

Determination of 9 UCMR4 Contaminants by EPA Method 525.3 using SPE and GC/MS Detection



UCT Part Numbers

ECUNI525-UCMR4

ENVIRO-CLEAN®

Proprietary sorbent for 525.3

UCMR4 compounds

1500mg/Universal Cartridge

ECUCTADP

ENVIRO-CLEAN®

Glass Cartridge Adaptor

ECUNIMSS

ENVIRO-CLEAN®

Muffled sodium sulfate

20g/Universal Cartridge

ECUNIBHD-PP

ENVIRO-CLEAN®

White Bottle Holder

ECUCTVAC6

ENVIRO-CLEAN®

6 Station Vacuum Manifold

Stainless Steel System

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, the EPA issues a list of no more than 30 unregulated contaminants, largely based on the Contaminant Candidate List (CCL), to be monitored in public water systems [1]. The 4th UCMR (UCMR4) listed 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 including chlorpyrifos, dimethipin, ethoprop, oxyfluorfen, profenofos, tebuconazole, total permethrin (cis- & trans-) and tribufos, plus 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 UCT's Enviro-Clean® 83-mL Universal Cartridge containing 1500 mg of proprietary sorbent mixture. The analytes are retained onto the sorbent and then eluted with a small amount of organic solvents. A drying cartridge with 20 grams of anhydrous sodium sulfate in 83 mL format is used to remove residual water in the SPE eluate. The dried extract is then concentrated to 1 mL and analyzed by GC/MS in SIM mode. EPA method 525.3 allows calibration standards be prepared in solvent (ethyl acetate) or matrix-matched (surrogates and target analytes post-spiked to the blank extracts) as matrix enhancement was observed in several analytes. In this study matrix-matched calibration was employed to compensate any matrix effect for more accurate quantitation results.



Sample Pretreatment:

- a) Preservatives, including 0.1 g of L-ascorbic acid, 0.35 g of EDTA trisodium salt, and 9.4 g of potassium dihydrogen citrate, are added to 1-L sample bottles prior to shipment to the sampling field.
- b) Before extraction, spike with surrogate (**Chem Service: M-SS5251B3-5ML**) and target analyte (**Chem Service: M-UCMR4PESTMIX1-1ML**) spiking solutions prepared in methanol, and mix well.

SPE Procedure:

1. Cartridge Conditioning

- a) Place the glass adaptors (**UCT: ECUCTADP**) on the 6-station vacuum manifold (**UCT: ECUCTVAC6**), attach the SPE cartridges (**UCT: ECUNI525-UCMR4**) to the glass adaptors, and then the bottle holders (**UCT: ECUNIBHD**) to the top of the SPE cartridges.
- b) Add 5 mL of 1:1 ethyl acetate:dichloromethane to the SPE cartridges by rinsing the bottle holders and the SPE cartridges, let solvent soak the SPE sorbent for 1 min before drawing to waste. Leave full vacuum on for 1 min.
- c) Release vacuum, add 10 mL of methanol to the SPE cartridges, let solvent soak the sorbent for 1 min, then draw (or by gravity) to waste leaving a thin methanol layer above the frit.
- d) Add 10 mL of DI water to the SPE cartridges, draw through leaving a thin layer above the frit.

2. Sample Extraction

- a) Load the sample bottles to the bottle holders on the manifold, and adjust vacuum for a fast dropwise flow (about 30 mL/min).
- b) Rinse the sample bottles with 10 mL of DI water, apply the bottle rinse to SPE cartridge, and draw to waste.

3. Cartridge Drying

- a) Dry the SPE cartridges under full vacuum for 10 min. Move the cartridges from the manifold during drying, and shake the cartridges to remove excess water from the bottom of the SPE cartridges.

4. Analyte Elution

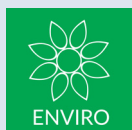
- a) Insert glass vials (40 or 50 mL VOA vials) into the SPE manifold to collect the SPE eluates.
- b) Rinse the sample bottles with 5 mL of ethyl acetate, apply the rinse to the SPE cartridges, let elution solvent soak sorbent for 1 min before drawing slowly to the collection vials. Leave full vacuum on for 1 min.
- c) Repeat 4.b) with 5 mL of dichloromethane, 5 mL of ethyl acetate, and 5 mL of dichloromethane.

5. Eluate Drying

- a) Remove the SPE cartridges with bottle holders from the glass cartridge adaptors, and remove the collection vials from the manifold.
- b) Place the sodium sulfate drying cartridges (**UCT: ECUNIMSS**) on the glass adaptors, rinse with 10 mL of dichloromethane.
- c) Insert new glass vials into the manifold, pass the SPE eluates through the drying cartridges and collect.
- d) Rinse the collection vials with 10 mL of dichloromethane, pass the rinse through and collect.

6. Concentration

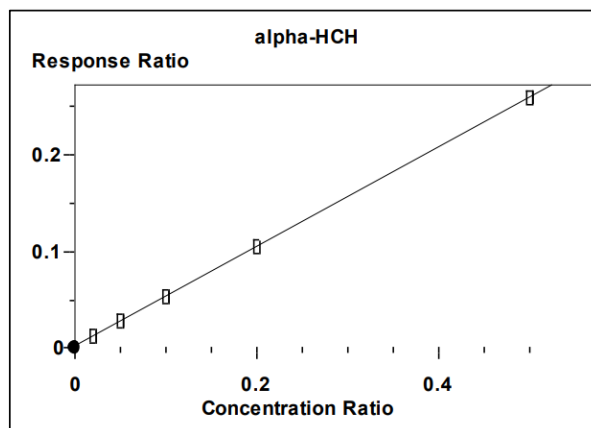
- a) Evaporate the eluates to 1 mL using TurboVap under a gentle stream of nitrogen (8-10 psi) at 40°C.
- b) Add internal standard (**Chem Service: M-IS525B3-5ML**), transfer the extracts to 2-mL autosampler vials, and adjust the final volume to 1 mL using ethyl acetate.
- c) Vortex the samples for 30 seconds, and inject 1 µL to GC/MS for analysis.



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 70 °C, hold for 1 min; ramp at 10 °C/min to 310 °C, and hold for 2 min
Temperatures	Transfer line 280 °C; Ion source 250 °C; Quadrupole 150 °C
Full scan range	45 - 450 amu

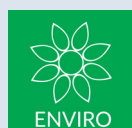
Retention Time and SIM Ions (Dwell time: 25 - 50 ms)				
Peak #	Compound Name	RT (min)	Quantitation ion	Confirmation ions
1	1,3-dimethyl-2-nitrobenzene Sur	6.888	77	79,134
2	Acenaphthene-d10 IS	10.950	162	164,160
3	Ethoprop	12.717	97	158,139
4	alpha-HCH	13.504	181	183,219
5	Dimethipin	13.973	54	53
6	Phenanthrene-d10 IS	14.494	188	189
7	Chlorpyrifos	16.377	97	199,197
8	Profenofos	18.256	97	139,339
9	Tribufos	18.369	57	169,202
10	Oxyfluorfen	18.441	252	300,361
11	Tebuconazole	20.112	125	83,250
12	Triphenyl phosphate Sur	20.173	77	325,326
13	Chrysene-d12 IS	20.858	240	236,241
14	Permethrin cis	22.519	183	163,184
15	Permethrin trans	22.641	183	163,184
16	Benzo(a)pyrene-d12 Sur	24.035	264	132,260

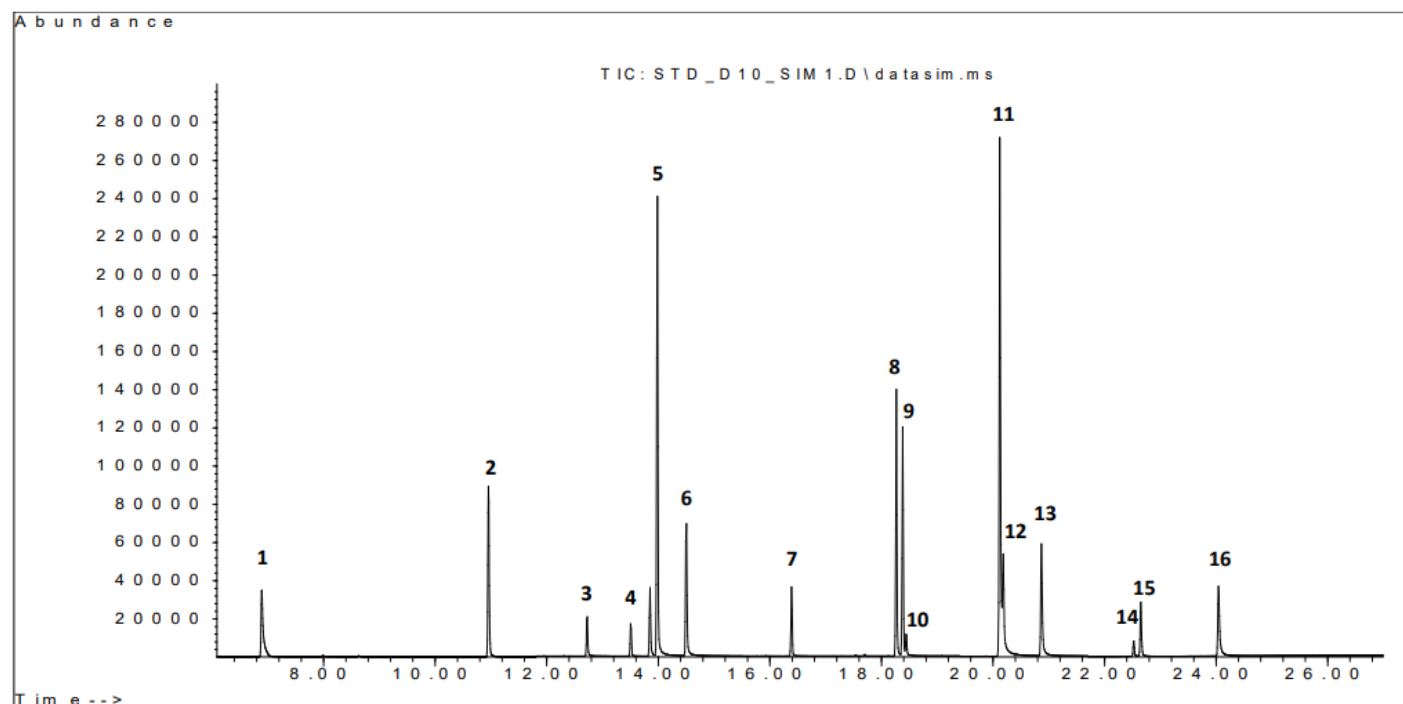
Matrix Matched Calibration Curve of alpha-Hexachlorocyclohexane ($R^2 = 1.0000$)

Results:

Accuracy and Precision Data in Laboratory Fortified Reagent Water					
		525.3 QC requirement		UCT reagent water (n = 4)	
Compound Name	Spiked at (µg/L)	Recovery%	RSD%	Recovery%	RSD%
1,3-dimethyl-2-nitrobenzene Sur	0.5	70 - 130	≤ 20	94.7	3.7
Ethoprop	0.3	70 - 130	≤ 20	102.1	7.3
alpha-HCH	0.1	70 - 130	≤ 20	94.7	4.0
Dimethipin	2.0	60 - 130	≤ 20	95.7	6.4
Chlorpyrifos	0.3	70 - 130	≤ 20	95.6	4.3
Profenofos	3.0	70 - 130	≤ 20	101.7	3.1
Tribufos	0.7	70 - 130	≤ 20	99.1	5.0
Oxyfluorfen	0.5	70 - 130	≤ 20	106.5	7.0
Tebuconazole	2.0	70 - 130	≤ 20	101.5	5.5
Triphenyl phosphate Sur	0.5	70 - 130	≤ 20	106.4	1.0
Total permethrin (cis & trans)	0.4	70 - 130	≤ 20	98.1	5.9
Benzo(a)pyrene-d12 Sur	0.5	70 - 130	≤ 20	98.8	1.8

Accuracy and Precision Data in Laboratory Tap Reagent Water					
		525.3 QC requirement		UCT reagent water (n = 4)	
Compound Name	Spiked at (µg/L)	Recovery%	RSD%	Recovery%	RSD%
1,3-dimethyl-2-nitrobenzene Sur	0.5	70 - 130	≤ 30	98.5	1.4
Ethoprop	0.3	70 - 130	≤ 30	113.3	1.2
alpha-HCH	0.1	70 - 130	≤ 30	97.7	0.5
Dimethipin	2.0	60 - 130	≤ 30	85.4	9.8
Chlorpyrifos	0.3	70 - 130	≤ 30	98.8	1.5
Profenofos	3.0	70 - 130	≤ 30	103.8	0.4
Tribufos	0.7	70 - 130	≤ 30	102.4	3.5
Oxyfluorfen	0.5	70 - 130	≤ 30	127.5	1.9
Tebuconazole	2.0	70 - 130	≤ 30	100.5	1.3
Triphenyl phosphate Sur	0.5	70 - 130	≤ 30	99.3	1.2
Total permethrin (cis & trans)	0.4	70 - 130	≤ 30	99.9	1.8
Benzo(a)pyrene-d12 Sur	0.5	70 - 130	≤ 30	98.6	3.1

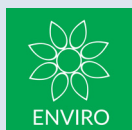




GC/MS SIM Chromatogram (Peak order can be found in the Retention Time and SIM Ion table on page 3)

Conclusion:

An efficient and straightforward SPE method using UCT's Enviro-Clean® 83 mL Universal Cartridges containing 1500 mg of proprietary sorbent has been demonstrated to extract 9 UCMR4 contaminants in drinking water by EPA method 525.3. Excellent analytical performance has been obtained, with recoveries ranged from 94.7 to 106.5% in laboratory fortified reagent water, and 85.4 to 127.5% in fortified tap water. The relative standard deviations (RSD%) were less than 10% in both reagent and tap water samples. All parameters have passed the QC acceptance criteria set by method 525.3, even for dimethipin, a polar compound with LogP of -1.51, which is usually difficult to retain on traditional silica based sorbent.



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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