EPA Method 538: Determination of Selected Organic Contaminants in Drinking Water by Aqueous Direct Injection and LC/MS/MS

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

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Summary:

This application outlines a direct aqueous injection-liquid chromatography/tandem mass spectrometry (DAI-LC/MS/MS) method for the determination of 11 selected organic contaminants in drinking water, including methamidophos, acephate, aldicarb sulfoxide, oxydemeton methyl, dicrotophos, aldicarb, diisopropyl methylphosphonate (DIMP), fenamiphos sulfone, fenamiphos sulfoxide, thiofanox, and quinoline [1]. Dicrotophos, oxydemeton methyl, methamidophos, and acephate are UCMR4 compounds.

An Aqueous C18 HPLC column was utilized for analyte retention and separation. Calibration curves were constructed using calibration standards prepared in reagent water with preservative reagents for analyte quantitation. The responses were linear over the entire analytical ranges ($R^2 \geq 0.9970$). Excellent accuracy (90 - 111%) and precision (RSD% < 20%, n=7) were achieved for fortified reagent water and tap water samples.

Procedure:

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.
3. Inject 50 µL onto LC/MS/MS equipped with an aqueous C18 HPLC column for analysis.

LC-MS/MS method:

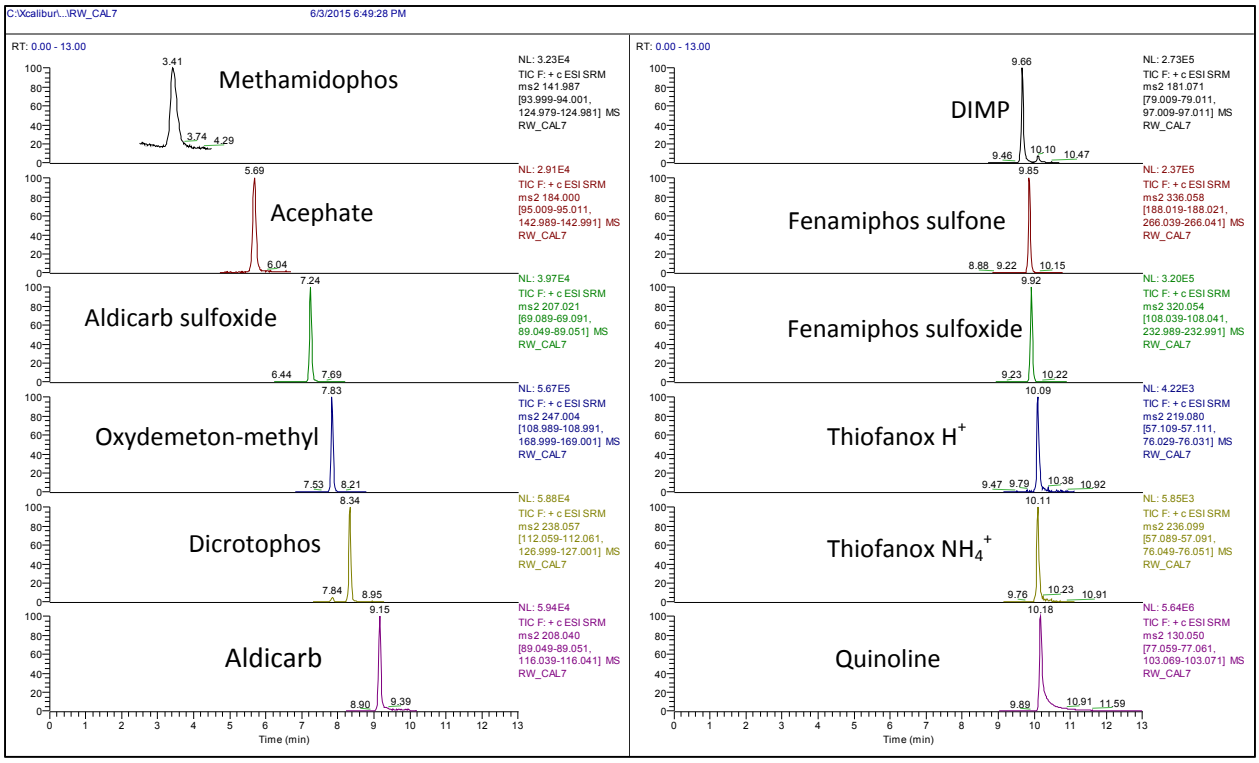
HPLC: Thermo Scientific Dionex UltiMate 3000® LC System		
Column: UCT, Selectra® Aqueous C18, 100 x 2.1 mm, 3 µm		
Guard column: UCT, Selectra® Aqueous C18, 10 x 2.0 mm, 3 µm		
Column temperature: 40 °C		
Column flow rate: 0.300 mL/min		
Auto-sampler temperature: 10 °C		
Injection volume: 50 µL		
Gradient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

Chromatogram – Reagent Water



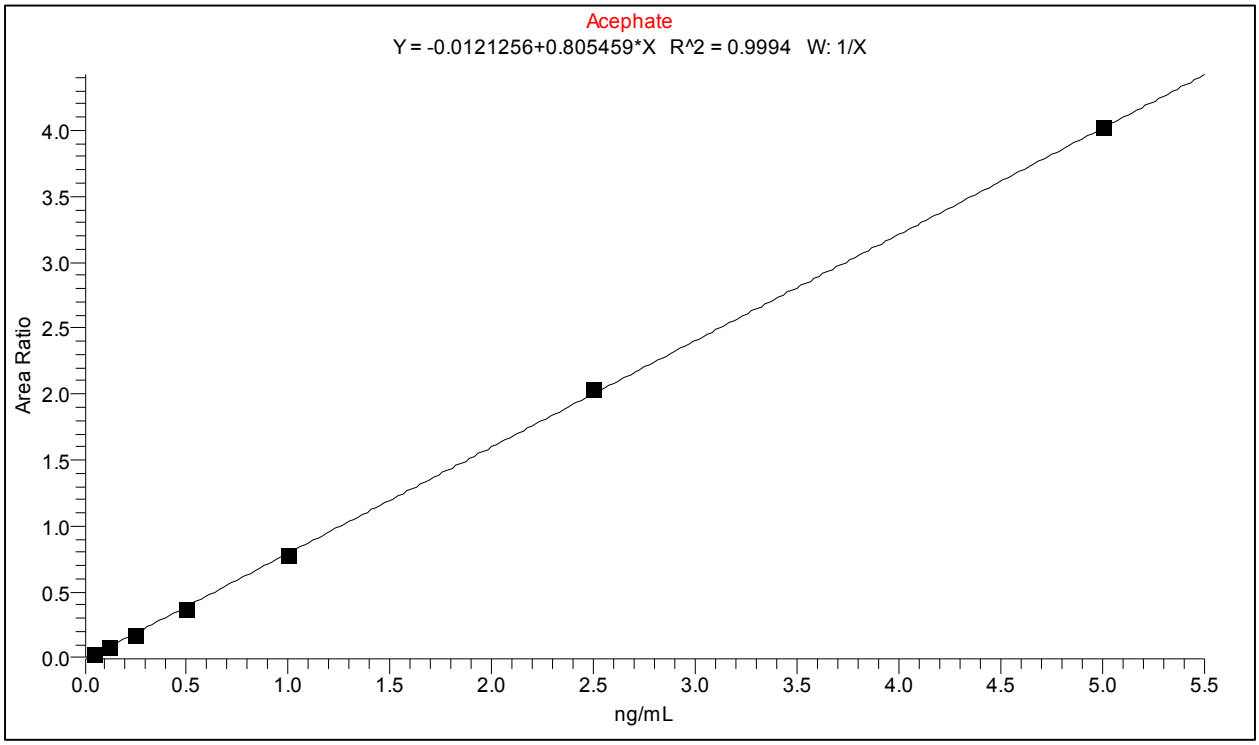
Results:

Analytical Range and Linearity Data

Compound Name	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, NH_4^+ adduct is more abundant than H^+ adduct, thus was selected for quantitation.

Calibration Curve of Acephate



Accuracy and Precision in Reagent Water Fortified at 0.125 - 5 ng/mL (n=7)

Compound Name	Spiked Conc. (ng/mL)	Ave Recovery%	RSD% (n=7)	Det. Limit (ng/mL)
Methamidophos	0.125	**103.0**	4.9	0.020
Acephate	0.125	**100.0**	6.6	0.026
Aldicarb sulfoxide	0.125	**101.6**	6.5	0.026
Oxydemeton-methyl	0.125	**101.1**	4.4	0.017
Dicrotophos	0.125	**104.8**	5.1	0.021
Aldicarb	0.25	**90.1**	10.7	0.076
DIMP	0.125	**97.2**	6.8	0.026
Fenamiphos sulfone	0.125	**96.9**	6.9	0.026
Fenamiphos sulfoxide	0.125	**97.1**	6.8	0.026
Thiofanox	0.5	**90.9**	18.3	0.261
Quinoline	5	**97.6**	4.6	0.700

Accuracy and Precision in Reagent Water Fortified at 1 - 40 ng/mL (n=7)

Compound Name	Spiked Conc. (ng/mL)	Ave Recovery%	RSD% (n=7)
Methamidophos	1	**100.3**	3.4
Acephate	1	**96.9**	3.9
Aldicarb sulfoxide	1	**103.9**	1.4
Oxydemeton-methyl	1	**95.7**	1.6
Dicrotophos	1	**104.0**	3.9
Aldicarb	2	**99.7**	4.7
DIMP	1	**97.6**	1.5
Fenamiphos sulfone	1	**100.2**	4.7
Fenamiphos sulfoxide	1	**100.9**	3.1
Thiofanox	4	**90.9**	6.5
Quinoline	40	**93.1**	3.7

Accuracy and Precision in Tap Water Fortified at 0.125 - 5 ng/mL (n=7)

Compound Name	Spiked Conc. (ng/mL)	Ave Recovery%	RSD% (n=7)
Methamidophos	0.125	**102.4**	8.7
Acephate	0.125	**98.6**	5.7
Aldicarb sulfoxide	0.125	**100.9**	6.1
Oxydemeton-methyl	0.125	**101.6**	2.8
Dicrotophos	0.125	**102.6**	9.6
Aldicarb	0.25	**94.5**	10.9
DIMP	0.125	**97.6**	3.0
Fenamiphos sulfone	0.125	**95.0**	5.1
Fenamiphos sulfoxide	0.125	**90.6**	8.5
Thiofanox	0.5	**92.7**	10.7
Quinoline	5	**96.7**	2.8

Accuracy and Precision in Tap Water Fortified at 1 - 40 ng/mL (n=7)

Compound Name	Spiked Conc. (ng/mL)	Ave Recovery%	RSD% (n=7)
Methamidophos	1	**102.8**	3.1
Acephate	1	**99.1**	2.0
Aldicarb sulfoxide	1	**110.6**	6.8
Oxydemeton-methyl	1	**98.9**	0.7
Dicrotophos	1	**105.7**	6.6
Aldicarb	2	**100.1**	3.7
DIMP	1	**99.5**	0.8
Fenamiphos sulfone	1	**97.3**	6.3
Fenamiphos sulfoxide	1	**98.0**	4.2
Thiofanox	4	**92.2**	6.9
Quinoline	40	**92.7**	3.8

References:

[1] http://www.epa.gov/nerlcwww/documents/Method538_Final.pdf

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