EPA Method 530: 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

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Summary:

Recently the US EPA published a list of 30 UCMR4 (the 4th Unregulated Contaminant Monitoring Rule) analytes which 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 hydroxyanisole (BHA), and dimethipin, are determined by EPA method 530 using solid phase extraction (SPE) and GC/MS detection.

1-liter 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. In this study, GC/MS SIM method with solvent standard calibration was carried out for data acquisition and analyte quantitation.

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 to a beaker containing DCM (5 mL x n samples). Let DCM soak the SPE sorbent for 1 min, draw DCM through and leave full vacuum on for 1 min.
   c) Condition the SPE cartridges with 10 mL methanol (x n samples), draw methanol through slowly and leave a thin layer above the frit.
   d) Equilibrate the SPE cartridges with 10 mL DI water (x n samples), draw water through 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 vacuum for a fast dropwise flow (about 15 mL/min).
3. Wash cartridge
   a) Rinse sample bottles with 10 mL DI water, and pass the rinse to SPE cartridges using the transfer tubes.
   b) Remove transfer tube from SPE cartridges, add 1 cartridge volume of DI water to each SPE cartridge to rinse off the preservatives left on the cartridge wall.
   c) Dry the SPE cartridges under full vacuum for 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 about 1" anhydrous sodium sulfate (**ECSS25K**) to SPE cartridges.
   c) Add 2 mL acetone to SPE cartridges, let acetone soak sorbent for 1 min, then pull through slowly, and leave full vacuum on for 1 min.
   d) Repeat Step 9) with 5 mL DCM, followed by sample bottle rinse of 5 mL DCM.
   e) Pre-rinse the drying cartridges (about 15 g sodium sulfate in 15 mL reservoirs) with 5 mL DCM, pass the SPE eluates through and collect in new glass vials. Rinse the eluate vials with 5 mL acetone*, apply the rinse to the sodium sulfate and collect.
   f) Concentrate the dried extract to 1 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 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 1 min
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	GC/MS SIM ions	
		(min)	Quantitation	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

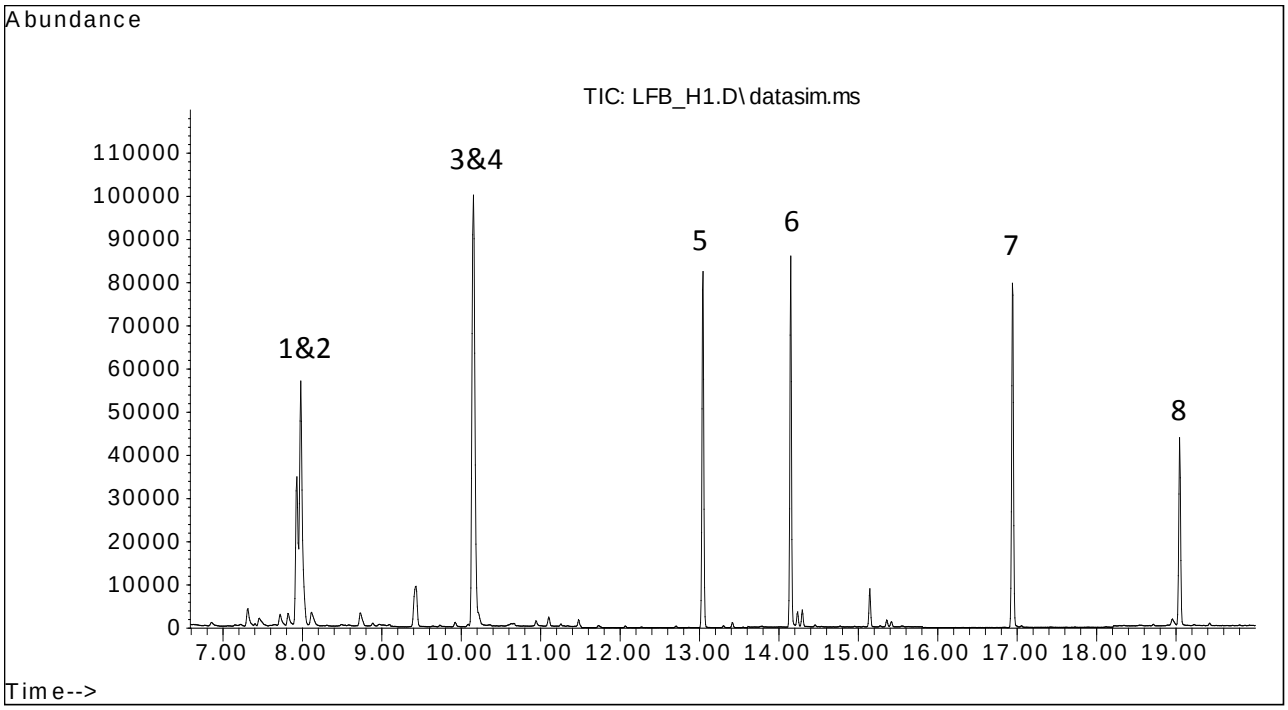

Figure 1: Chromatogram of a Laboratory Fortified Blank at 0.5 µg/L

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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%.*

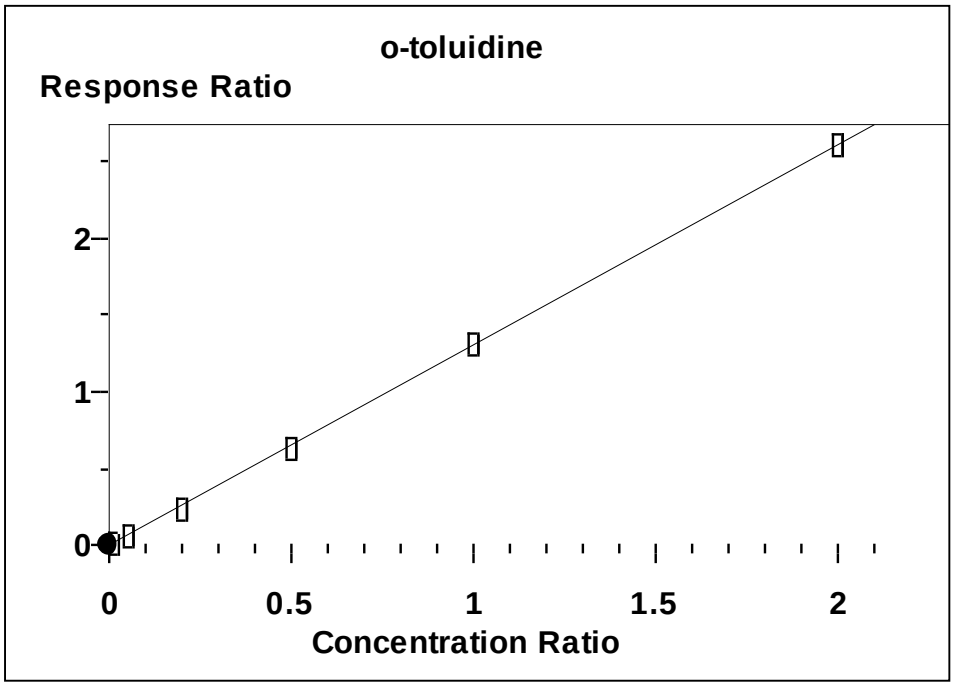

Figure 2: Solvent Standard Calibration Curve of o-toluidine (R^2 = 0.9998)

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

Compound	Spiked at 0.01 µg/L		Spiked at 0.1 µg/L		Spiked at 0.5 µg/L	
	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)

Compound	Spiked at 0.01 µg/L		Spiked at 0.1 µg/L		Spiked at 0.5 µg/L	
	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 easily 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%, which were within the method required limit of ≤ 20%.

UCT, LLC • 2731 Bartram Road • Bristol, PA 19007 800.385.3153 • 215.781.9255
www.unitedchem.com Email: methods@unitedchem.com

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