EPA Method 525.3: Determination of 9 UCMR4 Contaminants in Drinking Water by SPE and GC/MS

UCT Part Numbers

ECHLD156-P
ENVIRO-CLEAN® HLDVB
500 mg, 6 mL SPE cartridge PE Frit

VMF02125
12 position large
volume collection rack

VMFSTFR12
Large volume sample
transfer tubes

ECSS15M6
Enviro-Clean® Sodium Sulfate
5g, 6mL SPE cartridge Teflon Frit

VMF016GL
16 position glass
block manifold

AD0000AS
Cartridge Adapters
(1, 3, 6, 10, and 15 mL cartridges)

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

Summary:

The US EPA uses the Unregulated Contaminant Monitoring Rule (UCMR) program to collect occurrence data for contaminants that may be present in drinking water but do not have health-based standards set under SDWA. Once every five years EPA issues a list of no more than 30 unregulated contaminants, largely based on the Contaminant Candidate List (CCL), to be monitored by public water systems [1]. The 4th UCMR (UCMR4) was proposed on December 11, 2015 which outlines a list of 30 chemical contaminants to be monitored between 2018 and 2020. The monitoring will provide EPA a basis for future regulatory determinations and, as warranted, actions to protect public health [2]. Among the 30 contaminants, 8 pesticides (chlorpyrifos, dimethipin, ethoprop, oxyfluorfen, profenofos, tebuconazole, total permethrin (cis- & trans-), and tribufos), and 1 pesticide manufacturing byproduct (alpha-hexachlorocyclohexane), are determined by EPA method 525.3 using solid phase extraction (SPE) and GC/MS detection [3].

A 1-liter finished drinking water sample is extracted using a 6-mL SPE cartridge containing 500 mg of modified divinylbenzene(DVB) polymeric sorbent. The analytes are retained onto the sorbent and then eluted with a small amount of organic solvents. A drying tube with 5 grams of anhydrous sodium sulfate packed in 6 mL cartridge is attached to the bottom of the SPE cartridge during elution, providing a simultaneous drying of the SPE eluate. The dried extract is concentrated to 1 mL and analyzed by GC/MS equipped with a capillary GC column using either full scan or SIM mode. Calibration standards can be prepared in solvent (ethyl acetate) or matrix matched to compensate any possible matrix effect. In this study solvent standards were used as no matrix suppression or enhancement was encountered.

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Sample Pretreatment:

a) Preservatives, including 0.1 g of L-ascorbic acid (dechlorination), 0.35 g of EDTA (to inhibit metalcatalyzed hydrolysis), and 9.4 g of potassium dihydrogen citrate (pH 3.8 buffer and microbial inhibitor), are added to 1-L sample bottle prior to shipment to the sampling field.
b) Prior to extraction, spike the preserved samples with surrogate and appropriate amount of target analyte spiking solution prepared in water miscible solvents, such as methanol, and mix well.

SPE Procedure:

1. Cartridge Conditioning

a) Attach the SPE cartridges (**ECHLD156-P**) to the 16-position glass block manifold (**VMF016GL**), add 5 mL of ethyl acetate (EtOAc) to the SPE cartridges, let the solvent soak the sorbent for 1 min before drawing to waste, and leave full vacuum on for 1 min.
b) Repeat with 5 mL of methylene chloride (DCM).
c) Attach the large volume sample transfer tubes (**VMFSTFR12**) to the top of the SPE cartridges.
d) Insert the stainless steel ends of the transfer tubes into a beaker of methanol (10 mL per sample) and slowly draw the methanol through the SPE sorbent, leaving a thin layer of methanol above the SPE frit.
e) Repeat with reagent water (10 mL per sample), leaving a layer of about 1" above the frit.

2. Sample Extraction

a) Insert the stainless steel ends of the transfer tubes into the sample bottles. Adjust the vacuum so that the flow rate is approximate 15-20 mL/min (fast dropwise).

3. Cartridge Washing and Drying

a) Rinse the sample bottles with 10 mL reagent water and pass the rinsate to the SPE cartridges using the transfer tubes to remove any remaining sample preservatives.
b) Dry the SPE cartridges under full vacuum for 10 min.

4. Simultaneous Elution and Eluate Drying

a) Attach the drying tubes (**ECSS15M6**) to the manifold, and rinse with 5 mL of EtOAc.
b) Attach the drying tubes to the bottom of the SPE cartridges using the cartridge adapters (**AD0000AS**).
c) Insert the 12-position collection rack (**VMF02125**) with 40-60 mL VOA glass vials into the manifold to collect eluates.
d) Rinse the sample bottles with 5 mL of EtOAc and elute the retained analytes by slowly pulling the elution solution through the SPE cartridges using the transfer tubes Apply a low vacuum such that the elution solvent exits the cartridge in a slow dropwise fashion. After the solvent has passed through, apply full vacuum for 30 seconds so that all elution solvent is collected.
e) Repeat the elution with 10 mL of DCM.

5. Concentration

a) Evaporate the eluates to about 0.7 mL using TurboVap under a gentle stream of nitrogen (about 10 psi) at 40 °C.
b) Transfer the extracts to 2-mL autosampler vials, add internal standard, rinse the collection vials with small amount of EtOAc, transfer the rinsate to the 2-mL vials to bring the volume up to the 1-mL mark.
c) Vortex the samples for 30 seconds, and inject 1 µL to GC/MS for analysis.

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GC/MS Method:

Parameter	Conditions
GC/MS	Agilent 6890N GC coupled to 5975C MSD
Injection	1 µL splitless injection at 250 °C
GC liner (UCT: **GCLGN4MM-5**)	4 mm splitless gooseneck liner with deactivated glass wool
GC column	Restek Rxi®-5sil MS 30m x 0.25mm, 0.25µm with 10m integrated guard column
Carrier gas	Ultra high purity Helium at a constant flow of 1.2 mL/min
Oven temp. program	Initial temperature at 55 °C, hold for 1 min; ramp at 10 °C/min to 200 °C; ramp at 7 °C/min to 320 °C; and hold for 0.36 min
Temperatures	Transfer line 280 °C; Ion source 250 °C; Quadrupole 150 °C
Full scan range	45 - 500 amu

Results:

Accuracy and Precision in Fortified Reagent Water (n=5)		
Compound Name	**Recovery %**	**RSD %**
alpha-Hexachlorocyclohexane	86.2	1.8
Chlorpyrifos	95.6	2.5
Dimethipin	89.4	2.2
Ethoprop	98.9	2.4
Oxyfluorfen	99.5	3.8
Profenofos	105.6	3.7
Tebuconazole	92.9	4.0
Total permethrin (cis- & trans-)	98.5	3.6
Tribufos	88.2	3.8

Conclusion:

Excellent analytical performance has been obtained using UCT's DVB based sorbent for the extraction of 9 UCMR4 contaminants in drinking water by EPA method 525.3. Recoveries were ranged from 86.2 to 105.6% with relative standard deviations (RSD%) < 5%, which well passed the QC acceptance criteria required by Method 525.3, even for dimethipin, a problematic compound that is too polar (LogP = -1.51) to be retained on silica based C18 and some polymeric sorbents, such as the styrene divinylbenzene (SDVB) based sorbent.

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References:

[1] https://www.epa.gov/dwucmr/learn-about-unregulated-contaminant-monitoring-rule

[2] https://www.epa.gov/dwucmr/fourth-unregulated-contaminant-monitoring-rule

[3] https://www.ssi.shimadzu.com/industry/methods/m_525_3.pdf

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