

# 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 ALS058 - 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.

| <b>Determinand</b>          | <b>Maximum period of analyte stability prior to any extraction step (days)</b> | <b>Maximum period of analyte stability after to any extraction step (days)</b> | <b>Data is quoted from BS EN ISO 5667-3: 2018 ["ISO"] or ALS in-house data ["ALS IHD"]</b> |
|-----------------------------|--|--|--|
| ASULAM                      | 31   | N/A  | ALS IHD  |
| BENAZOLIN                   | 31   | N/A  | ALS IHD  |
| BENTAZONE                   | 31   | N/A  | ALS IHD  |
| BROMOXYNIL                  | 31   | N/A  | ALS IHD  |
| CLOPYRALID                  | 31   | N/A  | ALS IHD  |
| 2,4-D                       | 31   | N/A  | ALS IHD  |
| 2,4-DB                      | 31   | N/A  | ALS IHD  |
| DICAMBA                     | 31   | N/A  | ALS IHD  |
| 2,4-DP (DICHLORPROP)        | 31   | N/A  | ALS IHD  |
| FLUROXYPYR                  | 31   | N/A  | ALS IHD  |
| IMAZAPYR                    | 31   | N/A  | ALS IHD  |
| IOXYNIL                     | 31   | N/A  | ALS IHD  |
| MCPA                        | 31   | N/A  | ALS IHD  |
| MCPB                        | 31   | N/A  | ALS IHD  |
| MCPP (MECOPROP)             | 31   | N/A  | ALS IHD  |
| PENTACHLOROPHENOL           | 31   | N/A  | ALS IHD  |
| PICLORAM                    | 31   | N/A  | ALS IHD  |
| PROPAMOCARB                 | 31   | N/A  | ALS IHD  |
| 2,4,5-T                     | 31   | N/A  | ALS IHD  |
| 2,3,6-TRICHLOROBENZOIC ACID | 31   | N/A  | ALS IHD  |

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| <b>Determinand</b>  | <b>Maximum period of analyte stability prior to any extraction step (days)</b> | <b>Maximum period of analyte stability after to any extraction step (days)</b> | <b>Data is quoted from BS EN ISO 5667-3: 2018 ["ISO"] or ALS in-house data ["ALS IHD"]</b> |
|---------------------|--|--|--|
| 2,4,5-TP (FENOPROP) | 31   | N/A  | ALS IHD  |
| TRICLOPYR           | 31   | 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:

| Determinand | Direct Standards |       |               |       | Elvington (Hard Hardness) |        |
|-------------|------------------|-------|---------------|-------|---------------------------|--------|
|             | Low Standard     |       | High Standard |       | PCV Spike                 |        |
|             | Mean             | %RSD  | Mean          | %RSD  | %Rec                      | %RSD   |
| 2,3,6-TBA   | 49.43            | 3.37% | 201.35        | 4.35% | 96.96%                    | 5.00%  |
| 2,4,5-T     | 49.50            | 4.72% | 198.99        | 3.95% | 99.42%                    | 4.58%  |
| 2,4,5-TP    | 49.60            | 4.09% | 197.62        | 3.52% | 99.33%                    | 4.33%  |
| 2,4-D       | 49.44            | 5.28% | 202.24        | 4.03% | 98.95%                    | 3.28%  |
| 2,4-DB      | 49.90            | 6.33% | 198.50        | 4.71% | 99.03%                    | 5.08%  |
| 2,4-DP      | 50.41            | 4.25% | 198.23        | 2.98% | 100.75%                   | 4.35%  |
| Asulam      | 49.59            | 2.32% | 198.78        | 1.49% | 99.08%                    | 1.95%  |
| Benazolin   | 49.76            | 6.14% | 202.52        | 5.24% | 100.59%                   | 6.08%  |
| Bentazone   | 49.36            | 1.83% | 200.64        | 1.53% | 99.70%                    | 2.23%  |
| Bromoxynil  | 49.97            | 4.33% | 204.64        | 4.30% | 95.84%                    | 5.51%  |
| Clopyralid  | 48.58            | 4.09% | 195.67        | 3.72% | 88.32%                    | 10.08% |
| Dicamba     | 50.09            | 4.50% | 200.30        | 2.46% | 99.49%                    | 3.14%  |
| Fluroxypyr  | 49.93            | 3.66% | 201.86        | 4.84% | 100.04%                   | 3.75%  |
| Imazapyr    | 48.85            | 3.66% | 196.35        | 4.43% | 100.82%                   | 4.16%  |
| loxynil     | 49.65            | 3.80% | 199.88        | 4.26% | 98.12%                    | 4.01%  |
| MCPA        | 49.16            | 4.83% | 199.93        | 3.61% | 98.98%                    | 3.44%  |
| MCPB        | 50.00            | 5.84% | 198.70        | 4.44% | 99.47%                    | 4.08%  |
| MCPP        | 49.85            | 6.61% | 199.69        | 3.75% | 99.74%                    | 3.79%  |
| PCP         | 49.29            | 5.13% | 200.08        | 3.50% | 98.80%                    | 4.01%  |
| Picloram    | 49.45            | 6.13% | 200.90        | 4.27% | 108.93%                   | 5.75%  |
| Propamocarb | 49.96            | 4.83% | 203.64        | 4.83% | 101.94%                   | 5.11%  |
| Triclopyr   | 49.21            | 7.64% | 196.31        | 4.79% | 102.26%                   | 4.84%  |

**Instrument WQQQ2** performance testing dynamic MRM limit of quantification exercise March - April 2024.

**Instrument WQQQ10** performance testing, single matrix dynamic MRM comparability exercise March - April 2024.

| Determinand | WQQQ2<br>Limit of<br>Quantification (ng L <sup>-1</sup> ) | WQQQ10<br>Limit of Quantification<br>(ng L <sup>-1</sup> ) | METHOD<br>(Standardised)<br>LOQ (ng L <sup>-1</sup> ) |
|-------------|---|--|---|
| 2,3,6-TBA   | 5   | 6  | 6   |
| 2,4,5-T     | 5   | 13   | 13  |
| 2,4,5-TP    | 4   | 5  | 5   |
| 2,4-D       | 7   | 10   | 10  |
| 2,4-DB      | 12  | 7  | 12  |
| 2,4-DP      | 5   | 6  | 6   |
| Asulam      | 4   | 4  | 4   |
| Benazolin   | 9   | 14   | 14  |
| Bentazone   | 3   | 4  | 4   |
| Bromoxynil  | 4   | 7  | 7   |
| Clopyralid  | 12  | 9  | 12  |
| Dicamba     | 11  | 8  | 11  |
| Fluroxypyr  | 11  | 11   | 11  |
| Imazapyr    | 6   | 5  | 6   |
| loxynil     | 4   | 4  | 4   |
| MCPA        | 6   | 8  | 8   |

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| <b><u>Determinand</u></b> | <b>WQQQ2<br/>Limit of<br/>Quantification (ng L<sup>-1</sup>)</b> | <b>WQQQ10<br/>Limit of Quantification<br/>(ng L<sup>-1</sup>)</b> | <b>METHOD<br/>(Standardised)<br/>LOQ (ng L<sup>-1</sup>)</b> |
|---------------------------|--|---|--|
| MCPB                      | 7  | 11  | 11   |
| MCPP                      | 7  | 10  | 10   |
| PCP                       | 4  | 8   | 8  |
| Picloram                  | 16   | 9   | 16   |
| Propamocarb               | 3  | 4   | 4  |
| Triclopyr                 | 3  | 19  | 19   |

## 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.