Improving SPE Disk Extraction Technology for US EPA Wastewater Method 625.1

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Key Words: *Wastewater, US EPA Method 625.1, SPE, Solid Phase Extraction*

Introduction

The US EPA monitors a variety of chemicals in water that may cause harm to humans or wildlife in order to minimize exposure. Method 625 was developed by the Office of Science and Technology in the Clean Water program to monitor a large suite of semivolatile chemicals in wastewater for compliance with the National Pollution Discharge Elimination System (NPDES). NPDES is a system of permitting that regulates the characteristics of water that is released into a waterway, defined by industrial category. The permitting levels are set depending on the waterway's use. If the waterway is used for recreation or is an important wildlife habitat, the limit may be set lower.

The original method was developed in the early 1980s and has been updated several times since then to allow for the use of more modern technology. The latest update has taken place over the last few years and was proposed in a Method Update Rule (MUR) in 2015.[1] The latest version of the method includes a larger suite of analytes (up to 364) and an extensive set of labeled surrogates to better monitor the method performance throughout sample preparation and analysis steps.[2]

This note examines the results from an initial demonstration of capability (DOC) with one liter samples utilizing automated disk solid phase extraction (SPE) for US EPA method 625.1. Samples were evaluated and measured against the criteria listed in Table 6 of method 625.1. The analytes chosen for evaluation were from Tables 1, 2 and 3 in Method 625.1. Analytes from Table 3 do not have any acceptance criteria for comparison.

Experimental

One liter samples were processed as laboratory control samples (LCS), matrix spike (MS), matrix spike duplicate (MSD) and calibration verifications were evaluated. The samples were extracted using an Atlantic® One-pass SPE disk (Biotage) which is a mixed mode disk containing several functionalities. The process was automated with the Biotage® Horizon 5000 (previously known as the SPE-DEX® 5000) extraction system. A carbon cartridge (Max Detect, Biotage) was also used to ensure adequate retention of the light end compounds, such as N-Nitrosodi-n-propylamine.

The Fast Flow Disk Holder (FFSDH) was used with the samples because this method is known for varying levels of particulate matter and the sample size was 1 L. The FFSDH uses a 47 mm disk, but allows larger filters to be placed on top to shield the SPE disk from particulates that may cause clogging and maintain fast flow through the disk. The particulate material is retained on the filters and washed with solvent during the elution step, so any material that has been absorbed on the surface will be included in the extraction. Figure 1 shows a photo of the Biotage® Horizon 5000 configured with the One Pass kit, Carbon Cartridge and the Fast Flow Disk Holder.

Figure 1.
Biotage® Horizon 5000 (Previously known as the SPE-DEX 5000 Extractor).

The resulting extracts were dried using DryDisk® membrane drying system (Biotage) and evaporated to 1 mL with the DryVap® Automated In-line Drying and Concentration System (Biotage). The DryVap was chosen for its ability to in-line dry and concentrate extracts at a very low boiling point. Those two features preserve the extracted compounds concentration throughout the drying and concentration process, compared to traditional multistep processes. Figure 2 shows the DryVap system with DryDisk glassware holding the drying membranes in front. The dried extract is drawn into the concentration tube in the back and the evaporation occurs there. Residual water remains in the front reservoirs separated from the extract.

The extraction method used with the Biotage® Horizon 5000 is shown in Table 1. The conditions for operating the DryVap are shown in Table 2.

Figure 2. DryVap® System.

Table 1. Biotage® Horizon 5000 Extraction Method.

Step	Operation	Message	Attachment
1	Pause with Message	Part 1 of 3: Neutrals and Acids Elution. Have the Fast Flow Sediment Disk Holder with OnePass Disk, 1 µm filter, 5 µm filter, top screen over the filters, 250 mL collection flask, and carbon cartridge installed. The down spout of the water in valve must push down on the top screen. Click “Continue” to start Part 1.	None

Step	Operation	Solvent	Solvent Vol. (mL)	Purge Time (s)	Pump Rate (#)	Sat. Time (s)	Soak Time (s)	Drain Time (s)
2	Condition SPE	Acetone	40	60	4	2	60	60
3	Condition SPE	Reagent Water	20	60	4	2	60	60

Step	Operation	Sample Flow Rate (#)	Done Loading Sample Delay (s)
4	Load Sample	5	45

Step	Operation	Solvent	Solvent Vol. (mL)	Purge Time (s)	Pump Rate (#)	N2 Blanket	Sat. Time (s)	Soak Time (s)	Drain Time (s)
5	Wash Sample Container	Reagent Water	20	30	4	Off	2	5	30

Step	Operation	Dry Time (s)	Pump Rate (#)	N2 Blanket
6	Air Dry Disk Timer	360	6	Off

Step	Operation	Solvent	Solvent Vol. (mL)	Purge Time (s)	Pump Rate (#)	N2 Blanket	Sat. Time (s)	Soak Time (s)	Elute Time (s)
7	Elute Sample Container	Acetone	20	20	4	Off	2	180	180
8	Elute Sample Container	$MeCl_2$	17	15	4	Off	2	180	180
9	Elute Sample Container	$MeCl_2$	17	15	4	Off	2	120	120
10	Elute Sample Container	$MeCl_2$	17	15	4	Off	2	120	120
11	Elute Sample Container	$MeCl_2$	17	15	6	Off	2	120	180

Step	Operation	Message	Attachment
12	Pause with Message	Part 2 of 3: Ion Exchange Elution. Remove the 250 mL collection flask containing the neutrals and acids elution. Stopper the flask and set aside for part 3. Then install a clean 125 mL flask to collect the ion exchange elution. Click “Continue” to Start Part 2.	None

Step	Operation	Solvent	Solvent Vol. (mL)	Purge Time (s)	Pump Rate (#)	N2 Blanket	Sat. Time (s)	Soak Time (s)	Elute Time (s)
13	Elute Sample Container	Acetone	20	20	4	Off	2	0	180
14	Elute Sample Container	1% NH_4OH	20	30	4	Off	2	120	120
15	Elute Sample Container	Acetone	20	20	4	Off	2	180	120
16	Elute Sample Container	$MeCl_2$	17	15	4	Off	2	180	180
17	Elute Sample Container	$MeCl_2$	16	15	4	Off	2	120	180
18	Elute Sample Container	$MeCl_2$	16	15	4	Off	2	120	180
19	Elute Sample Container	$MeCl_2$	16	15	6	Off	2	120	180

Step	Operation	Message	Attachment
20	Pause with Message	Part 3 of 3: Carbon Cartridge Elution. Remove the carbon cartridge from the tubing lines. Connect the tubing ends together. Using a 20 cc syringe, plunge the carbon cartridge with air through the cap adapter to reseat the carbon bed on the frit. Replace the cap adapter with the funnel cartridge. Replace the disk holder with the cartridge. Replace the 125 mL flask with the 250 mL flask containing the neutrals and acids elution from Part 1. Stopper the 125 mL flask. Click “Continue” to start part 3.	None

Step	Operation	Dry Time (s)	Pump Rate (#)	N2 Blanket
21	Air Dry Disk Timer	60	6	Off

Step	Operation	Solvent	Solvent Vol. (mL)	Purge Time (s)	Pump Rate (#)	N2 Blanket	Sat. Time (s)	Soak Time (s)	Elute Time (s)
22	Elute Sample Container	Acetone	25	20	4	Off	3	60	60
23	Elute Sample Container	$MeCl_2$	17	15	4	Off	3	60	20
24	Elute Sample Container	$MeCl_2$	17	15	4	Off	3	60	20
25	Elute Sample Container	$MeCl_2$	17	15	4	Off	3	60	20
26	Elute Sample Container	$MeCl_2$	17	15	4	Off	3	60	20
27	Elute Sample Container	$MeCl_2$	17	15	6	Off	3	60	60

The samples were measured using GC/MS (6890GC/5975CMS, Agilent Technologies). The operational conditions are shown in Table 3.

All spiking standards used were from (Supelco, Bellefonte, PA). The surrogate mixes were from (Restek Corp, Bellefonte, PA.).

Results and Discussion

Table 6 in US EPA Method 625.1 (December 2014) lists criterion by analytes for a variety of characteristics to validate that the method applied with changes will meet the requirements of the original method for a variety of challenging matrices; representative of those that may be encountered in a commercial laboratory. This table is included in Appendix 1 for easy reference.

The first column of Table 6 in Method 625.1 is range in % for recovery of the calibration verification standard. The results for this standard during the testing of the extracts is shown in Table 4 and meets the criteria listed in Method 625.1 for compliance.

Table 2. DryVap® System Conditions.

Parameter	Setting
Dry Volume	200 mL
Heat Power	5
Heat Timer	OFF
Auto Rinse Mode	OFF
Nitrogen Sparge	20 psi
Vacuum	-7 in. Hg

Table 3. GC/MS Conditions.

Injection	
Volume	1 µL
Inlet Temperature	280 °C
Mode	Splitless
Gas Type	Helium
Column Conditions	**Zebron™ ZB-Semivolatiles (Phenomenex)**
Mode	Consistent Flow
Oven Program	45 °C hold for 1 min to 270 °C at 15 °C/min then to 318 °C at 6 °C/min
MS Ions Monitored	Scan masses 35-550

Table 4. Calibration Verification over the Course of Operation.

Analyte	Recovery (%)	Recovery (%)	Recovery (%)	Recovery (%)	Recovery (%)	Recovery (%)	Range for Q %	Pass/ Fail
NDMA	102.9	94.4	96.9	97.8	97.6	94.1	60-140	Pass
1,2,4,5-Tetrachlorobenzene	98.0	97.5	95.0	101.9	100.8	97.2	60-140	Pass
1,2,4-Trichlorobenzene	97.7	98.4	95.0	101.2	100.9	97.2	61-130	Pass
1,3,5,-Trinitrobenzene	95.5	94.7	92.1	97.1	94.6	92.8	60-140	Pass
1,4-Naphthoquinone	94.8	94.7	92.6	97.9	95.4	92.0	60-140	Pass
1-Naphthylamine	85.5	82.6	82.8	87.8	82.6	82.4	60-140	Pass
2,3,4,6-Tetrachlorophenol	93.9	93.5	93.5	98.1	96.3	93.6	60-140	Pass
2,4,5-Trichlorophenol	95.1	94.8	93.9	99.2	95.9	93.0	60-140	Pass
2,4-Dichlorophenol	96.7	96.2	94.4	99.5	96.3	93.1	64-130	Pass
2,4-Dimethylphenol	98.0	97.9	95.2	99.9	97.2	93.8	58-130	Pass
2,4-Dinitrophenol	80.2	81.2	85.7	87.9	85.6	82.1	39-173	Pass
2,4-Dinitrotoluene	93.5	94.2	94.0	98.6	96.9	93.9	53-130	Pass
2,6-Dichlorophenol	95.8	96.5	94.9	99.2	96.3	93.7	60-140	Pass
2,6-Dinitrotoluene	94.5	94.3	92.6	98.9	96.3	93.5	68-137	Pass
2-Chloronaphthalene	97.8	97.4	94.7	100.2	99.6	96.0	70-130	Pass
2-Chlorophenol	97.4	96.6	94.6	98.9	99.2	94.7	55-130	Pass
2-Fluorobiphenyl	99.0	97.9	97.3	100.0	92.5	91.0	60-140	Pass
2-Fluorophenol	99.9	95.8	97.8	95.4	96.3	94.3	60-140	Pass
2-Methylnaphthalene	96.7	98.4	95.3	100.5	98.8	95.3	60-140	Pass
2-Naphthylamine	68.6	70.4	66.2	71.8	65.5	66.7	60-140	Pass
2-Nitroaniline	95.1	94.3	93.4	98.1	94.9	92.5	60-140	Pass
2-Nitrophenol	95.2	96.5	93.7	98.2	96.1	93.7	61-163	Pass
3,3'-Dichlorobenzidine	107.2	106.0	100.4	108.2	102.7	102.2	18-213	Pass
3,3'-Dimethylbenzidine	80.2	84.5	80.1	92.8	86.1	88.0	60-140	Pass
3-Methylcholanthrene	95.0	96.1	92.4	99.4	95.9	94.4	60-140	Pass
3-Nitroaniline	99.2	96.0	96.2	100.6	97.8	96.1	60-140	Pass
4 Aminobiphenyl	87.9	88.2	79.6	86.2	79.9	80.4	60-140	Pass
4,6-Dinitro-2-methylphenol	89.0	90.5	90.9	96.2	94.0	90.7	56-130	Pass
4-Bromophenyl phenyl ether	96.6	99.8	96.0	103.5	100.8	98.1	70-130	Pass
4-Chloro-3-methylphenol	94.8	96.5	95.2	97.7	96.0	91.9	68-130	Pass
4-Chloroaniline	74.7	86.9	75.3	87.5	85.3	82.5	60-140	Pass
4-Chlorophenyl phenyl ether	95.3	97.9	94.9	101.0	98.8	97.5	57-145	Pass
4-Nitroaniline	96.3	92.4	94.9	94.6	94.6	89.9	60-140	Pass
4-Nitrophenol	96.4	89.3	91.5	91.7	90.0	86.8	35-130	Pass
4-Nitroquinoline-1-oxide	89.7	95.9	87.2	104.1	94.4	101.0	60-140	Pass
5-nitro-o-toluidine	94.3	92.9	92.7	98.6	96.3	93.5	60-140	Pass

	Recovery (%)	Recovery (%)	Recovery (%)	Recovery (%)	Recovery (%)	Recovery (%)	Range for Q	Pass/ Fail
7,12-Dimethylbenz(a)-anthracene	94.6	98.2	95.0	100.2	98.8	95.1	60-140	Pass
Acenaphthene	97.1	96.7	94.6	100.4	97.7	95.0	70-130	Pass
Acenaphthylene	96.9	96.5	94.6	100.5	97.2	94.6	60-130	Pass
Acetophenone	96.7	96.7	94.2	100.0	99.0	95.2	60-140	Pass
Acetylaminofluorene	97.0	95.8	92.1	98.5	94.4	93.7	60-140	Pass
Aniline	90.6	90.6	91.0	96.9	93.3	93.1	60-140	Pass
Anthracene	98.1	98.0	94.5	100.1	98.6	95.0	58-130	Pass
Benz(a)anthracene	96.6	95.1	94.1	98.2	97.2	94.3	42-133	Pass
Benzidine	81.9	84.7	76.3	87.4	82.0	85.3	60-140	Pass
Benzo(a)pyrene	96.5	96.0	93.7	99.3	97.1	94.7	32-148	Pass
Benzo(b)fluoranthene	93.7	94.6	92.2	98.2	96.2	93.2	42-140	Pass
Benzo(ghi)perylene	96.4	93.8	91.3	97.1	92.8	91.1	13-195	Pass
Benzo(k)fluoranthene	97.5	99.3	97.7	101.1	100.2	96.6	25-146	Pass
Benzoic acid	93.6	89.8	92.1	92.9	87.5	86.7	60-140	Pass
Benzyl alcohol	97.1	96.5	94.3	99.1	97.4	94.6	60-140	Pass
Bis(2-chlorethoxy)methane	96.7	98.9	94.3	100.6	98.4	95.5	52-164	Pass
Bis(2-chloroethyl)ether	99.6	99.8	94.7	100.1	99.1	96.5	60-140	Pass
Bis(2chloroisopropyl)ether	95.7	98.8	94.0	102.1	99.7	98.4	63-139	Pass
Bis(2-ethylhexyl) phthalate	85.3	98.6	91.0	102.3	99.9	98.4	43-137	Pass
Carbazole	100.0	96.6	95.1	98.2	97.6	93.5	60-140	Pass
Chrysene	97.4	96.1	94.8	98.1	97.6	93.9	44-140	Pass
Dibenz(ah)anthracene	91.2	93.5	91.1	98.2	94.2	92.5	13-200	Pass
Dibenzofuran	97.0	96.4	94.8	100.7	98.4	95.1	60-140	Pass
Diethyl phthalate	92.5	96.3	93.3	101.4	98.5	97.0	47-130	Pass
Dimethyl phthalate	93.7	95.7	93.3	99.4	97.4	94.4	50-130	Pass
Dimethylaminoazobenzene	90.2	97.7	93.3	99.5	97.9	95.5	60-140	Pass
Di-n-butyl phthalate	90.9	100.1	91.1	101.8	100.8	98.7	52-130	Pass
Di-n-octyl phthalate	89.3	99.2	92.2	102.3	99.4	98.4	21-132	Pass
Dinoseb	89.8	94.1	90.0	98.5	97.1	94.2	60-140	Pass
Diphenylamine	96.2	96.3	95.3	99.4	97.9	95.3	60-140	Pass
Ethylmethane Sulfonate	96.8	95.2	94.8	98.6	97.9	95.9	60-140	Pass
Fluoranthene	98.4	96.9	94.8	97.4	97.7	95.1	47-130	Pass
Fluorene	95.6	96.5	93.9	99.4	98.5	94.8	70-130	Pass
Hexachlorobenzene	96.1	99.6	94.4	101.3	99.4	96.2	38-142	Pass
Hexachlorobutadiene	97.9	101.3	95.5	104.7	103.5	100.3	68-130	Pass
Hexachlorocyclopentadiene	89.9	92.4	88.2	99.4	96.7	94.2	60-140	Pass

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	Recovery (%)	Recovery (%)	Recovery (%)	Recovery (%)	Recovery (%)	Recovery (%)	Range for Q	Pass/ Fail
Hexachloroethane	97.9	100.3	93.8	102.9	102.9	100.7	55-130	Pass
Hexachloropropene	97.5	98.9	93.8	101.4	100.6	97.1	60-140	Pass
Indeno(1,2,3-cd)pyrene	94.3	93.3	89.6	95.2	90.8	88.6	13-151	Pass
Isophorone	95.6	98.8	93.8	100.1	98.0	95.1	52-180	Pass
Methapyrilene	90.2	94.0	89.5	97.1	94.8	92.9	60-140	Pass
Naphthalene	98.5	97.9	95.0	100.2	98.8	95.6	70-130	Pass

Before running samples, the laboratory must first demonstrate their capability to use a method with an initial DOC, running four spiked reagent water samples through the complete sample preparation and analysis step. The results for recovery accuracy and precision are compared with the range specified for compliance. The range is included in Table 5 for easy comparison. Analytes with a * indicate that they are from Table 3 and do not have acceptance criteria in Table 6 within Method 625.1. It is up to the laboratory to generate their own acceptance criteria for Table 3 analytes.

Table 5. Initial demonstration of compliance.

Analyte	Average DOC	DOC Range	Pass/Fail	SD	Limit for s (%)	Pass/Fail
1,2,4,5-Tetrachlorobenzene*	61.89			5.24		
1,2,4-Trichlorobenzene	57.69	57-130	Pass	5.08	30	Pass
1,2-Dichlorobenzene*	51.60			4.49		
1,3,5,-Trinitrobenzene*	83.54			6.65		
1,3-Dichlorobenzene*	46.37			4.58		
1,3-Dinitrobenzene*	88.29			5.80		
1,4-Dichlorobenzene*	48.39			4.84		
1,4-Naphthoquinone*	77.21			2.15		
1-Naphthylamine*	89.88			1.58		
2,3,4,6-Tetrachlorophenol*	87.10			5.02		
2,4,5-Trichlorophenol*	84.55			4.56		
2,4-Dichlorophenol	86.09	53-122	Pass	4.45	30	Pass
2,4-Dimethylphenol	85.77	42-120	Pass	4.31	35	Pass
2,4-Dinitrophenol	83.62	D-173	Pass	5.97	79	Pass
2,4-Dinitrotoluene	88.97	48-127	Pass	4.91	25	Pass
2,6-Dichlorophenol*	85.58			4.19		
2,6-Dinitrotoluene	89.83	68-137	Pass	5.49	29	Pass
2-Chloronaphthalene	70.88	65-120	Pass	5.97	15	Pass
2-Chlorophenol	77.07	36-120	Pass	5.10	37	Pass
2-Fluorobiphenyl*	83.45			2.46		
2-Fluorophenol*	55.75			6.09		
2-Methyl phenol*	80.66			5.19		
2-Methylnaphthalene*	68.80			5.49		
2-Naphthylamine*	109.87			6.08		

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Analyte	Average DOC	DOC Range	Pass/Fail	SD	Limit for s (%)	Pass/Fail
2-Nitroaniline*	87.96			6.80		
2-Nitrophenol	75.83	*45-167*	*Pass*	3.66	79	*Pass*
2-Picoline*	47.44			2.09		
3,3'-Dichlorobenzidine	88.90	*8-213*	*Pass*	3.25	65	*Pass*
3,3'-Dimethylbenzidine*	94.17			2.61		
3+4 Methyl phenol*	82.47			6.41		
3-Methylcholanthrene*	84.77			5.18		
3-Nitroaniline*	91.89			4.77		
4 Aminobiphenyl*	112.58			6.89		
2-methyl-4,6-Dinitrophenol	87.21	*53-130*	*Pass*	5.66	122	*Pass*
4-Bromophenyl phenyl ether	82.74	*65-120*	*Pass*	4.84	26	*Pass*
4-Chloro-3-methylphenol	89.01	*41-128*	*Pass*	4.86	44	*Pass*
4-Chloroaniline*	118.22			8.03		
4-Chlorophenyl phenyl ether	79.56	*38-145*	*Pass*	4.55	36	*Pass*
4-Nitroaniline*	86.93		*Pass*	4.82		
4-Nitrophenol	92.06	*13-129*	*Pass*	4.99	79	*Pass*
4-Nitroquinoline-1-oxide*	90.69			7.66		
5-nitro-o-toluidine*	93.58			5.44		
7,12-Dimethylbenz(a)-anthracene*	84.98			4.36		
Acenaphthene	76.24	*60-132*	*Pass*	5.58	29	*Pass*
Acenaphthylene	77.33	*54-126*	*Pass*	5.81	45	*Pass*
Acetophenone*	75.52			3.75		
Acetylaminofluorene*	90.49			6.10		
Aniline*	80.22			6.18		
Anthracene*	85.84	*43-120*	*Pass*	6.38	40	*Pass*
Azobenzene*	82.72			4.95		
Benz(a)anthracene	86.41	*42-133*	*Pass*	5.20	32	*Pass*
Benzidine*	99.72			4.45		
Benzo(a)pyrene	86.46	*32-148*	*Pass*	5.17	43	*Pass*
Benzo(b)fluoranthene	87.03	*42-140*	*Pass*	4.62	43	*Pass*
Benzo(ghi)perylene	87.07	*D-195*	*Pass*	6.09	61	*Pass*
Benzo(k)fluoranthene	86.62	*25-146*	*Pass*	4.91	38	*Pass*
Benzoic acid*	57.15			6.57		
Benzyl alcohol*	78.97			3.41		
Bis(2-chlorethoxy)methane	82.26	*49-165*	*Pass*	3.42	32	*Pass*
Bis(2-chloroethyl)ether	68.31	*43-126*	*Pass*	2.05	65	*Pass*
Bis(2chloroisopropyl)ether	68.10	*63-139*	*Pass*	3.03	46	*Pass*
Bis(2-ethylhexyl) phthalate	91.34	*29-137*	*Pass*	6.66	50	*Pass*
Benzyl butyl phthalate	90.69	*D-140*	*Pass*	5.14	36	*Pass*
Carbazole*	89.33			7.42		
Chrysene	87.54	*44-140*	*Pass*	5.42	53	*Pass*
cis-Isosafrole*	75.74			4.98		

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Analyte	Average DOC	DOC Range	Pass/Fail	SD	Limit for s (%)	Pass/Fail
Dibenz(ah)anthracene	87.88	*D-200*	*Pass*	4.85	75	*Pass*
Dibenzofuran*	78.22			5.60		
Diethyl phthalate	90.84	*D-120*	*Pass*	4.45	60	*Pass*
Dimethyl phthalate	89.80	*D-120*	*Pass*	4.36	110	*Pass*
Dimethylaminoazobenzene*	91.85			4.54		
Di-n-butyl phthalate	90.70	*8-120*	*Pass*	6.31	28	*Pass*
Di-n-octyl phthalate	89.40	*19-132*	*Pass*	5.25	42	*Pass*
Dinoseb*	87.13			6.29		
Diphenylamine*	87.58			5.24		
Ethylmethane Sulfonate*	75.62			3.61		
Fluoranthene	87.77	*43-121*	*Pass*	6.82	40	*Pass*
Fluorene	81.07	*70-120*	*Pass*	5.80	23	*Pass*
Hexachlorobenzene	83.49	*8-142*	*Pass*	5.44	33	*Pass*
Hexachlorobutadiene	44.63	*38-120*	*Pass*	4.47	38	*Pass*
Hexachlorocyclopentadiene*	41.53			4.33		
Hexachloropropene*	45.64			4.68		
Indeno(1,2,3-cd)pyrene	85.73	*D-151*	*Pass*	5.28	60	*Pass*
Isophorone	82.02	*47-180*	*Pass*	3.88	56	*Pass*
Methapyrilene*	89.82			4.64		
Methyl Methane Sulfonate*	49.04			2.10		
Naphthalene	66.73	*36-120*	*Pass*	5.59	39	*Pass*
NDMA*	36.34			0.68		
Nitrobenzene	72.65	*54-158*	*Pass*	3.72	37	*Pass*
Nitrobenzene-d5	77.26	*15-314*	*Pass*	4.08		
N-Nitroso-diethylamine*	67.44			2.70		
N-nitroso-di-n-butylamine*	85.87			4.26		
N-nitroso-di-n-propylamine	79.49	*14-198*	*Pass*	4.52	52	*Pass*
N-Nitrosomethyl ethylamine	58.95			1.50		
N-Nitroso-morpholine*	78.99			7.92		
N-Nitroso-piperidine*	82.98			3.96		
N-Nitroso-pyrrolidine*	83.07			4.02		
o-toluidine*	95.47			6.77		
Pentachlorobenzene*	74.93			5.07		
Pentachloroethane*	49.71			4.29		
Pentachloronitrobenzene*	85.84			5.93		
Pentachlorophenol	88.93	*38-152*	*Pass*	7.50	52	*Pass*
Phenacetin*	89.68			6.07		
Phenanthrene	86.11	*65-120*	*Pass*	6.78	24	*Pass*
Phenol	57.80	*17-120*	*Pass*	4.35	39	*Pass*

Analyte	Average DOC	DOC Range	Pass/Fail	SD	Limit for s (%)	Pass/Fail
Phenol-d5	57.80	*8-424*	*Pass*	4.35		
p-Terphenyl-d14*	91.52			4.98		
Pyrene	87.34	*70-120*	*Pass*	7.55	30	*Pass*
Pyridine*	32.13			2.96		
Safrole*	78.46			5.28		
trans-Isosafrole*	77.99			5.67		

The criteria were met in all cases within the demonstrated Table 6 analytes in Method 625.1, indicating the analyte list is under control and further analysis can proceed.

Table 6 demonstrates the results for the matrix spike (MS) and matrix spike duplicate (MSD). The spike recovery data from the sample is shown in the second column, where the range criteria shown in Table 6 of Method 625.1 is presented. The spike and surrogates were added at 100 µg/mL in each liter of sample. The relative percent difference between the spike recovery and spike recovery duplicate is calculated using the equation in Method 625.1. If the data meets the criterion, a pass is indicated in the Pass/Fail. Analytes with a * indicate that they are from Table 3 and do not have acceptance criteria in Table 6 within Method 625.1. It is up to the laboratory to generate their own acceptance criteria for Table 3 analytes.

Table 6. Recovery Data: Matrix spike (MS) and matarix spike duplicate (MSD).

Analyte	Average MS, MSD Recovery %	Range P,Ps(%)	Pass/Fail	RPD %	(%) Limit	Pass/Fail
1,2,4,5-Tetrachlorobenzene*	67.1			9.11		
1,2,4-Trichlorobenzene	62.1	44-142	Pass	4.96	50	Pass
1,2-Dichlorobenzene*	56.5			5.31		
1,3,5,-Trinitrobenzene*	87.7			1.85		
1,3-Dichlorobenzene*	51.1			5.58		
1,3-Dinitrobenzene*	92.9			0.52		
1,4-Dichlorobenzene*	53.1			5.14		
1,4-Naphthoquinone*	82.5			4.89		
1-Naphthylamine*	92.3			5.45		
2,3,4,6-Tetrachlorophenol*	90.5			0.74		
2,4,5-Trichlorophenol*	87.5			1.04		
2,4-Dichlorophenol	89.0	39-135	Pass	0.47	50	Pass
2,4-Dimethylphenol	87.9	32-120	Pass	0.38	58	Pass
2,4-Dinitrophenol	87.5	D-191	Pass	7.00	132	Pass
2,4-Dinitrotoluene	92.9	39-139	Pass	1.44	42	Pass
2,6-Dichlorophenol*	87.8			1.90		
2,6-Dinitrotoluene	93.6	50-158	Pass	3.18	48	Pass
2-Chloronaphthalene	75.9	60-120	Pass	7.87	24	Pass
2-Chlorophenol	81.7	23-134	Pass	3.08	61	Pass
2-Fluorobiphenyl*	86.9			3.43		

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Analyte	Average MS, MSD Recovery %	Range P,Ps(%)	Pass/Fail	RPD %	RPD (%) Limit	Pass/Fail
2-Fluorophenol*	61.8			5.05		
2-Methyl phenol*	84.8			0.68		
2-Methylnaphthalene*	72.7			4.62		
2-Naphthylamine*	113.0			2.93		
2-Nitroaniline*	92.9			1.41		
2-Nitrophenol	80.7	29-182	Pass	4.36	55	Pass
2-Picoline*	49.2			6.96		
3,3'-Dichlorobenzidine	93.3	D-262	Pass	7.92	108	Pass
3,3'-Dimethylbenzidine*	99.3			0.90		
3+4 Methyl phenol*	86.4			1.17		
3-Methylcholanthrene*	87.9			8.34		
3-Nitroaniline*	95.4			4.75		
4 Aminobiphenyl*	114.6			2.36		
2-methyl-4,6-Dinitrophenol	91.9	D-181	Pass	1.83	203	Pass
4-Bromophenyl phenyl ether	85.0	53-127	Pass	3.90	43	Pass
4-Chloro-3-methylphenol	91.1	22-147	Pass	3.06	73	Pass
4-Chloroaniline*	120.7			0.11		
4-Chlorophenyl phenyl ether	82.3	25-158	Pass	4.57	61	Pass
4-Nitroaniline*	90.7			2.92		
4-Nitrophenol	97.3	D-132	Pass	4.31	131	Pass
4-Nitroquinoline-1-oxide*	95.8			1.99		
5-nitro-o-toluidine*	96.8			3.00		
7,12-Dimethylbenz(a)-anthracene*	86.9			5.42		
Acenaphthene	80.1	47-145	Pass	6.28	48	Pass
Acenaphthylene	81.3	33-145	Pass	4.75	74	Pass
Acetophenone*	80.2			5.11		
Acetylaminofluorene*	94.7			6.09		
Aniline*	84.0			7.85		
Anthracene*	89.2	27-133	Pass	7.17	66	Pass
Azobenzene*	86.6			3.64		
Benz(a)anthracene	89.2	33-143	Pass	8.15	53	Pass
Benzidine*	105.5			9.38		
Benzo(a)pyrene	88.8	17-163	Pass	9.10	72	Pass
Benzo(b)fluoranthene	89.2	24-159	Pass	6.83	71	Pass
Benzo(ghi)perylene	90.1	D-219	Pass	11.44	97	Pass
Benzo(k)fluoranthene	89.2	11-162	Pass	7.01	63	Pass
Benzoic acid*	58.7			6.47		
Benzyl alcohol*	81.3			2.07		
Bis(2-chlorethoxy)methane	85.4	33-184	Pass	0.19	54	Pass
Bis(2-chloroethyl)ether	74.6	12-158	Pass	6.50	108	Pass
Bis(2chloroisopropyl)ether	73.7	36-166	Pass	8.23	76	Pass
Bis(2-ethylhexyl) phthalate	92.3	8-158	Pass	0.81	82	Pass

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Analyte	Average MS, MSD Recovery %	Range P,Ps(%)	Pass/Fail	RPD %	(%) Limit	Pass/Fail
Benzyl butyl phthalate	91.7	D-152	Pass	1.99	60	Pass
Carbazole*	93.1			5.94		
Chrysene	89.4	17-168	Pass	10.27	87	Pass
cis-Isosafrole*	79.9			3.64		
Dibenz(ah)anthracene	91.2	D-227	Pass	6.46	126	Pass
Dibenzofuran*	82.7			6.37		
Diethyl phthalate	94.3	D-120	Pass	1.07	100	Pass
Dimethyl phthalate	93.2	D-120	Pass	0.97	183	Pass
Dimethylaminoazobenzene*	93.4			4.06		
Di-n-butyl phthalate	93.9	1-120	Pass	5.12	47	Pass
Di-n-octyl phthalate	90.7	4-146	Pass	2.69	69	Pass
Dinoseb*	91.0			1.83		
Diphenylamine*	91.3			2.03		
Ethylmethane Sulfonate*	79.1			3.34		
Fluoranthene	91.6	26-137	Pass	6.57	66	Pass
Fluorene	85.1	59-121	Pass	5.18	38	Pass
Hexachlorobenzene	86.1	D-152	Pass	6.56	55	Pass
Hexachlorobutadiene	48.8	24-120	Pass	5.56	62	Pass
Hexachlorocyclopentadiene*	46.5			4.15		
Hexachloropropene*	49.9			5.69		
Indeno(1,2,3-cd)pyrene	89.6	D-171	Pass	11.95	99	Pass
Isophorone	85.0	21-196	Pass	0.36	93	Pass
Methapyrilene*	92.8			3.99		
Methyl Methane Sulfonate*	53.4			8.39		
Naphthalene	71.4	21-133	Pass	4.06	65	Pass
NDMA*	38.6			17.34		
Nitrobenzene	77.4	35-180	Pass	5.18	62	Pass
Nitrobenzene-d5	82.0			5.54		
N-Nitroso-diethylamine*	71.4			6.09		
N-nitroso-di-n-butylamine*	88.2			0.45		
N-nitroso-di-n-propylamine	83.6	D-230	Pass	3.64	87	Pass
N-Nitrosomethyl ethylamine	62.8			11.95		
N-Nitroso-morpholine*	82.3			13.96		
N-Nitroso-piperidine*	85.7			2.10		
N-Nitroso-pyrrolidine*	85.7			0.86		
o-toluidine*	100.1			1.58		
Pentachlorobenzene*	78.8			7.32		
Pentachloroethane*	55.3			7.13		
Pentachloronitrobenzene*	89.1			5.28		
Pentachlorophenol	93.5	14-176	Pass	3.03	86	Pass

Analyte	Average MS, MSD Recovery %	Range P,Ps(%)	Pass/Fail	RPD %	(%) Limit	Pass/Fail
Phenacetin*	92.7			3.73		
Phenanthrene	88.8	54-120	Pass	6.07	39	Pass
Phenol	62.2	5-120	Pass	5.59	64	Pass
Phenol-d5	61.8			6.61		
p-Terphenyl-d14*	89.1			6.72		
Pyrene	90.8	52-120	Pass	7.51	49	Pass
Pyridine*	32.3			4.49		
Safrole*	83.0			3.83		
trans-Isosafrole*	82.8			1.56		

The matrix spike (MS) and matrix spike duplicate (MSD) were successfully spiked and measured recoveries were within the range specified in Table 6 in Method 625.1. The relative percent difference (RPD) between the matrix spike and duplicate sample showed excellent agreement when compared to the limit allowed. The agreement was generally well below the limit, sometimes more than an order of magnitude better.

Conclusion

US EPA Method 625 is an important method for evaluation of water pollution or clean-up. It allows a full suite of analytes to be evaluated at one time using GC/MS. Sample preparation is an important part of the process and disk solid phase extraction can provide advantages in using less solvent, eliminating emulsions and providing good extraction across the suite of analytes considered while minimizing exposure.

A number of analytes within Tables 1-3 were extracted simultaneously with a 1 liter sample volume. This was to challenge the extraction method and matrix components that may interfere with good adsorption and release of the analytes. The results show excellent performance of the One-Pass disk coupled with a Carbon Cartridge for capture of the analytes. Reduced sample volumes can be used for this method to improve method performance as long as all Method Detection Limits (MDLs) and reporting limits are met.

Solid phase extraction disks are another tool for the environmental laboratory to consider when evaluating their workflow for increased efficiency and safety. Other things can be considered once analytical performance is demonstrated, such as the ability to use less solvent, and reducing the need for evaporation and subsequent solvent recollection. Automation can also enhance reproducibility. Excellent duplicate agreement was shown here, even for the more difficult samples. Overall, the demonstrated analytical performance meets the criteria required and other favorable factors can be included in the decision making process to bring newer technology into today's modern laboratory.

References

1. 1. Method Update Proposed Rule, Federal Register, February 19, 2015, page 8946.
2. 2. Method 625.1, December 14 revision, can be found in the MUR, February 20, 2014. Or downloaded here:

https://nepis.epa.gov/Exe/ZyPDF.cgi/P100LVHC.PDF?Dockey=P100LVHC.PDF

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Appendix 1

Table 6 from US EPA Method 625.1, December 2014

Table 6 – QC Acceptance Criteria – Method 625 [1]					
Analyte	Range for Q (%) [2]	Limit for s (%) [3]	Range for $\bar{X}$ (%) [3]	Range for P, P_s (%) [3]	Limit for RPD (%)
Acenaphthene	70-130	29	60-132	47-145	48
Acenaphthylene	60-130	45	54-126	33-145	74
Aldrin	7-152	39	7-152	D-166	81
Anthracene	58-130	40	43-120	27-133	66
Benzo(a)anthracene	42-133	32	42-133	33-143	53
Benzo(b)fluoranthene	42-140	43	42-140	24-159	71
Benzo(k)fluoranthene	25-146	38	25-146	11-162	63
Benzo(a)pyrene	32-148	43	32-148	17-163	72
Benzo(ghi)perylene	13-195	61	D-195	D-219	97
Benzyl butyl phthalate	43-140	36	D-140	D-152	60
beta-BHC	42-131	37	42-131	24-149	61
delta-BHC	D-130	77	D-120	D-120	129
bis(2-Chloroethyl)ether	52-130	65	43-126	12-158	108
bis(2-Chloroethoxy)methane	52-164	32	49-165	33-184	54
bis(2-Chloroisopropyl) ether	63-139	46	63-139	36-166	76
bis(2-Ethylhexyl) phthalate	43-137	50	29-137	8-158	82
4-Bromophenyl phenyl ether	70-130	26	65-120	53-127	43
2-Chloronaphthalene	70-130	15	65-120	60-120	24
4-Chlorophenyl phenyl ether	57-145	36	38-145	25-158	61
Chrysene	44-140	53	44-140	17-168	87
4,4'-DDD	D-135	56	D-135	D-145	93
4,4'-DDE	19-130	46	19-120	4-136	77
4,4'-DDT	D-171	81	D-171	D-203	135
Dibenz(a,h)anthracene	13-200	75	D-200	D-227	126
Di-*n*-butyl phthalate	52-130	28	8-120	1-120	47
3,3'-Dichlorobenzidine	18-213	65	8-213	D-262	108
Dieldrin	70-130	38	44-119	29-136	62
Diethyl phthalate	47-130	60	D-120	D-120	100
Dimethyl phthalate	50-130	110	D-120	D-120	183
2,4-Dinitrotoluene	53-130	25	48-127	39-139	42
2,6-Dinitrotoluene	68-137	29	68-137	50-158	48
Di-*n*-octyl phthalate	21-132	42	19-132	4-146	69
Endosulfan sulfate	D-130	42	D-120	D-120	70
Endrin aldehyde	D-189	45	D-189	D-209	75
Fluoranthene	47-130	40	43-121	26-137	66
Fluorene	70-130	23	70-120	59-121	38
Heptachlor	D-172	44	D-172	D-192	74
Heptachlor epoxide	70-130	61	71-120	26-155	101
Hexachlorobenzene	38-142	33	8-142	D-152	55
Hexachlorobutadiene	68-130	38	38-120	24-120	62
Hexachloroethane	55-130	32	55-120	40-120	52
Indeno(1,2,3-cd)pyrene	13-151	60	D-151	D-171	99
Isophorone	52-180	56	47-180	21-196	93
Naphthalene	70-130	39	36-120	21-133	65
Nitrobenzene	54-158	37	54-158	35-180	62
N-Nitrosodi-*n*-propylamine	59-170	52	14-198	D-230	87

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Table 6 – QC Acceptance Criteria – Method 625 [1]					
Analyte	Range for Q (%) [2]	Limit for s (%) [3]	Range for $\bar{X}$ (%) [3]	Range for P, P_s (%) [3]	Limit for RPD (%)
PCB-1260	19-130	77	19-130	D-164	128
Phenanthrene	67-130	24	65-120	54-120	39
Pyrene	70-130	30	70-120	52-120	49
1,2,4-Trichlorobenzene	61-130	30	57-130	44-142	50
4-Chloro-3-methylphenol	68-130	44	41-128	22-147	73
2-Chlorophenol	55-130	37	36-120	23-134	61
2,4-Dichlorophenol	64-130	30	53-122	39-135	50
2,4-Dimethylphenol	58-130	35	42-120	32-120	58
2,4-Dinitrophenol	39-173	79	D-173	D-191	132
2-Methyl-4,6-dinitrophenol	56-130	122	53-130	D-181	203
2-Nitrophenol	61-163	33	45-167	29-182	55
4-Nitrophenol	35-130	79	13-129	D-132	131
Pentachlorophenol	42-152	52	38-152	14-176	86
Phenol	48-130	39	17-120	5-120	64
2,4,6-Trichlorophenol	69-130	35	52-129	37-144	58

[1] Acceptance criteria are based upon method performance data in Table 7 and from EPA Method 1625. Where necessary, limits for recovery have been broadened to assure applicability to concentrations below those used to develop Table 7.
[2] Test concentration = 100 µg/mL
[3] Test concentration = 100 µg/L

Q = Calibration verification (Sections 7.3.1 and 13.4)
s = Standard deviation for four recovery measurements in the DOC test (Section 8.2.4).
$\bar{X}$ = Average recovery for four recovery measurements in the DOC test (Section 8.2.4).
P, P_s = MS/MSD recovery (Section 8.3.2, Section 8.4.2).
RPD = MS/MSD relative percent difference (RPD; Section 8.3.3).
D = Detected; result must be greater than zero.

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Literature Number: AN123-HOR.V.1

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