METHOD DEVELOPMENT FOR THE 4TH UNREGULATED CONTAMINANT MONITORING RULE (UCMR4) COMPOUNDS

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Every 5 years, the US EPA issues a list of about 30 contaminants which do not have health-based standards set under the Safe Drinking Water Act, to be monitored in public drinking water systems [1]. UCMR3 contaminants are currently being monitored and will be completed by the end of 2015. The US EPA is now developing and publishing new methods for the UCMR4 compound list. Public drinking water systems will start monitoring the UCMR4 compounds no later than 2018. This poster discusses several UCMR4 methods developed in the Research and Development laboratory at UCT, such as EPA methods 525.3 [2], and 541 (to be published soon) using solid phase extraction (SPE) and GC/MS detection, and method 538 [3] using direct aqueous injection and LC/MS/MS techniques.

Part 1: Semi-volatile Organic Compounds by SPE and GC/MS (EPA Method 525.3)

Product Description	UCT Part Number
16 position glass block manifold	VMF016GL
SPE cartridge: 500 mg Enviro-Clean® HL DVB in 6 mL cartridge	ECHLD156-P
Large sample transfer tubes	VMFSTFR12
12 position large volume collection rack	VMF02125
Drying cartridge: 5 g anhydrous sodium sulfate in 6 mL cartridge	ECSS15M6
GC liner, 4mm splitless gooseneck, 4mm ID x 6.5mm OD x 78.5mm	GCLGN4MM-5

SPE Procedure for EPA Method 525.3	
Sample pretreatment (1 liter)	0.1 g/L of L-ascorbic acid 0.35 g/L of EDTA 9.4 g/L of potassium dihydrogen citrate
Cartridge conditioning	10 mL DCM; 10 mL MeOH; and 10 mL DI water
Sample loading	15-20 mL/min with large sample transfer tube
Cartridge wash	10 mL DI water (bottle and transfer tube rinse)
Cartridge drying	10 min under full vacuum
Elution with in-line drying	10 mL EtOAc; 10 mL DCM (bottle and transfer tube rinse)
Concentration	Nitrogen at 40 °C to 1 mL, add IS.

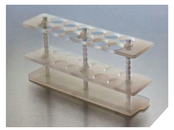
Instrumentation	
GC/MS	Agilent 6890N GC coupled to a 5975C MSD
Injection	1µL splitless injection at 250 °C
GC liner	4 mm splitless gooseneck, packed with deactivated glass wool
GC column	Restek Rxi®-5sil MS 30m x 0.25mm, 0.25µm with 10m integrated guard column
Carrier gas	Ultra high purity Helium at 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; Source 250 °C; Quadrupole 150 °C
Full scan range	45 - 500 amu

Accuracy and Precision in Spiked Reagent Water (5 µg/L)

Analyte	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

SPE Setup for EPA Method 525.3

Elution with In-line Eluate Drying



Collection Rack for 12 large vials (40, 50, or 60 mL)

Part 2: Small Polar Compounds by SPE and GC/MS (EPA Method 541)

Product Description	UCT Part Number
16 position glass block manifold	VMF016GL
SPE cartridge: 600 mg activated carbon in 3 mL cartridges	EU521163
Cartridge adaptors	AD0000AS
75 mL empty reservoirs	RFV0075P
Stopcocks	VMF02024
GC liner, 4mm splitless gooseneck, 4mm ID x 6.5mm OD x 78.5mm	GCLGN4MM-5
Sodium sulfate, anhydrous, ACS grade, granular 60 mesh, 25 kg	ECSS25K

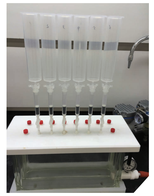
SPE Procedure for EPA Method 541	
Sample pretreatment (50 mL)	50 mg/L sodium sulfite 1000 mg/L sodium bisulfate
Cartridge conditioning	5 mL of 5% MeOH in DCM; 2 x2 mL MeOH; and 5 mL DI water
Sample loading	5 mL/min with 75-mL reservoir
Cartridge wash	5 mL DI water (bottle rinse) and 0.2 mL MeOH
Cartridge drying	30 sec under full vacuum followed by 10 min of N_2 at 5 L/min using a drying manifold.
Elution	2 x 1.3 mL of 5% MeOH in DCM
Eluate drying	Add IS and dry with 1-2 g Na_2SO_4 for 15 min, adjust final volume to 2 mL with 5% MeOH in DCM

Instrumentation	
GC/MS	Agilent 6890N GC coupled to a 5975C MSD
Injection	1µL splitless injection at 200 °C
GC liner	4 mm splitless gooseneck, packed with deactivated glass wool
GC column	Phenomenex ZB-WAX *plus*: 30m x 0.25mm x 0.5µm
Carrier gas	Ultra high purity Helium at a constant flow of 0.9 mL/min
Oven temp. program	Initial temperature at 35 °C, hold for 5 min; ramp at 10 °C/min to 105 °C; ramp at 30 °C/min to 240 °C; and hold for 3.5 min
Temperatures	Transfer line 240 °C; Source 250 °C; Quadrupole 150 °C

Analyte	Rt (min)	SIM ions (50 ms dwell time)			Linearity (R^2)
1,4-dioxane d8 (IS)	8.671	96.1	64.1	46	NA
1,4-dioxane	8.698	88	58	43	0.9998
2-propen-1-ol d6 (Surr)	9.704	61	63	46	NA
2-propen-1-ol	9.823	57	39	58	0.9997
1-butanol d10 (Surr)	10.309	64.1	46.1	50.1	NA
1-butanol	10.477	56	41	43.05	0.9996
2-methoxyethanol	11.099	45	76	47	0.9997
Chlorobenzene d5 (IS)	11.747	117	82	119	NA

Accuracy and Precision Data (n=5)

Analyte	Fortified reagent water		Fortified tap water	
	Recovery%	RSD%	Recovery%	RSD%
1,4-dioxane	89.5	5.2	87.7	1.9
2-propen-1-ol d6	92.9	4.6	82.5	4.8
2-propen-1-ol	85.5	3.4	84.1	2.8
1-butanol d10	101.0	3.6	88.0	5.3
1-butanol	96.4	3.3	91.9	2.1
2-methoxyethanol	97.6	4.0	94.8	2.6



SPE Setup for EPA Method 541

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Part 3: Selected Organic Contaminants by Direct Aqueous Injection and LC/MS/MS (EPA Method 538)

Product Description	UCT Part Number
Selectra® Aqueous C18, 100 x 2.1mm, 3µm	SLAQ100ID21-3UM
Guard Cartridge Holder	SLGRDHLDR
Selectra® Aqueous C18, Guard column, 10 x 2.0mm, 3µm	SLAQGDC20-3UM

Procedure for EPA Method 538:

1. Preserve drinking water sample with 64 mg/L of sodium omadine (antimicrobial) and 1.5 g/L of ammonium acetate (binding free chlorine).
2. Mix 0.99 mL of the preserved water sample with 10 µL of 0.4-12.5 ng/µL internal standard mixture, and vortex for 30 sec.

Instrumentation
HPLC: Thermo Scientific Dionex UltiMate 3000® LC System
Column: UCT, Selectra® Aqueous C18, 100 x 2.1 mm, 3 µm
Guard column: UCT, Selectra® Aqueous C18, 10 x 2.0 mm, 3 µm
Column temperature: 40 °C
Column flow rate: 0.300 mL/min
Auto-sampler temperature: 10 °C
Injection volume: 50 µL
Gradient program:

Time (min)	A% (20 mM ammonium formate)	B% (MeOH)
0	100	0
2	100	0
9	15	85
12	15	85
12.1	100	0
16	100	0

Divert mobile phase to waste from 0 - 2 and 14 - 16 min to prevent ion source contamination.

MS parameters	
Instrumentation	Thermo Scientific TSQ Vantage tandem MS
Polarity	ESI +
Spray voltage	5000 V
Vaporizer temperature	203 °C
Ion transfer capillary	208 °C
Sheath gas pressure	40 arbitrary units
Auxiliary gas pressure	5 arbitrary units
Q1 and Q3 peak width (FWHM)	0.2 and 1.0 Da
Collision gas and pressure	Ar at 1.5 mTorr
Cycle time	1 sec
Acquisition method	EZ Method (scheduled SRM)

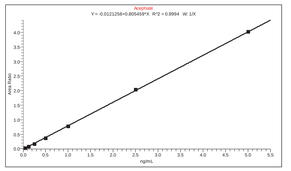
SRM Transitions							
Compound Name	Rt (min)	Precursor	Product 1	CE 1	Product 2	CE 2	S-lens
Methamidophos	3.41	142.0	94.0	14	125.0	12	69
Acephate-d6	5.63	190.0	149.0	5	98.0	24	64
Acephate	5.69	184.0	143.0	5	95.0	22	53
Aldicarb sulfoxide	7.24	207.0	89.1	13	69.1	15	60
Oxydemeton-methyl-d6	7.81	253.0	175.0	13	115.0	27	89
Oxydemeton-methyl	7.83	247.0	169.0	13	109.0	27	84
Dicrotophos	8.34	238.1	112.1	11	127.0	18	75
Aldicarb	9.15	208.0	116.0	5	89.1	14	45
DIMP-d14	9.62	195.1	99.0	12	80.0	35	61
DIMP	9.66	181.1	97.0	12	79.0	32	49
Fenamiphos sulfone	9.85	336.1	266.0	16	188.0	26	135
Fenamiphos sulfoxide	9.92	320.1	233.0	24	108.0	39	102
Thiofanox H^+	10.10	219.1	57.1	12	76.0	5	40
Thiofanox $NH4^+$	10.10	236.1	57.1	11	76.1	5	42
Quinoline-d7	10.14	137.1	81.1	33	109.1	26	78
Quinoline	10.18	130.1	77.1	32	103.1	25	101

Analytical Range and Linearity.

Analyte	Analytical range (ng / mL)	Linearity (R^2)
Methamidophos	0.05 - 5	0.9982
Acephate	0.05 - 5	0.9994
Aldicarb sulfoxide	0.05 - 5	0.9996
Oxydemeton-methyl	0.05 - 5	0.9996
Dicrotophos	0.05 - 5	0.9973
Aldicarb	0.1 - 10	0.9970
DIMP	0.05 - 5	0.9997
Fenamiphos sulfone	0.05 - 5	0.9996
Fenamiphos sulfoxide	0.05 - 5	0.9989
Thiofanox*	0.2 - 20	0.9993
Quinoline	2 - 200	0.9972

* For thiofanox, NH4+ adduct is more abundant than H+ adduct, thus was selected for quantitation..

Example Calibration Curve



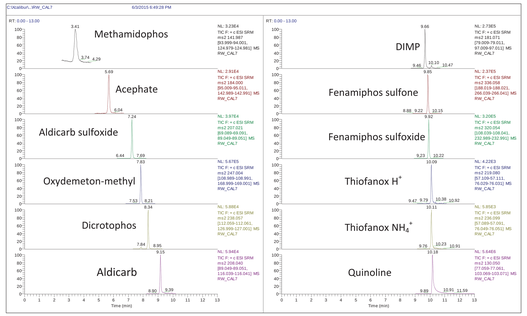
Accuracy and Precision in Fortified Reagent Water

Analyte	Low spike (n=7)		High spike (n=7)	
	Recovery%	RSD%	Recovery%	RSD%
Methamidophos	103.0	4.9	100.3	3.4
Acephate	100.0	6.6	96.9	3.9
Aldicarb sulfoxide	101.6	6.5	103.9	1.4
Oxydemeton-methyl	101.1	4.4	95.7	1.6
Dicrotophos	104.8	5.1	104.0	3.9
Aldicarb	90.1	10.7	99.7	4.7
DIMP	97.2	6.8	97.6	1.5
Fenamiphos sulfone	96.9	6.9	100.2	4.7
Fenamiphos sulfoxide	97.1	6.8	100.9	3.1
Thiofanox	90.9	18.3	90.9	6.5
Quinoline	97.6	4.6	93.1	3.7

Accuracy and Precision in Fortified Tap Water

Analyte	Low spike (n=7)		High spike (n=7)	
	Recovery%	RSD%	Recovery%	RSD%
Methamidophos	102.4	8.7	102.8	3.1
Acephate	98.6	5.7	99.1	2.0
Aldicarb sulfoxide	100.9	6.1	110.6	6.8
Oxydemeton-methyl	101.6	2.8	98.9	0.7
Dicrotophos	102.6	9.6	105.7	6.6
Aldicarb	94.5	10.9	100.1	3.7
DIMP	97.6	3.0	99.5	0.8
Fenamiphos sulfone	95.0	5.1	97.3	6.3
Fenamiphos sulfoxide	90.6	8.5	98.0	4.2
Thiofanox	92.7	10.7	92.2	6.9
Quinoline	96.7	2.8	92.7	3.8

Chromatogram



Conclusions:

Three EPA methods monitoring UCMR4 compounds have been demonstrated in this poster. Method 525.3 determines 11 semi-volatile organic compounds using a new polymeric SPE sorbent, method 541 analyzes 4 small polar compounds using the activated carbon SPE cartridge, while method 538 detects 11 selected organic contaminants using the direct aqueous injection technique and LC/MS/MS equipped with an Aqueous C18 column. Excellent accuracy and precision data have been achieved for all of the 3 methods developed in this study. UCT's R&D lab continues working on other UCMR4 compounds using EPA methods 542, 544 and 545.

References:

[1] http://water.epa.gov/lawsregs/rulesregs/sdwa/ucmr/
[2] http://www.epa.gov/microbes/documents/method525_3_feb21_2012%20final.pdf
[3] http://www.epa.gov/nerlcwww/documents/Method538_Final.pdf