Fast, Direct Injection Determination of HAAAs in Drinking Water with IC-MS/MS by EPA 557

Speaker: Paul Voelker, ThermoFisher Scientific

- **Webinar Starts at 11:45 Eastern Daylight Time**
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  - Be sure to enter your ID number when you call or it will not link the call properly to Webex.
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  - suzanne.rachmaninoff@nelac-institute.org or ilona.taunton@nelac-institute.org

NEMC

Meeting Mechanics

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Meeting Mechanics

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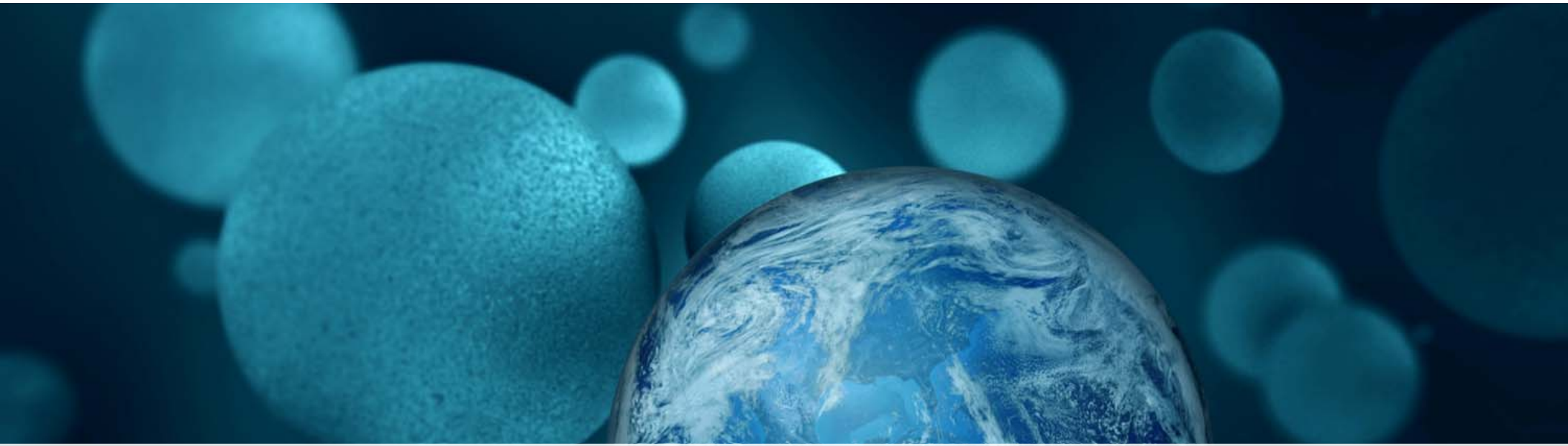

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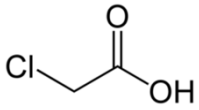
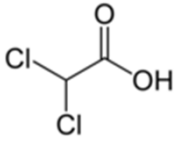
Fast, Direct Injection Determination of HAAs in Drinking Water with IC-MS/MS by EPA 557

Paul Voelker
IC/SP Product Marketing Manager

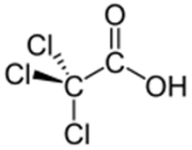
Haloacetic Acids



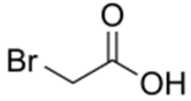
monochloroacetic acid (MCA)



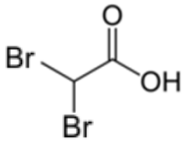
dichloroacetic acid (DCA)



trichloroacetic acid (TCA)



monobromoacetic acid (MBA)



dibromoacetic acid (DBA)

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Disinfection Byproducts in Drinking Water

Untreated Source Water

Pathogens:
Cryptosporidium
Giardia
Virus
Fecal Coliform
E. Coli

Water Treatment Plant

Disinfection:
Ozonation

Chlorination (Chloramine, Chlorine)

Bromide

Naturally occurring matter

Drinking Water

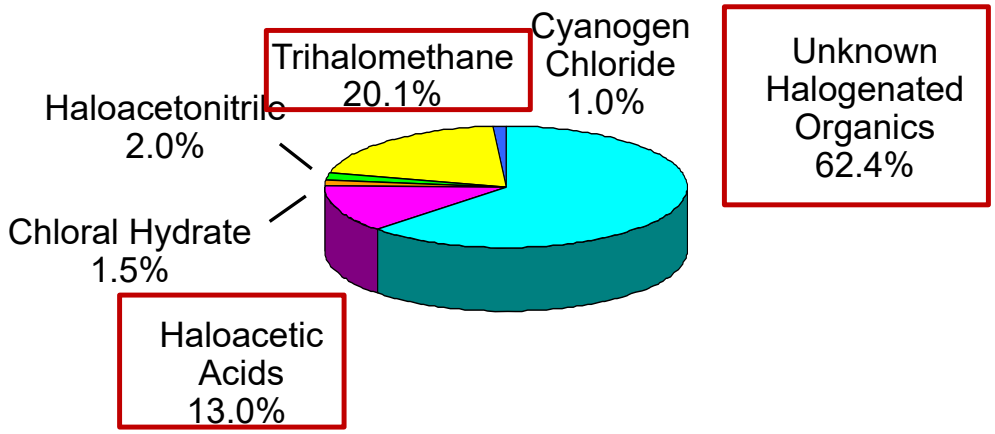
Disinfection Byproducts (DBPs):

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 (HAAs)

EPA Method 552.3 (GC-ECD)[1] or EPA Method 557 (IC-ESI-MS/MS)[2]

Analyte	CAS Registry Number	MRL[3]	MCLG[4]	HAA5 Group	HAA6Br Group	HAA9[7] Group
dichloroacetic acid (DCAA)	79-43-6	0.2 µg/L	0 µg/L	HAA5 Group MCL[5,6] = 60 µg/L		HAA9
monochloroacetic acid (MCAA)	79-11-8	2.0 µg/L	70 µg/L			
trichloroacetic acid (TCAA)	76-03-9	0.5 µg/L	20 µg/L			
monobromoacetic acid (MBAA)	79-08-3	0.3 µg/L	N/A		HAA6Br	
dibromoacetic acid (DBAA)	631-64-1	0.3 µg/L	N/A			
bromochloroacetic acid (BCAA)	5589-96-8	0.3 µg/L	N/A			
bromodichloroacetic acid (BDCAA)	71133-14-7	0.5 µg/L	N/A			
chlorodibromoacetic acid (CDBAA)	5278-95-5	0.3 µg/L	N/A			
tribromoacetic acid (TBAA)	75-96-7	2.0 µg/L	N/A			

[1]Gas Chromatography with Electron Capture Detection
[2]Ion Chromatography Electrospray Ionization Tandem Mass Spectrometry
[3]Minimum Reporting Level
[4]Maximium Contaminant Level Goals (MCLGs) established under the D/DBPRs
[5]Disinfection Byproduct Information Collection Rule (DBP ICR) (1997-1998)
[6]The HAA5 group is currently regulated in drinking water at a MCL of 60 µg/L per D/DBPRs
[7]PWSs are required to monitor for the indicators total organic carbon (TOC) and bromide in their source water at the same time as their HAA samples. Consecutive connections are not required to take TOC and bromide samples.

Source: EPA Public Meeting and Webinar: The Fourth Unregulated Contaminant Monitoring Rule (UCMR 4) Meeting Presentations, April 2017

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

- 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

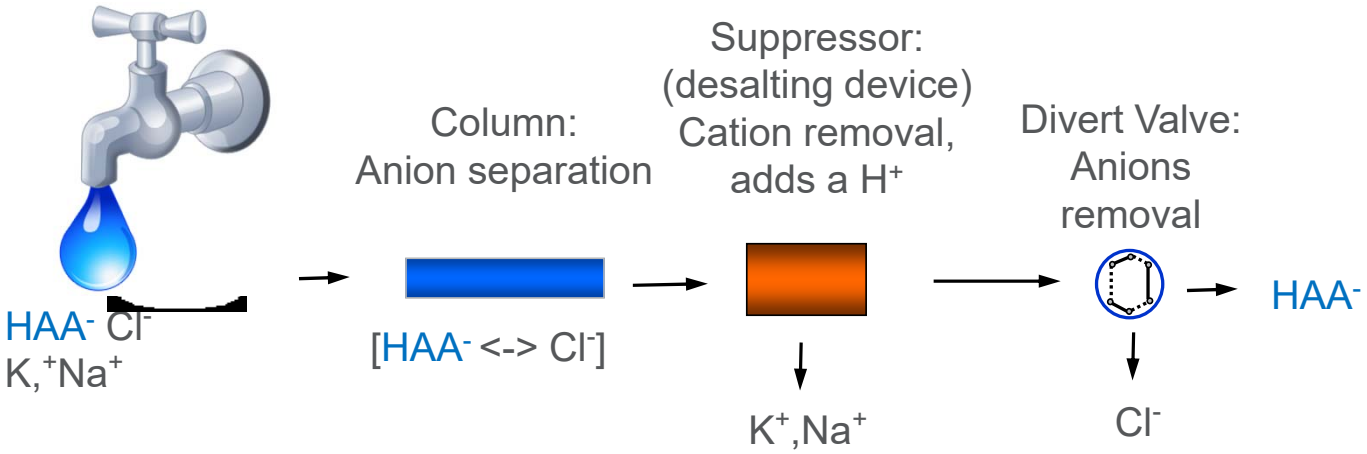
HAA by IC-MS/MS – a higher throughput method

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

EPA United States Environmental Protection Agency

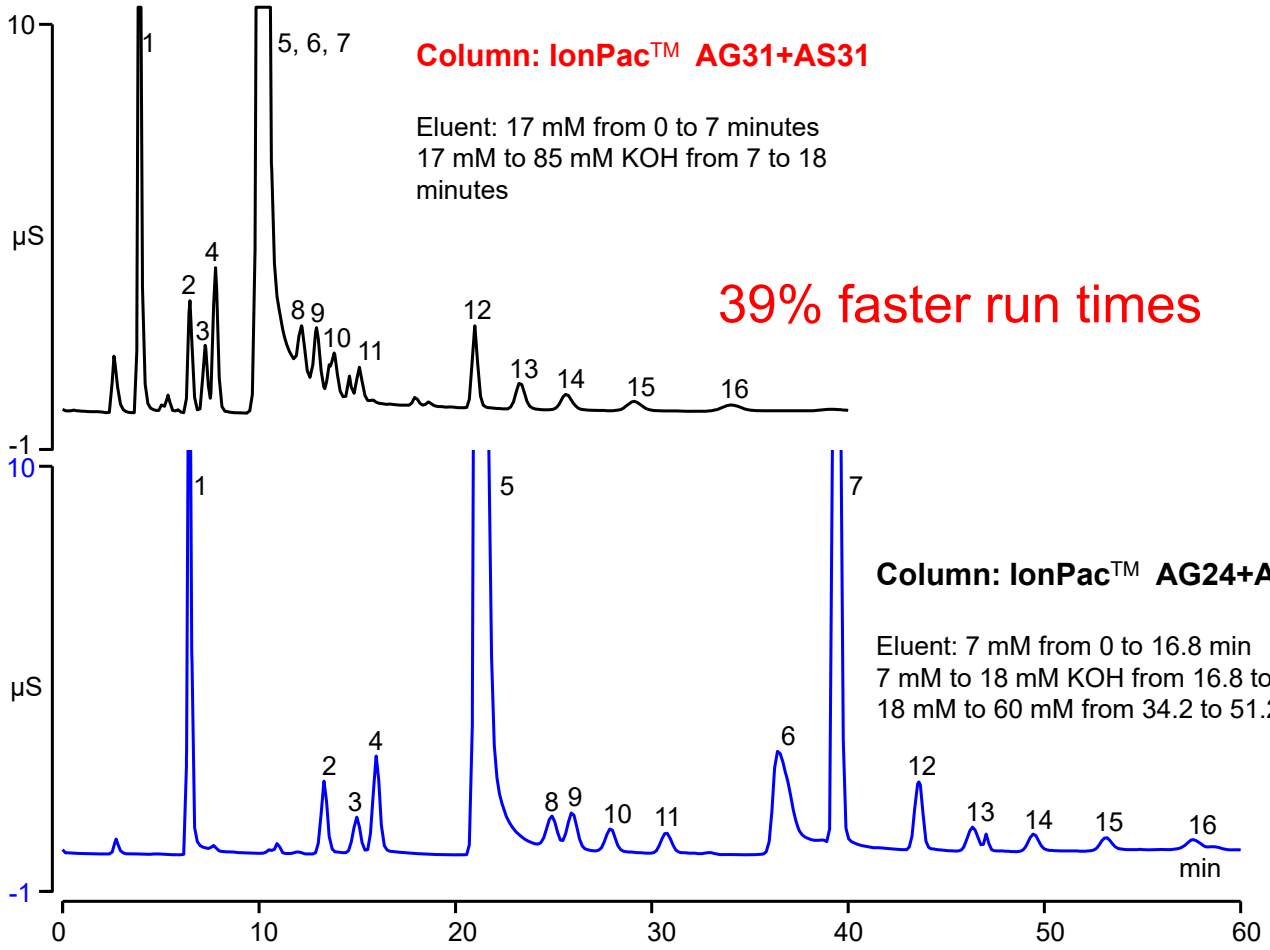
METHOD 557: DETERMINATION OF HALOACETIC ACIDS, BROMATE, AND DALAPON IN DRINKING WATER BY ION CHROMATOGRAPHY ELECTROSPRAY IONIZATION TANDEM MASS SPECTROMETRY (IC-ESI-MS/MS)

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: IonPac™ AG31+AS31

Eluent: 17 mM from 0 to 7 minutes
17 mM to 85 mM KOH from 7 to 18 minutes

39% faster run times

Column: IonPac™ AG24+AS24

Eluent: 7 mM from 0 to 16.8 min
7 mM to 18 mM KOH from 16.8 to 34.2 min
18 mM to 60 mM from 34.2 to 51.2 min

Column:	See Chromatogram
Eluent :	See Chromatogram
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 2mm 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

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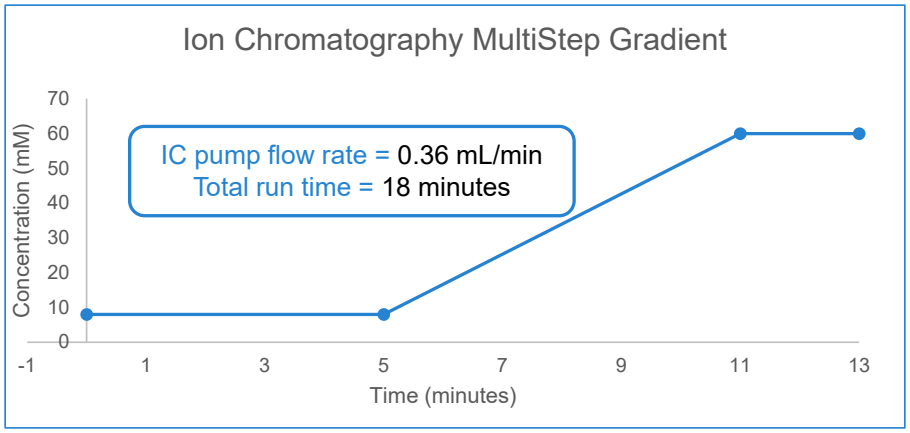
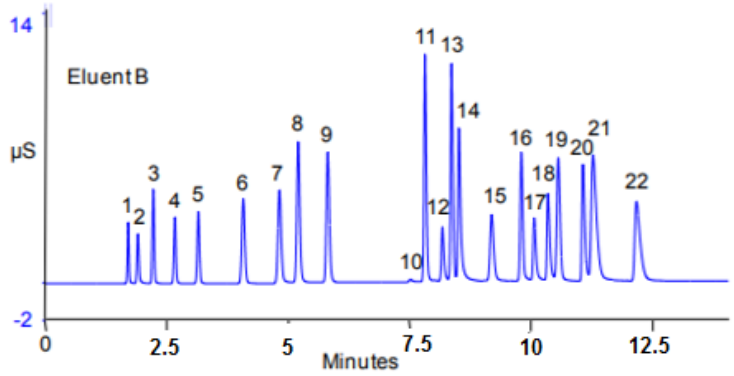
Multistep or Isocratic Gradient





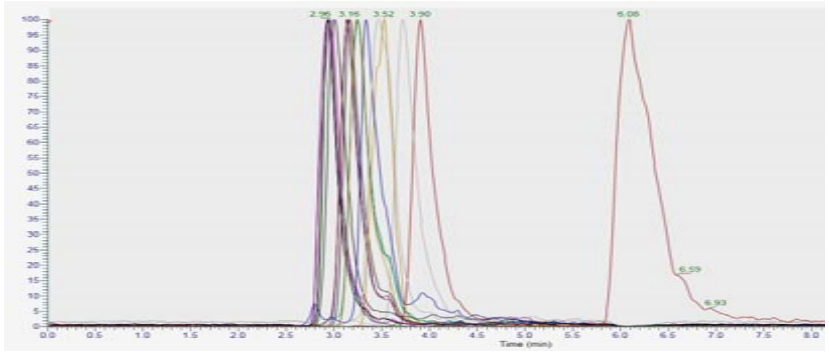
Multistep Gradient for ultimate resolution on IC peaks

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



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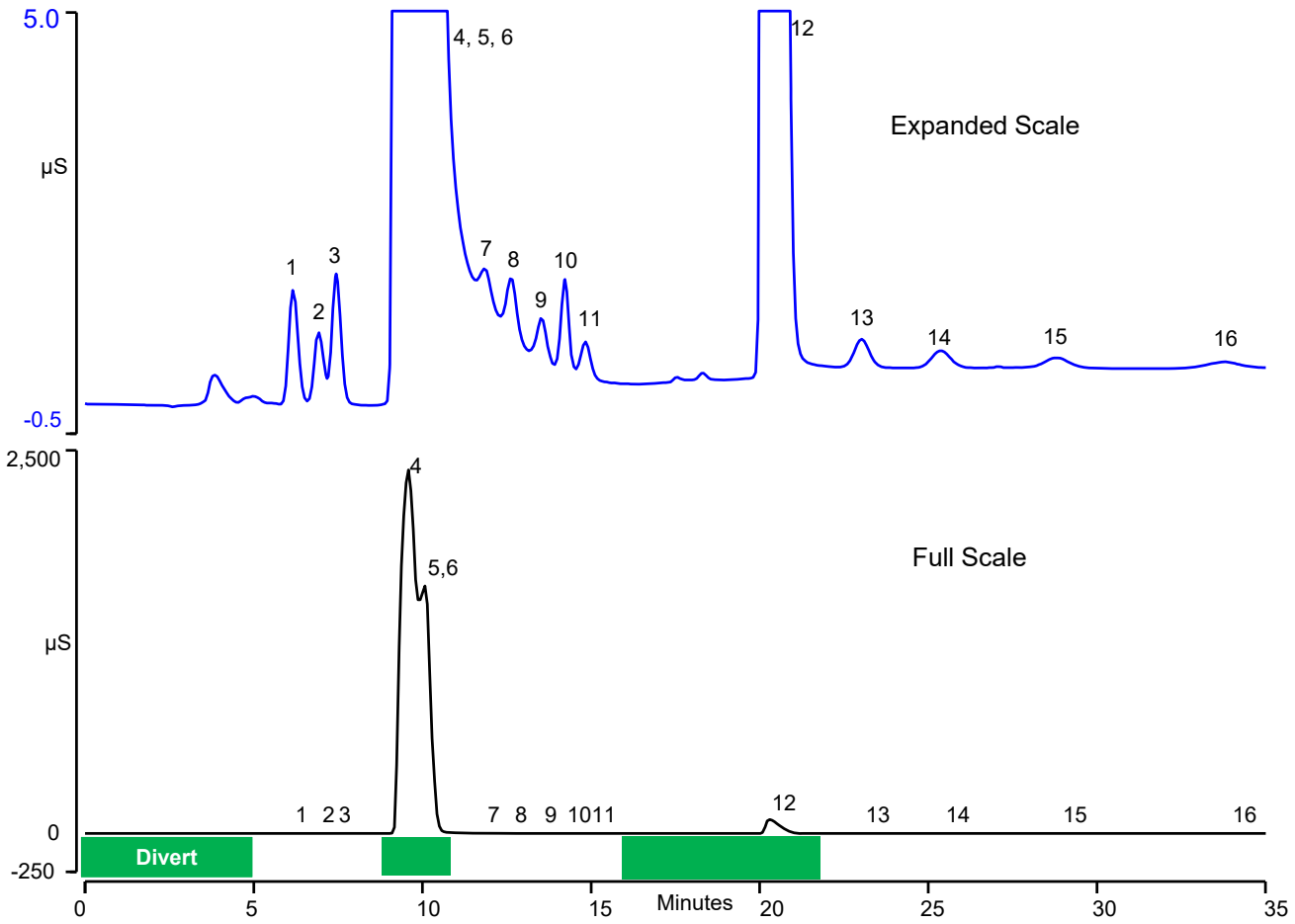
IC Separation: 9 HAAs, Dalapon & Bromate in LSSM Matrix



Column:	Dionex™ IonPac™ AG31 / AS31 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 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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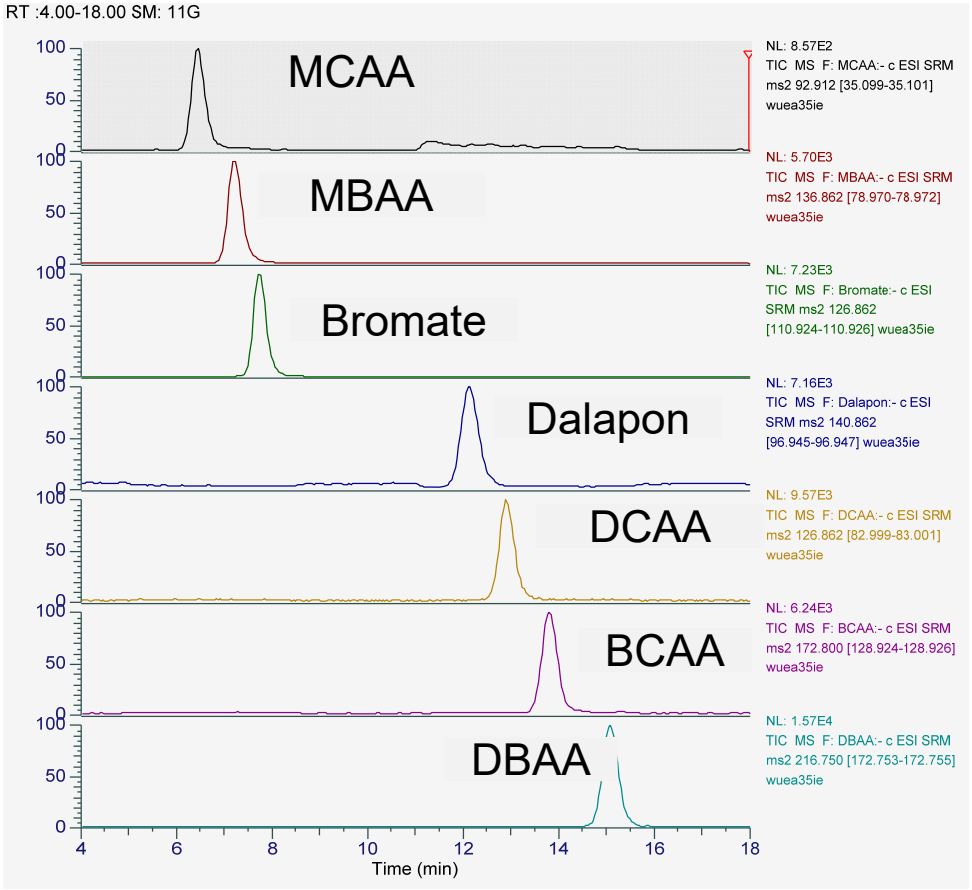
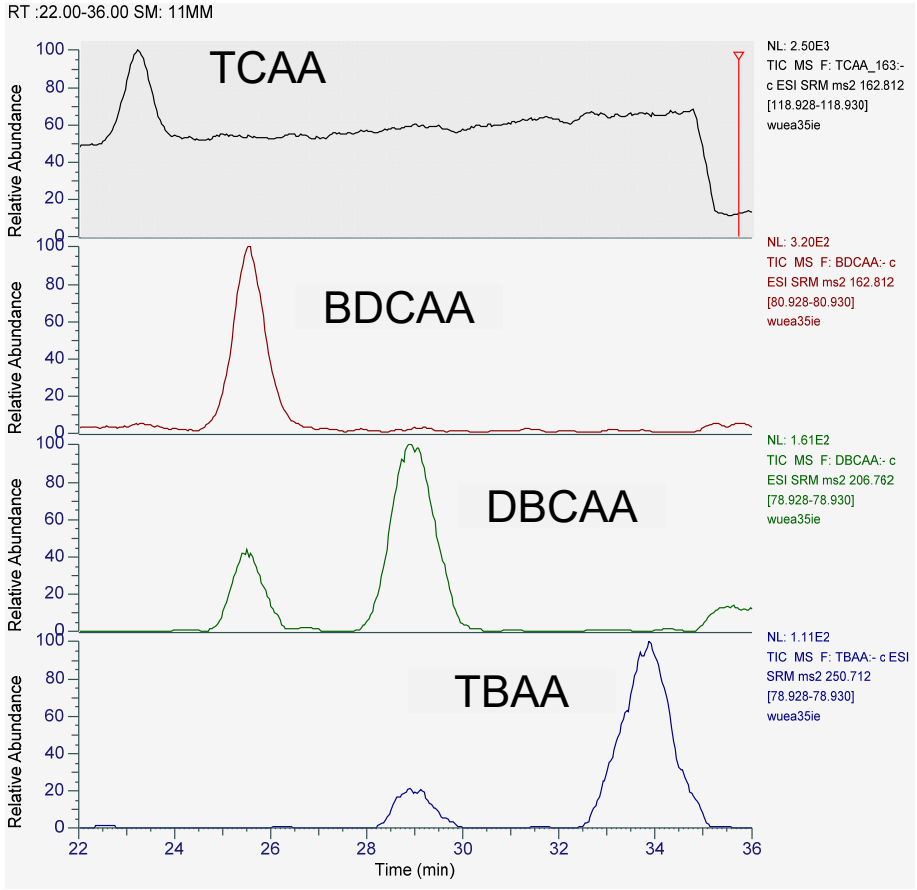
IC-MS/MS for 9 HAAs, Dalapon & Bromate (IonPac AS31 & TSQ Fortis)





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 Columns

MDL (µg/L, n=7)	Abbreviation	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

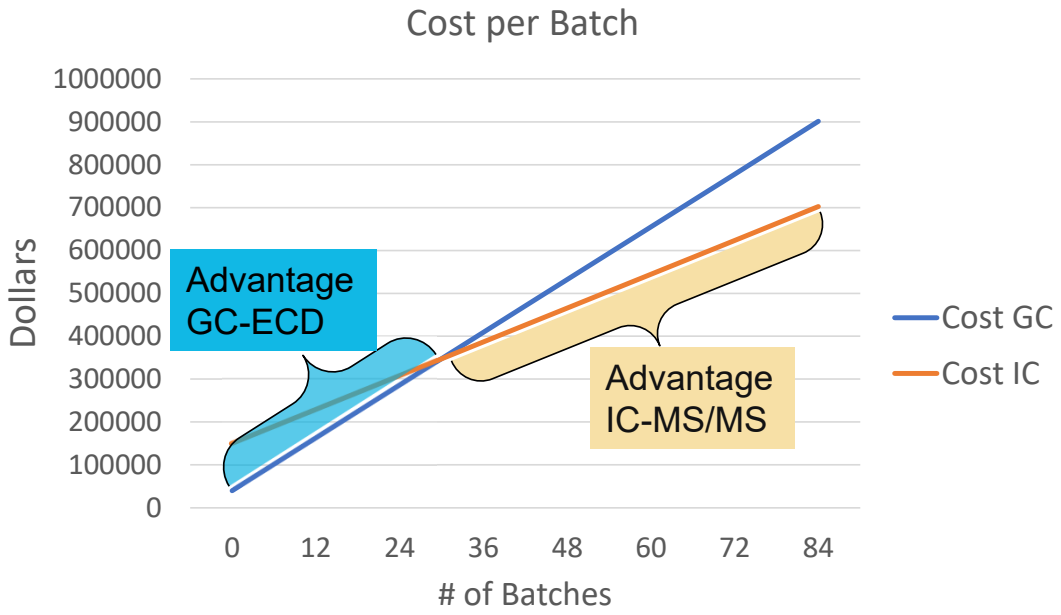
Comparable MDLs obtained for the target analytes

Cost of Ownership Comparison: GC-ECD vs IC-MS/MS

Y = X + (A*B)

	GC-ECD	IC-MS/MS
A = # Batches/Mo	0 – 84	0 – 84
B = Batch* cost/Mo	$10,250	$6,575
Sample cost/Mo	$410	$ 263
X= CapEx	$40K	$150K
Y= $ Value	$40K - $900K	$150K - $702K

# Batches / Mo	GC-ECD	IC-MS/MS
0	$40,000	$150,000
12	$163,000	$228,900
24	$286,000	$307,800
36	$409,000	$386,700
48	$532,000	$465,600
60	$655,000	$544,500
72	$778,000	$623,400
84	$901,000	$702,300



*1 Batch size = 25 samples

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What can we analyse?

IonPac AG19 & AS19 4µm column

ADRS600 2mm 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

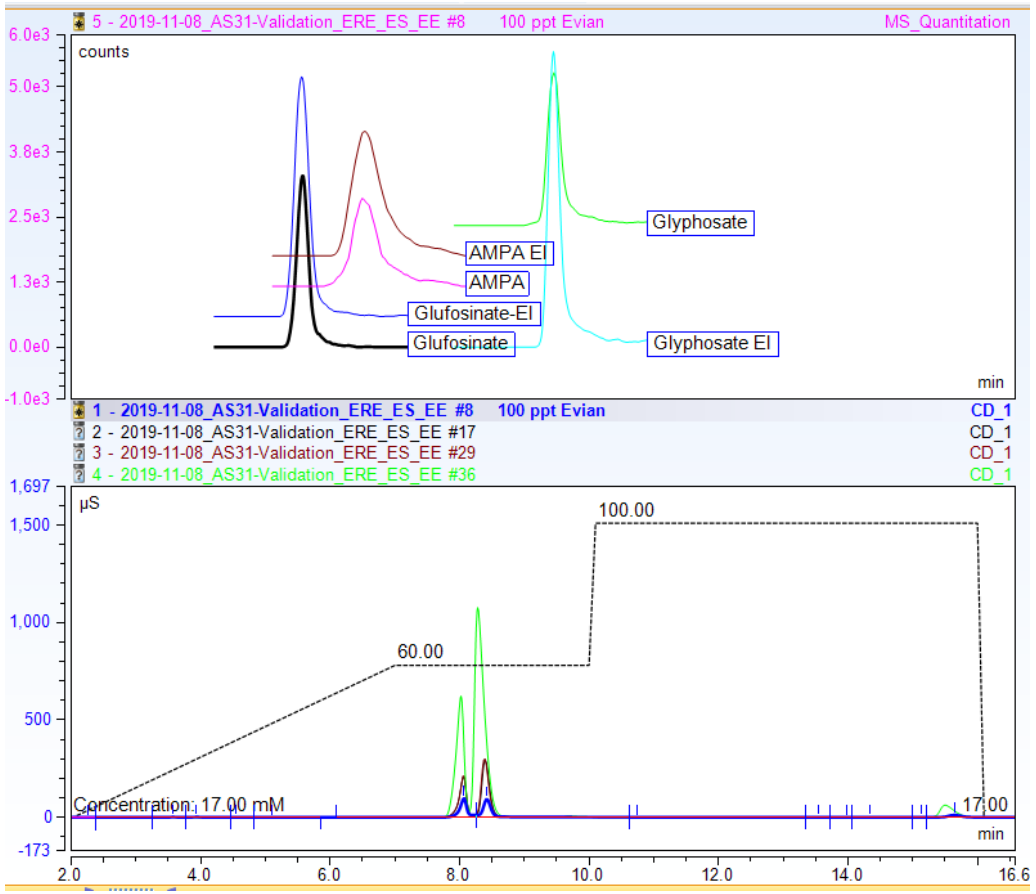
Polar Pesticides

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
- AS31 column, 30µL injection
- TSQ Altis MS
- Standards in bottled water
- Validation in surface, ground, and mineral water



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Thermo Scientific Ion Chromatography Portfolio

RFIC

HPIC

Dionex Aquion	Dionex Integrion	Dionex ICS-4000	Dionex ICS-6000

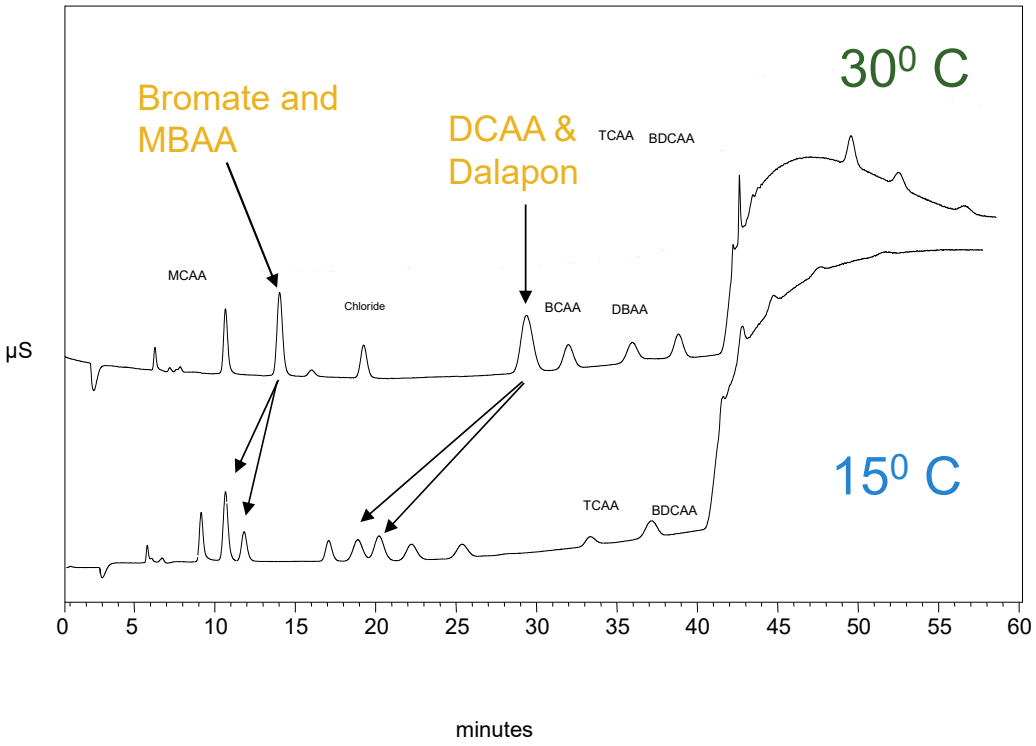
- Fast, high-resolution run times with high-pressure ion chromatography (HPIC)
- Always on, always ready with capillary IC (ICS-4000)
- Reagent-free IC integrated systems (RFIC)
- Superior separation column technology
- Chromeleon intelligent functionality and operational simplicity

Overview – HPIC Systems (Analytical flow)

- Dionex ICS-6000 HPIC System
  - Top-tier system
  - Modular for fast, easy expansion
  - Dual channel
  - Gradient Pump for carbohydrates
- Dionex Integrion HPIC System
  - Mid-tier system
  - Integrated, compact design
  - Flexible detector configurations

IC Features	Dionex ICS-6000	Dionex Integrion
Modular or Integrated Design	Modular	Integrated
Dual Channel	✓	✗
Gradient Pump	✓	✗
HPIC	✓	✓
RFIC	Optional	Optional
Column Cooling	✓	✗
Detector Cooling	✓	Optional
BioIC Compatible	✓	Limited
Validated Software Solution	✓	✓

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



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., TCAA)
  - *Lower MDLs*
- Faster separations

Thermo Scientific High-Pressure IC Systems (Analytical-flow HPIC) for HAAs

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

Dionex
ICS-6000

Addresses the full range of IC application needs and **solves complex challenges** with duality, modularity, capillary/hybrid support, provides **ultimate versatility**

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Thermo Scientific TSQ Product Portfolio

PERFORMANCE

VALUE

Environmental and Food Safety
Clinical Research
Pharma QA/QC

TSQ Fortis

- Mass Range m/z 5 – 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 support
- ***80,000:1 S/N***

Food Safety
Pharma
Clinical Research
Forensic Toxicology

TSQ Quantis

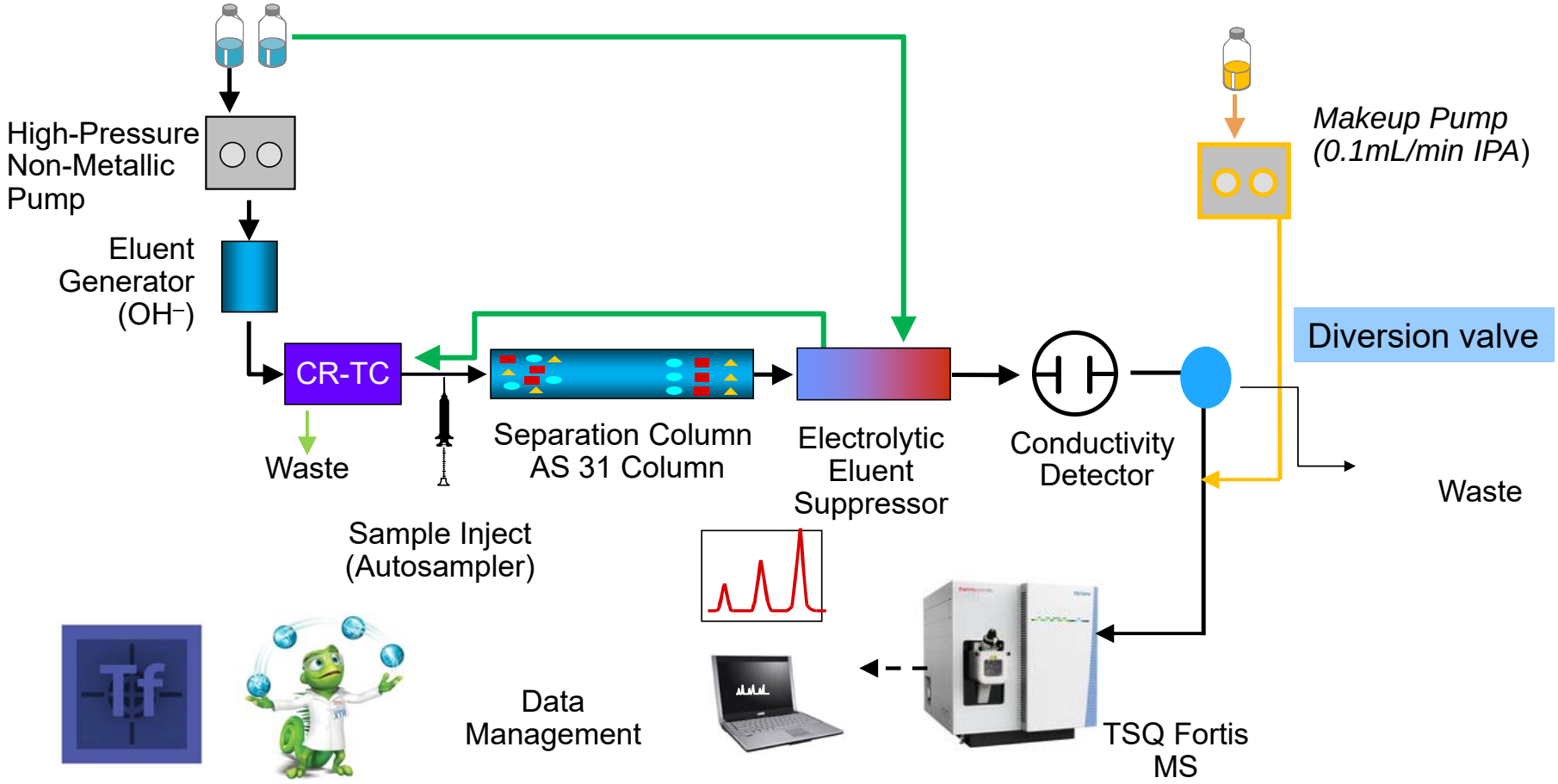
- Mass Range m/z 5 – 3000
- Max Resolution ***0.4 FWHM***
- Max 30,000 transitions per run
- Polarity Switching < 20 msec
- Dynamic interscan time
- 600 SRM/sec
- TNG software
- Chromeleon support
- ***200,000:1 S/N***

Pharma/Biopharma
Environmental and Food Safety
Omics

TSQ Altis

- Mass Range m/z 5 – 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 support
- ***500,000:1 S/N***

IC-MS System Setup



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Thermo Application Notes on HAAs

WP 72958

thermoscientific

Fast determination of haloacetic acids in drinking water

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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]

AN 73343

thermoscientific

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

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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

Thank you

Experimental: IC-MS/MS of HAAs (with IonPac™ AS31 Column)

Thermo Scientific™ Dionex™ ICS-6000 System and Thermo Scientific™ TSQ Fortis™ Mass Spectrometer

Column:	IonPac AS31 2 x 250 mm + 2 x 50 mm Guard
Eluent:	KOH Gradient (see Timed Events)
Suppressor:	ADRS® 600, 2-mm, external water, 0.3 mL/min
Suppressor Current:	64 mA
Analytical Flow Rate:	0.3 mL/min
Column Temp:	15 ° C
Injection Volume:	100 µL
Detector:	CD, TSQ Fortis

TSQ Fortis Tune Parameters:

Ion Source Type:	H-ESI (Negative Polarity)
Spray Voltage:	3200 V
Cycle Time:	2.3 secs
Resolution:	Q1 (FWHM) 0.7
	Q3 (FWHM) 0.7
CID Gas:	2 mTorr
Sheath Gas:	50 Arb
Aux Gas :	10 Arb
Sweep Gas:	3 Arb
Ion Transfer Tube Temp:	225° C
Vaporizer Temp:	275° C

Timed Events

Time	[KOH], mM	Divert Valve
-5.0 Begin	17.0	Eluent to Waste
0.0	17.0	
5.0	17.0	Eluent to MS
7.0	17.0	
8.5		Eluent to Waste
11.1		Eluent to MS
15.6		Eluent to Waste
18.0	85.0	
21.7		Eluent to MS
35.0	85.0	Eluent to Waste
35.1	17.0	
36.0 End		

Divert valve used to shunt high concentration anions (e.g., Cl^-) to waste, preventing fouling of TSQ ion source