

METHOD STATEMENT



Determinand:

Determination of chlormequat, diquat and mepiquat.

Matrix:

Sample Type: Treated, Ground and Raw Waters.

Principle of Method:

Samples are adjusted to pH7 with a phosphate buffer prior to extraction by weak cation exchange solid phase extraction cartridges. The solid phase extraction cartridges are eluted with Acetonitrile: Formic Acid, 4: 1. The sample extracts are analysed by HPLC 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 multiple reaction monitoring (MRM) 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.

Storage - samples should be analysed as soon as possible after collection. When this is not possible they can be stored under refrigeration at 1-5°C until analysis can begin. 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 ["STS-AS IHD"]
CHLORMEQUAT CATION	21	N/A	ALS IHD
DIQUAT CATION	21	N/A	ALS IHD
MEPIQUAT CATION	21	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:

<u>Determinand</u>	<i>Operational Calibration Range</i>
CHLORMEQUAT	LOQ - 0.150 µg/l
DIQUAT	LOQ - 0.150 µg/l
MEPIQUAT	LOQ - 0.150 µg/l

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

<u>DETERMINAND</u>	<u>LOQ</u> (ng L ⁻¹)	<u>UoM</u>	<u>DIRECT STANDARDS</u>				<u>ELVINGTON TREATED (Hard Hardness)</u>	
			<u>LOW STANDARD</u>		<u>HIGH STANDARD</u>		<u>PCV SPIKE</u>	
			<u>RECOVERY</u>	<u>RSD</u>	<u>RECOVERY</u>	<u>RSD</u>	<u>RECOVERY</u>	<u>RSD</u>
CHLORMEQUAT	2	6.75%	99.09%± 1.27%	2.84%	100.41%± 1.01%	2.39%	102.29%± 1.05%	2.00%
DIQUAT	14	12.18 %	97.85%± 1.87%	3.87%	100.33%± 1.34%	2.64%	100.99%± 1.34%	2.87%
MEPIQUAT	3	5.14 %	98.39%± 1.50%	3.02%	100.40%± 1.01%	2.22%	100.47%± 0.89%	1.79%

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.

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