

METHOD STATEMENT



Determinand:

Determination of Chlormequat, Diquat and Mepiquat.

Matrix:

Sample Type: Treated, Ground and Raw Waters

Principle of Method:

The method is a direct aqueous injection procedure. Samples are prepared by adding acetonitrile, 0.25% formic acid and ammonium formate, 1.5M (aq) prior to analysis. The sample is analysed by HILIC high performance liquid chromatography using a triple quadrupole mass spectrometer as a detector. The analytes 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 are taken in PE/HD bottles, with screw tops containing sample preservative – sodium thiosulfate 1.8% w/v (aq).

Storage – samples should be analysed as soon as possible after collection. When this is not possible they can be stored under refrigeration at $3\pm2^{\circ}\text{C}$. 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 any extraction step (days)	Data is quoted from BS EN ISO 5667-3: 2003 ["ISO"] or ALS in-house data ["ALS IHD"]
Chlormequat Cation	31	N/A	ALS IHD
Diquat Cation	31	N/A	ALS IHD
Mepiquat Cation	31	N/A	ALS IHD

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:

Determinand	Operational Calibration Range (Instrument Asset Number 2572)
Chlormequat Cation	LOQ - 0.150 µg/L
Diquat Cation	LOQ - 0.150 µg/L
Mepiquat Cation	LOQ - 0.150 µg/L

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

<u>Determinand</u>	<u>LoQ,</u> <u>ng/L</u>	<u>UoM,</u> <u>%</u>	<u>Direct Standards</u>				<u>Elvington</u> <u>Treated</u> <u>(Hard Water)</u>	
			Low Standard		High Standard		PCV Spike	
			Recovery	RSD	Recovery	RSD	Recovery	RSD
Chlormequat Cation	8	± 9.90	93.6%	9.8%	99.3%	3.0%	99.5%	3.8%
Diquat Cation	10	± 15.53	94.7%	10.3%	98.8%	4.0%	97.7%	6.6%
Mepiquat Cation	8	± 10.32	94.0%	8.0%	99.4%	2.8%	98.6%	4.0%

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 6400 Series Triple Quadrupole 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.

A Manual on Analytical Quality Control for the Water Industry, R.V. Cheeseman, A.L. Wilson, revised by M. J. Gardner, NS 30, Water Research Centre, 1989. ISBN 0-902156-85-3.