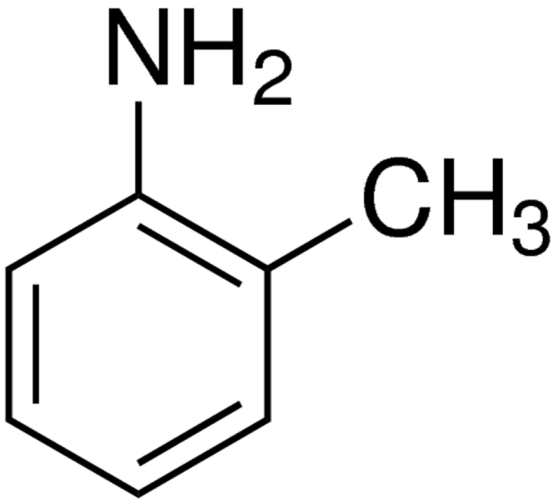
Determination of Selected Semivolatile Organic Chemicals in Drinking Water by SPE and GC/MS



UCT Part Numbers

ECHLD156-P
ENVIRO-CLEAN® HL DVB 500 mg, 6 mL cartridge

VMFSTFR12
Large volume sample transfer tubes

VMF016GL
16 position glass block manifold

VMF02125
12 position large volume collection rack

RFV1F15P
15 mL reservoirs with 1 frit, 10-micron porosity

ECSS25K
Sodium sulfate, anhydrous, ACS grade, granular, 60 mesh.

GCLGN4MM-5
GC liner, 4mm splitless gooseneck, 4mm ID x 6.5mm OD x 78.5mm

Summary:

Recently the US EPA published a list of 30 UCMR4 (the 4th Unregulated Contaminant Monitoring Rule) analytes that may potentially be present in tap water but are not yet subject to EPA's drinking water standards set under the Safety Drinking Water Act. 4 among the 30 UCMR4 compounds, including o-toluidine, quinoline, butylated hydroxy-anisole (BHA), and dimethipin, are determined by EPA method 530 using solid phase extraction (SPE) and GC/MS detection.

1-liter of preserved drinking water is passed through a 6-mL SPE cartridge containing 500 mg divinylbenzene (DVB) based sorbent, the analytes are retained on the sorbent and later eluted with a small quantity of organic solvents. The extract is dried using anhydrous sodium sulfate and concentrated to 1 mL. The final extract is analyzed by GC/MS under full scan or SIM mode. Calibration standards prepared in solvent or matrix matched standards can be used for constructing calibration curves. This study used the GC/MS SIM method with solvent standard calibration for data acquisition and analyte quantitation.

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Sample Pretreatment:

All samples are preserved with 0.1 g/L L-ascorbic acid (dechlorination), 0.35 g/L EDTA·Na3 (inhibit metal-catalyzed hydrolysis of targets), 1 g/L diazolidinyl urea (microbial inhibitor), and 7.75 g/L Trizma® pH 7 buffer* (reduce acid and base catalyzed hydrolysis of target analytes).

**: Trizma buffer caused an interfering peak in GC/MS full scan chromatogram (around 10.7 min), which luckily did not interfere analyte quantitation.*

SPE Procedure:

1. SPE conditioning

a) Connect the large sample transfer tubes **(VMFSTFR12)** to the top of the SPE cartridges (**ECHLD156-P)**. Attach the connected SPE cartridges to a 16-position glass block manifold **(VMF016GL)**.
b) Insert the stainless-steel ends of the transfer tubes into a beaker containing DCM and draw some of the solvent through the cartridge. Let the DCM soak in the SPE sorbent for 1 min, and draw the remainder of the DCM through the cartridge to waste. Draw full vacuum through the cartridges for 1 minute.
c) Condition the SPE cartridges with 10 mL of methanol, draw the methanol through the cartridges slowly and leave a thin layer above the frit.
d) Equilibrate the SPE cartridges with 10 mL of DI water, draw the water through the cartridges and leave a layer (about 1") above the frit.

2. Sample extraction

a) Insert the stainless-steel end of each transfer tube to each corresponding sample bottle. Adjust the vacuum for a fast dropwise flow (about 10 mL/min).

3. Wash cartridge

a) Rinse each of the sample bottles with approx. 10 mL of DI water and pass the water to the SPE cartridges using the transfer tubes.
b) Remove the transfer tubes from the SPE cartridges, add 1 cartridge volume of DI water to each SPE cartridge to rinse off the preservatives from the cartridge wall.
c) Dry the SPE cartridges under full vacuum for about 10 min.

4. Elution

a) Insert the collection rack (VMF02125) with glass vials (40 - 60 mL) into the manifold to collect the SPE eluates.
b) Add ~2 mL of acetone to the sample bottle, and rinse the inside walls thoroughly. Allow the solvent to settle to the bottom of the bottle, then transfer it to the cartridge. Draw the solvent through the cartridge using vacuum and collect it.
c) Add 5 mL of DCM to the sample bottle and rinse the inside walls thoroughly. Allow the solvent to settle to the bottom of the bottle, and then transfer it to the cartridge using vacuum pressure. Draw about half of the solvent through the cartridge, stop vacuum pressure at the cartridge, and allow the cartridge to soak for one minute. Draw the remaining solvent through the cartridge. Repeat the above step with another 5 mL of DCM and collect all of the DCM. Pre-rinse the drying cartridges (about 7g sodium sulfate) with 3 mL of DCM.
d) Pass the SPE eluates through the drying column and collect it in new glass vials. Rinse the eluate vials with 3 mL of DCM and pass the DCM through the sodium sulfate anhydrous and collect the extract.
e) Concentrate the dried extract to 0.71 mL using a TurboVap under a gentle stream of nitrogen (about 9-10 psi) in a water bath of 40 °C. Add internal standards and bring to a 1 mL final volume with DCM. Inject 1 µL to GC/MS for analysis.
**: Acetone can release o-toluidine and o-toluidine d9 in sodium sulfate much better than DCM.*

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GC/MS SIM Method:

Parameter	Conditions
GC column	Restek Rtx®-1701 w/Integra-Guard® 30 m, 0.25 mm ID, 0.25 µm df
GC liner **(GCLGN4MM-5)**	4 mm, single gooseneck, packed with deactivated glass wool
Injection	1 µL at 250 °C, splitless injection, purge flow of 30 mL/min at 1min
Carrier gas and flow rate	Helium at 1.0 mL/min (constant flow)
GC temperature program	60 °C hold for 1 min, ramp at 10 °C/min to 280 °C, and hold for 2 min
Solvent delay	6.5 min (acquire data from 6.5 to 20 min)
MS source temperature	250 °C
MS quadrupole temperature	150 °C
GC/MS interface	280 °C
Tune	dftpp tune
Acquisition mode	SIM

Peak #	Compound	Retention (min)	(GC/MS SIM ions) Quantitation	(GC/MS SIM ions) Confirmation
1	o-toluidine d9	7.93	114	112
2	o-toluidine	7.98	106	107
3	Quinoline d7	10.14	136	108
4	Quinoline	10.16	129	102
5	Acenaphthene d10	13.04	162	164
6	BHA	14.15	165	137
7	Phenanthrene d10	16.94	188	189
8	Dimethipin	19.04	54	118

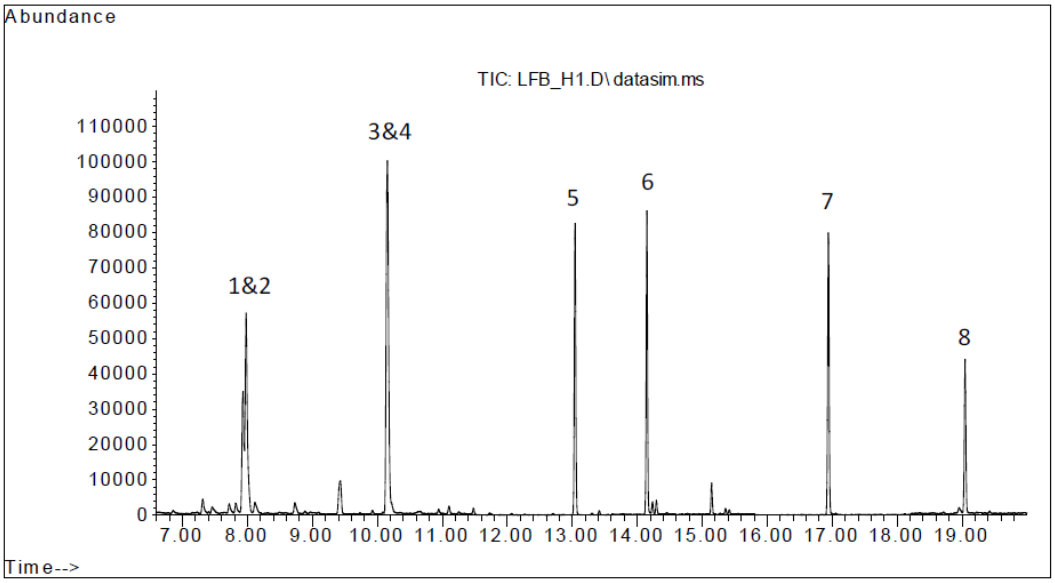

Figure 1: Chromatogram of a Laboratory Fortified Blank at 0.5 µg/L

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Results:

Linearity and Detection Limit

Compound	Linearity range (ng/mL)	Linearity (R^2)	Detection Limit* (µg/L)
o-toluidine	5 - 1000	0.9998	0.001
Quinoline	5 - 1000	0.9999	0.002
BHA	5 - 1000	0.9986	0.001
Dimethipin	5 - 1000	0.9998	0.001

**: Detection limits were calculated from 7 replicated laboratory fortified blanks at 0.01 µg/L, which also met the minimum reporting limit criteria, with the upper prediction interval results being ≤ 150% while the lower prediction interval results ≥ 50%.*

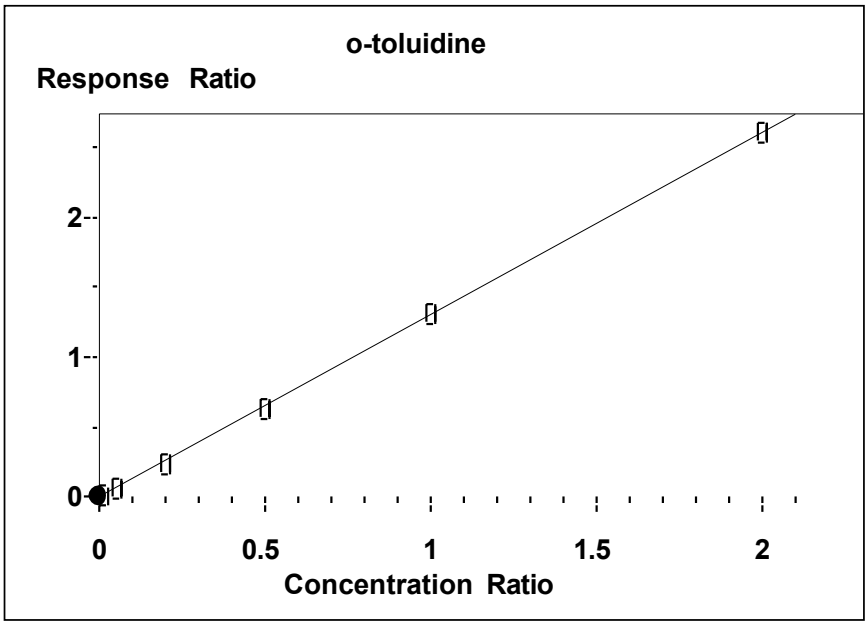

Figure 2: Solvent Standard Calibration Curve of o-toluidine (R^2 = 0.9998)

Accuracy and Precision in Fortified Reagent Water (n = 4)

	Spiked at 0.01 µg/L		Spiked at 0.1 µg/L		Spiked at 0.5 µg/L	
Compound	Avg Recovery %	RSD%	Avg Recovery %	RSD%	Avg Recovery %	RSD%
o-toluidine d9	**87.1**	2.9	**98.7**	1.8	**101.5**	1.4
o-toluidine	**98.5**	1.3	**98.3**	2.0	**98.2**	0.9
Quinoline d7	**95.0**	3.4	**96.6**	2.6	**99.9**	0.6
Quinoline	**100.5**	6.3	**97.0**	3.0	**99.5**	0.9
BHA	**119.1**	2.2	**111.3**	2.7	**102.1**	1.2
Dimethipin	**127.3**	1.9	**115.7**	1.5	**106.0**	1.2

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Accuracy and Precision in Fortified Tap Water (n = 4)

	Spiked at 0.01 µg/L		Spiked at 0.1 µg/L		Spiked at 0.5 µg/L	
Compound	**Avg Recovery %**	**RSD%**	**Avg Recovery %**	**RSD%**	**Avg Recovery %**	**RSD%**
o-toluidine d9	**84.3**	1.3	**92.6**	2.8	**89.9**	1.4
o-toluidine	**96.9**	3.0	**93.8**	1.6	**86.9**	1.6
Quinoline d7	**92.4**	1.0	**95.2**	1.0	**100.2**	1.1
Quinoline	**107.3**	0.7	**97.3**	2.9	**96.2**	0.5
BHA	**113.1**	2.1	**113.7**	1.3	**104.5**	1.7
Dimethipin	**121.2**	2.3	**116.5**	3.5	**106.9**	1.4

**: Tap water source: Delaware river and wells*

Conclusion:

Excellent recovery and reproducibility have been achieved using UCT's DVB-based polymeric sorbent for the determination of four UCMR4 analytes in reagent and tap water samples. Recoveries ranged from 84.3 to 127.3% for low-level spiked samples (0.01 µg/L), which well passed the QC requirement of 50 to 150%. For median (0.1 µg/L) and high (0.5 µg/L) spiking levels, recoveries ranged from 86.9 to 116.5%, which also passed the QC acceptance criteria of 70 to 130% (50 to 130% for o-toluidine and o-toluidine d9).
The relative standard deviations (n = 4) for all 3 spiking levels in both reagent and tap water were ≤ 6.3%, within the method-required limit of ≤ 20%.

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