Vacuum Assisted Sorbent Extraction (VASE) and a Dual-Column Thermal Desorption Approach for GC-MS Analysis of Trace-Level Polycyclic Aromatic Hydrocarbons

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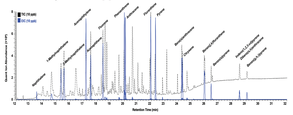
Overview:
- A new instrument design and methodology for trace-level headspace analysis of polycyclic aromatic hydrocarbons is described.
- Using a 1 mL sample of water, quantitation from 5 ppt – 10 ppb is demonstrated for a wide range of polycyclic aromatic hydrocarbons from Naphthalene (BP 218°C) to Benzo(g,h,i) pyrene (BP 550°C).

Recovery of a 10 ppb PAH mixture from 10 mL water

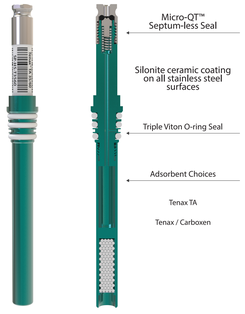


Introduction

- Since its conception in 1989 (Belardi & Pawliszyn, 1989), solid phase **headspace** (HS) sampling coupled to thermal desorption (TD) gas chromatography-mass spectrometry (GC-MS) has become a powerful technique for both targeted and untargeted chemical analysis of volatile and semi volatile organic compounds (VOCs & SVOCs).
- We recently developed a HS sampling approach, termed **vacuum assisted sorbent extraction** (VASE), in which the sample is positioned in a disposable sample vial and placed in a reduced pressure environment in the presence of a packed **headspace sorbent pen** (HSP).
- Following a controlled, diffusive headspace extraction with optional heat and agitation, the HSP containing adsorbed analytes is thermally desorbed directly onto the GC column via an inline sorbent pen thermal desorption unit (SPDU).
- Here we present a configuration and operating mode of the SPDU specifically designed for trace-level analysis of SVOCs, and we apply this operating mode in conjunction with VASE to analyze polycyclic aromatic hydrocarbons (PAHs) in water.
- In comparison to traditional operating modes of the SPDU, this dual-column setup enables simultaneous split-mode analysis of VOCs (which are unretained on column 1) and spitless analysis of SVOCs.
- Using 1 mL of sample volume, quantitation from 5 ppt – 10 ppb is demonstrated for a wide range of polycyclic aromatic hydrocarbons from Naphthalene (BP 218°C) to Benzo(g,h,i)pyrene (BP 550°C).

Methods

Headspace Sorbent Pen™



Schematic of the **Headspace Sorbent Pen (HSP)**, showing the Micro-QT vacuum seal and the internal sorbent bed. The HSP can be packed with a variety of sorbents, including multi-component beds of varying physical properties. For the purposes of this work, ~80 mg of Tenax TA (35/60 mesh) was used.

The Vacuum Assisted Sorbent Extraction Process

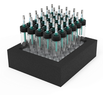
1 Vacuum Application

Step 1: The sample is placed in a vial and brought under vacuum using a 2-stage diaphragm pump. Sample vials from 5 - 1000 mL are available however the typical sample size is less than 1 mL.

2 Diffusive Headspace Extraction

Step 2: The samples are heated and agitated while under vacuum. Diffusive headspace extraction conditions promote adherence of analyte to the front of the sorbent bed, enabling flash desorption and narrow chromatographic peaks. Typical extractions require 1–24 h.

3 Water Management



Step 3: The sample vials are placed onto a chilled block to remove water from the sorbent bed and HSP.

4 Storage

Step 4: Extracted Sorbent Pens are placed in isolation sleeves, where they can typically be stored for up to 1 week prior to TD-GC-MS.

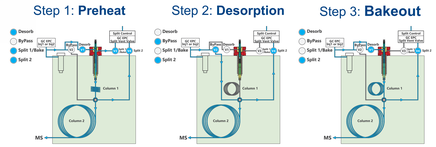
Thermal Desorption GC-MS

Sorbent Pen Thermal Desorption (SPDU) and **Sample Preparation Rail** (SPR) positioned on top of a Thermo GC-MS. The SPR transfers Sorbent Pens between the SPDU and air-tight isolation sleeves. The SPDU is connected directly to a capillary GC column held within the GC oven, which helps to minimize the flow path and mitigate analyte loss and/or carryover. Important optimization parameters include flow rate, preheat temperature & duration, desorption temperature & duration, and bakeout temperature & duration.

Split-Mode TD for VOCs & SVOCs

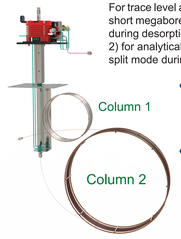
For analysis of the widest range of compounds (i.e., **VOCs & SVOCs**), the SPDU is arranged using an inert Silonite coated metal tubing (column 1) as an expansion loop and a capillary column (column 2) for analytical separation. The system is operated in split mode for adequate flow of desorption gas through the sorbent bed.

- During **preheat**, the **bypass** and **split 2** valves (**V2 & V4**) are open while the **desorb** and **split 1** valves (**V1 & V3**) are closed to allow heating without flow.
- During **desorption**, the **bypass** valve is closed and the **desorb** valve is opened so that the desorb gas can flow through the HSP and onto column 1 and column 2.
- During **bakeout**, the **split 1** valve is opened, enable effective flushing.



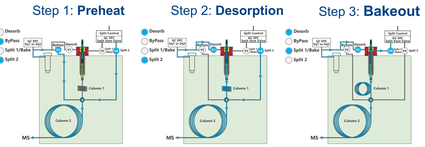
Thermal Desorption: 30 sec 70°C Preheat, 6 min 325°C Desorption, 21 min 325°C Bakeout
GC-MS: Thermo TRACE 1310 ISQ (50-300 amu), 15:1 Split, Entech inert expansion loop (Column 1), Agilent DB-5MS (30m×0.25mm×0.5µm) (Analytical Column)

Dual-Column Spitless TD for trace SVOCs



For trace level analysis of **SVOCs**, the SPDU is arranged using a short megabore capillary precolumn (column 1) to retain analytes during desorption and a more retentate capillary column (column 2) for analytical separation. The system is effectively operated in split mode during desorption and splitlessly during bakeout.

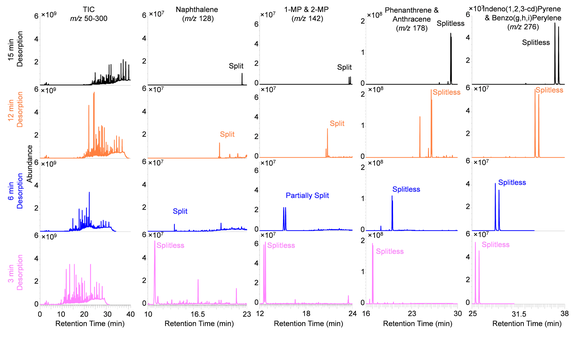
- During preheat, the **bypass** and **split 2** valves (**V2 & V4**) are open while the **desorb** and **split 1** valves (**V1 & V3**) are closed to allow heating without flow.
- During **desorption**, the **bypass** valve is closed and the desorb valve is opened so that the desorb gas can flow through the HSP and onto column 1. SVOCs are retained on column 1 and lighter compounds are split at the oven cross.
- During **bakeout**, the **split 1** valve is opened and the **split 2** valve is closed to allow SVOCs to pass splitlessly onto the analytical column.



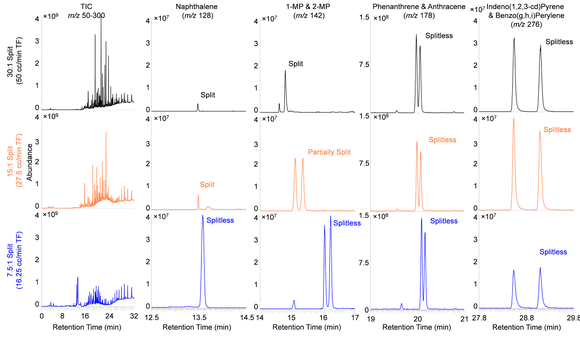
Thermal Desorption: 30 sec 70°C Preheat, 6 min 325°C Desorption, 21 min 325°C Bakeout
GC-MS: Thermo TRACE 1310 ISQ (50-300 amu), 15:1 Split, Quadrex UAC-1MS/HT (7m×0.53mm×0.25µm) (Column 1), Agilent DB-5MS (30m×0.25mm×0.5µm) (Analytical Column)

Method Development: Adjusting the Split/Splitless Cutoff

Variation in Desorption Time

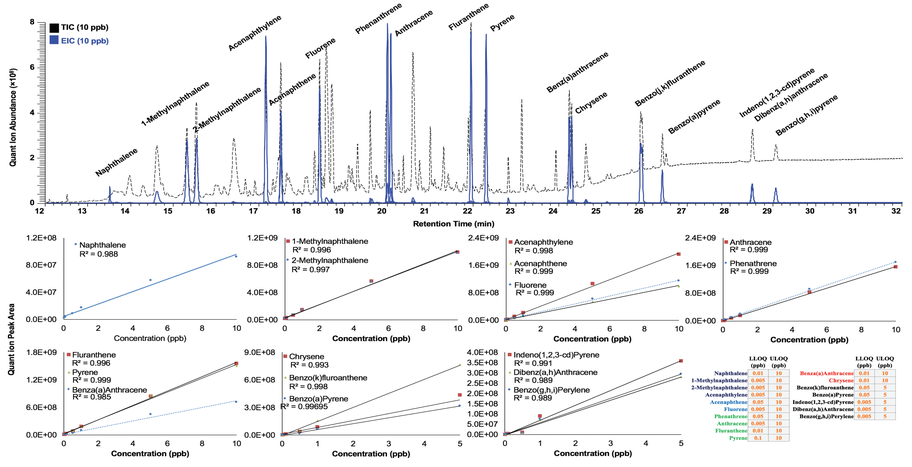


Variation in Desorption Flow



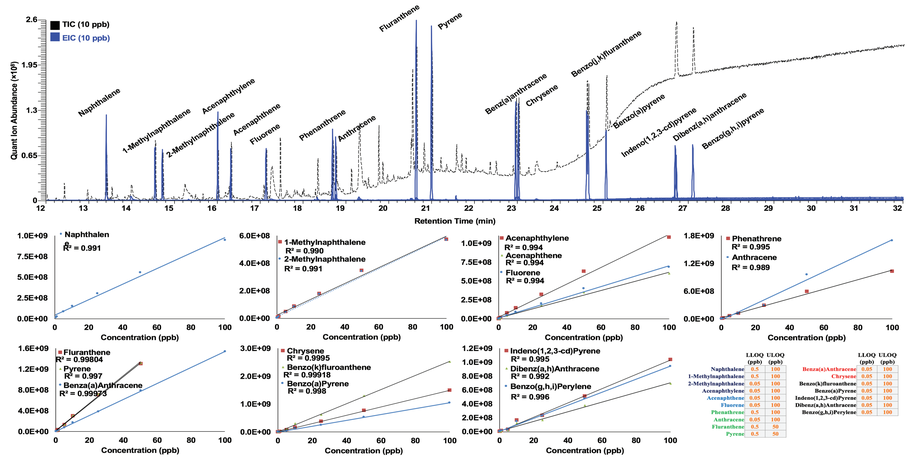
Results: Quantitative Recovery of Parts-Per-Trillion Level 6-Ring PAHs from 1 mL Water

Quantitative Recovery of PAHs from Water Using VASE & Splitless-Mode TD-GC-MS



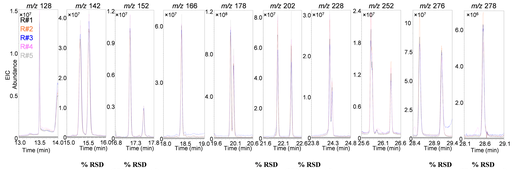
	LLOQ (ppb)	ULOQ (ppb)
Naphthalene	0.01	10
1-Methylnaphthalene	0.005	10
2-Methylnaphthalene	0.005	10
Acenaphthylene	0.005	10
Acenaphthene	0.05	10
Fluorene	0.005	10
Phenanthrene	0.05	10
Anthracene	0.005	10
Fluoranthene	0.01	10
Pyrene	0.1	10
Benzo(a)Anthracene	0.01	10
Chrysene	0.01	10
Benzo(k)fluoranthene	0.05	5
Benzo(a)Pyrene	0.05	5
Indeno(1,2,3-cd)Pyrene	0.005	5
Dibenz(a,h)Anthracene	0.005	5
Benzo(g,h,i)Perylene	0.005	5

Quantitative Recovery of PAHs from Water Using VASE & Split-Mode TD-GC-MS



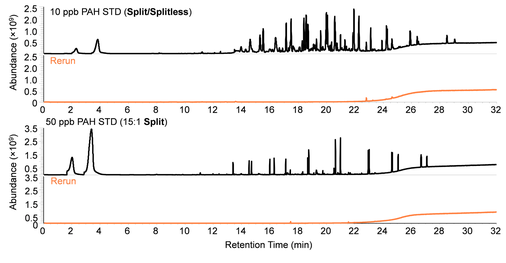
	LLOQ (ppb)	ULOQ (ppb)
Naphthalene	0.5	100
1-Methylnaphthalene	0.5	100
2-Methylnaphthalene	0.05	100
Acenaphthylene	0.05	100
Acenaphthene	0.05	100
Fluorene	0.05	100
Phenanthrene	0.5	100
Anthracene	0.05	100
Fluoranthene	0.5	50
Pyrene	0.5	50
Benza(a)Anthracene	0.05	100
Chrysene	0.05	100
Benzo(k)fluoranthene	0.05	100
Benzo(a)Pyrene	0.05	100
Indeno(1,2,3-cd)Pyrene	0.05	100
Dibenz(a,h)Anthracene	0.05	100
Benzo(g,h,i)Perylene	0.05	100

Reproducibility (5 ppb replicates, n = 5)



	% RSD (Raw)	% RSD (IS Normalized)
Naphthalene	4.4%	1.9%
1-Methylnaphthalene	5.1%	1.8%
2-Methylnaphthalene	6.8%	1.4%
Acenaphthylene	5.6%	0.8%
Acenaphthene	5.6%	2.1%
Fluorene	6.7%	2.9%
Phenanthrene	6.1%	6.1%
Anthracene	6.8%	1.1%
Flouranthene	8.9%	3.8%
Pyrene	15%	6.8%
Benza(a)Anthracene	10%	3.0%
Chrysene	9.7%	1.3%
Benzo(k)fluoranthene	11%	5.7%
Benzo(a)Pyrene	12%	6.7%
Indeno(1,2,3-cd)Pyrene	9.9%	6.6%
Dibenz(a,h)Anthracene	9.3%	8.1%
Benzo(g,h,i)Perylene	11%	7.9%

Carryover: HSP Reruns in Split and Splitless Modes



Conclusions

- A dual column split/splitless operation of the sorbent pen thermal desorption unit (SPDU) is described.
- The split/splitless operating mode enables lower limits of detection for SVOCs, with a cutoff point dependent on desorption time, desorption flow, and the physical properties of the pre-column.
- In combination with VASE, limits of detection as low as 5 ppt are demonstrate for PAHs extracted from 1 mL of water.
- With 5 technical replicates, RSDs of less than 10% are demonstrated for the full range of standards examined (BP 218°C to 550°C).

References

R.G. Belardi & J. Pawliszyn, "The application of chemically modified fused silica fibers in the extraction of organics from water matrix samples and their rapid transfer to capillary columns", Water Pollut. Res. J. Can. 24 (1989) 179-191

Acknowledgements

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