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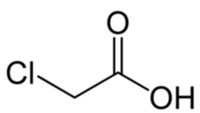
Fast validated direct injection determination of HAAs in drinking water with IC-MS/MS by EPA 557

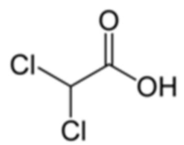
Paul Voelker
Product Marketing Manager IC/SP
August 10, 2021

The world leader in serving science

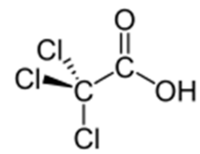
Haloacetic acids



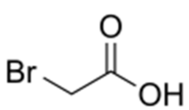
monochloroacetic acid (MCA)



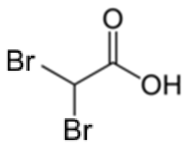
dichloroacetic acid (DCA)



trichloroacetic acid (TCA)



monobromoacetic acid (MBA)



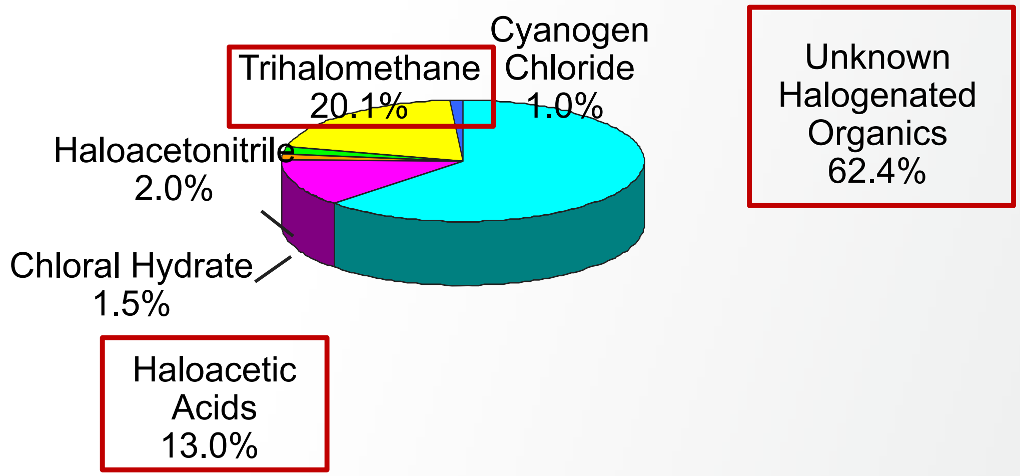
dibromoacetic acid (DBA)

Disinfection byproducts in drinking water

Untreated Source Water	Water Treatment Plant		Drinking Water
			
Pathogens: *Cryptosporidium* *Giardia* Virus Fecal Coliform *E. Coli*	**Disinfection:** Ozonation Chlorination (Chloramine, Chlorine)	*Bromide* *Naturally occurring matter*	**Disinfection Byproducts (DBPs):** Bromate Chlorate, chlorite Trihalomethanes (THM) Haloacetic Acids (HAA)

Occurrence of disinfectant treatment byproducts

Haloacetic acids are formed when chlorine or other disinfectants react with naturally occurring organic and inorganic matter in water



Haloacetic acids (HAA5, HAA6Br, and HAA9)

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Acid	HAA	Formula	pK_a
Monochloroacetic Acid	MCAA	$ClCH_2CO_2H$	2.86
Dichloroacetic Acid	DCAA	Cl_2CHCO_2H	1.25
Trichloroacetic Acid	TCAA	Cl_3CCO_2H	0.63
Monobromoacetic Acid	MBAA	$BrCH_2CO_2H$	2.87
Dibromoacetic Acid	DBAA	Br_2CHCO_2H	1.47
Tribromoacetic Acid	TBAA	Br_3CCO_2H	0.66
Bromochloroacetic Acid	BCAA	$BrClCHCO_2H$	1.39
Chlorodibromoacetic Acid	CDBAA	Br_2ClCCO_2H	1.09
Bromodichloroacetic Acid	BDCAA	Cl_2BrCCO_2H	1.09

HAA5

HAA6Br

HAA9

UCMR* 4 (2017-2021, 30 contaminants)

Regulated (EPA)

**Unregulated Contaminant Monitoring Rule*

Emerging drinking water regulations

METHOD 557: DETERMINATION OF HALOACETIC ACIDS, BROMATE, AND DALAPON IN DRINKING WATER BY ION CHROMATOGRAPHY ELECTROSPRAY IONIZATION TANDEM MASS SPECTROMETRY (IC-ESI-MS/MS)

Regulation in China: validation is underway

EU: HAA5 Regulation Enacted Feb 5, 2020 – sum not to exceed 60 ppb

- *Excellent opportunity for IC-MS/MS*
- *Next MOI HAA's and Ionic Pesticides*

HAA by GC-ECD – the most common technique today

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- EPA 552.3 - Method Steps:
  - Adjust pH to 0.5 then
  - Extract with either with methyl tert-butyl ether (MTBE) or
    tert-amyl methyl ether (TAME)
  - Convert HAAs to their methyl esters by addition of acidic methanol and heat for **two hours**
  - Separate from the acidic methanol by adding a concentrated aqueous solution of sodium sulfate
  - Neutralize with saturated solution of sodium bicarbonate
  - Analyze by GC/ECD: run time 25–30 min

Total Time ≈ 4+ hrs. per sample

- ***Sample prep is a major pain point***
- Long and tedious sample preparation complaints motivated the EPA to develop an IC-MS/MS method

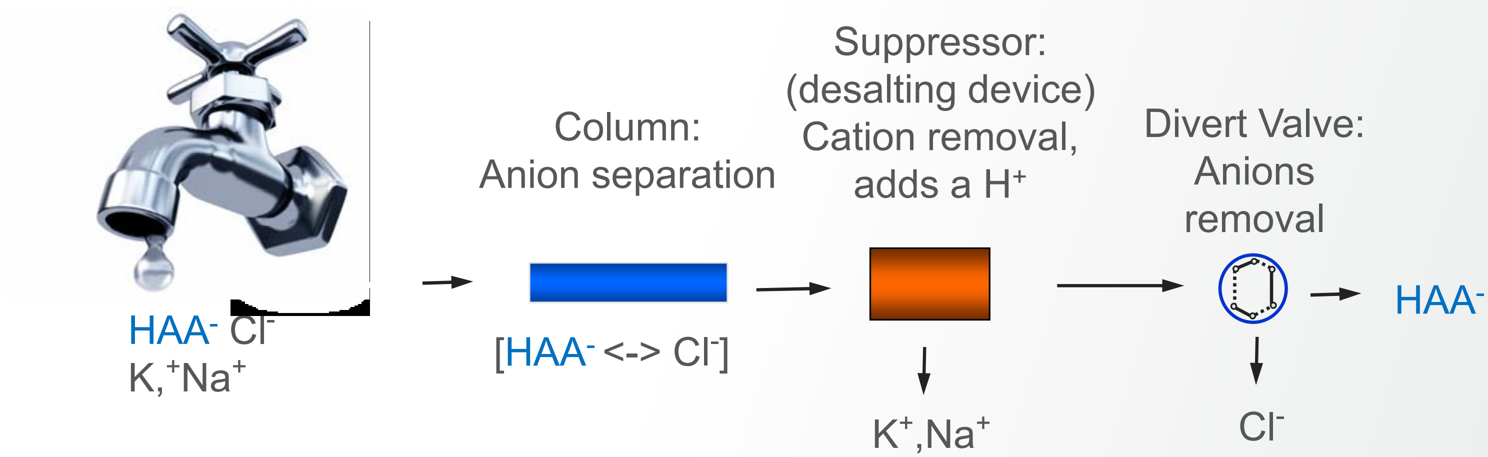
HAA by IC-MS/MS – a higher throughput method

- Sample Prep
  - None - Direct injection
- Analysis
  - Analyze by IC-MS/MS run time ~35 min

EPA United States Environmental Protection Agency

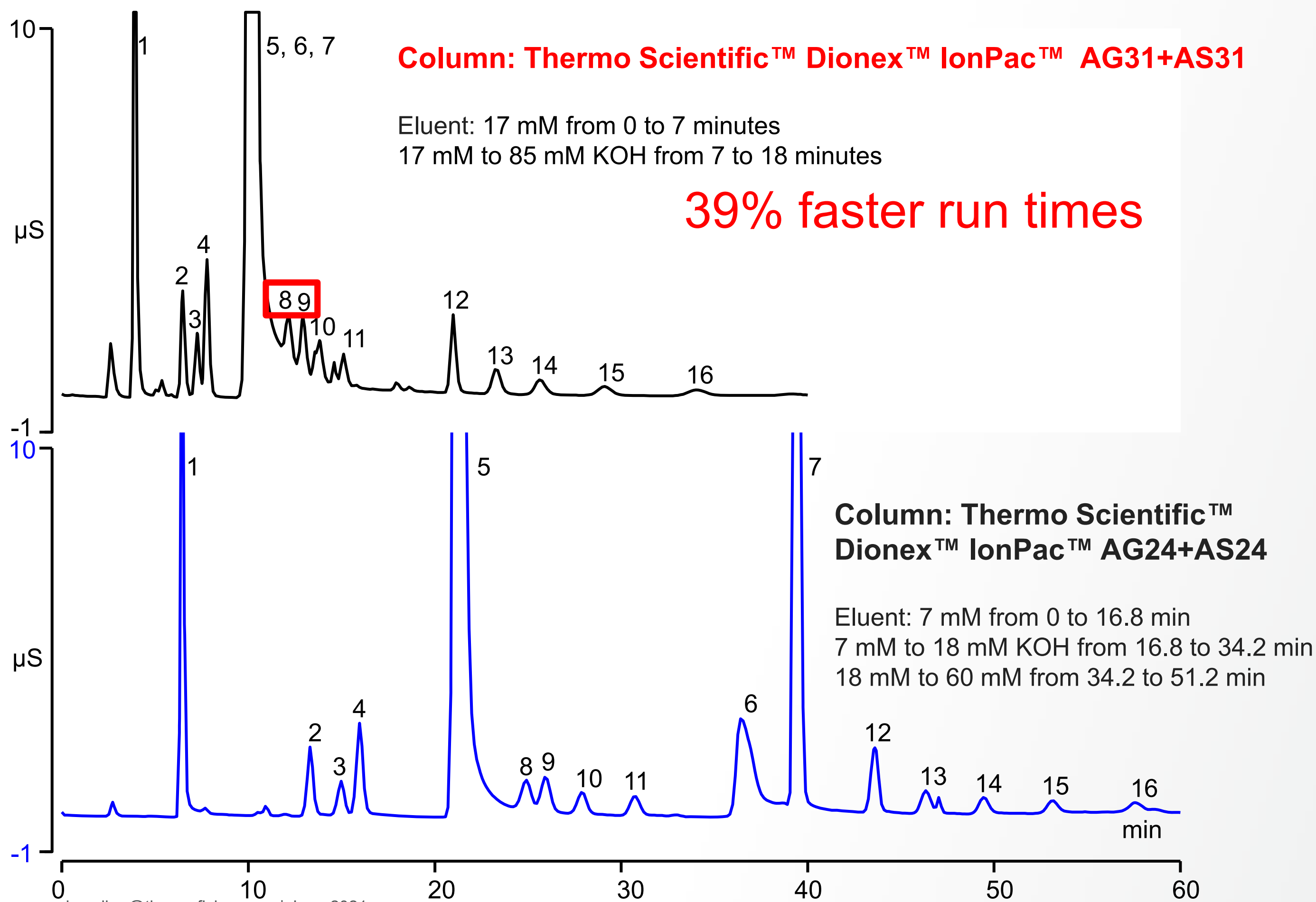
METHOD 557: DETERMINATION OF HALOACETIC ACIDS, BROMATE, AND DALAPON IN DRINKING WATER BY ION CHROMATOGRAPHY ELECTROSPRAY IONIZATION TANDEM MASS SPECTROMETRY (IC-ESI-MS/MS)

Matrix elimination of anions and cations by ion exchange chromatography



Strategy to eliminate signal suppression in the MS

IonPac AS24 & AS31 for separation of HAAs, dalapon & bromate (drinking water)

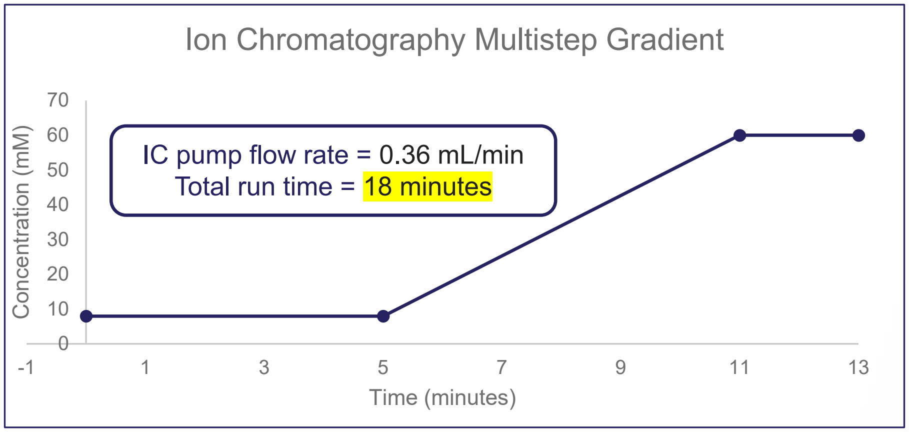


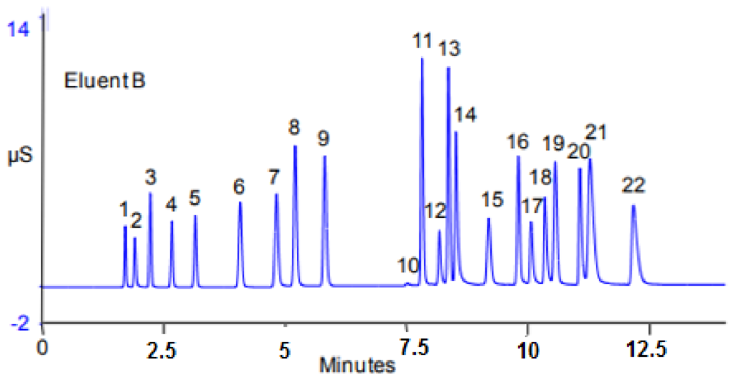
Column:	See Chromatogram
Eluent :	See Chromatogram
Eluent Source:	Thermo Scientific™ Dionex™ EGC-500 KOH cartridge
Flow Rate:	0.30 mL/min
Inj. Volume:	100 µL
Temperature:	15 ˚C
Detection:	Suppressed Conductivity, Thermo Scientific™ Dionex™ ADRS 600 Suppressor, 2 mm AutoSuppression, recycle mode
Sample	Municipality Drinking Water Spiked with 9HAAs, Dalapon and Bromate

Peaks (Standard):	mg/L
1. Fluoride	NQ
2. Monochloroacetate	1.0
3. Monobromoacetate	1.0
4. Bromate	1.0
5. Chloride	NQ
6. Sulfate	NQ
7. Carbonate	NQ
8. Dalapon	1.0
9. Dichloroacetate	1.0
10. Bromochloroacetate	1.0
11. Dibromoacetate	1.0
12. Nitrate	NQ
13. Trichloroacetate	1.0
14. Bromodichloroacetate	1.0
15. Chlorodibromoacetate	1.0
16. Tribromoacetate	1.0

NQ: Not Quantified

Multistep or isocratic gradient





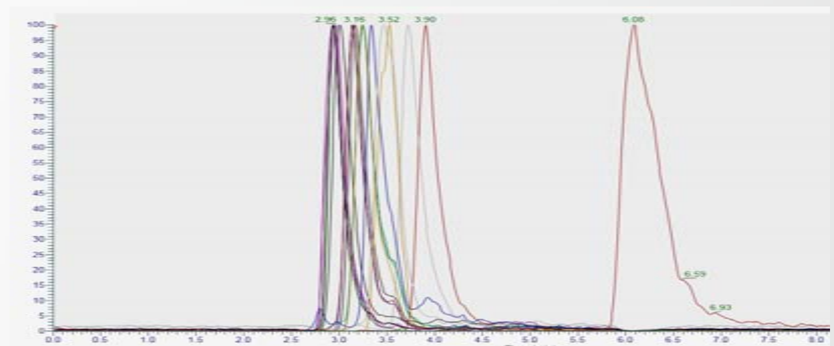
Multistep Gradient for ultimate resolution on IC peaks

OR..

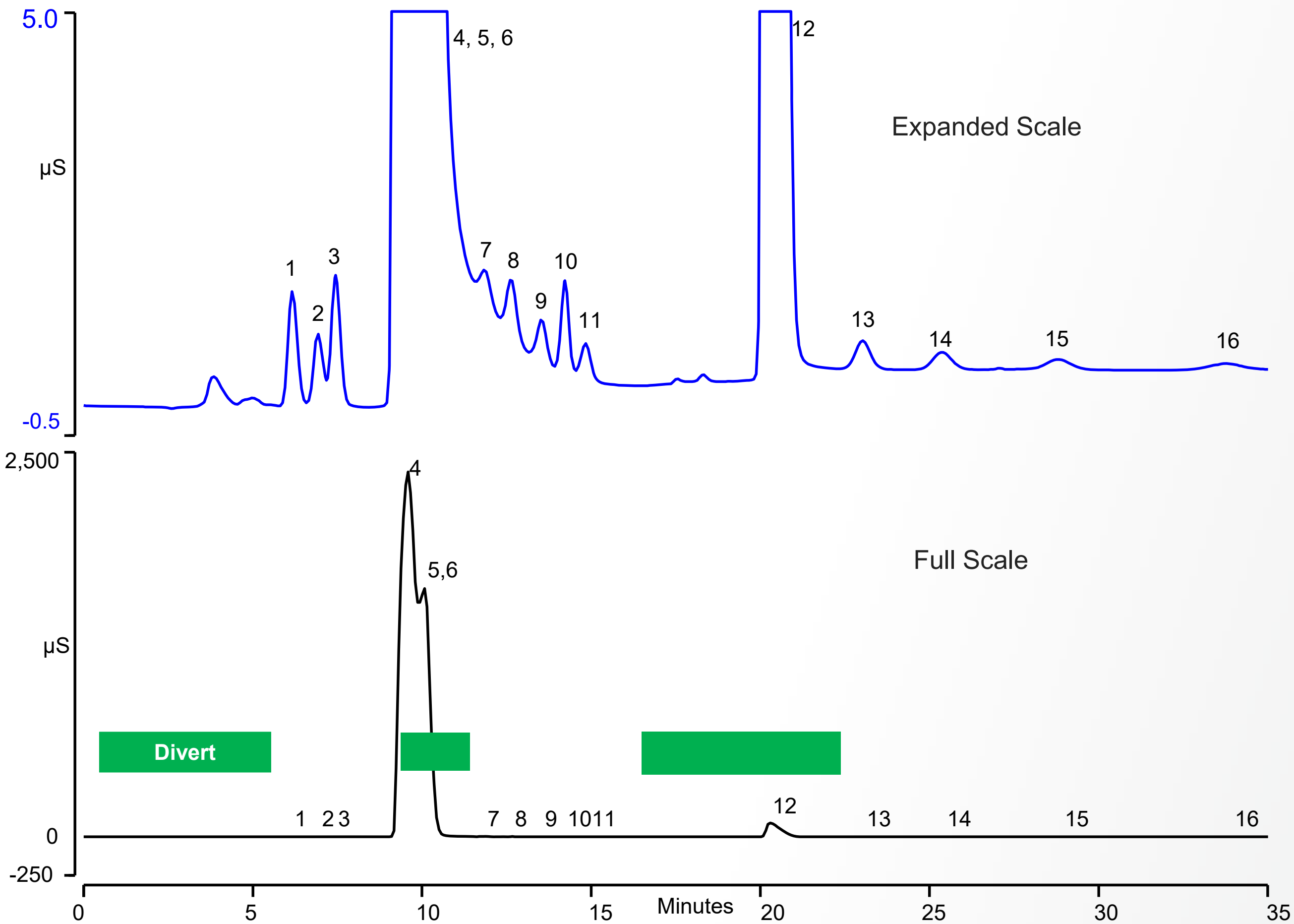
Ion Chromatography Isocratic Gradient

IC pump flow rate = 0.36mL/min
Concentration (mM) = 60mM
Total Run Time = 8 minutes

Sacrifice IC resolution for faster method & use mass resolution of mass spectrometry instrument to analyse peaks



IC separation: 9 HAAs, dalapon & bromate in LSSM matrix



Column:	Dionex IonPac AG31 / AS31 column 2 x 150 mm
Eluent :	17 mM from 0 to 7 minutes 17 mM to 85mM KOH from 7 to 18 mins 85 mM KOH from 18-35 mins
Eluent Source:	Dionex EGC-500 KOH cartridge
Flow Rate:	0.30 mL/min
Inj. Volume:	100 µL
Temperature:	15˚C
Detection:	Suppressed Conductivity, Dionex ADRS 600 Suppressor, 2 mm AutoSuppression, recycle mode

Peaks (Standard):	mg/L
1. Monochloroacetate	0.5
2. Bromate	0.5
3. Monobromoacetate	0.5
4. Chloride	316
5. Carbonate	150
6. Sulfate	250
7. Dalapon	0.5
8. Dichloroacetate	0.5
9. Bromochloroacetate	0.5
10. Nitrite	0.15
11. Dibromoacetate	0.5
12. Nitrate	20.0
13. Trichloroacetate	0.5
14. Bromodichloroacetate	0.5
15. Chlorodibromoacetate	0.5
16. Tribromoacetate	0.5

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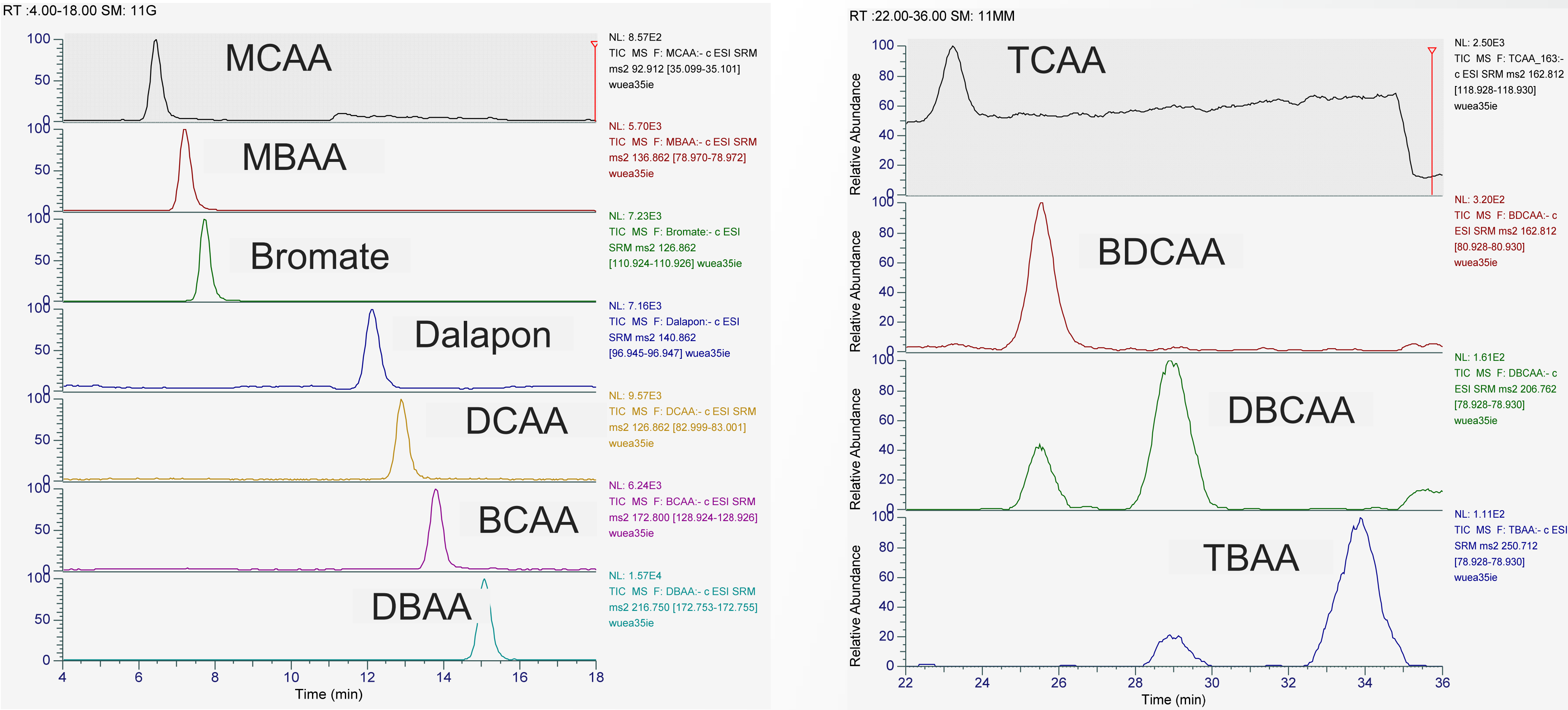
IC-MS/MS for 9 HAAs, dalapon & bromate (IonPac AS31 column and TSQ Fortis MS)



Concentrations of 9 HAAs, Dalapon & Bromate are 5 ppb in 100 ppm NH_4Cl

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Recovery data: 2 µg/L HAAs, dalapon & bromate in reagent water and LSSM

Analyte	Reagent Water Spiked with Analytes at 2µg/L		LSSM Spiked with Analytes at 2µg/L	
	% Recovery	% RSD (n=7)	% Recovery	% RSD (n=7)
MCAA	99.6	3.4	104.5	5.1
MBAA	101.6	3.8	103.5	4.2
Bromate	103.9	2.8	101.1	5.3
Dalapon	104.2	1.8	99.2	3.2
DCAA	109.7	1.8	110.1	2.0
BCAA	103.5	2.4	106.8	4.1
DBAA	101.7	0.6	101.0	2.8
TCAA	102.2	6.7	105.8	8.6
BDCAA	98.2	3.1	97.0	4.4
DBCAA	92.0	6.7	93.3	7.3
TBAA	92.0	3.7	98.4	7.4
AVG	100.8	3.4	101.9	4.9

All recoveries within 90-110 % with all %RSDs ≤10 to meet the EPA requirements

IC-MS/MS method detection limits: IonPac AS31 column

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MDL (µg/L, n=7)	Abbreviation	AS24 EPA Calculated DL	AS31 Calculated DL
Monochloroacetic acid	MCAA	0.2	0.19
Monobromoacetic acid	MBAA	0.064	0.021
Bromate	Bromate	0.02	0.014
Dalapon	Dalapon	0.038	0.079
Dichloroacetic acid	DCAA	0.055	0.019
Bromochloroacetic acid	BCAA	0.11	0.086
Dibromoacetic acid	DBAA	0.015	0.009
Trichloroacetic acid (163/119)	TCAA	0.09	0.073
Bromodichloroacetic acid	BDCAA	0.05	0.087
Chlorodibromoacetic acid	DBCAA	0.041	0.19
Tribromoacetic acid	TBAA	0.067	0.067

Comparable MDLs obtained for the target analytes

Cost of ownership comparison: GC-ECD vs. IC-MS/MS

Select currency: USD

Sample cost: 15 $/month

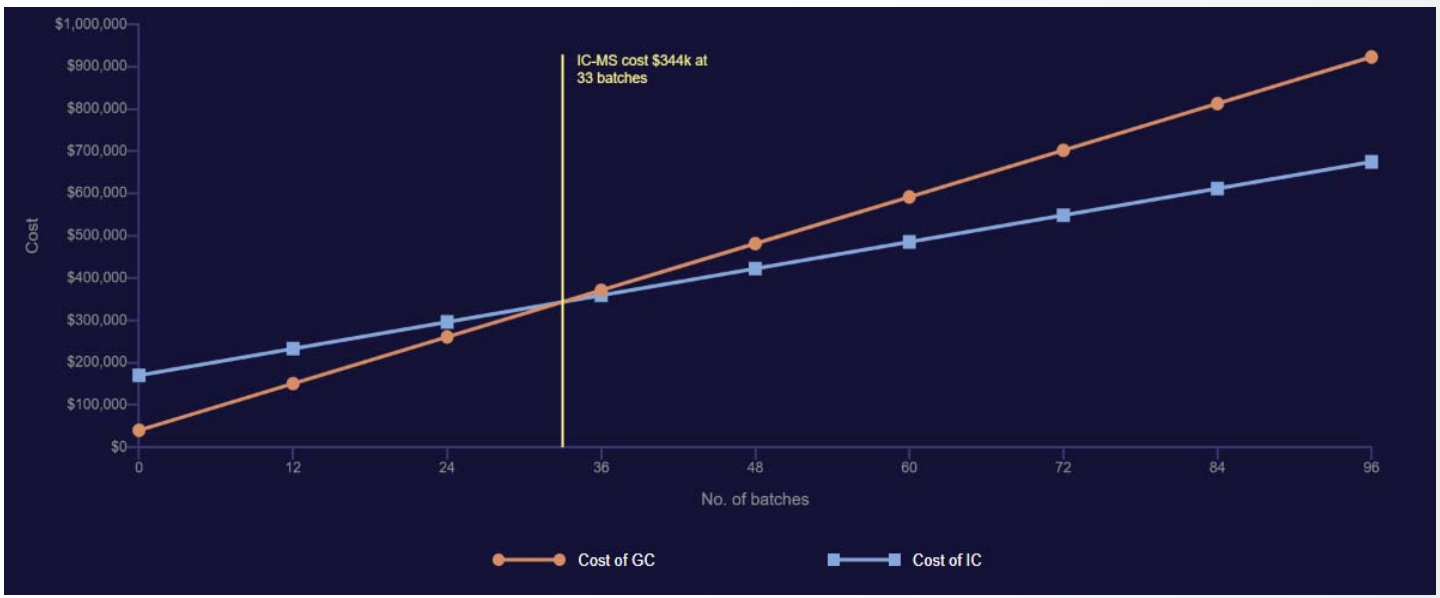
Labor cost: 40 $/hour

Derivatization time: 4 hours

GC-ECD CapEx: 40000 $

IC-MS CapEx: 170000 $

Reset | Share results | Download PDF | Recalculate costs



Link to webpage

1 Batch size = 20 samples, not including: reagent blanks, calibration checks, fortified blanks and internal standards

What can we analyse?

IonPac AG19 & AS19 4µm column

ADRS600 2 mm Suppressor

Mass Spectrometer

One Ion Chromatography Mass Spectrometry setup allows the flexibility of several different workflows

Haloacetic Acids

Quantification of all 9 Haloacetic Acids

Anions

Analysis of 22 environmental anions; such as Bromate, Bromide & Perchlorate

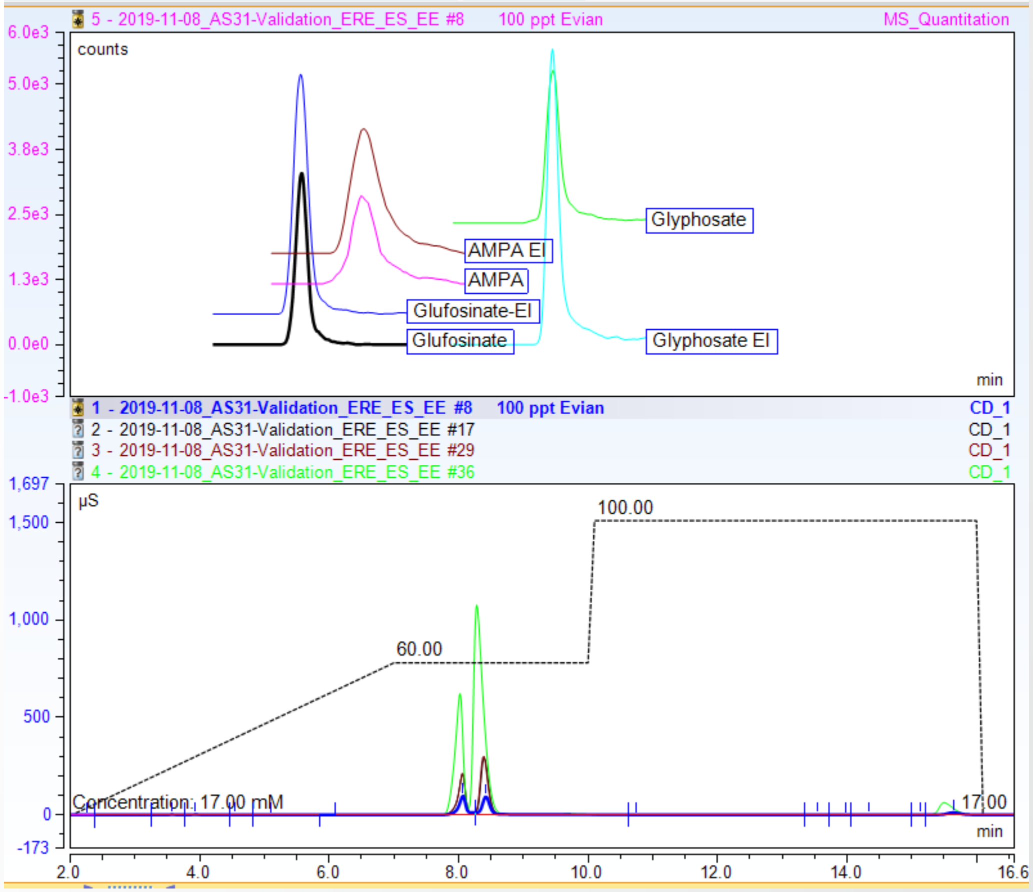
Polar Pesticides

Anionic polar pesticides such as Glyphosate, Glufosinate & AMPA

Separation of polar pesticides using IC-MS/MS

Conditions

- The analytical LQ for AMPA, glufosinate, and glyphosate is 10 ppt
- IonPac AS31 column, 30 µL injection
- Thermo Scientific™ TSQ Altis™ MS
- Standards in bottled water
- Validation in surface, ground, and mineral water



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Separation of HAAs using IC-MS/MS: 15 °C vs. 30 °C

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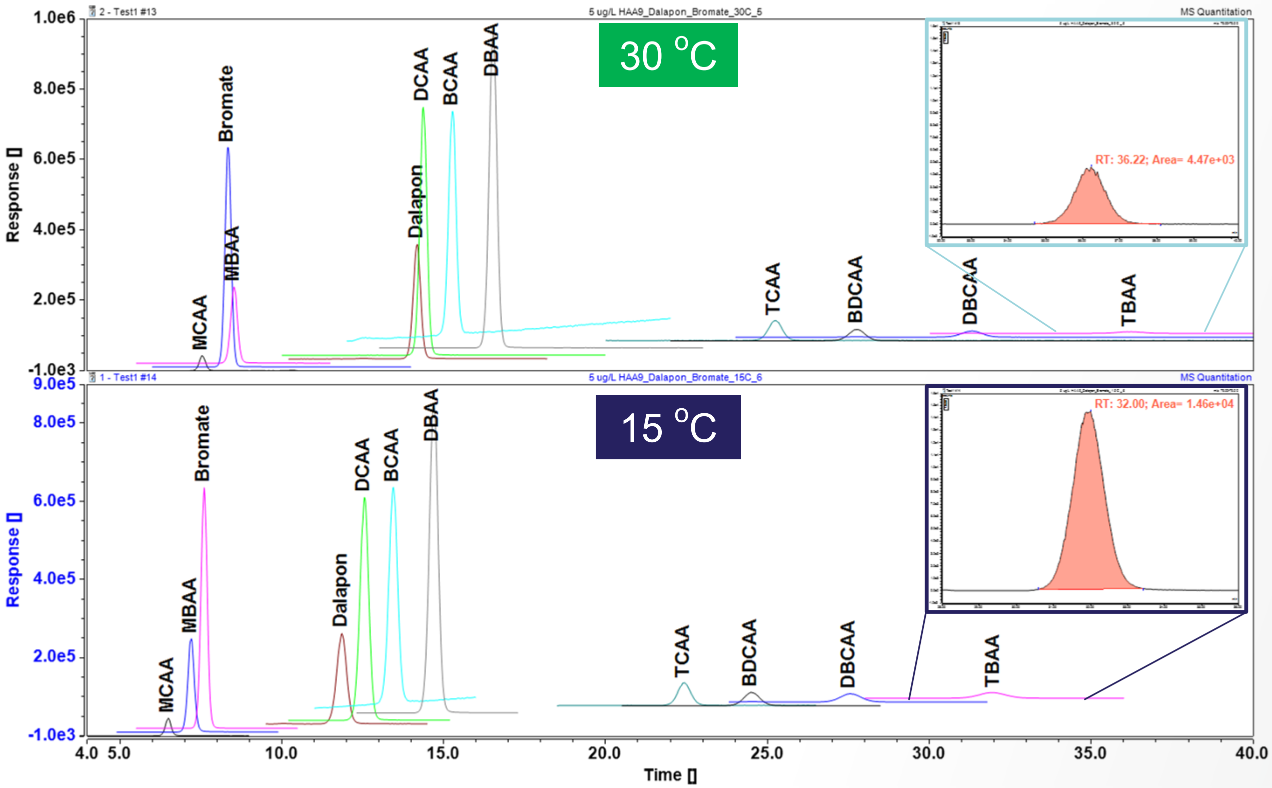

Higher Temperature

- Compound co-elutions
- Higher MDLs

Lower temperature

- Separation of bromate & MBAA
- Separation of Dalapon & DCAA
- Significantly lower degradation rate of unstable analytes (e.g., TBAA, insets)
  - *Lower MDLs*
- Faster separations

***Inset chromatograms for TBAA show 3-fold decrease in area at higher IC column temperature**

Data Format: IC Quantitation and MS Quantitation

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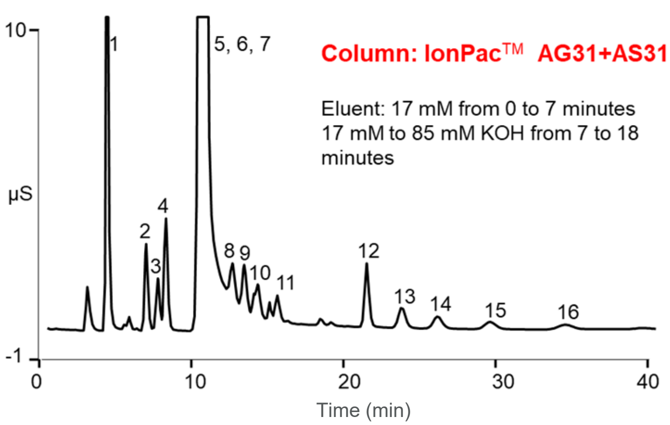
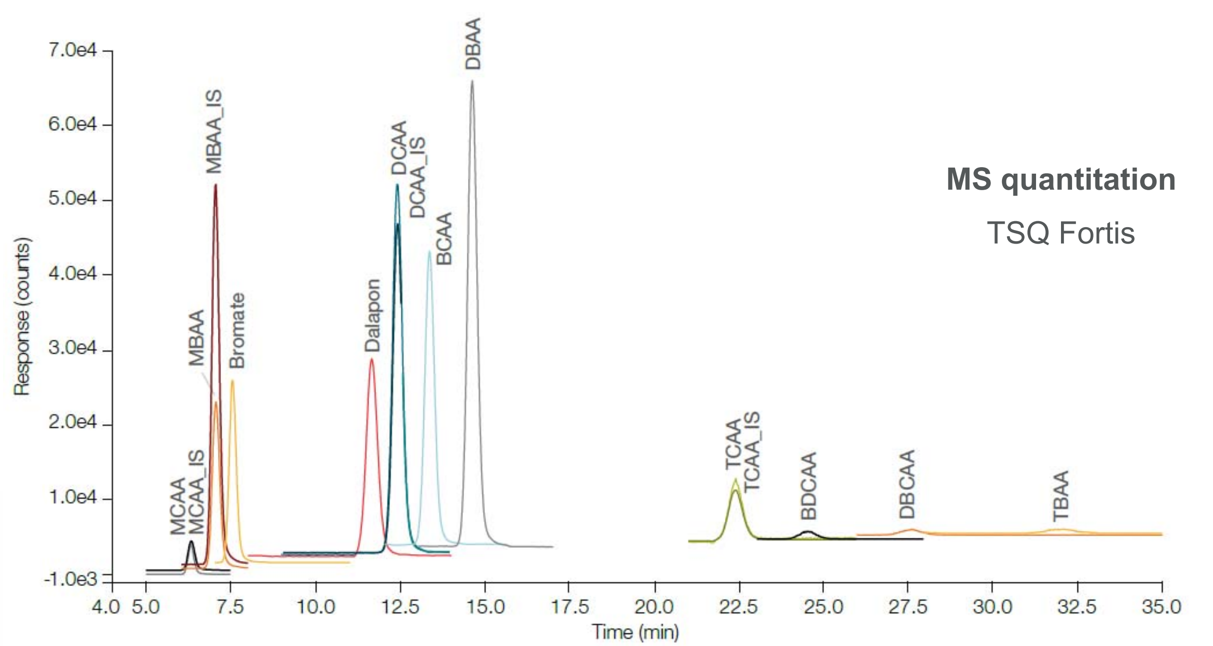
Sample: Municipality Drinking Water
Spiked with 9HAAs, Dalapon & Bromate

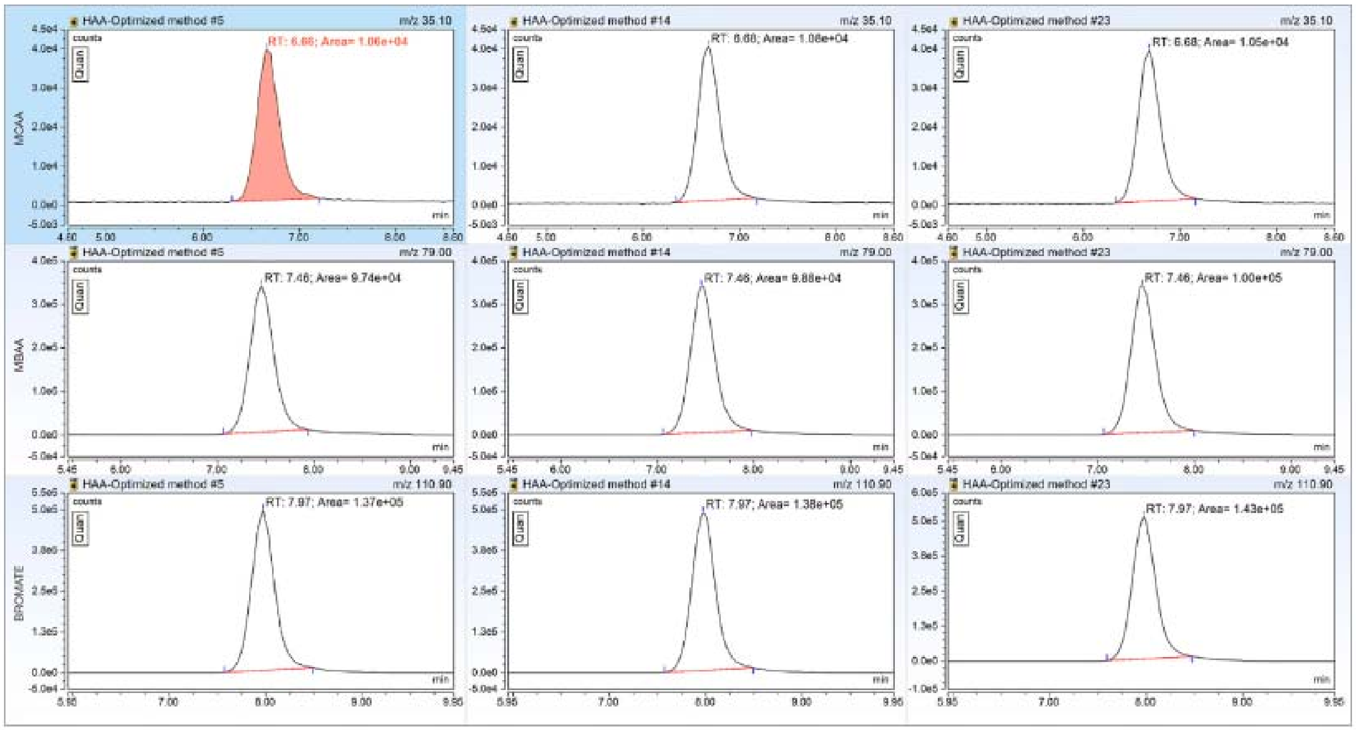
Peaks (Standard):	mg/L	Peaks (Standard):	mg/L
1. Fluoride	NQ	9. Dichloroacetate	1.0
2. Monochloroacetate	1.0	10. Bromochloroacetate	1.0
3. Monobromoacetate	1.0	11. Dibromoacetate	1.0
4. Bromate	1.0	12. Nitrate	NQ
5. Chloride	NQ	13. Trichloroacetate	1.0
6. Sulfate	NQ	14. Bromodichloroacetate	1.0
7. Carbonate	NQ	15. Chlorodibromoacetate	1.0
8. Dalapon	1.0	16. Tribromoacetate	1.0

IC





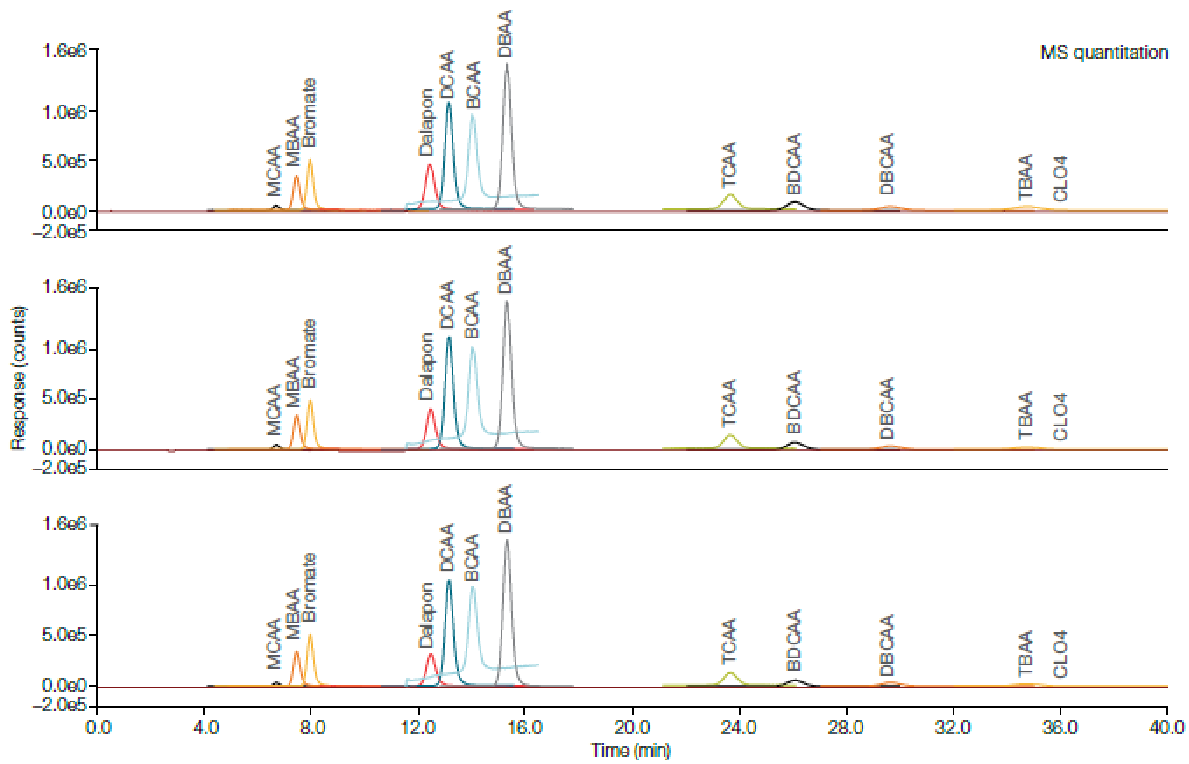
Verification: Peak Area Count Repeatability



1 instrument; 1 operator

SRM Peak Area below 10%

Verification: Retention Time Repeatability



1 instrument; 1 operator – 3 replicate injections at 5.0 µg/L

Retention time below 3%

Validation: Retention Time Repeatability

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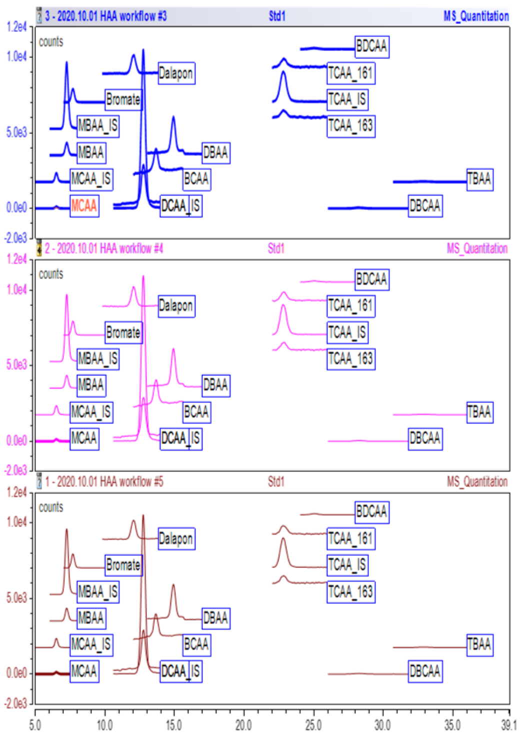
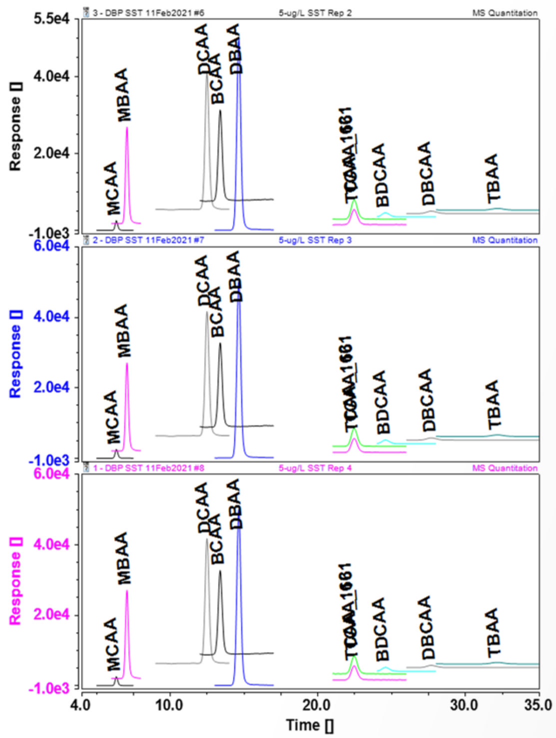
TSQ Fortis MS #1



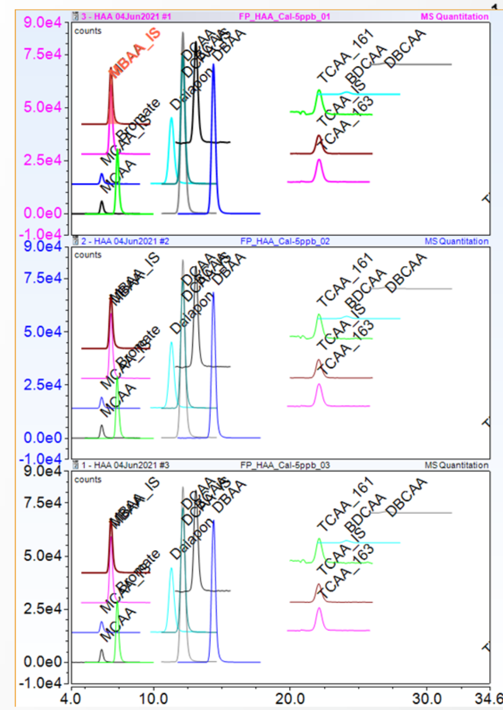
HAA at 1.0 µg/L

TSQ Fortis MS #2



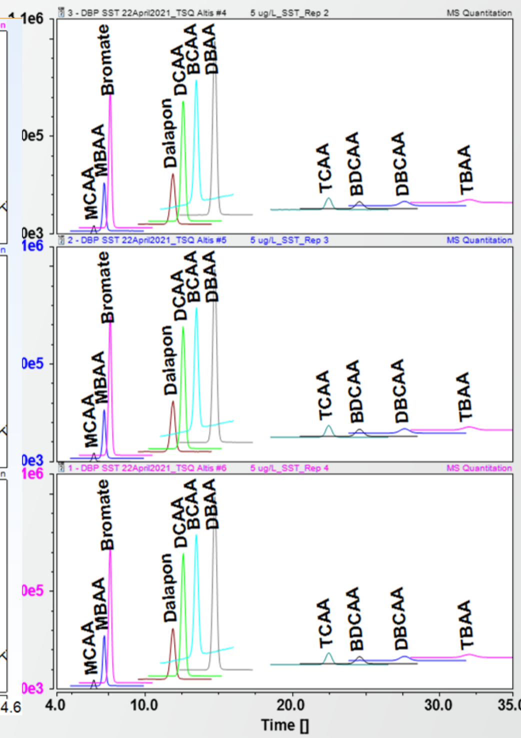
HAA at 5.0 µg/L

TSQ Fortis Plus MS #3



HAA at 5.0 µg/L

TSQ Altis MS #1



HAA at 5.0 µg/L

4 instruments; Multiple operators

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Thermo Scientific high-pressure IC systems (analytical-flow HPIC) for HAAs

Dionex Integrion HPIC System

Dionex ICS-6000
Standard and/or Capillary HPIC System

Separation of HAAs requires sub-ambient temperature control of column not provided on Integrion
Integrion is not EPA 557 compliant

Thermo Scientific TSQ MS product portfolio

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PERFORMANCE

Environmental and Food Safety
Clinical Research
Pharma QA/QC

TSQ Fortis MS

- Mass Range m/z 2 – 3000
- Max Resolution ***0.4 FWHM***
- Max 30,000 transitions per run
- Polarity Switching < 20 msec
- Dynamic interscan time
- 600 SRM/sec
- TNG software
- Chromeleon CDS software support
- ***80,000:1 S/N***

Food Safety
Pharma
Clinical Research
Forensic Toxicology

Thermo Scientific™ TSQ Quantis™ MS

- Mass Range m/z 2 – 3000
- Max Resolution ***0.4 FWHM***
- Max 30,000 transitions per run
- Polarity Switching < 20 msec
- Dynamic interscan time
- 600 SRM/sec
- TNG software
- Chromeleon CDS software support
- ***200,000:1 S/N***

Pharma/Biopharma
Environmental and Food Safety
Omics

TSQ Altis MS

- Mass Range m/z 2 – 2000
- Max Resolution ***0.2 FWHM***
- Max 30,000 transitions per run
- Polarity Switching < 20 msec
- Dynamic interscan time
- 600 SRM/sec
- TNG software
- Chromeleon CDS software support
- ***500,000:1 S/N***

VALUE

Summary

- IC-MS/MS System Advantages
  - Direct injection – no sample prep (save 4+ hrs)
  - Capability to analyze HAA9, Bromate, and Dalapon
  - Allows the flexibility of several different workflows: HAAs and Polar Pesticides

- AS 31Column Advantages
  - High ion exchange capacity and allow large loop injections for trace analysis (µg/L) without sample pre-treatment.
  - Operates at 15°C for increased sensitivity and improved resolution of specific co-eluents* resolving so a Thermo Scientific Dionex ICS-5000+ or ICS-6000 HPIC system is required
  - Meets or exceeds the performance requirements of EPA Method 557.
  - Delivers 39% faster run times relative to IonPac AS24 columns, reducing the EPA Method 557 run time from 57 minutes to 35 minutes

*Thermo Scientific™ Dionex™ ICS-5000+ or ICS-6000 HPIC system is required

Resources

Thermo Fisher SCIENTIFIC

White Paper


thermoscientific

WHITE PAPER 72958

Fast determination of haloacetic acids in drinking water

Authors
Dr. Detlef Jensen
Thermo Fisher Scientific GmbH,
Im Steingrund 4-6,
63303 Dreieich, Germany
E-mail:
Detlef.Jensen@thermofisher.com

Keywords
Automation, eluent generation, haloacetic acids (HAA), ion chromatography (IC), IC-MS/MS, mass spectrometry (MS)

Introduction
As a result of current government proposals and developments, haloacetic acids (HAA) are in the focus of modern water analysis. The established methods use gas chromatography with electron capture detection (GC-ECD) or mass spectrometry (GC-MS). However, the drawback of these methods is the need for time-consuming derivatization and multiple extraction steps. Can the analysis be simplified? Can sensitive and rapid detection be achieved without sample pretreatment? In this paper, these questions are answered based on current developments in IC-MS/MS.

Discussion
Right2Water
In response to the "Right2Water" initiative, supported by 1.6 million Europeans, the European Commission proposed a revision of the Drinking Water Directive in January 2018.[1] The obligatory and extended list of criteria contains 18 new or revised entries, including chlorate and HAAs.[2]

App Notes


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APPLICATION NOTE 73343

Fast determination of nine haloacetic acids, bromate, and dalapon at trace levels in drinking water samples by tandem IC-MS/MS

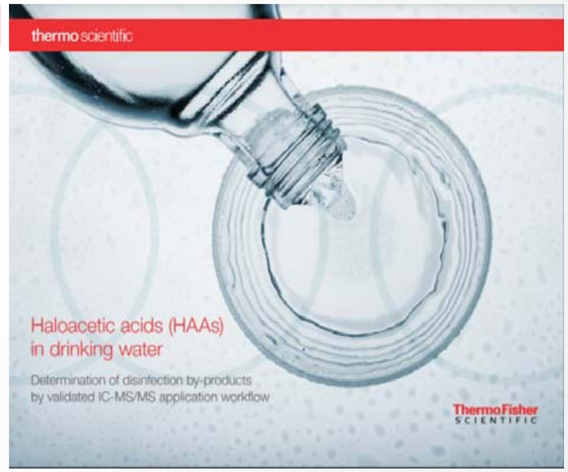
Authors: Xin Zhang, Charanjit Saini, Chris Pohl, and Yan Liu
Thermo Fisher Scientific, Sunnyvale, CA

Keywords: IC-MS/MS, HAA5, HAA9, disinfection byproducts (DBPs), EPA 557, Dionex IonPac AS31 column, Dionex ICS-6000 ion chromatography system, TSQ Fortis triple quadrupole mass spectrometer

Goal
To identify and quantify low concentrations of haloacetic acids, bromate, and dalapon in drinking water according to U.S. EPA Method 557 using a Thermo Scientific™ Dionex™ ICS-6000 ion chromatography system and a Thermo Scientific™ Dionex™ IonPac™ AS31 column coupled with triple quadrupole electrospray mass spectrometry

developmental, reproductive, and hepatic toxicity,[1-4] the World Health Organization (WHO)[5] has established

Brochure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Haloacetic acids (HAAs) in drinking water

Determination of disinfection by-products by validated IC-MS/MS application workflow

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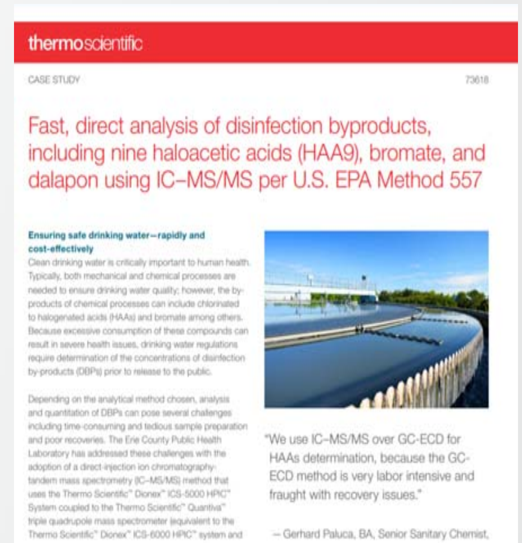
Case Study


thermoscientific

CASE STUDY 73618

Fast, direct analysis of disinfection byproducts, including nine haloacetic acids (HAA9), bromate, and dalapon using IC–MS/MS per U.S. EPA Method 557

Ensuring safe drinking water—rapidly and cost-effectively
Clean drinking water is critically important to human health. Typically, both mechanical and chemical processes are needed to ensure drinking water quality; however, the by-products of chemical processes can include chlorinated to halogenated acids (HAAs) and bromate among others. Because excessive consumption of these compounds can result in severe health issues, drinking water regulations require determination of the concentrations of disinfection by-products (DBPs) prior to release to the public.

Depending on the analytical method chosen, analysis and quantitation of DBPs can pose several challenges including time-consuming and tedious sample preparation and poor recoveries. The Erie County Public Health Laboratory has addressed these challenges with the adoption of a direct-injection ion chromatography-tandem mass spectrometry (IC-MS/MS) method that uses the Thermo Scientific™ Dionex™ ICS-5000 HPIC™ System coupled to the Thermo Scientific™ Quantiva™ triple quadrupole mass spectrometer (equivalent to the Thermo Scientific™ Dionex™ ICS-6000 HPIC™ system and

"We use IC–MS/MS over GC-ECD for HAAs determination, because the GC-ECD method is very labor intensive and fraught with recovery issues."

— Gerhard Paluca, BA, Senior Sanitary Chemist,

https://www.thermofisher.com/haaworkflow.html

Thank you