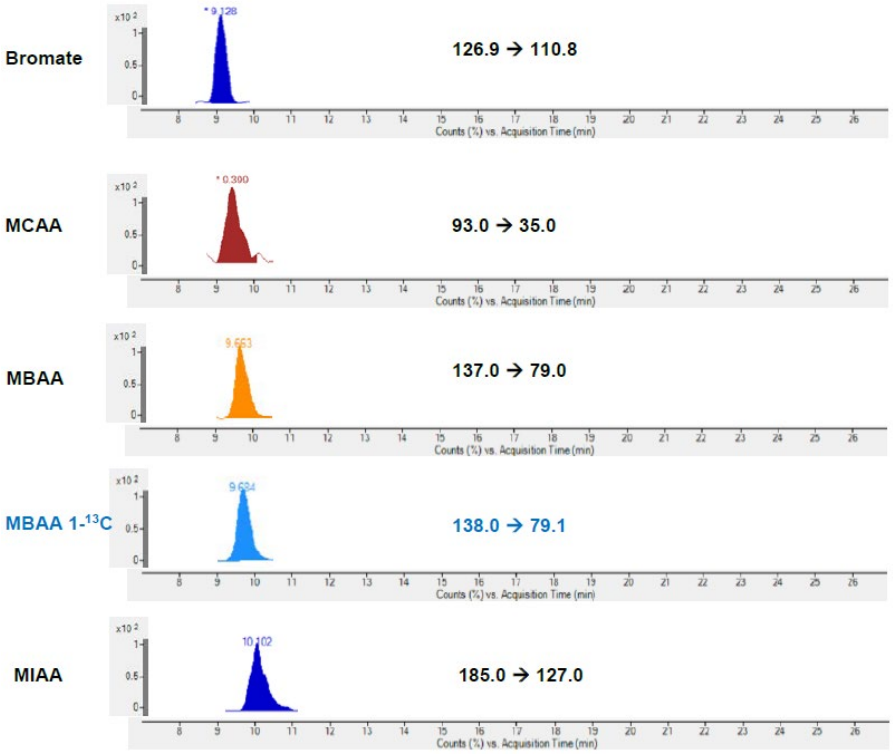
IC Application Note M–15

Trace haloacetic acids, dalapon, and bromate in water

Determination as per US EPA 557 applying IC-MS/MS



Highly sensitive and selective trace analysis of disinfection byproducts: Extracted Ion Chromatograms of 50 µg/L MBAA (monobromoacetic acid) 1-^{13}C (internal standard), bromate, MCAA (monochloroacetic acid), MBAA (monobromoacetic acid), and MIAA (monoiodoacetic acid), respectively (further chromatograms and results see below)

Chlorine in various forms remains the primary disinfection method for municipal water systems. Chlorine can form µg/L levels of disinfection byproducts (DBP's) in water supplies, which include haloacetic acids (HAA's). These HAA's are thought to pose potential cancer risks with high levels of exposure. As a precaution, the US EPA, has defined a maximum threshold of HAA content in municipal waters. To address the need for measuring low µg/L levels of various haloacetic acids (HAA's), a method was developed using ion chromatography/mass spectrometry (IC/MS), which conforms to USEPA Method 557. The benefit of using MS/MS with a triple-quadrupole mass spectrometer over using MS with a single quadrupole mass spectrometer is the ability to avoid potential interferences while achieving lower detection limits and enhanced selectivity.

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Sample

Fortified matrix sample, water

Sample preparation

None

Columns

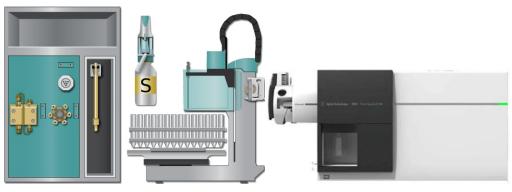
Metrosep A Supp 7 – 250/4.0	6.1006.630
Metrosep A Supp 5 Guard/4.0	6.1006.500

IC Solutions

Eluent A	50 mmol/L potassium hydroxide 7 mmol/L sodium carbonate 15 % (v/v) acetonitrile
Eluent B	Ultrapure water
Regenerant Dosino	1 mol/L nitric acid 10 % (v/v) acetonitrile
Rinsing	10 % (v/v) acetonitrile

Instrumentation

940 Professional IC Vario ONE/SeS/HPG	2.940.1440
Agilent 6470A Triple Quadrupole Mass Spectrometer w/Jet Stream ESI Source	
858 Professional Sample Processor	2.858.0020
800 Dosino	2.800.0010
Remote Box MSB	6.2148.010
MSM-HC Rotor	6.2842.000
IC equipment: Dosino Regeneration	6.5330190
MagIC Net Professional	6.6059.322
Agilent Mass Hunter Software	Ver. B.08.00



Parameters IC

Flow rate	0.7 mL/min
Injection volume (MiPT)	100 µL
P_{max}	150 MPa
Column temperature	45 °C
Recording time	28 min

Parameters MS/MS

Nebulizer	45 psig
Drying gas flow	12 L/min
Drying gas temperature	150 °C
Sheath gas heater temp.	245 °C
Sheath gas flow	12 L/min
Capillary voltage	3500 V
Charging voltage	500 V
Resolution	Unit (0.7 amu)

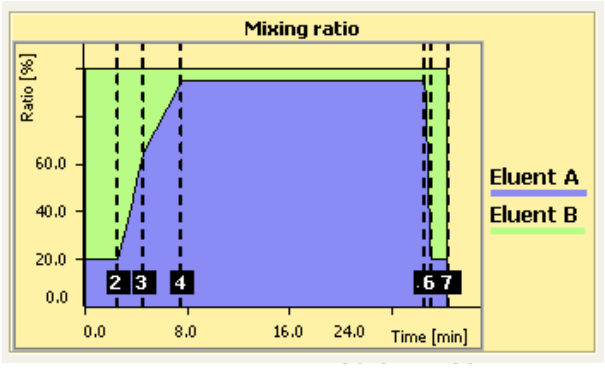
Analysis

MS/MS detection (triple quad)

IC Gradient

Gradient

	Time [min]	Eluent A [%]	Eluent B [%]	Curve	Flow
▶ 1	Start	20	80		0.7
2	2.6	20	80	Linear	0.7
3	4.6	65	35	Linear	0.7
4	7.6	95	5	Linear	0.7
5	26.6	95	5	Linear	0.7
6	27.1	20	80	Linear	0.7
7	28.5	20	80	Linear	0.7



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MS/MS acquisition parameter

Compound Name	ISTD Ref.	Precursor Ion [amu]	Product Ion [amu]	Dwell Time [ms]	Fragment Voltage [V]	Collision Energy [V]	Cell Accel. [V]	Polarity
DBAA	#2	216.8	173.0	40	60	10	2	Negative
DBAA*	#2	216.8	78.9	40	60	35	2	Negative
MIAA	#1	185.0	127.0	40	40	10	2	Negative
BCAA	#2	173.0	129.0	80	60	10	2	Negative
BCAA*	#2	173.0	80.9	80	60	25	2	Negative
Dalapon	#2	141.0	97.0	80	100	5	2	Negative
MBAA 1-13C (ISTD #1)	-	138.0	79.1	80	60	10	2	Negative
MBAA	#1	137.0	79.0	40	60	10	2	Negative
DCAA 2-13C (ISTD #2)	-	128.0	84.0	80	80	10	2	Negative
DCAA*	#2	127.0	83.0	80	80	10	2	Negative
DCAA	#2	127.0	34.8	80	80	25	2	Negative
Bromate*	#1	126.9	110.8	40	120	25	2	Negative
Bromate	#1	126.9	95.0	40	120	35	2	Negative
MCAA	#1	93.0	35.0	40	80	10	2	Negative
CDBAA	#3	206.9	81.0	90	100	15	2	Negative
CDBAA*	#3	206.7	79.1	90	100	15	2	Negative
BDCAA*	#3	163.0	81.0	90	100	10	2	Negative
BDCAA	#3	163.0	78.9	90	100	10	2	Negative
TCAA	#3	161.0	117.0	90	40	5	2	Negative
TCAA 2-13C (ISTD #3)	-	162.1	118.1	90	80	15	2	Negative
TCAA*	#3	117.0	34.9	90	100	15	2	Negative

* components chosen for quantification

DBAA: dibromoacetic acid
MIAA: monoiodoacetic acid
BCAA: bromochloroacetic acid
MBAA: monobromoacetic acid
DCAA: dichoroacetic acid
MCAA: monochloroacetic acid
CDBAA: chlorodibromoacetic acid
BDCAA: bromodichloroacetic acid
TCAA: trichloroacetic acid

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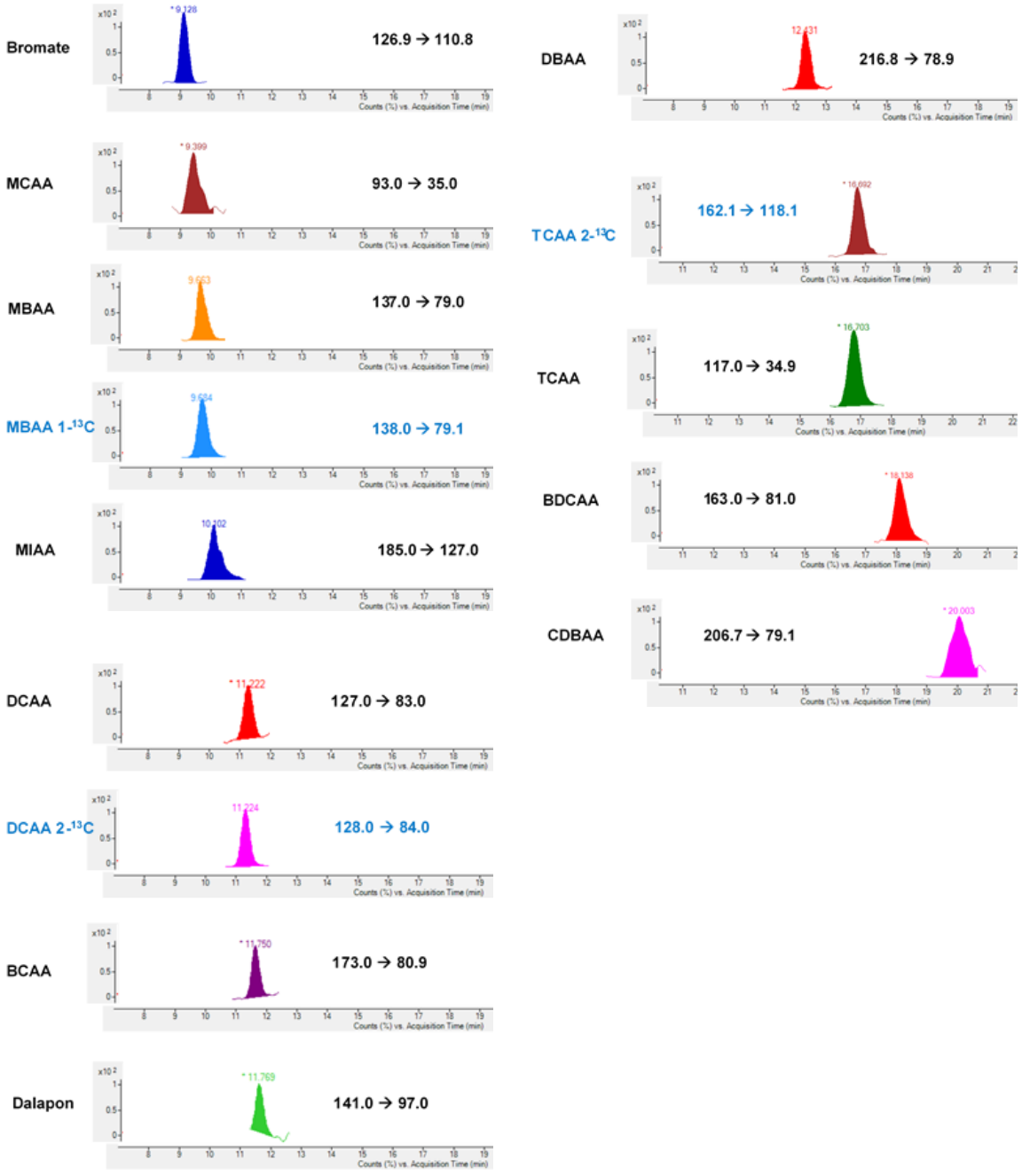
Extracted Ion Chromatograms of 50 µg/L of all analytes



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Results

Calibration results

Linear calibration is applied with 10 Calibration levels from 1 through 500 µg/L. Each standard solution is injected threefold.

Analyte	Transition [amu]	RT [min]	Correlation coefficient
Bromate	126.9 → 110.8	9.14	0.9989
MCAA	93.0 → 35.0	9.38	0.9903
MBAA	137.0 → 79.0	9.69	0.9981
MIAA	185.0 → 127.0	10.05	0.9868
DCAA	127.0 → 83.0	11.24	0.9987
BCAA	173.0 → 80.9	11.77	0.9988
Dalapon	141.0 → 97.0	11.80	0.9826
DBAA	216.8 → 78.9	12.46	0.9940
TCAA	117.0 → 34.9	16.74	0.9951
BDCAA	163.0 → 81.0	18.17	0.9977
CDBAA	206.7 → 79.1	20.03	0.9924

Spiked water results

Ultrapure water is spiked with 25 µg/L of each analyte. The spike solution is gravimetrically prepared from certified reference standards.

Analyte	Mean [µg/L]	RSD [%]	Expected [µg/L]	Recovery [%]
Bromate	39.4	4.5	35.0	112
MCAA	29.5	9.6	24.8	119
MBAA	25.6	13.3	23.9	107
MIAA	46.2	6.7	36.5	127
DCAA	24.8	2.2	24.0	103
BCAA	17.6	2.8	18.1	97
Dalapon	25.8	4.5	24.7	104
DBAA	24.7	5.7	25.1	99
TCAA	22.9	6.0	24.8	92
BDCAA	25.8	4.9	24.1	107
CDBAA	21.6	8.7	24.8	87

Municipal water results

Two different municipal water samples are analyzed. The results are based on a fivefold injection of the samples. Both samples contain lower concentrations of the target analytes than the limits set by the US EPA guidelines for total haloacetic acids.

Analyte	Water #1 [µg/L]	Water #2 [µg/L]
Bromate	4.0	n.d.
MCAA	n.d.	n.d.
MBAA	1.3	n.d.
MIAA	n.d.	n.d.
DCAA	2.2	12.3
BCAA	1.3	4.8
Dalapon	n.d.	n.d.
DBAA	n.d.	n.d.
TCAA	3.0	9.0
BDCAA	< 1	2.0
CDBAA	<1	n.d.
Total HAA's	**11.8**	**28.1**

n.d. = not detected