U.S. EPA Method 625.1 – New Method and New Instrumentation for Semi-volatiles with Solid Phase Extraction

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Introduction

US EPA method 625 is used to determine acidic, basic, and neutral semi-volatile organic compounds (SVOC) in municipal and industrial wastewater. Revision A of this method is applied to a total possible list of 364 compounds that include; polynuclear aromatic hydrocarbons, chlorinated hydrocarbons, pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolones, aromatic nitro compounds, and phenols.

The current method outlines an extraction procedure utilizing either liquid-liquid extraction (LLE) or continuous liquid-liquid extraction (CLLE), followed by sodium sulfate drying. While it is not specifically outlined in the method, solid phase extraction (SPE) may be utilized for sample preparation, provided the Alternate Testing Procedure (ATP) process is followed.

Solid phase extraction is a well-established technique for automating traditional acid-base-neutral LLE methods; however, the method typically involves a multi-pass procedure where the solutions must be passed through the extraction media following 2 separate pH adjustments.

The work presented here demonstrates successful sample preparation using an automated, one-pass SPE system. In this configuration, all analytes of interest are extracted with a single pH adjustment. The success of the extraction is due to the use of a mixed mode SPE disk which contains several functionalities.

Experimental

Conditions

All samples were prepared for analysis using the workflow illustrated in the figure below. Sample extractions were performed on the Biotage® Horizon 5000 (previously known as the SPE-DEX 5000). The DryVap® In-line Drying and Concentration System from Biotage was used for solvent drying following the extraction.

Figure 1. *Extraction and drying systems used for sample preparation: the Biotage® Horizon 5000 (previously known as the SPE-DEX 5000) (left) and the DryVap® System (right).*

Conditions

All samples were prepared and analyzed according to the conditions listed in Table 1 below.

Extraction Parameters	
Parameter	**Value**
Extraction System	Biotage® Horizon 5000 Automated Extraction System
SPE Disk	Atlantic® 8270 One Pass SPE Disk (47 mm)
Disk Holder	Fast Flow Disk Holder
Carbon Cartridge	8270 Max Detect Carbon Cartridge
Drying/Concentration Parameters	
Parameter	**Value**
Solvent Drying System	DryVap® In-line Drying and Concentration System with DryDisk® Separation Disks
Dry Volume	200 mL
Heat Power	5
Heat Timer	OFF
Nitrogen Sparge	20 psi
Vacuum	-7 in. Hg
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. *Extraction, drying and analysis conditions for the analysis of wastewater samples.*

Samples

Nine water samples were prepared for analysis. The samples consisted of wastewater, seawater and effluent water to demonstrate proof of concept in a wide range of sample matrices. The sample names and descriptions are listed in Table 2 below.

Sample Name	Description
Synthetic wastewater	Prepared following ASTM D 5905 - 98
Synthetic seawater	Prepared from Instant Ocean, a commercially available product closely matching the composition of seawater
POTW Influent 1	Geographical coverage of the southern section including residential and treated industrial waste
POTW Effluent	Effluent from a large treatment plant
POTW Effluent plus O&G > 20 mg/L	To ensure the criterion is met, the effluent was spiked with 24 mg/L of Oil & Grease Standard
Industrial Effluent 1-RC1	PART 446—Paint formulating point source category
Industrial Effluent 2-RC2	PART 437— The centralized waste treatment point source category
Industrial Effluent 3-ES	PART 432—Meat and poultry products point source category
Industrial Effluent 4-Alpha	Part 414 - Organic Chemicals, Plastics and Synthetic fibers (OCPSF)

Table 2. *Sample names and descriptions.*

SPE Protocol

Outline

- Precondition both the SPE disk and the carbon cartridge
- Acidify the sample to pH 2
- Pass the acidified sample through the disk and cartridge to retain analytes on both
- Elute acidic and neutral semi-volatile organic analytes from the disk using acetone and methylene chloride
- Elute remaining organic bases from the disk using acetone, 1% ammonium hydroxide and methylene chloride
- Remove the disk holder and elute the light-end semi-volatile organic analytes from the carbon cartridge using acetone and methylene chloride

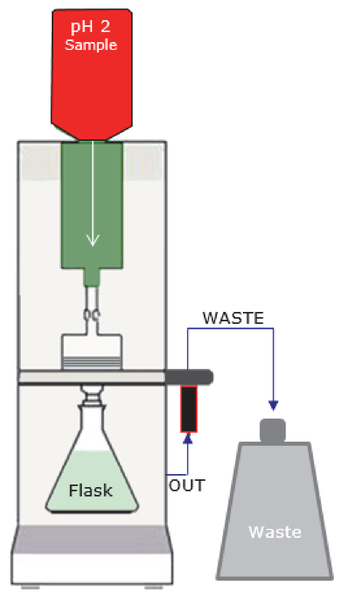

Figure 2. *Schematic representation of SPE protocol using automated SPE with a one-pass configuration.*

Results and Discussion

Prior to analyzing samples, the laboratory performed all necessary experiments to generate data demonstrating compliance with EPA Method 625.1. All results indicated that the laboratory met all demonstration of compliance (DOC) requirements (data not shown).

Following compliance verification, a series of synthetic water samples were analyzed. Results for one of the synthetic wastewater samples are listed in Table 3. Analyte results that are listed as measured spikes are from Table 3 in Method 625.1 and do not have official acceptance criteria. For those analytes, it is the responsibility of each laboratory to generate their own acceptance data.

Superscripts in Table 3 highlight those analytes that were eluted off the carbon cartridge or off the ion exchange portion of the Atlantic® One-Pass SPE disk. All other analytes were eluted from the One-Pass SPE disk under acidic conditions.

All measured analyte concentrations and relative percent difference (RPD) results were within the passing criteria for EPA Method 625.1.

Conclusions

- A robust workflow was developed for extracting a full suite of analytes in compliance with EPA Method 625.1
- Data collected for synthetic water samples indicated that analyte recoveries were within the acceptable limits of Method 625.1
- The use of the Atlantic® One Pass Disk, combined with the carbon cartridge, allowed for the extraction of semi-volatile and light-end semi-volatile organic compounds under acidic and neutral conditions, with a single pass of the solution
- The automation of the extraction improved the accuracy and reproducibility of the data, which improves the ease with which a laboratory can maintain EPA compliance
- Additional solid phase extraction benefits include: reduced solvent usage, reduced hazardous waste generation, reduced exposure to solvent vapors and reduced solvent evaporation and recollection requirements

Results and Discussion

Analyte	Avg Measured Conc (µg/L)	Acceptable Range (µg/L)	RPD Limit	Analyte	Measured Spike Conc (µg/L)	Measured Spike Conc (µg/L)	RPD
1,2,4-Trichlorobenzene	49.04	44-142	50	1,2,4,5-Tetrachlorobenzene*	59.02	55.11	3.43
2,4-Dinitrotoluene	76.57	39-139	42	1,3,5,-Trinitrobenzene*	45.95	41.48	5.11
2,6-Dinitrotoluene	78.08	50-158	48	1,3-Dinitrobenzene*	77.48	74.87	1.71
2-Chloronaphthalene	64.25	60-120	24	1,4-Naphthoquinone*	55.16	54.26	0.82
3,3'-Dichlorobenzidine[a]	41.09	D-262	108	1-Naphthylamine*	50.35	49	1.36
4-Bromophenyl phenyl ether	75.46	53-127	43	2,3,4,6-Tetrachlorophenol*	86.75	83.82	1.72
4-Chlorophenyl phenyl ether	72.32	25-158	61	2,4,5-Trichlorophenol*	79.16	76.03	2.02
Acenaphthene	68.17	47-145	48	2,6-Dichlorophenol*	80.06	77.36	1.72
Acenaphthylene	69.43	33-145	74	2-Methylnaphthalene*	61.72	60.31	1.16
Anthracene	74.38	27-133	66	2-Naphthylamine*	67.09	20.23	53.66
Benz(a)anthracene	75.73	33-143	53	2-Nitroaniline*	79.7	77.05	1.69
Benzo(a)pyrene	73.99	17-163	72	2-Picoline*	28.22	30.72	4.24
Benzo(b)fluoranthene	75.72	24-159	71	3,3'-Dimethylbenzidine*	4.03	3.04	14.00
Benzo(ghi)perylene	75.08	D-219	97	3-Methylcholanthrene*	76.67	71.44	3.53
Benzo(k)fluoranthene	75.68	11-162	63	3-Nitroaniline*	68.52	67.74	0.57
Bis(2-chlorethoxy)methane	75.90	33-184	54	4 Aminobiphenyl*	32.18	30.11	3.32
Bis(2chloroisopropyl)ether	65.00	36-166	76	4-Chloroaniline*	54.28	56.11	1.66
Bis(2-ethylhexyl) phthalate	87.59	8-158	82	4-Nitroaniline*	60.13	59.59	0.45
Chrysene	75.09	17-168	87	4-Nitroquinoline-1-oxide*	11.48	9.3	10.49
2,4,6-Trichlorophenol	78.33			5-nitro-o-toluidine*	73.13	71.42	1.18
2,4-Dichlorophenol	78.66	39-135	50	7,12-Dimethylbenz(a)-anthracene*	75.6	71.17	3.02
2,4-Dimethylphenol	80.11	32-120	58	Acetophenone*	66.76	68.85	1.54
2,4-Dinitrophenol	86.95	D-191	132	Acetylaminofluorene*	83.57	79.91	2.24
2-Chlorophenol	72.64	23-134	61	Aniline*	49.11	54.18	4.91
2-Nitrophenol	68.86	29-182	55	Benzoic acid*	117.29	121.83	1.90
4,6-Dinitro-2-methylphenol	76.27	D-181	203	Benzyl alcohol*,[b]	73.73	75.64	1.28
4-Chloro-3-methylphenol	83.33	22-147	73				
4-Nitrophenol	85.60	D-132	131				
Pentachlorophenol	97.61	14-176	86				
Phenol[b]	46.58	5-120	64				

Table 3. *Analyte measurements for a synthetic water sample after demonstrating laboratory compliance with Method 625.1 requirements.*
[a]Eluted with ion exchange conditions using the Atlantic® One-Pass SPE Disk
[b]Eluted with the carbon cartridge
**No official acceptance criteria in Method 625.1*

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