Solvent-Free Extraction Technique for Determination of Semi-Volatile Organic Compounds in Water Samples by EPA Method 8270

Application Note:

V-3742-01

Authors

Daniel B. Cardin
Victoria L. Noad
Entech Instruments
Simi Valley, CA 93065

Overview

The need for accurate monitoring of semi-volatile organic compounds (SVOCs) in water samples using methods such as US EPA Method 8270 continues to grow in importance as the comprehension of their adverse effects on human health evolves. Improvements in analytical technology for accurate determination down to sub-PPB levels is critical to obtain the most comprehensive monitoring possible. Current techniques for extraction of base/neutral/acid SVOCs include solvent extraction and separatory funnel extraction, however these methods require many steps and environmentally unfriendly solvents. Additionally, there are many analytical challenges due to matrix interferences, contamination, and the broad range of chemical properties.

A new solvent-free automated technique for extracting SVOCs in water using Vacuum Assisted Sorbent Extraction (VASE) paired with GCMS is presented. VASE performs an in-vial extraction for gas, liquid, and solid samples followed by direct thermal desorption into the GC. VASE is a powerful extraction technique which places a sample vial under vacuum in the presence of a 70mg adsorbent cartridge (Sorbent Pen) to effect near exhaustive extractions of GC compatible compounds. VASE allows reliable extraction with minimal matrix effects due to the high phase ratio and surface area of the adsorbent. After the vacuum source is removed, the vial remains under vacuum causing transfer to the adsorbent to occur faster than at atmospheric or higher pressures. Repeated heating and cooling of the sample creates an evaporation and condensation action in a closed system which effectively transfers SVOCs and recovery surrogate standards onto the adsorbent. Sample injection is performed with a thermal desorption unit fitted into a GC injection port. Extracted compounds remain near the front of the adsorbent ensuring quantitative recovery.

This paper pairs the VASE technique with a newly introduced way to accelerate the transmission of heavy organic compounds into the gas phase during vacuum extraction. Using a new process called “Pulsed Vacuum Assisted Sorbent Extraction", or Pulsed VASE, a water sample is heated and cooled during vacuum extraction to cycle between evaporating some, most, or all of the water off of the bottom of a 20 or 40mL vial with condensation then occurring on the sides or top of the vial, followed by re-condensation of the water sample on the bottom of the vial by cooling it back down. Repeating this process on up to 30 sample vials simultaneously ensures the complete or near complete transfer of very heavy or highly polar

Headspace Analysis

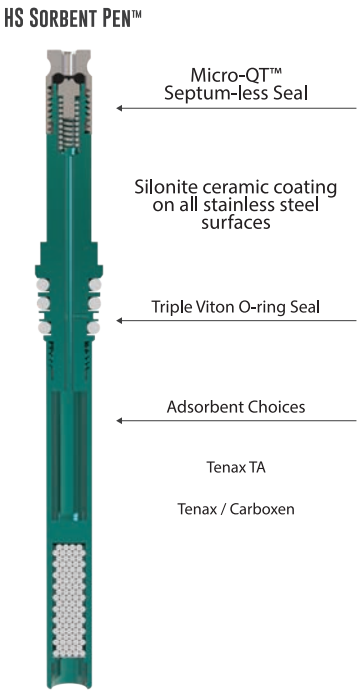


Figure 1 - The adsorbent inside the Headspace Sorbent Pen is positioned starting 3mm recessed from the bottom to provide protection from aerosols generated during rapid agitation. A hole between the bottom two O-rings allows the desorb gas to back-desorb the extracted sample into the GC when an upstream valve is turned on.

SVOCs to the headspace and then to the adsorbent in the Sorbent Pen. VASE recoveries consistent and SVOC extraction times are reduced. After the final cycle, the bottom of the vial is cooled for a longer period to ensure that no liquid water remains inside of the Sorbent Pen which might otherwise affect the subsequent GCMS analysis.

Calibration curves for SVOCs such as pesticides, active compounds found in cannabis, and polycyclic aromatic hydrocarbons (PAHs) are presented. Data reveals both the reproducibility and lack of carryover achieved by this new technique resulting in accurate analysis of SVOCs.

Introduction

0ver the last 30 years, a range of sample preparation techniques have been developed to selectively extract and enrich volatile organic compounds (VOCs) from gas, liquid, and solid samples to improve sensitivity while eliminating matrix related interferences. Headspace techniques have been successful at eliminating most of the non-GC compatible matrix to achieve either qualitative or quantitative analysis of VOCs. Compounds in the SVOC range boiling from 230°C to 500°C have not been successfully analyzed using headspace techniques, yet full immersion techniques using polydimethylsiloxane (PDMS) to extract the heavier compounds have resulted in successful analyses. Although solvent extraction has been the mainstay for extracting heavy volatile and semi-volatile compounds for gas chromatography (GC) analysis, compounds incompatible with GC can still be extracted requiring additional clean up stages to prevent both column contamination and the creation of breakdown products from the introduction of non-volatile or thermally labile chemicals. This is generally labor intensive and can provide highly variable results when multiple cleanup steps are required due to the increased potential for errors. It is in the interest of many laboratories world-wide to utilize new analytical techniques which minimize the use of solvents and sample preparation steps without comprising the analytical results in terms of accuracy, sensitivity, and robustness.

A new solvent-free automated technique for extracting SVOCs in water using Vacuum Assisted Sorbent Extraction (VASE) paired with GCMS is presented. VASE performs an in-vial extraction for gas, liquid, and solid samples followed by direct thermal desorption into the GC.

Samples are analyzed using a unique dual column injector installed onto the GC or GCMS called the 5800 Sorbent Pen Desorption Unit (SPDU), which can be used in either split or splitless modes depending on whether high or trace-level analysis was to be performed. The 5800 SPDU allows a precolumn to be plumbed in prior to a second split location to allow faster desorptions while still achieving a splitless injection of all compounds retained by the precolumn.

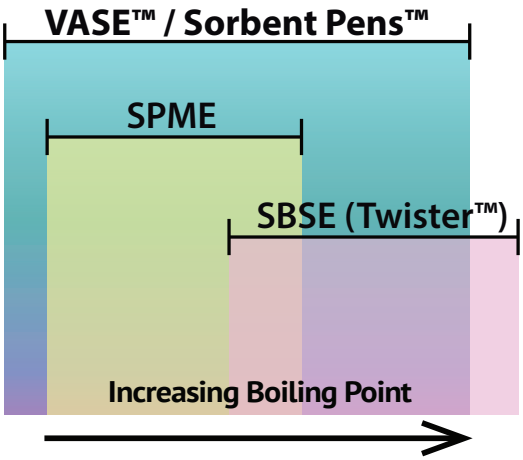


Figure 2 - Using Sorbent Pens, the VASE technique recovers compounds starting even lighter than SPME and out to compounds nearly as heavy as those recovered by SBSE. Most applications achieved by SPME or SBSE can be more easily performed with a wider compound range, higher sensitivity, and better reproducibility using VASE.

VASE Advantages Include:

- Solvent-free extractions with and without heating
- Amount of phase is increased approximately 150 times relative to SPME
- Ability to perform exhaustive extractions
- Sample extracts much faster under vacuum than while at atmospheric pressure, enhancing the recovery of low volatility compounds
- Static headspace technique allows analytes to diffuse onto and collect at front of adsorbent bed allowing recovery of heavier compounds while eliminating carryover and channeling
- Not in contact with matrix, fewer artifacts created and longer adsorbent life time
- Cost effective, simple to use and maintainable by lab chemist
- Manual or automated

Dual-Column 5800 SPDU Trace Analysis Procedure

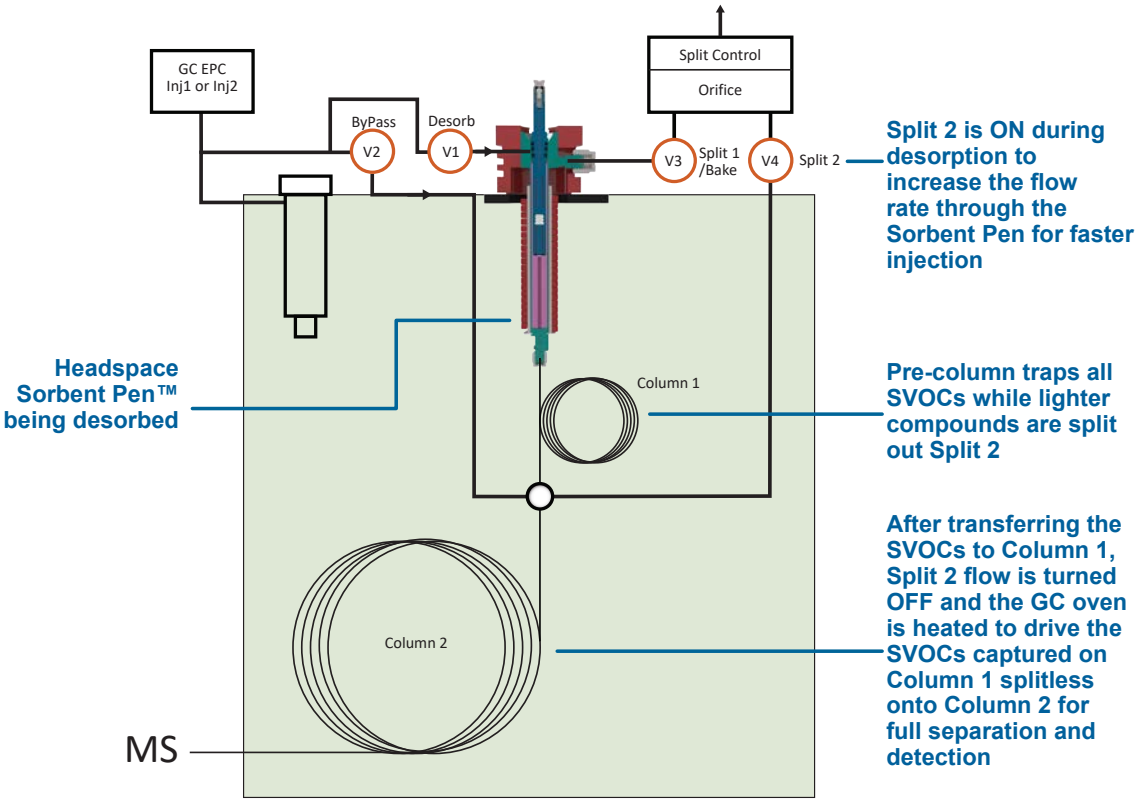


Figure 3 - 5800 Sorbent Pen Desorption Unit (SPDU) diagram. Using a series of two columns in the flow path after thermal desorption, with forward and backward flushing capabilities for the first column, a wide range of applications can be performed to analyze compounds ranging in boiling points from -100°C to 500°C. Water management is performed through condensation, splitting, and back flushing. A series of 4 valves controls each method process and the location of each valve is shown: Desorb, Valve 1 (V1); Bypass, Valve 2 (V2), Split 1/Bake, Valve 3 (V3), and Split 2, Valve 4 (V4). The Trace Analysis Procedure is outlined here.

Figure 4 - A 5800 Sorbent Pen Desorption Unit (SPDU) and Entech Sample Preparation Rail (SPR) Autosampler installed onto an Agilent GCMS. After sample extraction via Pulsed VASE, the fully automated SPR transfers the Sorbent Pens from the vials in the Pulsed VASE tray to isolation sleeves prior to transferring each Sorbent Pen in sequence to the 5800 SPDU for direct thermal desorption onto the GC column.

Sample Preparation

The combined approach of using greater amounts of phase, vacuum to speed up the extraction process, and a unique GC injector/thermal desorption unit to introduce the extracted sample quantitatively makes VASE distinctively capable of recovering both VOCs and SVOCs from gas, liquid, or solid samples with boiling points from -50°C to over 500°C. However, when combined with another sample preparation technique, called Pulsed Vacuum Assisted Sorbent Extraction, or Pulsed VASE, this process can be accelerated significantly for SVOCs. Instead of allowing the adsorbent and sample come to equilibrium at room temperature or with the traditional addition of heat and RPM agitation, the sample can be heated and cooled repeatedly causing evaporation and re-condensation to occur in cycles, thereby maximizing the surface area of the sample to ensure all target compounds are forced into the headspace where they can diffuse onto the adsorbent. In many cases, such as water analysis, the heating of the sample does not alter the sample as it would with natural products which should not be heated over 40°C. By heating the sample and creating a boiling effect, heavier or very polar compounds can be delivered more effectively into the gas phase. A slow heating creates a carrier gas effect right at the liquid/headspace boundary as water vaporizes, carrying low volatility compounds into the headspace and towards the adsorbent where they can be collected more efficiently. Once maximum temperature is achieved, the boiling stops, and at the increased pressures, the diffusion rates are slower. By quickly lowering the temperature of the bottom sample while keeping the headspace at least 20°C warmer, excess water condenses, and the vacuum is again restored, allowing the entire evaporation/condensation process to be performed repeatedly in cycles. A final cooling of the bottom of the vial further drives out any excess water back into the aqueous matrix at the bottom of the vial. Any remaining gas phase water is effectively managed by using an initial split injection during desorption.

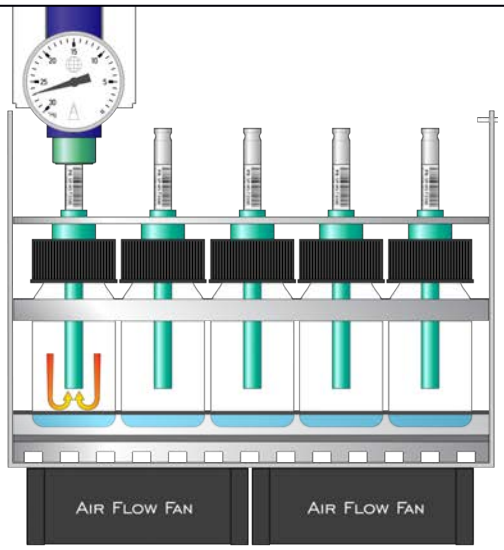
Steps of Pulsed Vacuum Assisted Sorbent Extraction (Pulsed VASE)

VASE Vial Evacuation

Evacuation of the vial containing a 1mL water sample begins to boil at room temperature as the vacuum in the vial drops below 29" Hg.

This increases target compound volatility and diffusion rates to the adsorbent.

1



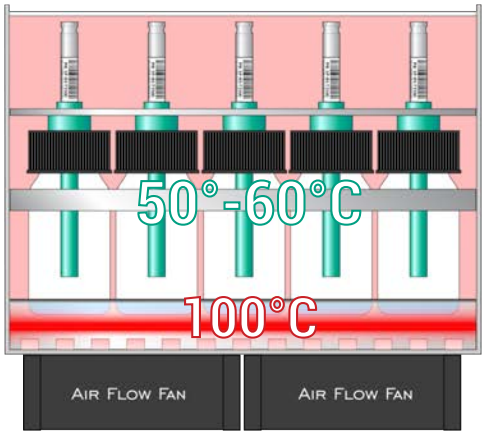
Slow Boil in Closed System

Heat Applied to Bottom

Sample comes to a slow boil by heating the bottom of the vials to approximately 100°C.

The upper portion of the vial containing the adsorbent remains between 50°-60°C.

2



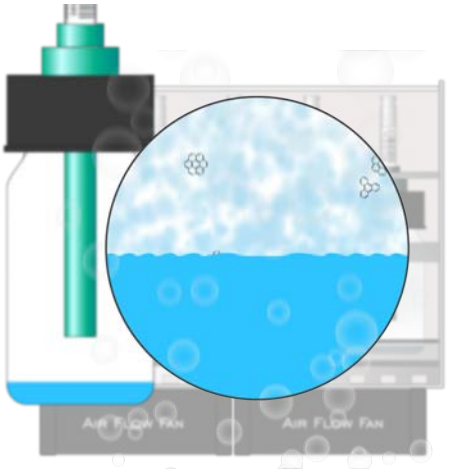
Differential Heating

Carrier Gas Effect

By slowly heating the bottom of the sample and keeping the upper portion of the vial between 50°-60°C, a carrier gas effect is created at the liquid/headspace boundary.

This carries low volatility or very polar compounds further into the headspace and towards the adsorbent where they may be collected faster.

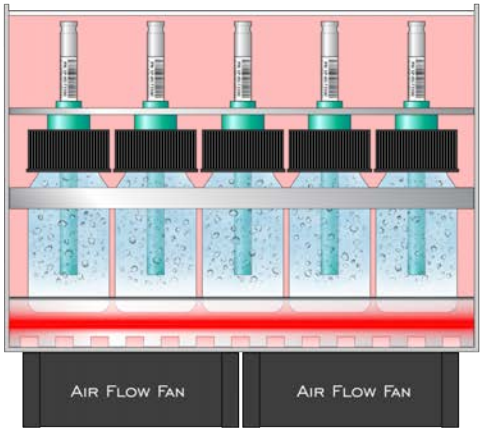
3



Sample Evaporation

Vaporization and condensation onto the cooler section of the vial surface maximizes the opportunity for transfer of SVOCs into the headspace and onto the adsorbent.

4



Recondensation To The Bottom of Vial

Cooling the bottom of the vial to room temperature (about 30°C), causes the excess water to condense back down to the bottom of the vial. Initial vacuum is again restored.

5

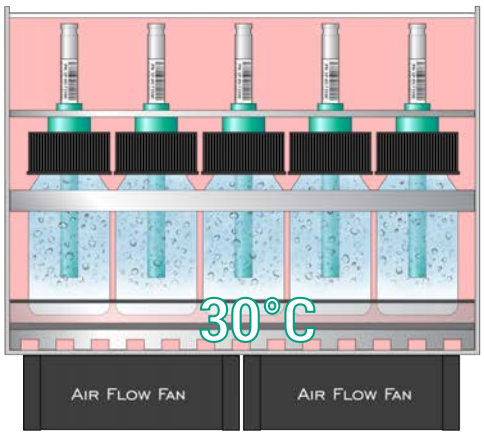


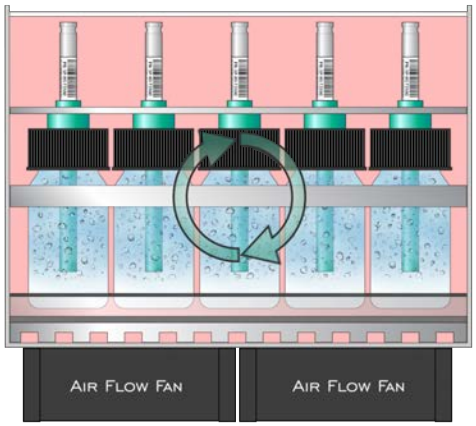
Figure 5 - An outline of the Pulsed Vacuum Assisted Sorbent Extraction (Pulsed VASE) automated sample agitation process. Repeated heating and cooling of the sample creates cycles of fully automated agitation by boiling and condensing the sample matrix in a closed system which effectively transfers even the heaviest SVOCs and recovery surrogate standards into the adsorbent. A final cooling further drives out any excess water back into the aqueous matrix at the bottom of the vial. Any remaining gas phase water is further managed by using an initial split injection during desorption. After desorption, the Split 2 valve closes and compounds C8 and above are splitlessly transferred onto the analytical column as the oven temperature ramps up for full separation and trace level detection.

Heating & Cooling Cycle Repeats

The entire sample evaporation and condensation agitation cycle repeats based on method specifications, enabling automated exhaustive recovery of SVOCs for quantitative analysis.

A final cooling of the bottom of the vial while the top remains at 70°C further condenses out any excess water back into the aqueous matrix at the bottom of the vial for water management before injection into the water sensitive GCMS.

6

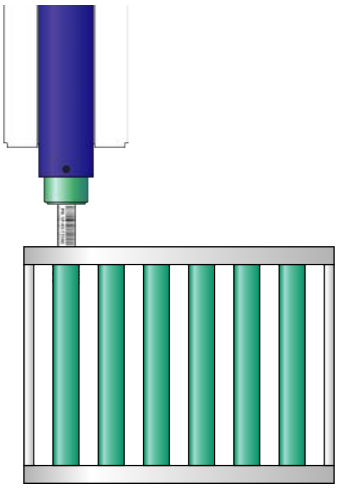


Transfer of Pens to ISO Tray

Fully automated, the Sample Preparation Rail (SPR) transfers the Sorbent Pens™ into the isolation tray prior to desorption.

Utilizing the Trace Analysis Procedure (TAPs) and the Entech 5800 SPDU, compounds C8 and above may be injected splitless for quantitative trace level analysis.

7

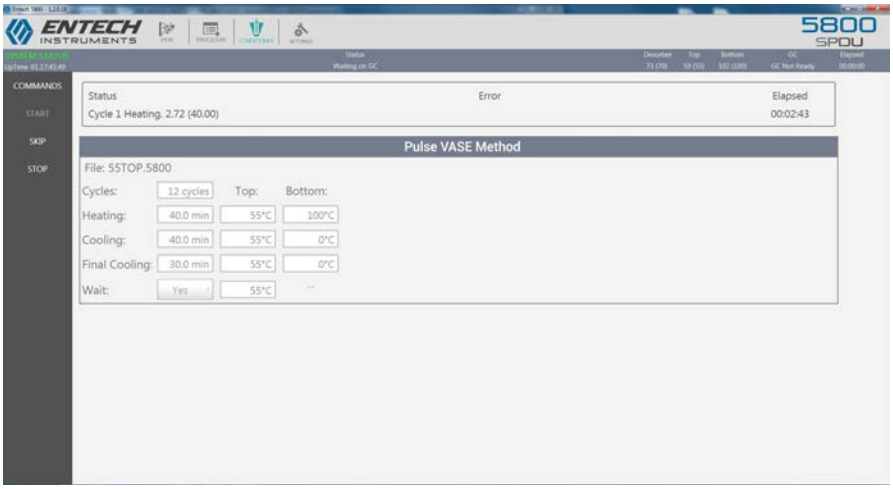


Methods

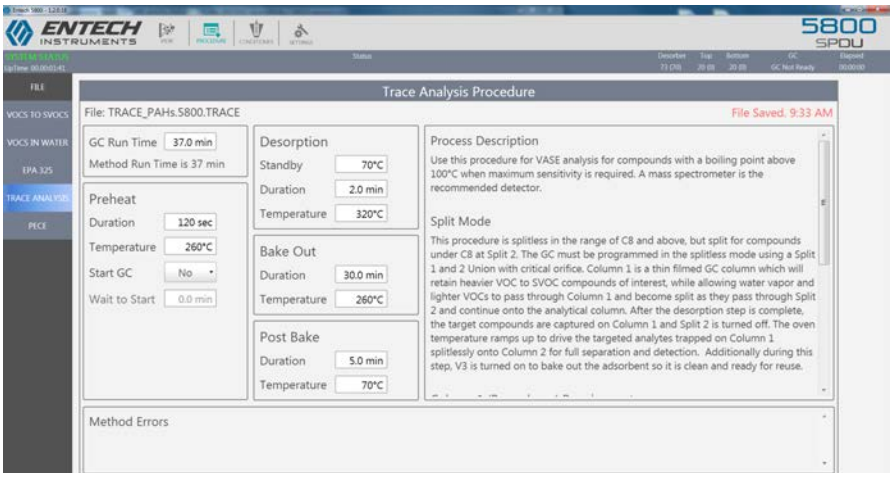
Water samples were spiked with SVOCs and these target compounds were extracted using Sorbent Pens for each level by Pulsed VASE to create linear calibration curves. Pulsed VASE, or “Vacuum Assisted Sorbent Extraction" uses pulsed heating and cooling in a closed vial to create evaporation and condensation cycles which vastly increase the surface area of the sample. Under the vacuum conditions of VASE, Vacuum Assisted Sorbent Extraction, headspace diffusion of 4-6 aromatic compounds, phenols, and other low volatility compounds to the adsorbent are accelerated by using Pulsed VASE. The 5800 Sorbent Pen Desorption Unit (SPDU) was used to thermally desorb the collected compounds onto a dual column system. The first column traps 100% of the SVOCs while operating at an elevated flow rate of about 10cc/min while splitting downstream of the first collection column. After collection of the SVOCs on the first column, the split is turned off allowing 100% of the sample to be transmitted to the second column as the GC oven temperature ramps up and are ultimately delivered to the MS detector. Recovery of 100% of the sample allows equivalent detection limits using just 1cc of water by Pulsed VASE, instead of using a full 1L of water while performing solvent extraction where only 1µL is injected after drying down the final solvent volume to 1cc. This thermal desorption procedure was used for all of the analyses presented here using a 5800 SPDU on a 7890B/5977 GCMS (Agilent, Palo Alto, CA).

Instrument Parameters:

Entech Pulsed VASE Parameters:



5800 SPDU Procedure Parameters:



GCMS Parameters:

Instrument: 5800 Sorbent Pen Desorption Unit (SPDU)
Run Date: January 2018
Sample Description: SVOCs
Amount of Sample: 1mL water
Sample Conditions: 20mL vial
Split Mode: Splitless w/ 0.0010 restrictor on Split 1 & 2 Union (Total Flow = 15cc/min
Precolumn: DB1 metal 5m x 0.530mm ID x 0.250 µm film thickness
Column: DB-5MS UI 30m x 0.250mm ID x 0.50µm film thickness
Carrier: Helium 1.5mL/min
MS Operation: Full Scan, 33-450, 3 scans/sec
AUX: 250°C

GC Oven Program:

	Rate (°C/min)	Value (°C)	Hold Time (min)	Run Time (min)
Initial		40	2	2
Ramp 1	15	150	0	9.3333
Ramp 2	10	310	11.67	37.003

Results

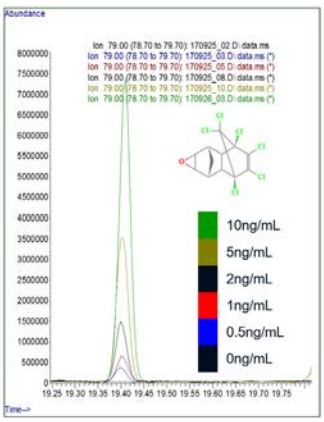
Linear calibration curves down to sub-ppb levels for SVOCs were generated using separate Sorbent Pens for each level to show the consistency of each Sorbent Pen and therefore the ability to use many Sorbent Pens simultaneously to perform parallel extractions. Included in the study were a range of pesticides, cannabis active compounds, and polycyclic aromatic hydrocarbons (PAHs). Standards were spiked into vials containing a final volume of 5mL water samples for pesticide and THC samples and a final volume of 1mL water samples for PAH analyses. Standards and internal surrogate standards were prepared in methanol and added in equal amounts to each vial for each level. The GCMS operated in full scan mode for all compounds and Scan/SIM mode for PAH Group 5 compounds. Tables 2, 4, and 6 below show Response Factors for within individual points for calibration curves various SVOCs. Data reveals both the reproducibility and lack of carryover achieved by this automated solvent-free technique, resulting in accurate analysis of SVOCs from water samples. Since VASE is a diffusive sampling technique performed under vacuum where the speed of sampling increases significantly, the extent of sample penetration into the adsorbent caused by the channeling effect inherent with Dynamic Headspace techniques is virtually eliminated, significantly reducing carryover and improving recovery of heavy compounds.

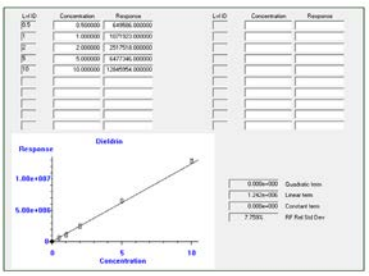
Table 1: Pesticide Target Compounds

Analyte	CAS Number	Retention Time	Formula	MW (g/mol)	Boiling Point (ºC)	Quantification Ion	Qualifier Ions
a-BHC	319-84-6	11.908	$C_6H_6Cl_6$	288	288	219	181, 111
b-BHC	319-85-7	14.932	$C_6H_6Cl_6$	288	288	109	181, 219
Heptachlor	76-44-8	16.667	$C_{10}H_5Cl_7$	370	NA	272	247, 270, 337
Aldrin	309-00-2	17.407	$C_{12}H_8Cl_6$	362	145	263	265, 261, 293
Heptachlor Epoxide	1024-57-3	18.142	$C_{10}H_5Cl_7O$	386	NA	353	355, 351
4,4'-DDE	72-55-9	19.177	$(ClC_6H_4)_2C{=}CCl_2$	316	336	218	318, 248
Dieldrin	60-57-1	19.399	$C_{12}H_8Cl_6O$	378	385	79	81, 82
4,4'-DDD	72-54-8	19.985	$(ClC_6H_4)_2CHCHCl_2$	318	193	165	237

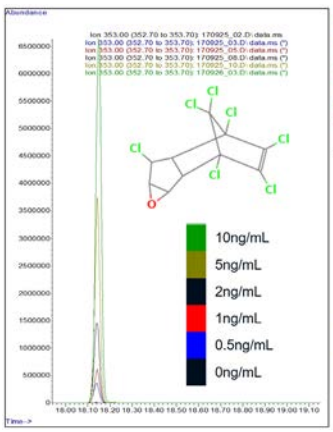
Table 2: Pesticide Response Factor Results (ppb)

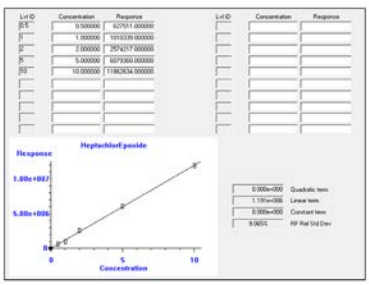
Analyte	0.5ppb	1ppb	2ppb	5ppb	10ppb	Average	%RSD
b-BHC	5.79	3.85	5.30	5.11	4.97	5.01	**14.36**
a-BHC	3.22	3.58	3.26	3.46	3.27	3.36	**4.62**
Heptachlor	2.42	2.16	1.52	2.45	2.48	2.21	**18.29**
Aldrin	5.98	4.63	5.23	5.19	4.85	5.18	**9.91**
Heptachlor Epoxide	1.26	1.01	1.29	1.22	1.19	1.19	**9.06**
4,4DDE	1.54	0.98	1.31	1.20	1.12	1.23	**17.27**
Dieldrin	1.30	1.07	1.26	1.30	1.29	1.24	**7.76**
4,4DDD	1.30	0.90	1.17	1.26	1.11	1.15	**13.62**





Compound: Dieldrin
Retention Time (min): 19.399
MW (g/mol): 378
Quant Ion: 79
Qualifier Ions: 81, 82
%RSD: 7.759





Compound: Heptachlor Epoxide
Retention Time (min): 18.142
MW (g/mol): 386
Quant Ion: 353
Qualifier Ions: 355, 351
%RSD: 9.065

Table 3: Cannabis Target Compounds

Analyte	CAS Number	Retention Time	Formula	MW (g/mol)	Boiling Point (ºC)	Quantification Ion	Qualifier Ions
Delta-9-THC D3	81586-39-2	25.406	$C_{21}H_{32}O_2$	317	157	302	317
Delta-9-THC	1972-08-3	25.415	$C_{21}H_{30}O_2$	314	157	299	231, 314
Cannabidiol	13956-29-1	24.859	$C_{21}H_{30}O_2$	314	160	231	246, 314

Table 4: THC Response Factor Results (ppb)

Analyte	0.5ppb	1ppb	2ppb	10ppb	20ppb	Average	%RSD
Delta-9-THC D3							
Delta-9-THC	1.32	1.17	1.36	1.14	1.16	1.23	8.19
Cannabidiol	7.56	6.98	6.24	8.84	6.56	7.24	14.14

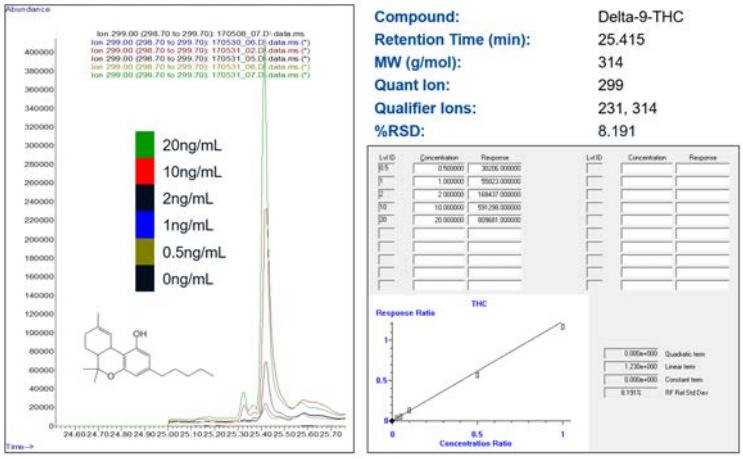
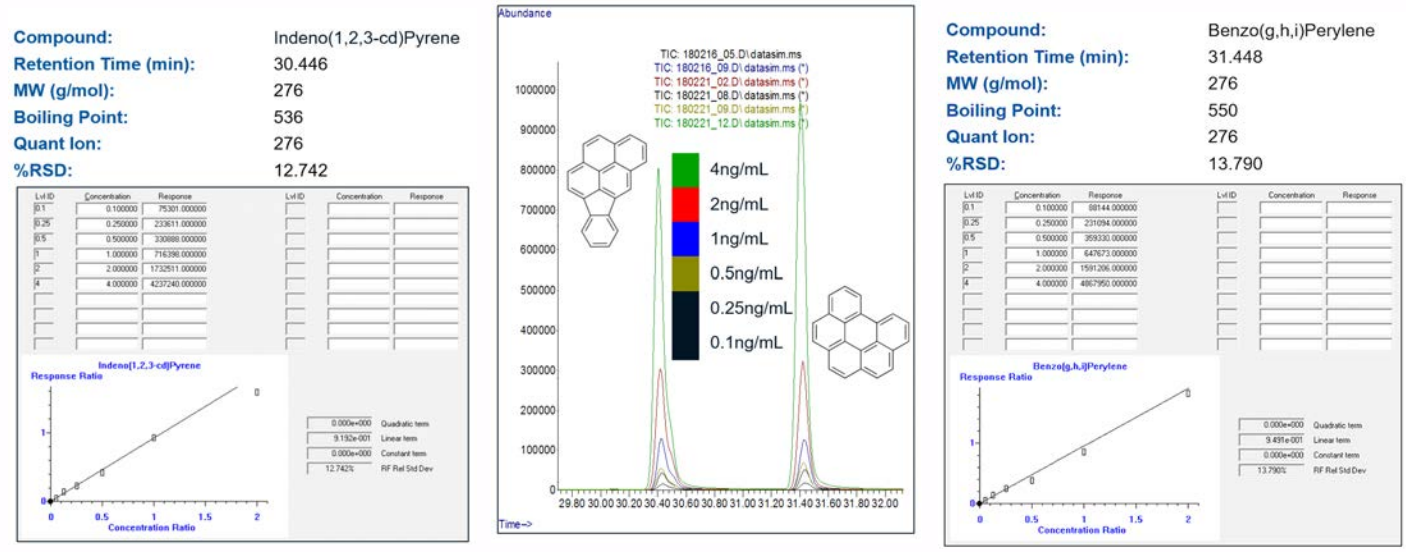


Table 5: PAH Target Compounds

Analyte	CAS#	Retention Time	Formula	MW (g/mol)	Boiling Point (ºC)	Quantification Ion	Qualifier Ions
Napthalene-d8 Group 1	1146-65-2	10.201	$C_{10}D_8$	136	218	136	108, 137
Naphthalene	91-20-3	10.245	$C_{10}H_8$	128	218	128	127, 129
Acenaphthylene	208-96-8	13.590	$C_{12}H_8$	152	280	152	76, 151
Acenaphthene-d10 Group 2	15067-26-2	13.912	$C_{12}D_{10}$	164	279	164	164, 160
Acenaphthene	83-32-9	13.983	$C_{12}H_{10}$	154	279	154	76, 151
Fluorene	86-73-7	15.133	$C_{13}H_{10}$	166	298	166	164, 165
Phenanthrene-d10 Group 3	1517-22-2	17.279	$C_{14}D_{10}$	188	340	188	189
Anthracene	120-12-7	17.455	$C_{14}H_{10}$	178	340	178	76, 89
Fluranthene	206-44-0	20.169	$C_{16}H_{10}$	202	384	202	101, 200
Pyrene	129-00-0	20.7104	$C_{16}H_{10}$	393	384	202	200, 201
Chrysene-d12 Group 4	1719-03-5	23.620	$C_{18}D_{12}$	240	448	240	236, 241
Benza(a)Anthracene	56-55-3	23.601	$C_{18}H_{12}$	228	437	228	114, 226
Chrysene	218-01-9	23.685	$C_{18}H_{12}$	228	448	228	114, 226
Perylene-d12 Group 5	1520-96-3	27.045	$C_{20}D_{12}$	264	468	264	260, 265
Benzo(k)Fluroanthene	205-99-2	26.088	$C_{20}H_{12}$	252	481	252	126, 250
Benzo(a)Pyrene	50-32-8	26.901	$C_{20}H_{12}$	252	495	252	126, 250
Indeno(1,2,3-cd)Pyrene	193-39-5	30.446	$C_{22}H_{12}$	276	539	276	138, 274
Benzo(g,h,i)Perylene	191-24-2	31.448	$C_{22}H_{12}$	276	550	276	138, 274

Table 6: PAH Response Factor Results (ppb)

Analyte	0.1ppb	0.25ppb	0.5ppb	1ppb	2ppb	4ppb	Average	%RSD
Napthalene-d8 Group 1								
Napthalene	1.30	0.95	0.81	0.84	0.83	0.78	0.92	21.31
Acenaphthylene	1.00	1.08	0.96	0.89	0.86	0.86	0.94	9.50
Acenaphthene-d10 Group 2								
Acenaphthene	1.14	1.00	0.83	0.93	0.87	0.73	0.92	15.36
Fluorene	0.98	1.13	0.96	1.00	0.82	0.79	0.95	13.27
Phenanthrene-d10 Group 3								
Anthracene	0.71	0.89	0.87	0.84	0.85	0.74	0.82	8.93
Fluranthene	0.75	0.87	0.81	0.75	0.76	0.69	0.77	8.34
Pyrene	0.73	0.89	0.83	0.80	0.81	0.71	0.80	8.44
Chrysene-d12 Group 4								
Benza(a)Anthracene	1.09	1.19	1.08	1.11	1.17	0.94	1.10	8.24
Chrysene	1.07	1.07	0.99	1.03	1.06	0.84	1.01	8.82
Perylene-d12 Group 5								
Benzo(k)Fluroanthene	1.21	1.43	1.20	1.54	1.55	1.04	1.33	15.76
Benzo(a)Pyrene	0.77	0.99	0.96	1.06	1.09	0.82	0.95	13.46
Indeno(1,2,3-cd)Pyrene	0.88	1.13	0.94	0.85	0.93	0.79	0.92	12.74
Benzo(g,h,i)Perylene	1.03	1.12	1.02	0.76	0.85	0.91	0.95	13.79



Conclusions and Future Work

VASE, or Vacuum Assisted Sorbent Extraction, has shown to extend the amount of applications compatible with headspace extraction by:

- ☑ Extracting various SVOCs previously requiring solvent-extraction including pesticides, delta-9-THC, and PAHs from spiked water samples reproducibly without carryover.
- ☑ Quantitatively recovering low volatility compounds from water using a headspace extraction technique without having to perform isotope dilution for each target compound.
- ☑ Combing VASE with automated Pulsed Vacuum Assisted Sorbent Extraction (Pulsed VASE) to speed up the extraction by increasing the surface area of the sample with cycles of evaporation and condensation in a closed system.

VASE has the potential to provide an accurate, sensitive, and reproducible solution to replace solvent extraction and solid phase extraction cleanup methods for analysis of SVOCs in water samples by EPA Method 8270 with minimal sample preparation and without the use of solvents. In combination with Pulsed VASE to help speed up the extraction process, VASE has shown to be very effective in trace analysis of organochlorine pesticides, 2-6 ring polycyclic aromatic hydrocarbons, and cannabis compounds from water. The results show linear calibration curves with and without the addition of surrogate internal standards, demonstrating the use of VASE for routine analyses of these compounds down to sub-ppb levels. Future work will include extraction from actual ground and surface water samples.

Entech Instruments shall not be liable for errors contained herein or for incidental or consequential damages in connection with the furnishing, performance, or use of this material.

Information, descriptions, and specifications in this publication are subject to change without notice.

Learn more about us:


entechinst.com


facebook.com/entechinst


twitter.com/entechinst


linkedin.com/company/entech-instruments-inc

Entech Instruments
2207 Agate Court
Simi Valley, CA 93065
Phone: 805-527-5939