ENVIRONMENTAL ANALYSIS

MONITORING FOR HALOACETIC ACIDS IN TREATED WATERS USING DIRECT AQUEOUS INJECTION ON THE AGILENT 6460 LC/QQQ

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Solution Note

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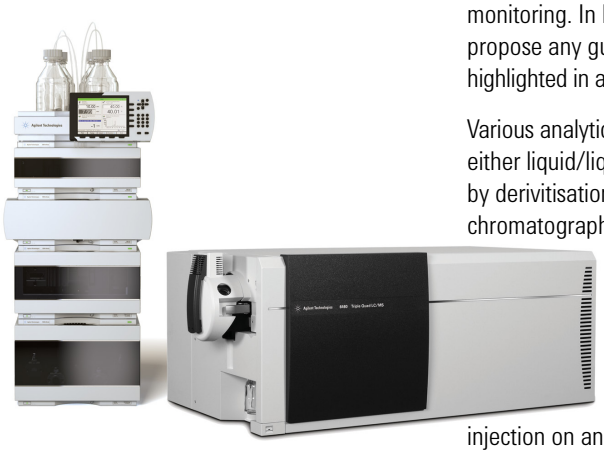
Abstract

A method for the determination of Haloacetic acids and Dalapon in treated drinking waters has been developed on the Agilent 6460 LC/QQQ. The method utilises direct aqueous injection onto the LC/QQQ and achieves limits of detection of less than 0.25 µg/L.

Introduction

Haloacetic Acids (HAAs) are a group of disinfection by-products (DBPs) produced when chlorine or other disinfectants used to control microbial contaminants in drinking water react with naturally occurring organic and inorganic matter in the water. HAAs have been linked to possible human health effects. In the US, they are regulated by the US Environment Protection Agency (EPA) which has established a Maximum Contaminant Level (MCL) of 60 µg/L for five of the HAAs, known as the HAA5, namely monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), dichloroacetic acid (DCAA), dibromoacetic acid (DBAA) and trichloroacetic acid (TCAA). The HAA5, along with tribromoacetic acid (TBAA), bromochloroacetic acid (BCAA), bromodichloroacetic acid (BDCAA) and chlorodibromoacetic acid (CDBAA), make up the HAA9, which are recommended for monitoring. In Europe, the Drinking Water Directive 98/83/EC (DWD) does not currently propose any guideline values for HAAs in drinking water. However, they have been highlighted in a report to the European Commission as a possible future regulated parameter.



Various analytical techniques are used to determine HAAs in water. These typically involve either liquid/liquid extraction (LLE) or solid phase extraction (SPE) extraction, followed by derivitisation to convert the HAAs to their methyl esters and analysis by GC/ECD (gas chromatography with electron capture detection) [1] or GC/MS (gas chromatography with mass spectrometer detection). Methods using direct injection IC/MS/MS (Ion chromatography with triple quadrupole detection) have also been developed.

Anglian Water has developed a method for the determination of the HAAs and Dalapon in treated drinking water using direct aqueous injection on an Agilent 6460 LC/QQQ (high performance liquid chromatography with mass spectrometer triple quadrupole detection) system. This method can determine all nine HAAs as well as Dalapon. It benefits from requiring no sample preparation but is sensitive enough to achieve LODs of less than 0.25 µg/L for all HAAs. The range of application for this method is up to 50 µg/L.

Analytical Technique

Sample Preparation

- Direct aqueous injection onto the Agilent 6460 LC/QQQ

Instrumentation

Agilent 1200 Series HPLC System consisting of the following:

- Autosampler G1329C
- Micro Vacuum Degasser G1379B
- 2 Position / 6 Port Valve G4231A
- Binary Pump G1312B
- Column Compartment G1316A

Agilent 6460 QQQ System with Jet Stream Interface

Agilent 1200/6460 LC/QQQ Operating Conditions

LC Conditions		
Analytical Column	C18 2.0 x 250 mm x 5 µm	
Column Temperature	40° C	
Injection Volume	15 µL	
Mobile Phase	A = 0.05 % Formic Acid B = Methanol	
Run Time	23 minutes	
MS Conditions	Acquisition Parameters: MRM Mode, ESI Negative	
	Initial Conditions	Conditions @ 9 minutes
Gas Temperature	225 °C	150 °C
Gas Flow	8 L/min	6 L/min
Nebuliser Pressure	40 psi	40 psi
Sheath Gas Temperature	225 °C	175 °C
Sheath Gas Flow	11 L/min	9 L/min
Capillary Voltage	4000 V	4000 V
Nozzle Voltage	0 V	0 V

MRM Transitions – Negative Ion Mode

Peak	Compound		Molecular Weight	Precursor Ion (m/z)	Product Ion (m/z)	Fragmentor Voltage (V)	Collision Energy (V)
1	Monochloroacetic acid	MCAA	94.0	93.0	35.0	80	7
2	Monobromoacetic acid	MBAA	138.0	137.0	79.0	80	8
3	Dichloroacetic acid	DCAA	128.0	127.0	83.0	85	6
4	Dibromoacetic acid	DBAA	216.0	217.0	173.0	85	3
5	Trichloroacetic acid	TCAA	162.0	161.0	117.0	65	2
6	Tribromoacetic acid	TBAA	294.0	250.7	78.7	50	12
7	Bromochloroacetic acid	BCAA	172.0	173.0	129.0	80	6
8	Bromodichloroacetic acid	BDCAA	206.0	163.0	81.0	60	6
9	Chlorodibromoacetic acid	CDBAA	250.0	207.0	79.0	80	8
10	2,2-Dichloropropionic acid	Dalapon	142.0	141.0	97.0	90	4

Results and Discussion

Direct aqueous injection eliminates the need for costly and time consuming sample preparation techniques. The sample matrix is also cleaner than if derivitisation had been performed, which is beneficial to the instrument and its performance. Also, smaller sample volumes are required to be taken and results can be obtained faster. The method should also be more reproducible as there are no extraction variables.

The calibration range for each HAA was 0 to 50 µg/L with standards at 0, 5, 10, 25 and 50 µg/L. Figure 1 shows a typical chromatogram of a 5 µg/L standard. It demonstrates good chromatography for all HAAs and Dalapon. Figure 2 shows a typical calibration for dichloroacetic acid (DCAA) with a real sample containing 9.8 µg/L of DCAA. Table 1 shows method performance. Recoveries for both the 5 µg/L and 37.5 µg/L spikes for all HAAs are in the range of 90 to 110 % and LODs range from 0.07 µg/L to 0.21 µg/L.

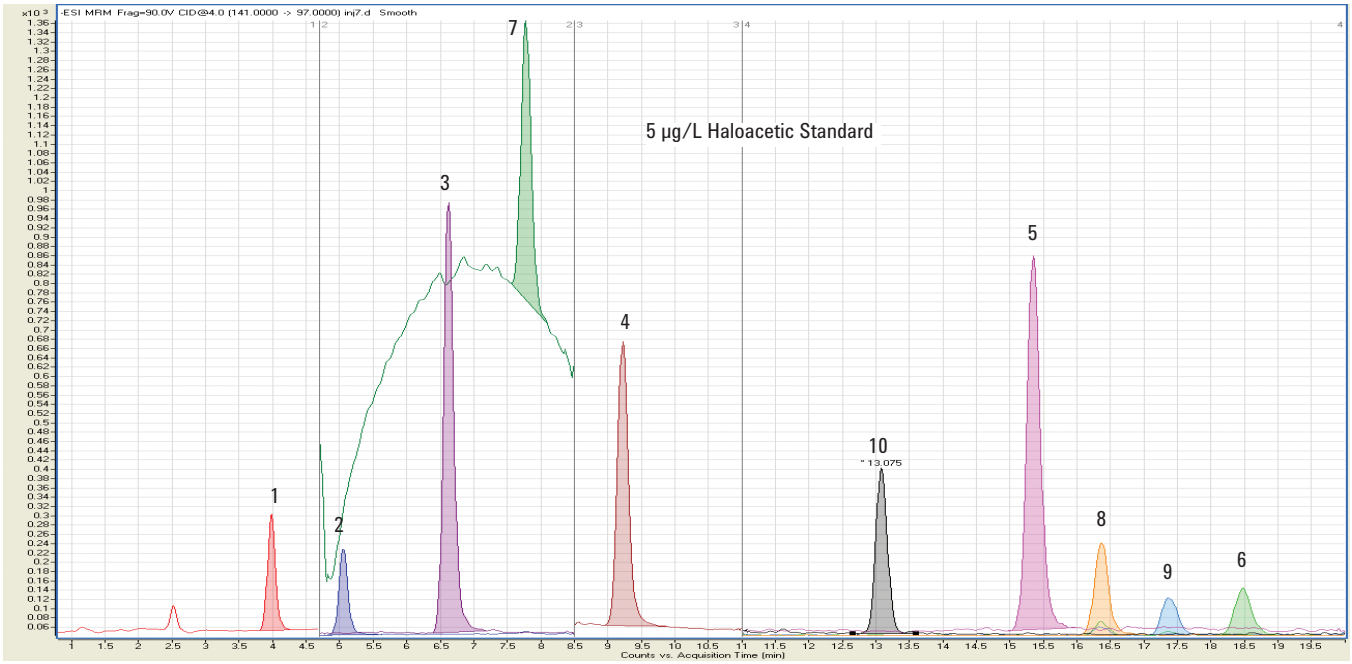


Figure 1: 5 µg/L Haloacetic Standard Chromatogram (Refer to Table 1 for Compound Names).

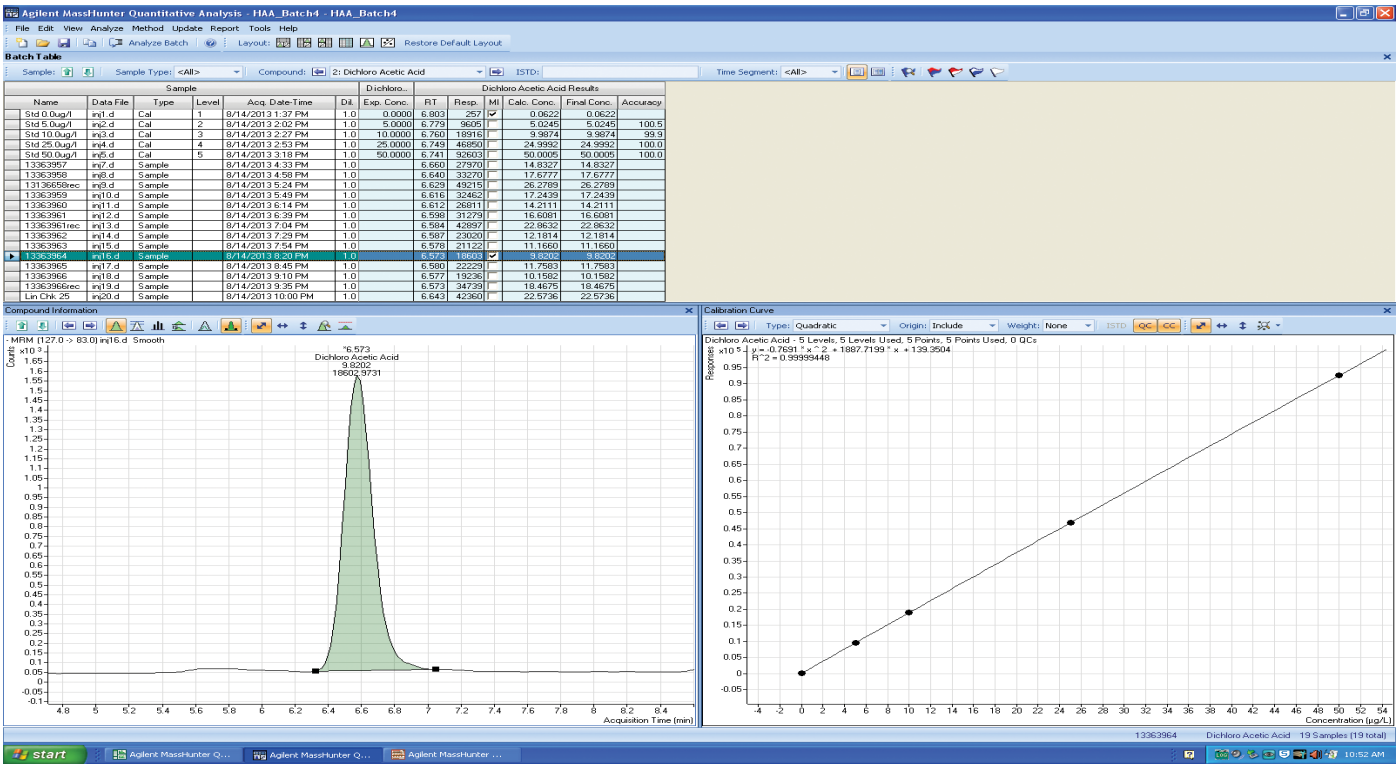


Figure 2: Dichloroacetic Acid (DCAA) in a treated water sample at a concentration of 9.8 µg/L.

Compound	% Recovery of 5 µg/L Spike	% Recovery of 37.5 µg/L Spike	LOD, µg/L
MCAA	90.1	92.5	0.07
MBAA	93.0	94.7	0.18
DCAA	94.5	99.0	0.07
DBAA	88.2	92.8	0.08
TCAA	94.0	97.5	0.08
TBAA	102.0	101.4	0.21
BCAA	90.7	97.0	0.13
BDCAA	96.6	98.5	0.17
CDBAA	93.7	96.1	0.20
Dalapon	94.6	92.8	0.16

Table1: Performance Data

Conclusions

A method has been developed for the determination of HAAs in treated drinking water using direct aqueous injection on the Agilent 6460 LC/QQQ. This method demonstrates excellent sensitivity and is capable of achieving LODs of less than 0.25 µg/L.

References

1. Doris Smith and Ken Lynam, "Determination of Haloacetic Acids in Water by GC/µECD Using Agilent J&W DB-35ms Ultra Inert and DB-XLB Columns," Agilent Technologies publication, 5990-8765EN, August 2011.

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