METHOD STATEMENT

Determinand:
Haloacetic Acids and Dalapon

Matrix:
Sample Types: Treated and Raw waters.

Principle of Method:
The method is a direct aqueous injection procedure. Samples are analysed by high performance liquid chromatography using a triple quadrupole mass spectrometer as a detector. The aqueous sample is injected and the organic compounds are separated and then identified and quantified with mass spectrometric detection (MSD) in selected reaction monitoring (SRM) mode. Quantitation is based on an internal standardisation procedure.

Sampling and Sample Preparation:
Sampling, samples should be collected in 250 mL coloured glass bottles with PTFE lined screw caps containing 250 µL of 10% w/v ammonium chloride solution as preservative, i.e. STL430.
Storage – samples should be analysed as soon as possible after collection. When this is not possible, they are stored under refrigeration at 1-5□C until analysis can begin. The maximum permissible storage time prior to analysis is given below:

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: 2003 ["ISO"] or ALS in-house data ["ALS-AS IHD"]***
MCAA	10	N/A	ALS IHD
DCAA	14	N/A	ALS IHD
TCAA	21	N/A	ALS IHD
MBAA	14	N/A	ALS IHD
DBAA	14	N/A	ALS IHD
TBAA	21	N/A	ALS IHD
BCAA	14	N/A	ALS IHD
BDCAA	21	N/A	ALS IHD
DBCAA	21	N/A	ALS IHD
Dalapon	21	N/A	ALS IHD

Interferences
HPLC-QQQ is an extremely selective technique and interferences should only be encountered very rarely. Any interfering compounds would have to display the identical SRM 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:
LOQ to 150 µg L^{-1}
Samples producing results above this range should be diluted and re-extracted.

Limit of Quantification:

Determinand	Method Limit of Quantification (µg L^{-1})
Monochloroacetic acid (MCAA)	1.3
Dichloroacetic acid (DCAA)	1.2
Trichloroacetic acid (TCAA)	1.7
Monobromoacetic acid (MBAA)	1.2
Dibromoacetic acid (DBAA)	1.6
Tribromoacetic acid (TBAA)	1.2
Bromochloroacetic acid (BCAA)	1.0
Bromodichloroacetic acid (BDCAA)	1.3
Dibromochloroacetic acid (DBCAA)	1.5
Dalapon	1.2

Recoveries of Compounds, Bias and Uncertainty of measurement:

Determinand	Uncertainty of Measurement (UoM) (%)	Direct Standards				Elvington Treated Water	
		Low Standard		High Standard		PCV Spike	
		Recovery	SD	Recovery	SD	Recovery	SD
MCAA	10.554	98.39%± 1.50%	3.20%	100.33%± 1.41%	3.10%	101.18%± 1.72%	3.53%
DCAA	21.971	102.06%± 2.16%	4.79%	100.70%± 2.43%	4.86%	110.32%± 2.70%	4.85%
TCAA	9.695	99.34%± 1.50%	3.35%	100.77%± 1.36%	2.73%	101.39%± 1.45%	2.72%
MBAA	10.865	100.91%± 1.72%	3.79%	101.60%± 1.59%	3.46%	101.71%± 1.32%	2.87%
DBAA	17.824	100.76%± 1.78%	3.69%	101.41%± 2.14%	4.47%	106.17%± 2.36%	4.40%
TBAA	17.343	106.43%± 2.17%	4.03%	100.87%± 2.61%	5.29%	106.83%± 2.86%	5.08%
BCAA	17.734	98.32%± 1.79%	4.32%	99.79%± 2.45%	5.05%	106.21%± 2.95%	5.47%
BDCAA	19.815	100.96%± 2.66%	5.03%	100.41%± 3.33%	6.56%	106.46%± 3.82%	6.72%
DBCAA	18.732	103.77%± 2.21%	4.17%	101.30%± 3.12%	6.13%	107.19%± 2.94%	5.19%
DALAPON	10.879	99.11%± 2.36%	5.16%	101.74%± 1.41%	3.63%	101.24%± 1.59%	3.28%

References:

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