Determination of the 11 Fourth Unregulated Contaminant Monitoring Rule (UCMR4) Compounds by EPA Method 525.3

UCT Part Numbers:
ECHLD156P - 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:

The US Environmental Protection Agency (EPA) uses the Unregulated Contaminant Monitoring Program to collect data for contaminants suspected to be present in drinking water but do not have health-based standards set under the Safe Drinking Water Act [1]. Every five years the US EPA reviews and issues a list of contaminants (30 or less) to be monitored; largely based on the Contaminant Candidate List. The US EPA and its contracting laboratories are currently developing and publishing testing methods for the UCMR4 contaminants. These compounds will be monitored by public drinking water systems no later than 2018. Among the EPA issued UCMR4 compound list there are 11 analytes (disulfoton, ethoprop, alpha-Hexachlorocyclohexane, trans- permethrin, cis-permethrin, tribufos, profenofos, oxyfluorfen, vinclozolin, dimethipin, and tebuconazole) that can be analyzed by EPA Method 525.3.

A 1-liter finished drinking water sample is extracted using a 6 mL solid phase extraction (SPE) cartridge containing 500 mg of DVB based polymeric sorbent. The analytes are retained on the sorbent and then eluted with a small amount of organic solvents. The extract is dried using anhydrous sodium sulfate and concentrated to 1 mL. The final extract is analyzed by GC/MS equipped with a capillary column using either full scan or SIM mode. Calibration standards can be prepared in solvent (ethyl acetate) or matrix

matched standards obtained by spiking known amounts of target analytes to the 1-mL final extracts from the extracted blank samples.

Sample Preservation:

Preservation reagents, including 0.1 g of L-ascorbic acid (dechlorination), 0.35 g of EDTA (to inhibit metal-catalyzed hydrolysis), and 9.4 g of potassium dihydrogen citrate (pH 3.8 buffer and microbial inhibitor), are added to each 1-L sample bottle prior to shipment to the sampling field.

SPE Procedure:

1. Add surrogates to the 1-L preserved water sample, and target analytes for spiked samples, and mix well.

   Note: Spiking solutions should be prepared in water miscible solvents, such as methanol and acetone.
2. Attach the SPE cartridges (**ECHLD156P**) to the 16 position glass block manifold (**VMF016GL**).
3. Wash the SPE cartridges with 6 mL dichloromethane (DCM), let the sorbent soak for 1 min, draw the DCM through and leave full vacuum on for 1 min. Repeat the wash with 6 mL DCM.
4. Condition the SPE cartridges with 10 mL methanol, draw the methanol through slowly and leave a thin solvent layer above the frit. Equilibrate the SPE cartridges with 10 mL DI water, draw the water through and leave about 1” layer above the frit.
5. Attach the large volume sample transfer tubes (**VMFSTFR12**) to the top of the SPE cartridges. Adjust the vacuum for a fast dropwise flow (about 15 to 20 mL/min).
6. Rinse sample bottles with 10 mL DI water, and pass the rinsates to the SPE cartridges using the transfer tubes to remove the sample preservatives.
7. Dry the SPE cartridges under full vacuum for 10 min.

8. Insert the collection rack (**VMF02125**) with glass vials (40 - 60 mL volumes) into the manifold to collect the SPE eluates.
9. Rinse sample bottles with 10 mL ethyl acetate (EA), draw 1/3 though the SPE cartridges and let soak 2 min before passing the remaining EA through the SPE cartridges in a slow dropwise fashion. Leave full vacuum on for 1 min.
10. Repeat Step 9) with 10 mL DCM.
11. Dry the eluates by passing through the 15 mL reservoirs (**RFV1F15P**) holding about 15 g of anhydrous sodium sulfate (**ECSS25K**) and collect in a new glass vial (40 - 60 mL). Rinse the eluate vials with 10 mL DCM and apply the rinses to the sodium sulfate and collect.
12. Concentrate the dried eluates to about 0.8 mL using a TurboVap under a gentle stream of nitrogen in a water bath of 40 °C.
13. Transfer the concentrated extracts to 2-mL auto-sampler vials, rinse the glass vials with small quantities of EA and transfer the rinses to the 2-mL vials until 1 mL final volume is reached.
14. Add internal standards and inject 1 µL to GC/MS for analysis.

GC/MS method:

GC/MS	Agilent 6890N GC coupled to a 5975C MSD
Injection	1 µL splitless injection at 250 ºC
GC liner	UCT p/n **GCLGN4MM-5 -** 4 mm splitless gooseneck 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 ºC, hold for 1 min; ramp at 10 ºC/min to 200 ºC; ramp at 7 ºC/min to 320 ºC; and hold for 0.36 min
Temperatures	Transfer line 280 ºC; Source 250 ºC; Quadrupole 150 ºC
Full scan range	45 - 500 amu

Results:

Recovery and RSD% of 1-L Drinking Water Spiked with 5 µg/L of Target Analytes

Compound Name	Recovery%	RSD% (n=5)
alpha-Hexachlorocyclohexane	86.2	1.8
Dimethipin	89.4	2.2
Disulfoton	90.7	3.4
Ethoprop	98.9	2.4
Oxyfluorfen	99.5	3.8
Permethrin, cis-	102.4	3.9
Permethrin, trans-	94.6	3.4
Profenofos	105.6	3.7
Tebuconazole	92.9	4.0
Tribufos+Merphos	88.2	3.8
Vinclozolin	89.7	2.5

References:

[1] http://water.epa.gov/lawsregs/rulesregs/sdwa/ucmr/

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