

METHOD STATEMENT

Determinand:

Determination of selected triazines, phenyl ureas, carbamate, organophosphorus and neutral compounds.

Matrix:

Sample Type: Treated, Ground and Raw Waters.

Principle of Method:

The method is a large volume injection on-line solid phase extraction procedure. Samples are analysed by high performance liquid chromatography using a triple quadrupole mass spectrometer as a detector. The aqueous sample is injected by large volume injection (LVI) onto an enrichment column. The analytes trapped on the enrichment column are back flushed on to the analytical column. The aqueous sample is injected and the organic compounds are separated and then identified and quantified with mass spectrometric detection (MSD) in multiple reaction monitoring (MRM) mode. Quantitation is based on an internal standardisation procedure.

Interferences:

HPLC-MS/MS is an extremely selective technique and interferences should only be encountered very rarely. Any interfering compounds would have to display the identical MRM transition at the same retention time, this is extremely unlikely in potable water samples. However, any compound, which passes through the extraction procedure, and has a similar liquid chromatographic retention time and mass spectrometric properties to the compound of interest, will cause interference. Samples containing high humic or fulvic loading have been demonstrated to not cause significant ion suppression for the compounds.

Performance of Method:

Range of Application:

Instrument Q5 and Q6

<u>Determinand</u>	<u>Operational Calibration Range</u>
AMETRYN	LOD - 0.25 µg/l
ATRAZINE-DESETHYL	LOD - 0.25 µg/l
ATRAZINE-DESIOPROPYL	LOD - 0.25 µg/l
AZINPHOS-METHYL	LOD - 0.25 µg/l
CARBENDAZIM	LOD - 0.25 µg/l
CHLORFENVINPHOS	LOD - 0.25 µg/l
DICHLORVOS	LOD - 0.25 µg/l
DIMETHOATE	LOD - 0.25 µg/l
ETHOFUMESATE	LOD - 0.25 µg/l
ETHOPROPHOS	LOD - 0.25 µg/l
FENPROPIDIN	LOD - 0.25 µg/l
FENPROPIMORPH	LOD - 0.25 µg/l
FLUXAPYROXAD	LOD - 0.25 µg/l
LENACIL	LOD - 0.25 µg/l
MALATHION	LOD - 0.25 µg/l
METHABENZTHIAZURON	LOD - 0.25 µg/l
METHIOCARB	LOD - 0.25 µg/l
METRIBUZIN	LOD - 0.25 µg/l
METSULFURON-METHYL	LOD - 0.25 µg/l
MEVINPHOS	LOD - 0.25 µg/l
PIRIMICARB	LOD - 0.25 µg/l
PIRIMIPHOS-METHYL	LOD - 0.25 µg/l
PROMETRYN	LOD - 0.25 µg/l



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Determinand	Operational Calibration Range
PROPAZINE	LOD - 0.25 µg/l
PROPETAMPHOS	LOD - 0.25 µg/l
SPIROXAMINE	LOD - 0.25 µg/l
TERBUTHYLAZINE	LOD - 0.25 µg/l
TERBUTRYN	LOD - 0.25 µg/l
TRIAZOPHOS	LOD - 0.25 µg/l

Limit of Detection, Uncertainty of measurement and Recoveries of Compounds

Instrument Q5:

Determinand	LOD ng/litre	Direct Standards				Elvington Treated Water (Hardness)		
		Low Standard		High Standard		PCV Spike		
		% Recovery	% RSD	% Recovery	% RSD	% Recovery	% RSD	Uncert
AMETRYN	2	101.1%	2.9%	100.3%	1.4%	100.5%	1.5%	± 3.48%
ATRAZINE-DEISOPROPYL	1	100.6%	2.9%	99.9%	1.9%	99.7%	1.9%	± 4.00%
ATRAZINE-DESETHYL	1	100.2%	3.0%	99.8%	1.9%	100.7%	1.9%	± 4.42%
AZINPHOS-METHYL	1	101.2%	3.0%	99.7%	2.2%	100.6%	2.1%	± 4.83%
CARBENDAZIM	1	101.7%	3.2%	101.2%	1.1%	102.1%	1.8%	± 5.64%
CHLORFENVINPHOS	3	101.0%	6.0%	100.1%	4.6%	100.9%	5.1%	± 11.05%
DICHLORVOS	1	100.6%	3.0%	100.3%	1.7%	100.3%	2.3%	± 4.90%
DIMETHOATE	2	101.1%	3.7%	100.9%	1.1%	101.3%	2.2%	± 5.66%
ETHOFUMESATE	1	103.9%	4.2%	99.8%	3.8%	104.2%	2.6%	± 9.38%
ETHOPROPHOS	2	99.0%	3.6%	99.9%	2.8%	101.3%	3.1%	± 7.47%
FENPROPIDIN	1	99.9%	3.5%	99.5%	1.4%	101.1%	2.3%	± 5.59%
FENPROPIMORPH	1	100.1%	3.3%	100.1%	1.5%	101.3%	2.1%	± 5.44%
FLUXAPYROXAD	2	101.6%	4.7%	100.7%	2.0%	101.6%	2.1%	± 5.77%
LENACIL	2	100.6%	3.8%	100.2%	2.5%	100.7%	2.6%	± 5.85%
MALATHION	2	100.2%	3.7%	100.2%	1.9%	100.6%	2.4%	± 5.37%
METHABENZTHIAZURON	1	101.0%	2.8%	100.3%	1.0%	101.3%	1.3%	± 3.92%
METHIOCARB	2	101.1%	4.3%	100.2%	1.7%	100.9%	2.2%	± 5.35%
METRIBUZIN	1	101.6%	2.8%	101.7%	2.5%	101.0%	2.5%	± 5.90%
METSULFURON-METHYL	2	101.9%	6.1%	101.0%	4.5%	99.9%	7.9%	± 15.79%
MEVINPHOS	2	100.3%	3.3%	100.1%	1.3%	100.3%	2.2%	± 4.76%
PIRIMICARB	1	99.5%	2.6%	99.4%	1.4%	99.3%	1.4%	± 3.44%
PIRIMIPHOS-METHYL	1	98.8%	4.0%	100.6%	4.8%	100.0%	4.2%	± 8.40%
PROMETRYN	1	100.7%	2.9%	99.9%	1.1%	100.6%	1.6%	± 3.67%
PROPAZINE	1	100.8%	3.0%	100.4%	1.6%	101.3%	1.6%	± 4.49%
PROPETAMPHOS	2	100.5%	4.5%	99.4%	2.3%	101.0%	3.0%	± 6.90%
SPIROXAMINE	1	98.6%	3.6%	99.2%	2.6%	101.2%	2.5%	± 6.27%
TERBUTHYLAZINE	1	100.5%	2.9%	100.1%	1.4%	101.7%	1.6%	± 5.01%
TERBUTRYN	1	100.5%	2.6%	100.1%	1.2%	100.9%	1.1%	± 3.12%
TRIAZOPHOS	2	99.9%	4.4%	100.2%	3.6%	100.3%	4.0%	± 8.40%

Instrument Q6:

Determinand	LOD ng/litre	Direct Standards				Elvington Treated Water (Hardness)		
		Low Standard		High Standard		PCV Spike		
		% Recovery	RSD	% Recovery	RSD	% Recovery	RSD	Uncert
AMETRYN	2	99.7%	2.5%	100.6%	1.3%	99.7%	1.5%	± 3.20%
ATRAZINE-DEISOPROPYL	1	99.6%	3.8%	100.4%	1.1%	98.9%	1.9%	± 4.94%
ATRAZINE-DESETHYL	1	100.1%	3.5%	100.6%	1.4%	100.1%	2.2%	± 4.50%
AZINPHOS-METHYL	1	100.1%	2.9%	100.2%	1.0%	101.1%	1.7%	± 4.54%
CARBENDAZIM	1	100.1%	2.2%	101.4%	1.8%	101.6%	1.5%	± 4.58%



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Determinand	LOD ng/litre	Direct Standards				Elvington Treated Water (Hardness)		
		Low Standard		High Standard		PCV Spike		
		% Recovery	RSD	% Recovery	RSD	% Recovery	RSD	Uncert
CHLORFENVINPHOS	2	100.0%	7.2%	97.3%	7.5%	102.0%	4.2%	± 10.37%
DICHLORVOS	2	99.6%	3.8%	100.4%	1.7%	100.1%	2.5%	± 5.07%
DIMETHOATE	1	100.5%	3.2%	101.0%	1.6%	100.3%	1.8%	± 3.88%
ETHOFUMESATE	2	101.6%	4.9%	99.2%	3.3%	102.6%	2.9%	± 8.48%
ETHOPROPHOS	2	100.2%	4.5%	100.9%	2.7%	102.3%	3.2%	± 8.78%
FENPROPIDIN	1	99.6%	4.3%	99.8%	1.4%	100.4%	2.4%	± 5.22%
FENPROPIMORPH	1	98.7%	3.7%	100.2%	1.8%	101.1%	2.8%	± 6.59%
FLUXAPYROXAD	2	99.2%	4.5%	100.9%	4.1%	99.9%	3.9%	± 7.96%
LENACIL	2	99.9%	3.7%	100.2%	2.2%	100.7%	2.5%	± 5.68%
MALATHION	2	100.8%	4.1%	100.4%	1.5%	100.9%	2.5%	± 5.86%
METHABENZTHIAZURON	1	100.2%	3.7%	101.0%	1.5%	100.6%	2.1%	± 4.72%
METHIOCARB	3	101.2%	4.8%	101.7%	2.8%	101.4%	3.5%	± 8.43%
METRIBUZIN	1	101.1%	3.4%	101.3%	2.1%	100.2%	2.5%	± 5.27%
METSULFURON-METHYL	3	98.1%	4.8%	97.4%	2.7%	93.5%	4.0%	± 14.48%
MEVINPHOS	1	100.1%	3.3%	100.7%	1.8%	100.7%	1.9%	± 4.48%
PIRIMICARB	1	100.5%	4.2%	100.3%	1.4%	99.5%	2.3%	± 5.01%
PIRIMIPHOS-METHYL	1	96.5%	4.0%	98.3%	1.9%	97.6%	2.0%	± 6.40%
PROMETRYN	1	99.6%	3.1%	100.5%	1.2%	100.3%	1.8%	± 3.84%
PROPAZINE	1	99.7%	2.4%	100.5%	1.4%	100.0%	1.7%	± 3.42%
PROPETAMPHOS	3	100.4%	5.0%	99.3%	3.2%	101.1%	3.9%	± 8.85%
SPIROXAMINE	1	98.8%	4.8%	99.1%	3.3%	101.7%	3.6%	± 8.95%
TERBUTHYLAZINE	1	100.0%	2.5%	100.6%	1.6%	101.0%	1.7%	± 4.27%
TERBUTRYN	1	99.9%	2.7%	100.6%	1.0%	100.1%	1.5%	± 3.10%
TRIAZOPHOS	2	98.0%	3.7%	98.9%	2.1%	99.2%	3.7%	± 8.26%

References:

- Agilent 1200 Series, Reference Manuals.
- Agilent 6400 QQQ LC/MS Techniques and Operation, Agilent Technologies Course Number R1893A, Student Manuals Volumes 1 and 2.
- Agilent 6460 Triple Quad LC/MS System, Quick Start Guide
- Agilent 6400 Triple Quad LC/MS, Maintenance and Familiarization Guides.
- Agilent 6400 Triple Quad LC/MS System, Concept Guide.

