Trace-Level Quantification of SVOCs in Water via Vacuum Assisted Sorbent Extraction (VASE) Thermal Desorption-GC-MS

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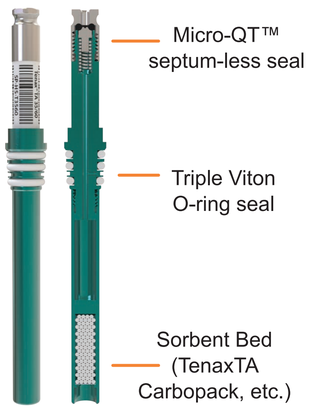
Overview

- Current analytical methods for evaluating **volatile and semi volatile organic compounds (VOCs & SVOCs)** in water often require large sample volumes (1 L or more), are labor intensive, and rely upon liquid-liquid extraction into organic solvents.
- Here we present a sensitive, solvent-free method – termed **vacuum assisted sorbent extraction (VASE)** – for extraction and pre-concentration of VOCs and SVOCs in preparation for thermal desorption-GC-MS.
- In VASE, the sample (often 1 mL or less for water) is evacuated in the presence of a **headspace sorbent pen (HSP)**, which is a vacuum-tight cartridge containing sorbent. In combination with optional heat and agitation, the static reduced pressure environment promotes compounds into the headspace for adherence to an internal sorbent bed.
- Here we demonstrate the application of VASE for extraction and quantitation of several **water pollutants routinely analyzed by EPA method 8270**. Compounds with boiling points ranging from 80°C to over 550°C are examined, including 2-6-ring polyaromatic hydrocarbons, phenols, pesticides, chlorinated hydrocarbons, and disinfection by-products.

Sorbent Pens & Vacuum Assisted Sorbent Extraction (VASE)

Headspace Sorbent Pen



1 Sorbent Pen Insertion and Vacuum Application

2 Parallel Extraction with Optional Heat and Agitation

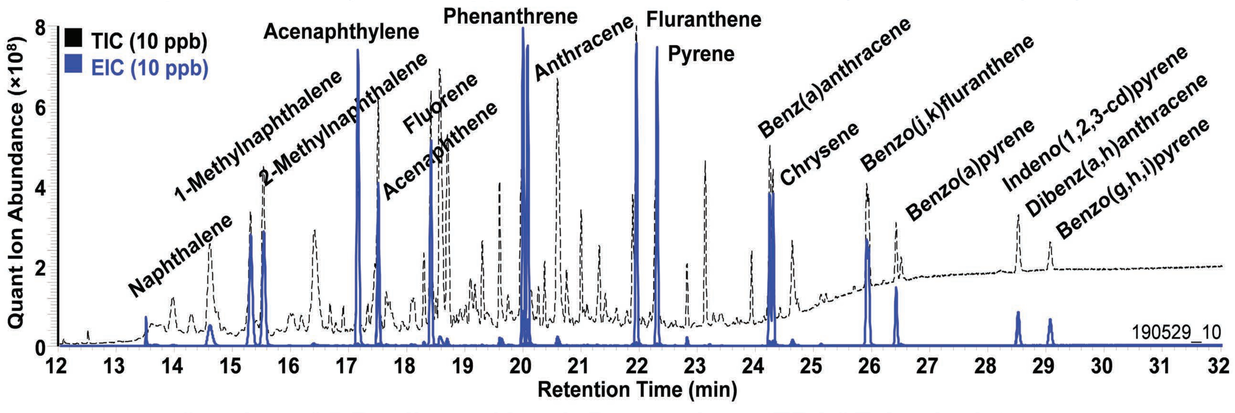
3 Water Management via Cold Block Condensation

4 Safe Storage of Extracted Sorbent Pens in Air-Tight Isolation Sleeves

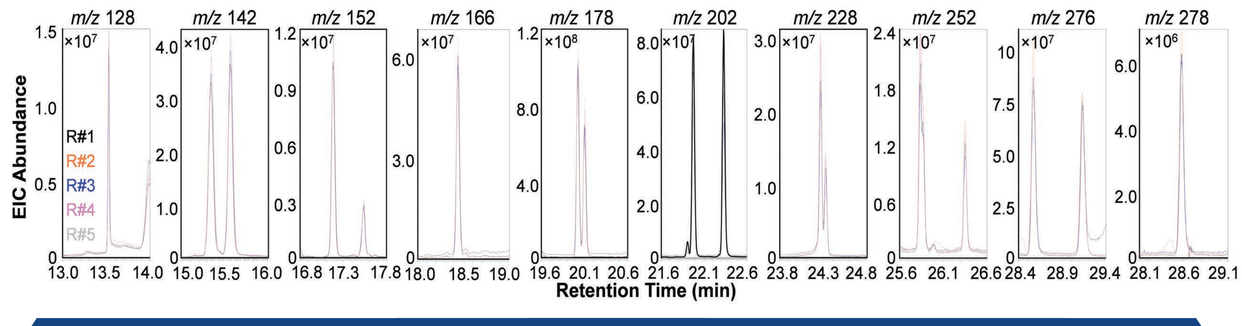
5 Automated Thermal Desorption of Sorbent Pens

Polycyclic Aromatic Hydrocarbons (PAHs)

Composite Overlay of a 10 ppb PAH Standard Mixture (TRACE Analysis)



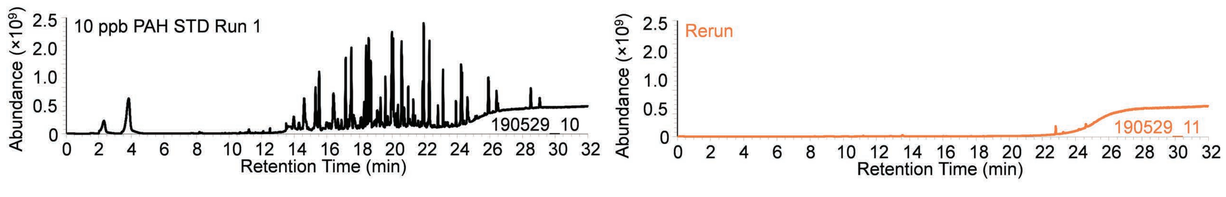
Overlay of 5 Replicate 10 ppb Desorptions (TRACE Analysis)



Analyte	BP (°C)	Q Ion	EPA LOQ* (ng/L)	Linear Range (ng/L) TRACE Analysis	Linear Range (ng/L) Split Analysis	R²	RSD (Raw)	RSD (IS Normalized)
Naphthalene	218	128	10, 000	10 – 10,000	500 – 100,000	0.998	4.4%	1.9%
1-Methylnaphthalene	240	142	NA	5 – 10,000	500 – 100,000	0.996	5.1%	1.8%
2-Methylnaphthalene	241	142	NA	5 – 10,000	50 – 100,000	0.997	6.8%	1.4%
Acenaphthylene	280	152	10, 000	5 – 10,000	50 – 100,000	0.998	5.6%	0.8%
Acenaphthene	279	154	10, 000	50 – 10,000	50 – 100,000	0.999	5.6%	2.1%
Fluorene	298	166	10, 000	5 – 10,000	50 – 100,000	0.999	6.7%	2.9%
Phenathrene	336	178	10, 000	50 – 10,000	500 – 100,000	0.999	4.1%	6.1%
Anthracene	340	178	10, 000	5 – 10,000	50 – 100,000	0.999	6.8%	1.1%
Fluranthene	384	202	10, 000	10 – 10,000	500 – 50,000	0.996	8.9%	3.8%
Pyrene	384	202	10, 000	100 – 10,000	500 – 50,000	0.999	15%	6.8%
Benza(a)Anthracene	437	228	10, 000	10 – 10,000	50 – 100,000	0.985	10%	3.0%
Chrysene	448	228	10, 000	10 – 10,000	50 – 100,000	0.993	9.7%	1.3%
Benzo(k)fluroanthene	481	252	10, 000	50 – 5,000	50 – 100,000	0.998	11%	5.7%
Benzo(a)Pyrene	495	252	10, 000	50 – 5,000	50 – 100,000	0.997	12%	6.7%
Indeno(1,2,3-cd)Pyrene	539	276	10, 000	5 – 5,000	50 – 100,000	0.991	9.9%	6.6%
Dibenz(a,h)anthracene	524	278	10, 000	5 – 5,000	50 – 100,000	0.989	9.3%	8.1%
Benzo(g,h,i)Perylene	550	276	10, 000	5 – 5,000	50 – 100,000	0.989	11%	7.9%

*Data from Table 2 Example lower limits of quantitation for semivolatile organics, EPA Method 8270D, Revision 4, February 2007.

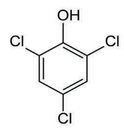
Clean HSP After Desorption Enables Repeat Sampling Without Additional Cleanup Step



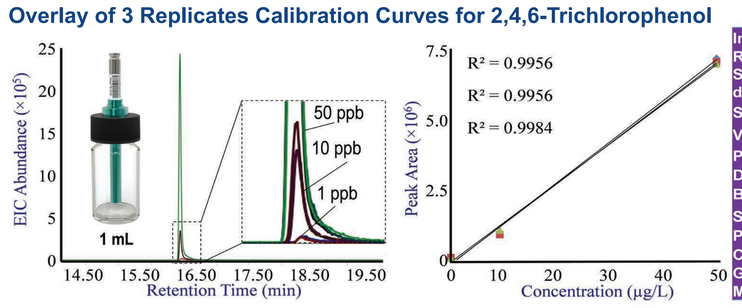
Phenols

Analyte	BP (°C)	Q Ion	EPA LOQ (µg/L)*	Linear Range (µg/L)	R²*
Phenol	182	94	10	1-50	0.997
2-Chlorophenol	175	128	10	1-50	0.998
o-Cresol	191	108	NA	1-50	0.994
m/p-Cresol	202	107	NA	1-50	1.000
2,4-Dimethylphenol	212	122	10	1-50	0.997
2,4-Dichlorophenol	210	162	10	1-50	0.995
2,6-Dichlorophenol	220	162	10	1-50	1.000
4-Chloro-3-methylphenol	235	107	20	1-50	0.995
2,4,6-Trichlorophenol	**246**	**196**	**10**	**1-50**	**0.997**
2,4,5-Trichlorophenol	253	196	10	1-50	1.000
2,3,4,6-Tetrachlorophenol	164	232	10	1-50	0.998
Pentachlorophenol	310	266	50	1-50	0.989
Dinoseb	332	211	20	1-50	0.994

*Data from Table 2 Example lower limits of quantitation for semivolatile organics, EPA Method 8270D, Revision 4, February 2007.
*R² refers to average R² value of n=3, 3-point calibration curves.



Overlay of 3 Replicates Calibration Curves for 2,4,6-Trichlorophenol



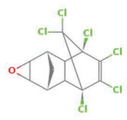
VASE, TD, and GC-MS Conditions

Instrument	5800 SPDU Trace Analysis Procedure
Run date	12-Mar-19
Sample description	Phenols, AccuStandard
Sample Quantity	**1 mL DI water**
VASE conditions	20 mL vial, 5% NA_2SO_4, pH 2, 70ºC, 250 rpm, 8 hr
Preheat	30 sec at 70ºC
Desorption	3 min at 300ºC
Bake-out	19 min at 280ºC
Split Mode	Splitless with 20 cc/min total flow
Precolumn	DB-1: 5 m x 0.530 mm ID x 0.250 µm
Column	DB-5MS UI: 30 m x 0.250 mm ID x 0.50 µm
GC-MS	Agilent 7890B GC; 5975C MS
MS Operation	Full Scan 33-450, >3 scans/sec

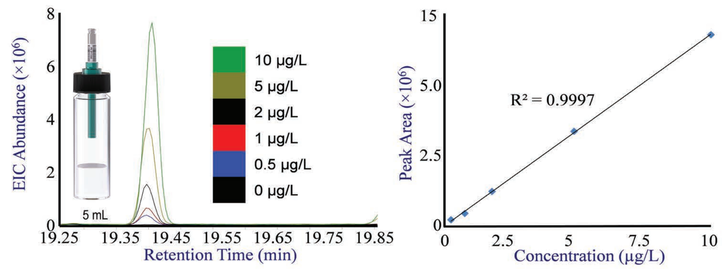
Pesticides

Analyte	BP (°C)	Q Ion	Linear Range (µg/L)	R²*
Aldrin	145	263	0.5-10	0.998
4,4'-DDD	193	165	0.5-10	0.993
a-BHC	288	219	0.5-10	0.999
b-BHC	288	109	0.5-10	0.999
4, 4'-DDE	336	318	0.5-10	0.998
Dieldrin	**385**	**79**	**0.5-10**	**1.000**
Heptachlor	NA	272	0.5-10	0.994
Heptachlor Epoxide	NA	353	0.5-10	0.999

*R² refers to R² value of n=1, 5-point calibration curves.



Calibration Curve for Dieldrin



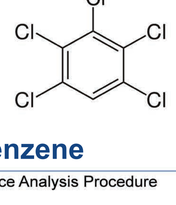
VASE, TD, and GC-MS Conditions

Instrument:	5800 SPDU Trace Analysis Procedure
Run date:	1-Sep-17
Sample description:	Organochlorine Pesticides, AccuStandard
Sample quantity	**5 mL tap water**
VASE conditions	40 mL vial, 3% NA2SO4, 16 hr at 70ºC
Preheat:	1 min at 260ºC
Desorption:	3 min at 275ºC
Bake-out:	18 min at 260ºC
Split mode:	Splitless with 9cc/min total flow
Precolumn:	DB-1: 2m x 0.530mm ID x 0.150 µm
Column:	DB-5MS UI: 30m x 0.250mm ID x 0.50µm
GC-MS:	Agilent 7890B GC; 5977A MS
MS Operation:	Full Scan 33-450, >3 scans/sec

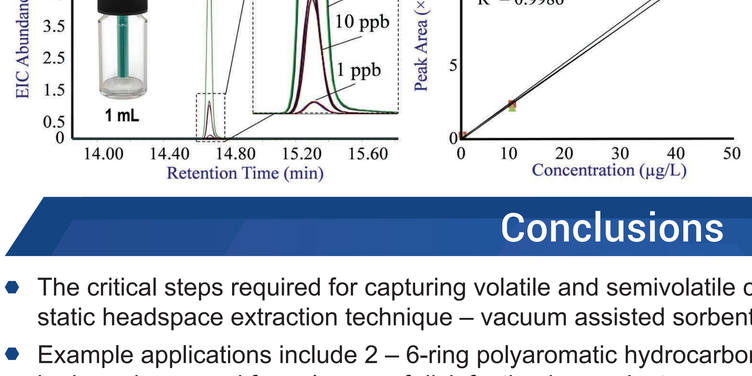
Chlorinated Hydrocarbons

Analyte	BP (°C)	Q Ion	EPA LOQ (µg/L)*	Linear Range (µg/L)	R²**
Pentachloroethane	162	167	10	1-50	0.998
1,2-Dichlorobenzene	180	146	10	1-50	0.999
1,3-Dichlorobenzene	173	146	10	1-50	0.999
1,4-Dichlorobenzene	174	146	10	1-50	0.999
Hexachloroethane	187	117	10	1-50	0.999
1,2,4-Trichlorobenzene	214	180	10	1-50	0.999
Hexachloropropene	210	213	10	1-50	0.997
Hexachlorobutadiene	215	225	10	1-50	0.999
1,2,4,5-Tetrachlorobenzene	245	216	10	1-50	0.999
Hexachlorocyclopentadiene	239	237	10	1-50	0.990
2-Chloronaphthalene	255	127	10	1-50	0.999
Pentachlorobenzene	**277**	**248**	**10**	**1-50**	**0.999**
Hexachlorobenzene	322	286	10	1-50	0.999

*Data from Table 2 Example lower limits of quantitation for semivolatile organics, EPA Method 8270D, Revision 4, February 2007.
*R² refers to average R² value of n=3, 3-point calibration curves.



Overlay of 3 Replicates Calibration Curves for Pentachlorobenzene

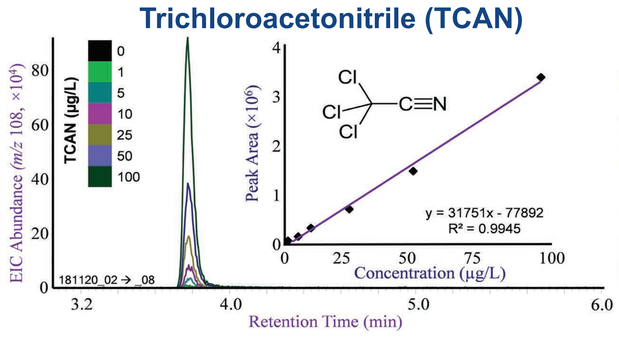


VASE, TD, and GC-MS Conditions

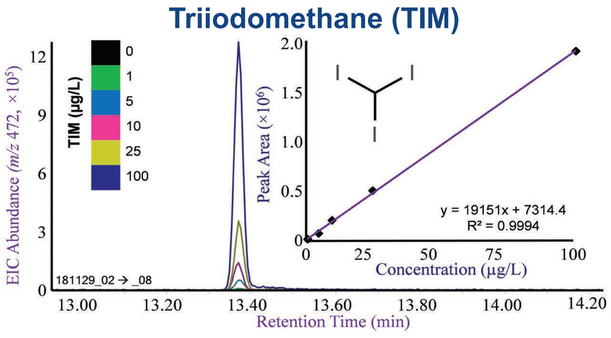
Instrument	5800 SPDU Trace Analysis Procedure
Run date	5-Mar-19
Sample description	Chlorinated hydrocarbons, AccuStandard
Sample quantity	**1 mL DI water**
VASE conditions	20 mL vial, 5% NA2SO4, 70ºC, 250rpm, 16 hr
Preheat	30 sec at 70ºC
Desorption	3 min at 300ºC
Bake-out	19 min at 280ºC
Split Mode	Splitless with 12cc/min total flow
Precolumn	DB-1: 5m x 0.530mm ID x 0.250 µm
Column	DB-5MS UI: 30m x 0.250mm ID x 0.50µm
GC-MS	Agilent 7890B GC; 5975C MS
MS Operation	Full Scan 33-450, >3 scans/sec

Disinfectant By-products (DBPs)

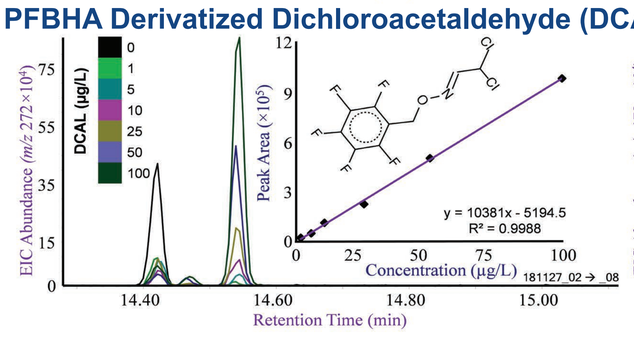
Trichloroacetonitrile (TCAN)



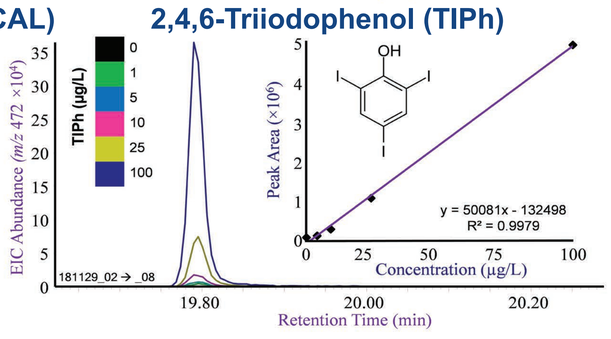
Triiodomethane (TIM)



PFBHA Derivatized Dichloroacetaldehyde (DCAL)



2,4,6-Triiodophenol (TIPh)



Conclusions

- The critical steps required for capturing volatile and semivolatile compounds from water via a reduced-pressure static headspace extraction technique – vacuum assisted sorbent extraction (VASE) – are shown.
- Example applications include 2 – 6-ring polyaromatic hydrocarbons, phenols, pesticides, chlorinated hydrocarbons, and four classes of disinfection by-products.
- Using 1 mL of water adulterated with PAHs, LODs as low as 5 ng/L and RSDs better than 10% are obtained, demonstrating the low detection limits and exceptional repeatability of VASE.

References

U.S. EPA. 2014. "Method 8270E (SW-846): Semivolatile Organic Compounds by Gas Chromatography/ Mass Spectrometry (GC/MS)," Washington, DC.

Acknowledgments

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