Advancements in Determining Semi-Volatile Organic Compounds in Groundwater

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Introduction

Semivolatile organic compounds (SVOC) have a variety of chemical properties that have been found to cause harmful effects to both humans and the environment. Accurate measurements are challenging to obtain because SVOCs readily adsorb onto surfaces and are found in common household items such as cleaning agents, personal care products, electrical components, pesticides, water and food. Laboratories around the world measure these compounds in water, soil, and leachates from waste sites. US EPA Method 8270E can be used to determine the concentration of SVOCs extracted from liquid, solid and leachate samples in effort to limit exposure and the spread of these persistent organic pollutants. 1

While almost all laboratories test for less than the full list of 243 compounds included in the method, typical laboratories will often measure a large suite of 80 to 100 compounds. Compound classes that can be extracted using this method include: polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols.

This application will demonstrate the results of Initial Demonstration of Proficiency (IDP) evaluations for compliance with US EPA Method 8270E to determine a list of semi-volatile organic compounds that are neutral, acidic, and basic. Solid phase extraction (SPE) is described as a suitable sample preparation alternative in Method 8270E and method US EPA 3535 outlines the general use of SPE. Suitable sorbent material in disk format for this list of analytes and a modern system for automation will be demonstrated.

Experimental

Sample Preparation Procedure

The SVOCs in this method were extracted using automated sample preparation solutions for SPE, drying and concentration. The samples were extracted using an Atlantic® One Pass Disk which is a mixed mode disk containing several functionalities in line with a One-Pass Carbon Cartridge Max Detect to ensure adequate retention of difficult to obtain light end compounds, such as NDMA and N-Nitrosomethyl ethylamine. One Atlantic Fast Flow 1 µm pre filter was used as well.

The Fast Flow Disk Holder was used because groundwater samples can, at times, have varying levels of particulate matter. The Fast Flow Disk Holder uses a 47 mm disk but allows larger diameter pre-filters to be placed on top to shield the SPE disk from particulates that may cause clogging and allow for a quicker sample flow through the disk. The particulates are retained on the filters and washed with solvent during the elution steps, so any compounds that have been adsorbed on the particulates will be included in the extraction.

The extraction was completed using the Biotage® Horizon 5000 (Figure 1), an automated extractor which allows various types of liquid samples to be processed directly from the original sample container. The system includes intuitive software for easy programming, and automatic sample and solvent delivery.

Each 1 L of reagent water was prepared by adding 1 mL of hydrochloric acid, bringing the sample to a pH less than 2. A method blank containing 50 ug/L of surrogates and six samples containing 50 ug/L of surrogates as well as 50 ug/L of 8270 spike mix were extracted using the Biotage Horizon 5000 in conjunction with the one pass method (Figure 2).

Upon completion of the extraction, the samples were dried using the DryDisk® Solvent Drying System (SDS) in conjunction with the DryDisk®-R utilizing the parameters outlined in table 1. The dried extracts were transferred to 200 mL evaporation tubes (with an endpoint of 0.9 mL) for use in the TurboVap® II. Since the final volume of the dried extracts exceeded 200 mL, the samples were added to the concentration tubes in two portions. The first portion was concentrated to approximately 15 mL before adding the final extract volume as well as glassware rinses. The samples were concentrated using the parameters outlined in table 1.

After concentration on the TurboVap® II, the samples were brought to 1 mL with methylene chloride and transferred to GC-MS vials. Internal standard was added to an aliquot of each of the completed 1 mL extracts and analyzed using the GC/MS using instrument parameters outlined in table 1.

Figure 1. *Extraction and concentration system used for sample preparation: the Biotage® Horizon 5000 (left) and the TurboVap® II (right).*

SPE Protocol: Automated

- Ensure the sample is at ~~a~~ pH 2 before placing on the Biotage® Horizon 5000
- Load sample(s) onto the extractor and load the one pass method onto each active position. All extraction ~~steps~~ and air-dry steps are fully automated with the extraction method.
- Condition the one pass disk with acetone and reagent water.
- Filter and extract the acidified sample through the disk and cartridge to retain analytes on media and air-dry.
- Elute acidic and neutral semi-volatile organic analytes from the disk using acetone and methylene chloride. Take off collection flask, cap, and place aside.
- Place new collection flask(s) on each position used and elute remaining organic bases from the disk using acetone, 1% ammonium hydroxide and methylene chloride.
- Remove collection flask and disk holder and replace with the carbon cartridge.
- Place the acidic extract flask back onto each station and elute the light-end semi-volatile organic analytes from the carbon cartridge using acetone and methylene chloride.

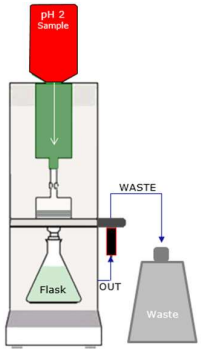

Figure 2. *Schematic representation of SPE protocol using automated SPE with a one-pass configuration.*

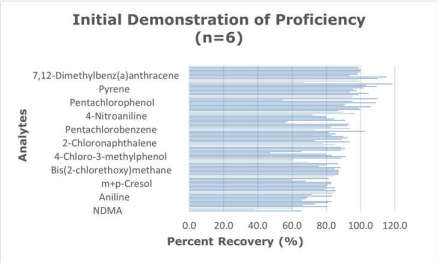

Chart 1. *Initial Demonstration of Proficency (IDP) Demonstrating 108 8270E analytes extracted, dried and concentrated (n=6).*

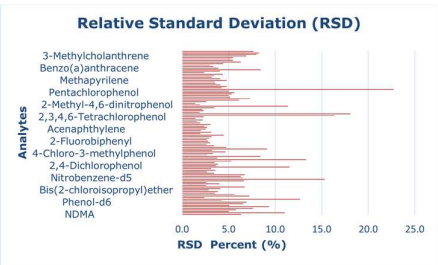

Chart 2*. Relative Standard Deviation of the IDP samples.*

Conditions

Solvent Drying System (SDS) Parameters	
Parameter	**Value**
Vacuum	-8 in.Hg
TurboVap® II Concentration Parameters	
Parameter	**Value**
Inlet Nitrogen Pressure	87 psi
Heat Timer	2.8 mL/min
Water Bath Temperature	40 °C
GC/MS Parameters	
Parameter	**Value**
GC/MS System	Agilent Technologies 6890 GC
GC/MS Detector	5973 Mass Selective Detector
Injection Volume	1 µL
Inlet Temperature	280 °C
Mode	Splitless
Gas Type	Helium
GC Column	Zebron™ ZB-Semivolatiles
Oven Program	Set to 45 °C, hold for 1 min
	Ramp from 45 °C to 270 °C, at 15 °C/min
	Ramp from 270 °C to 318 °C, at 6 °C/min
MS Ions Monitored	Masses 35-550 were scanned

Table 1. *SDS, TurboVap® II and GC/MS parameters.*

Results and Discussion

This study performed all necessary protocols to generate data demonstrating the IDP with 108 EPA Method 8270 analytes.

According to EPA Method 8270E analyte list in Section 1.1 suggests that method operation is considered appropriate if average recovery falls between 50 – 150 % and that relative standard deviations should be below 20%. This note explains that actual recoveries may vary depending on the sample matrix, number of constituents being analyzed concurrently, analytical instrumentation, and the preparation method used.

Section 13.1 suggests that performance criteria should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method, and use the method suggested criteria for guidance purposes only.

Results in chart 1 show that one compound out of the 108 was below the suggested 50% recovery limit. That compound pyridine averaged 38.3% recovery. This indicates a possible issue with acidification of the sample and or combining the extracts during the drying step. If the acidic extract is exposed to basic water, then there is the possibility of certain compounds within the one pass method to back extract into the basic water. With this method this can only happen when drying extracts through the DryDisk®-R or sodium sulfate. Users should take great care and ensure that the acid extracts are poured into the SDS reservoir and dried first. Then pour out any residual acidic water before drying the basic extract with the SDS. When using sodium sulfate, It is recommended to not use the same sodium sulfate when drying each acid and basic extract.

Chart 2 clearly shows only one compound that exceeds the suggested 20% RSD limit. The compound 4 Aminobiphenyl resulted In an RSD of 22.7 %. This compound did show some erratic recovery in the six samples and could have been a result in degradation during sample storage prior to drying and concentrating.

Table 2*. Ordering information.*

Part Number	Item Description	Pack Size
Consumables		
47-2346-11	Atlantic® One Pass Disk, 47mm	24
FFAP-100-HS1	Atlantic® Fast Flow Pre-Filter, 90 mm, Fine 1.0 µm	50
49-2620-01	One-Pass Carbon Cartridge Max Detect	16
40-1000-HT	DryDisk-R 65 mm	100
Instruments		
SDS-101-19/22	Solvent Drying System (19/22 taper)	1
SPE-DEX 5000	Biotage® Horizon 5000 3-Station Extractor Module (Includes Utility Kit with Waste Lines)	1
415001	TurboVap® II	1