and 10 ppb (µg/kg) were prepared too:

OIL 1: C18-C32 range (elution window in method 1: 14-26 min)

OIL 2: C24-C40 range (elution window in method 1: 20-34 min)

For easy comparison, only the results for benzo(a)anthracene (BaA), chrysene (Chrys), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), indeno(123cd)pyrene (Ipyr) and benzoghi)perylene (BghiP) are discussed.

METHOD 1: GC-MSD

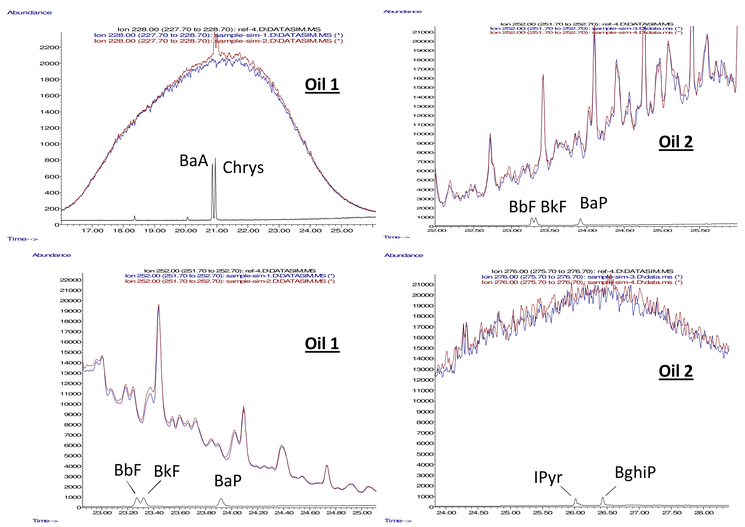
Direct injection of a 10% dilution, using 1/10 split ratio
with GC-MSD in SIM mode

Analytical parameters

Instrument: Agilent 7890A GC & 5975 MSD
Inlet: SSL at 280 °C, 1 µL, split ratio 10:1
Column: 30 m x 0.25 mm ID x 0.25 µm HP-5MS
Oven: 70 °C – 1 min – 10 °C/min – 325 °C – 8.5 min
MSD: SIM mode, ions 228, 252, 276 (50 ms dwell time)

Results

Below the extracted ion chromatograms (from SIM) are given for both oils. In each case, overlays are shown for respectievely the blank oil (blue trace), the oil spiked at 100 ppb (= 10 pg/µL in solution, red trace) and a 10 pg/µL reference standard (black trace). The PAHs cannot be detected in the oils due to the very high background.



METHOD 2: GC-MS/MS

Direct injection of a 10% dilution, using 1/10 split ratio
with GC-triple quadrupole MS in MRM mode

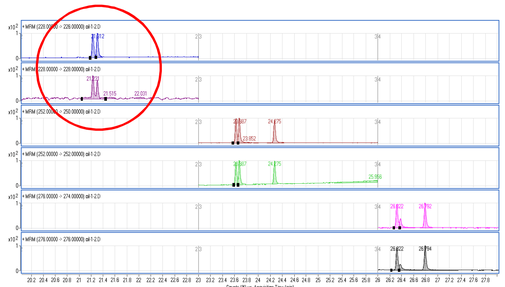
Analytical parameters

Instrument: Agilent 7890A GC & 7000A QQQ
Inlet: SSL at 280 °C, 1 µL, split ratio 10:1
Column: 30 m x 0.25 mm ID x 0.25 µm HP-5MS
Oven: 70 °C – 1 min – 10 °C/min – 325 °C – 8.5 min
MSD: MRM mode, 2 transitions per target compound

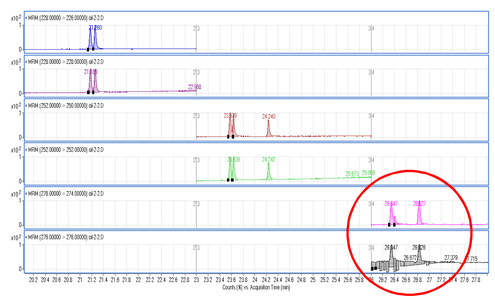
Results

Below the extracted ion chromatograms (from MRM) are given for respectievely oil 1 and oil 2 spiked at 100 ppb. All PAHs are detected. A higher background is observed for BaA/Chrys in oil 1 and Ipyr/BghiP in oil 2. LOD (S/N = 3) ≈ 15 ppb.

After several analyses of oil 2, source contamination was observed as well.



Oil 1
S/N = 2 for BaA/Chrys measured on sample spiked at 10 ppb level (228 – 226 transition)



Oil 2
S/N = 2 for IPyr/BghiP measured on sample spiked at 10 ppb level (276 – 274 transition)

METHOD 3: GC-GC-MS/MS

Direct injection of a 10% dilution, using 1/10 split ratio
with 2D-GC and MS/MS in MRM mode

Analytical parameters

Instrument: Agilent 7890A GC & 7000A QQQ with capillary flow Deans switch
Inlet: 1 µL, MMI in split mode
100 °C – 720 °C/min – 300 °C (5min)
^{1}D column: HP-5MS, 30 m x 0.25 mm x 0.25 µm – **boiling point separation**
^{1}D gas flow: 1.4 mL/min, helium, constant flow
GC oven: 80 °C (1 min) – 10 °C /min – 325 °C (30 min)
^{2}D column: DB-17MS, 30 m x 0.25 mm x 0.25 µm - **ΔRI ≈ 500**
^{2}D gas flow: 146 kPa, helium, constant pressure
LTM oven: 40º °C (27.8 min) – 20 °C/min – 250 °C – 7 °C /min – 320 °C – 5 °C /min – 330 °C
Heart-cuts: windows set at retention times measured at FID, +/- 0.1 min
Detection: FID (monitor detector) and MS (in MRM mode)
MRM: 2 transitions per target compound

Results

Below the extracted ion chromatograms (from MRM) are given for oil 1 and oil 2 spiked at **10 ppb**. Using 2D-GC-MS/MS, both the selectivity of the separation and detection are enhanced. **LOD (S/N = 3) < 5 ppb**. No source contamination was observed.