

METHOD STATEMENT



Determinand:

Determination of selected phenoxyalkanoic, benzonitrile and other compounds

Matrix:

Sample Type: Treated, Ground and Raw Waters.

Principle of Method:

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.

Sampling and Sample Preparation:

Sampling, samples should be collected in 500mL brown glass bottles with PTFE lined screw caps and contain either 0.500mL of sample preservative - ascorbic acid 3% w/v. or 0.500mL 18g/L sodium thiosulphate solution.

Storage - samples should be analysed as soon as possible after collection. When this is not possible they should be stored under refrigeration at $3\pm 2^{\circ}\text{C}$ in the dark, until analysis can begin. The maximum permissible storage time prior to analysis is given below which is either derived from BS EN ISO 5667-3:2018 "Water Quality - Sampling - Part 3: Guidance on the preservation and handling of water samples (BS 6068-6.3:2003) or from ALS in-house data ["ALS IHD"] which is held by the Quality section.

Determinand	Maximum period of analyte stability prior to any extraction step (days)	Maximum period of analyte stability after to any extraction step (days)	Data is quoted from BS EN ISO 5667-3:2018 ["ISO"] or ALS in-house data ["ALS IHD"]
ASULAM	21	N/A	ALS IHD
BENAZOLIN	21	N/A	ALS IHD
BENTAZONE	21	N/A	ALS IHD
BROMOXYNIL	21	N/A	ALS IHD
CLOPYRALID	21	N/A	ALS IHD
2,4-D	21	N/A	ALS IHD
2,4-DB	21	N/A	ALS IHD
DICAMBA	21	N/A	ALS IHD
2,4-DP (DICHLORPROP)	21	N/A	ALS IHD
FLUROXYPYR	21	N/A	ALS IHD
IMAZAPYR	21	N/A	ALS IHD
IOXYNIL	21	N/A	ALS IHD
MCPA	21	N/A	ALS IHD
MCPB	21	N/A	ALS IHD
MCPP (MECOPROP)	21	N/A	ALS IHD
PENTACHLOROPHENOL	21	N/A	ALS IHD
PICLORAM	21	N/A	ALS IHD
PROPAMOCARB	21	N/A	ALS IHD
2,4,5-T	21	N/A	ALS IHD
2,3,6-TRICHLOROBENZOIC ACID	21	N/A	ALS IHD

METHOD STATEMENT



Determinand	Maximum period of analyte stability prior to any extraction step (days)	Maximum period of analyte stability after to any extraction step (days)	Data is quoted from BS EN ISO 5667-3: 2018 ["ISO"] or ALS in-house data ["ALS IHD"]
2,4,5-TP (FENOPROP)	21	N/A	ALS IHD
TRICLOPYR	21	N/A	ALS IHD

Any additional comments:-

As the samples are analysed by direct aqueous injection, no data is available for analyte stability after any extraction step.

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:

<u>Determinand</u>	Operational Calibration Range
ASULAM	LOQ - 0.250 µg/l
BENAZOLIN	LOQ - 0.250 µg/l
BENTAZONE	LOQ - 0.250 µg/l
BROMOXYNIL	LOQ - 0.250 µg/l
CLOPYRALID	LOQ - 0.250 µg/l
2,4-D	LOQ - 0.250 µg/l
2,4-DB	LOQ - 0.250 µg/l
DICAMBA	LOQ - 0.250 µg/l
2,4-DP (DICHLORPROP)	LOQ - 0.250 µg/l
FLUROXYPYR	LOQ - 0.250 µg/l
IMAZAPYR	LOQ - 0.250 µg/l
IOXYNIL	LOQ - 0.250 µg/l
MCPA	LOQ - 0.250 µg/l
MCPB	LOQ - 0.250 µg/l
MCPP (MECOPROP)	LOQ - 0.250 µg/l
PICLORAM	LOQ - 0.250 µg/l
PENTACHLOROPHENOL	LOQ - 0.250 µg/l
PROPAMOCARB	LOQ - 0.250 µg/l
2,4,5-T	LOQ - 0.250 µg/l
2,3,6-TRICHLOROBENZOIC ACID	LOQ - 0.250 µg/l
2,4,5-TP (FENOPROP)	LOQ - 0.250 µg/l
TRICLOPYR	LOQ - 0.250 µg/l

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Limit of Quantification, Recoveries of Compounds, Bias and Uncertainty of measurement:

Instrument Q1.

Determinand	Direct Standards				Elvington (Hard Hardness)	
	Low Standard		High Standard		PCV Spike	
	Mean	%RSD	Mean	%RSD	%Recovery	%RSD
2,3,6-TrichloroBenzoic Acid	48.9	6.0%	201.6	4.0%	99.9%	3.8%
2,4,5-T	50.6	8.3%	201.7	6.4%	101.6%	5.6%
2,4,5-TP (Fenoprop)	50.9	6.3%	201.0	6.7%	99.9%	5.5%
2,4-D	50.2	9.3%	202.8	4.7%	99.5%	5.6%
2,4-DB	49.0	8.7%	196.1	6.0%	98.7%	4.7%
2,4-DP (Dichloroprop)	51.3	9.0%	198.6	5.6%	101.6%	6.5%
Asulam	49.6	4.3%	200.7	1.9%	100.1%	2.7%
Benazolin	50.3	7.8%	204.8	4.4%	99.9%	6.3%
Bentazone	49.2	3.3%	200.6	1.3%	99.8%	2.7%
Bromoxynil	49.9	7.5%	206.9	4.5%	105.1%	5.9%
Clopyralid	49.1	7.2%	200.7	6.3%	100.4%	4.3%
Dicamba	49.5	5.0%	203.5	3.4%	100.2%	7.2%
Fluroxypyr	50.5	8.2%	202.0	4.8%	100.1%	5.2%
Imazapyr	49.7	5.8%	200.6	4.6%	107.8%	6.1%
Ioxynil	50.3	6.3%	202.0	5.4%	102.9%	4.9%
MCPA	49.4	6.9%	201.3	5.1%	99.5%	5.5%
MCPB	51.0	6.0%	199.7	5.9%	101.1%	5.7%
MCPP	50.2	6.8%	201.0	4.3%	100.0%	6.6%
PCP	49.3	9.8%	199.3	9.2%	99.6%	7.9%
Picloram	50.4	5.1%	205.5	3.5%	110.1%	4.0%
Propamocarb	48.8	4.4%	201.2	2.2%	99.2%	2.8%
Triclopyr	50.6	12.3%	199.8	8.6%	98.2%	8.4%

Instrument Q2

Determinand	Direct Standards				Elvington (Hard Hardness)	
	Low Standard		High Standard		PCV Spike	
	Mean	%RSD	Mean	%RSD	%Recovery	%RSD
2,3,6-Trichlorobenzoic acid	49.9	4.8	200.8	4.9%	98.0%	4.0%
2,4,5-T	51.9	6.2	199.7	4.0%	101.9%	4.4%
2,4,5-TP (Fenoprop)	51.7	6.5	198.5	3.6%	101.3%	4.8%
2,4-D	50.8	4.5	199.3	5.2%	99.3%	4.5%
2,4-DB	51.9	7.1	199.9	5.0%	98.7%	6.3%
2,4-DP (Dichloroprop)	51.5	6.1	198.5	3.8%	101.0%	5.0%
Asulam	50.4	3.0	200.4	2.8%	99.7%	3.5%
Benazolin	51.7	4.7	201.0	5.2%	98.6%	4.7%
Bentazone	49.1	1.6	200.7	1.3%	98.1%	1.4%
Bromoxynil	50.4	4.4	200.4	5.5%	102.5%	5.7%
Clopyralid	51.5	4.6	200.2	4.7%	102.7%	5.0%
Dicamba	50.3	4.3	199.7	3.4%	99.9%	3.5%
Fluroxypyr	51.2	5.0	201.6	4.6%	98.6%	4.8%
Imazapyr	49.1	4.7	196.9	4.4%	106.3%	6.0%
Ioxynil	49.5	3.8	196.4	4.6%	100.5%	4.9%
MCPA	51.4	5.4	198.9	4.1%	100.1%	4.5%
MCPB	51.1	6.0	200.6	4.0%	101.7%	4.7%
MCPP (Mecoprop)	51.1	6.1	199.4	4.4%	101.8%	5.1%
Pentachlorophenol	49.8	6.8	194.2	5.3%	98.3%	5.6%
Picloram	50.8	4.8	199.2	4.1%	119.5%	5.4%
Propamocarb	50.5	4.5	201.6	1.8%	101.6%	3.2%
Triclopyr	50.2	7.4	199.5	5.1%	100.4%	3.6%

Determinand	METHOD (Standardised) LOQ (ng L ⁻¹)
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Determinand	METHOD (Standardised) LOQ (ng L⁻¹)
2,3,6-TBA	9
2,4,5-T	11
2,4,5-TP	9
2,4-D	12
2,4-DB	17
2,4-DP	11
Asulam	14
Benazolin	11
Bentazone	2
Bromoxynil	9
Clopyralid	11
Dicamba	14
Fluroxypyr	12
Imazapyr	4
Ioxynil	7
MCPA	8
MCPB	18
MCPP	7
PCP	15
Picloram	13
Propamocarb	6
Triclopyr	15

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.