The Use of 2-D IC for the Determination of Haloacetic Acids in Drinking Water – Redux

Richard F. Jack, Ph.D.
Rong Lin, Ph. D.
Kannan Srinivasan, Ph.D.

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Overview

- Haloacetic Acids Analysis (HAA)
  - Background
  - Current Methods
- 2-D IC
  - Matrix removal
  - New columns
  - System configuration
- Analysis of HAA9 with 2-D IC
- Conclusions

What Are HAAs?

Acid	Abbreviation	Chemical Formula	pKa	Boiling Point °C
Monochloroacetic Acid	MCAA*	$ClCH_2CO_2H$	2.86	187.8
Dichloroacetic Acid	DCAA *	Cl_2CHCO_2H	1.25	194
Trichloroacetic Acid	TCAA *	Cl_3CCO_2H	0.63	197.5
Monobromoacetic Acid	MBAA *	$BrCH_2CO_2H$	2.87	208
Dibromoacetic Acid	DBAA *	Br_2CHCO_2H	1.47	195
Tribromoacetic Acid	TBAA	Br_3CCO_2H	0.66	245
Bromochloroacetic Acid	BCAA	$BrClCHCO_2H$	1.39	193.5
Dibromochloroacetic Acid	DBCAA	Br_2ClCCO_2H	1.09	NA
Dichlorobromoacetic Acid	DCBAA	Cl_2BrCCO_2H	1.09	NA

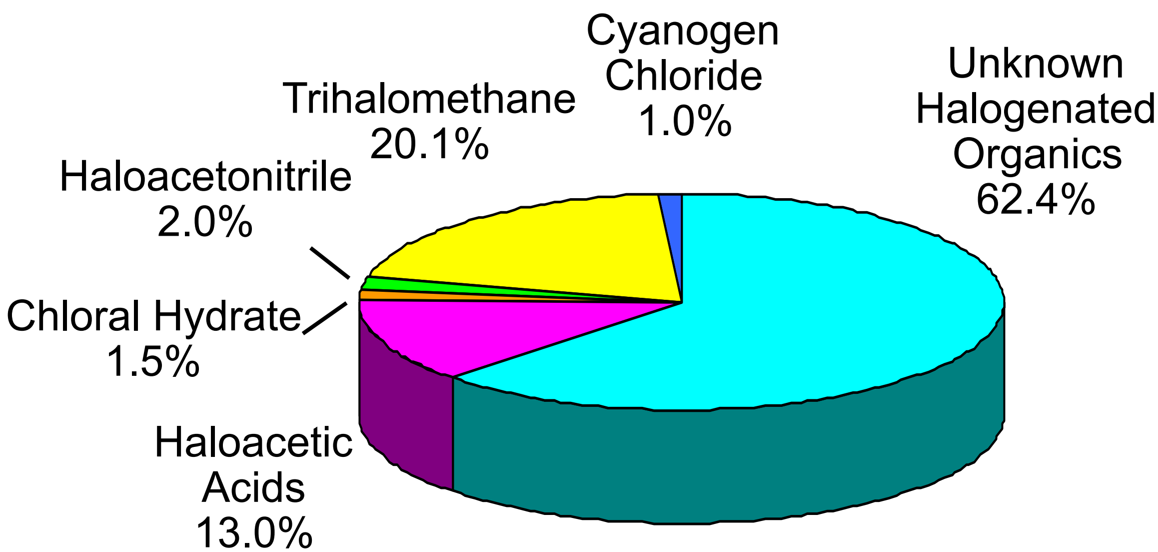
* MCAA, DCAA, TCAA, MBAA, DBAA are collectively referred to as HAA5

Formation of HAA's in Drinking Water

- Disinfection treatment is essential to eliminate waterborne disease-causing microorganisms
- Ozonation – bromate
- Chlorination (chlorine or chloramine)
  - Chlorite, chlorate
  - Trihalomethanes (THM) and haloacetic acids (HAAs)
- Highly regulated due to associated health issues
  - Chlorite: nervous system, affects fetal development, anemia
  - Bromate: carcinogenic
  - Chlorate: produce gastritis, blood diseases, and acute renal failure.
  - THM & HAAs: chronic exposure could increase risk of cancer
- Regulated under Safe Drinking Water Act
- EPA promulgated to the states

Drinking Water Disinfection: Treatment and Byproducts

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



Disinfectant Byproducts (DBPs) Regulation

- Total Trihalomethanes (TTHMs) in 1970s
- 1998 U.S. EPA Stage 1 Disinfectants/Disinfection Byproducts (D/DBP) Rule:
  - Seven new regulations, including HAA5 and bromate
  - Monitoring of HAA5 at all plants that disinfect with chlorine
  - Report total MCAA, MBAA, DCAA, DBAA, and TCAA
  - Maximum Contamination Level (MCL) = 0.060 mg/L annual average
  - MCL Goal (MCLG): DCAA should not be present; TCAA < 0.030 mg/L

- 2006 U.S. EPA Stage 2 D/DBP Rule: Reduced MCLG
  - Total HAA5 MCL < 0.060 mg/L
  - MCAA < 0.07 mg/L; TCAA < 0.02 mg/L
  - DCAA should not be present

Summary of EPA Methods for HAAs

Technique	EPA Method	Dionex IonPac Columns	MDL (ppb)
1) Liquid/Liquid Extraction 2) Derivitization 3) GC-ECD	552.2 552.3	GC-ECD	Mono: 0.13–0.20 Di: 0.02–0.08 Tri: 0.03-0.10
IC-MS, IC-MS/MS	557	Dionex IonPac AG24 precolumn + Dionex IonPac AS24 separation column (2 mm i.d.)	Mono: 0.06–0.20 Di: 0.02–0.11 Tri: 0.04–0.09
2D-IC Suppressed Cond. (direct)	Pending through 302.0, 314.2	First dimension: Dionex IonPac AG24A precolumn + Dionex IonPac AS24A separation column (4 mm i.d.) Second dimension: Dionex IonPac AG26 precolumn + Dionex IonPac AS26 separation column(0.4 mm i.d.)	Mono: 0.17–0.45 Di: 0.06–0.13 Tri: 0.08–0.27

U.S. EPA Method 552.3

- Sample Handling
  - Add 100 mg/L of granular ammonium chloride to convert residual free chlorine to combined chlorine
- Workflow
  - Acidify 40 mL of sample to pH = 0.5
  - Liquid/Liquid extraction: methyl *tert*-butyl ether (MTBE) or *tert*-amyl methyl ether (TAME)
  - Derivitization: Add acidic methanol and heat for ***2 h*** to convert HAAs to methyl esters
  - Separate sample: Add a concentrated sodium sulfate and discard aqueous layer
  - Neutralize: Add saturated sodium bicarbonate solution
  - Analysis: GC/ECD with a run time 25–30 min
  - Total time ***~ 3–4 h***

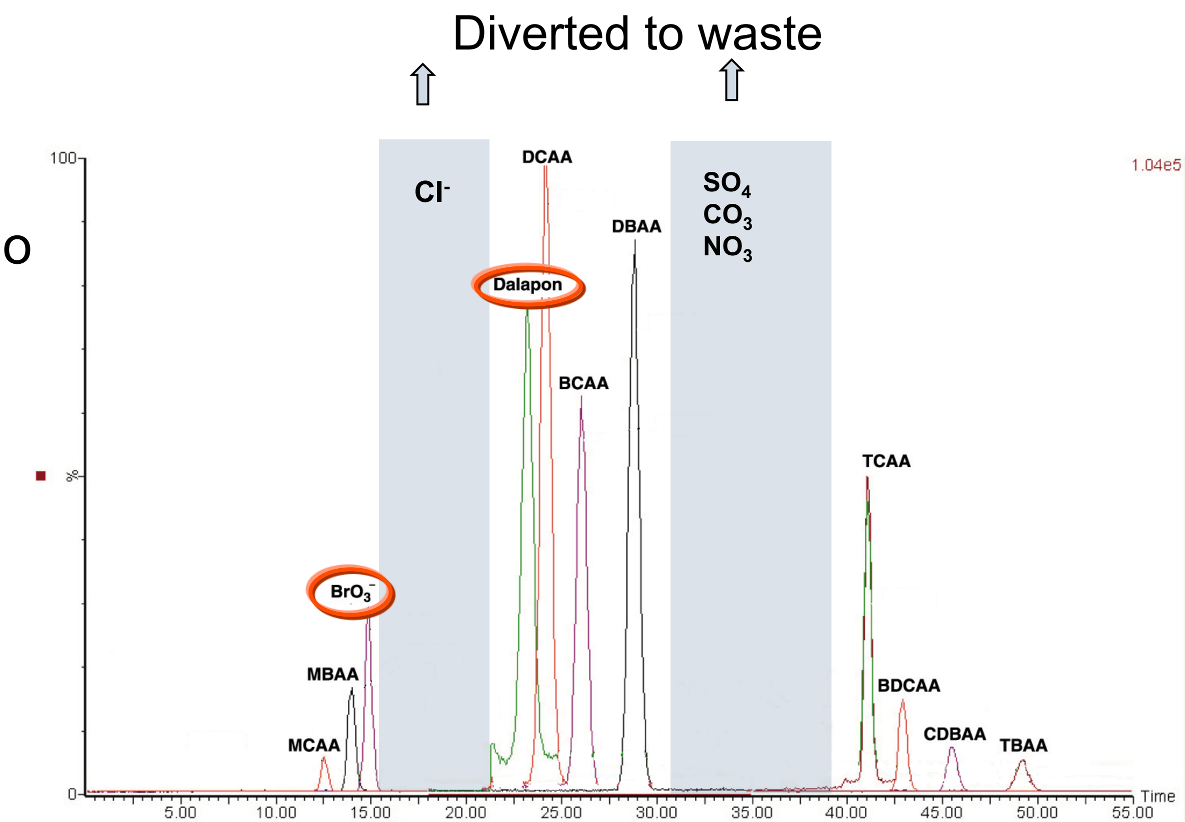
U.S. EPA Method 552.3 Reported Detection Limits

- **Advantages**
  - Good selectivity
  - Low MDLs
  - Wide applicable concentration range
  - 0.5–30 µg/L
- **Limitations**
  - Requires sample pretreatment
  - Time consuming
  - Labor intensive
  - Subject to multiple procedural errors

Analyte	Detection Limits (µg/L)	% Recovery
MCAA	**0.20**	**81**
MBAA	**0.13**	**91**
DCAA	0.084	98
BCAA	0.029	103
DBAA	0.021	105
TCAA	0.024	107
BDCAA	0.031	113
CDBAA	0.035	112
TBAA	0.097	109

EPA 557: Determination of Bromate, Dalapon, and HAA9 by Direct Injection Using IC-MS/MS

- **IC-MS/MS**
  - Suppressed ion chromatography with MS or MS-MS detection
  - No need for liquid-liquid extraction or sample pretreatment
  - Direct injection
  - MRL ppb level
  - Matrix diversion setup
  - No need for derivatizatio
  - Fully automated
  - Recovery >90%



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2-D IC for Haloacetic Acids

- Why another method for HAA's?
  - Avoid sample prep
  - Lower cost alternative

- EPA 2-D IC methods
  - *EPA 302.0: DETERMINATION OF BROMATE IN DRINKING WATER USING TWO-DIMENSIONAL ION CHROMATOGRAPHY WITH SUPPRESSED CONDUCTIVITY DETECTION*
  - *EPA 314.2: DETERMINATION OF PERCHLORATE IN DRINKING WATER USING TWO-DIMENSIONAL ION CHROMATOGRAPHY WITH SUPPRESSED CONDUCTIVITY DETECTION*

- Challenge: HAA
  - Matrix
  - Multiple time cuts
  - New columns to improve selectivity

Possible Anions in Drinking Water

- Common Anions
  - Fluoride, chloride, nitrite, bromide, nitrate, sulfate, and phosphate
  - High ionic water (HIW, Specified in EPA Methods)

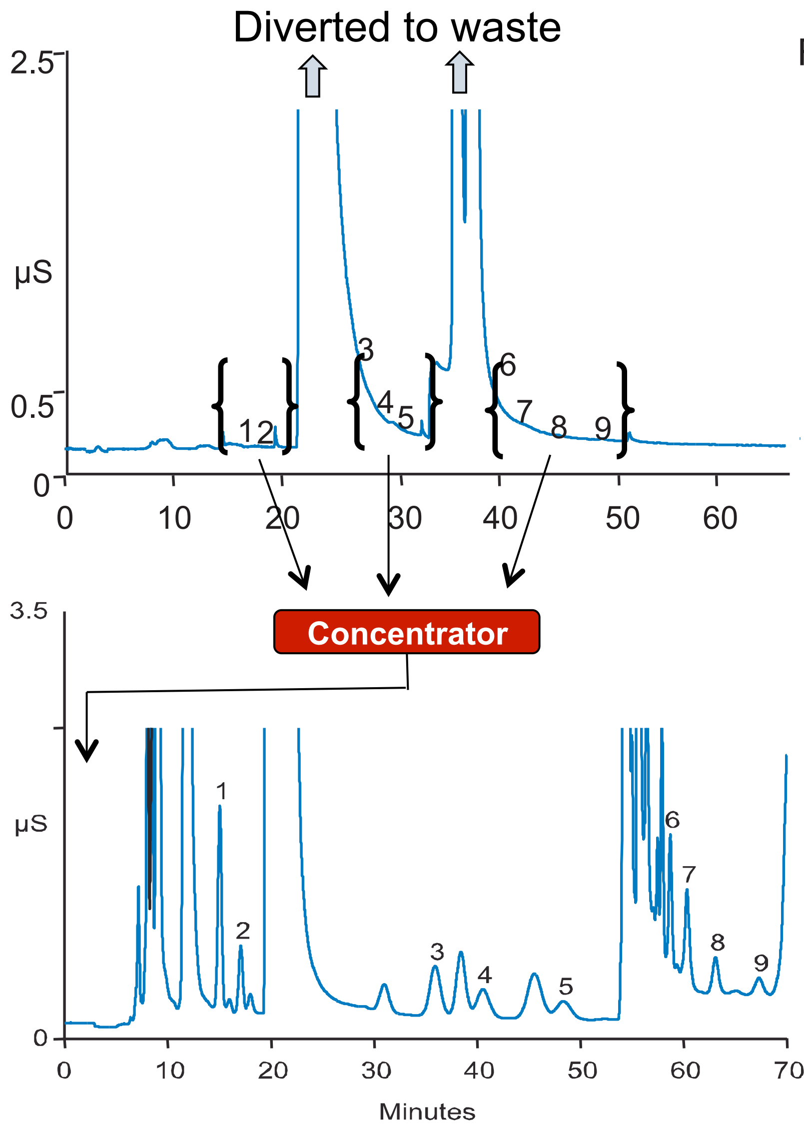
Chloride	350 mg/L
Bicarbonate	150 mg/L
Sulfate	250 mg/L
Nitrogen (Nitrate)	20 mg/L

- Oxyhalide
  - Chlorite, bromate, chlorate
- Organic Acids
  - Acetate, formate, benzoate, etc.

Matrix Elimination with 2-D Ion Chromatography

- Allows Large-Loop Injection in the First Dimension (4 mm column)
  - Possible to inject a larger loop volume than the standard approach because the capacity and selectivity of the analytical column in the first dimension dictates the recovery, and the analyte of interest is analyzed in the second dimension
- Focuses Ions of Interest in a Concentrator Column After Suppression in the First Dimension
  - Hydroxide eluent converted to DI water, providing an ideal environment for focusing or concentrating the ions of interest
- Provides Analysis in the Second Dimension Using a Smaller Column Format with a Smaller Cross-Sectional Area, Yielding Enhanced Sensitivity
  - For example, the cross-sectional area of a 1 mm column is one sixteenth the area of a 4 mm column, providing a sensitivity enhancement factor of ~16
- Provides Analysis in the Second Dimension Using a Different Chemistry
  - Enhanced selectivity

2D-IC Analysis of HAAs in a Fortified Matrix



First Dimension

Second Dimension

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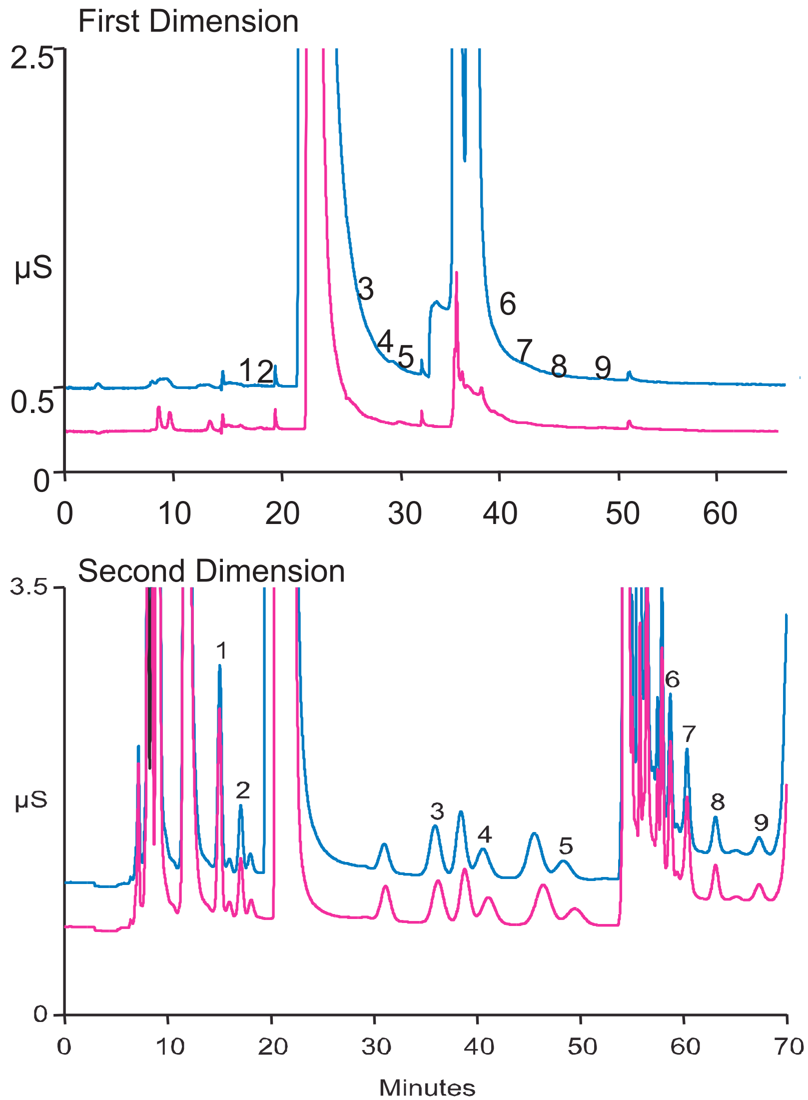
2D-IC Analysis of HAAs in Simulated Samples Using the Dionex IonPac AS24A and AS26 Columns



First Dimension Conditions

Column:	Dionex IonPac AS24A/AG24A (4 × 250 mm)
Eluent:	KOH: 7 mM from 0 to 12 min, 7 to 18 mM from 12 to 42 min, step to 65 mM at 42 min
Eluent Source:	Dionex EGC III KOH cartridge
Flow Rate:	1.0 mL/min
Inj. Volume:	500 µL
Temperature:	15 °C
Detection:	Suppressed Conductivity, Dionex ASRS 300, AutoSuppression, external water mode

Second Dimension Conditions:

Column:	Dionex IonPac AS26/AG26 Capillary (0.4 × 250 mm)
Eluent:	KOH: 6 mM from 0 to 50 min, step to 160 mM at 50 min, 160 mM from 50 to 57 min, step to 130 mM at 57 min
Eluent Source:	Dionex EGC III KOH capillary cartridge
Flow Rate:	0.012 mL/min
Concentrator:	Dionex IonSwift MAC-200
Temperature:	14 °C
Detection:	Suppressed Conductivity, Dionex ACES 300, AutoSuppression, external water mode

Peaks:

	µg/L		µg/L
1. MCAA	5	6. TCAA	5
2. MBAA	5	7. BDCAA	5
3. DCAA	5	8. CDBAA	5
4. BCAA	5	9. TBAA	5
5. DBAA	5		

Pink Trace: 100 ppm ammonium chloride

Blue Trace: High Ionic Water (250 ppm Chloride, 250 ppm Sulfate, 150 ppm Bicarbonate, 20 ppm nitrate and 100 ppm ammonium chloride)

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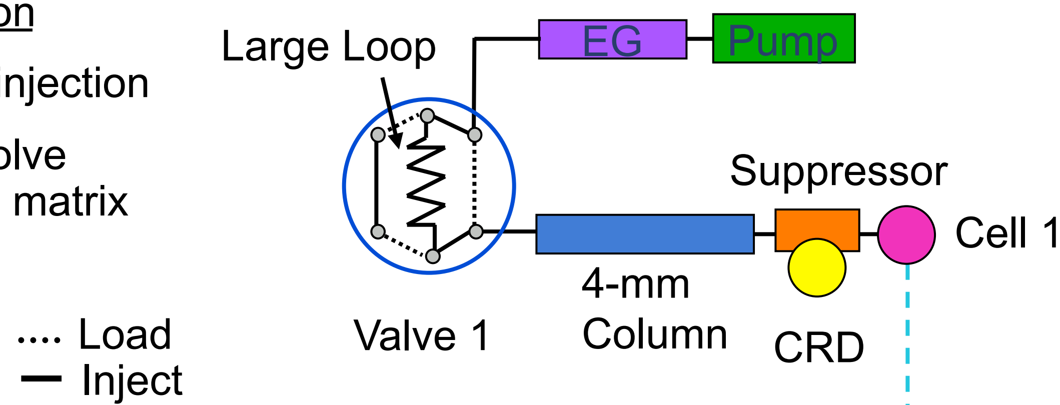
Sensitivity Improvement increased with Capillary IC

<u>1st Dimension</u>

Large Loop injection

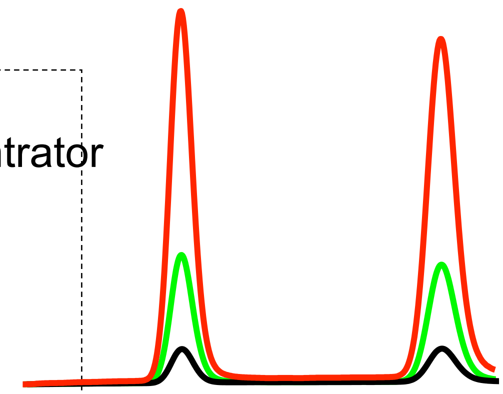
Partially resolve analyte from matrix



<u>Intermediate Step</u>

Transfer cut volume

Trap and focus ions of interest

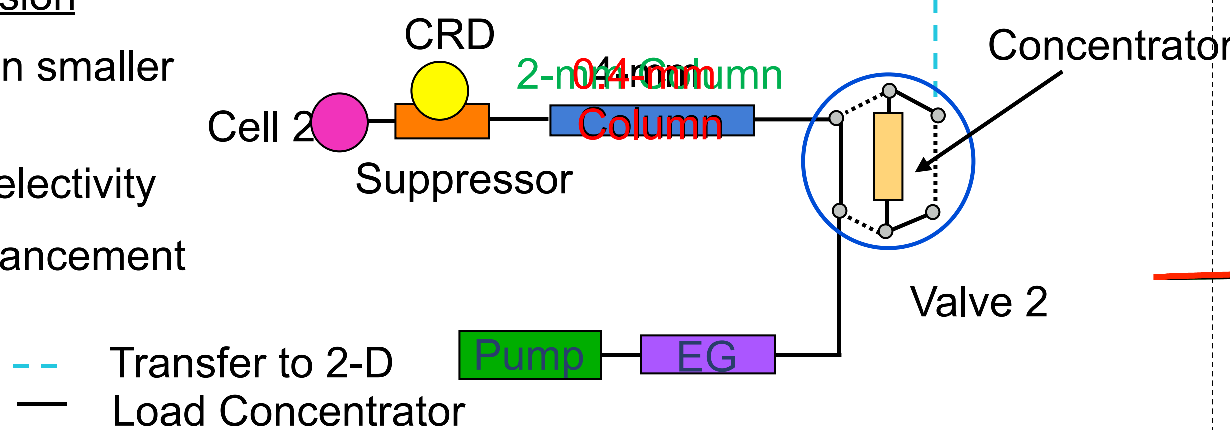


<u>2nd Dimension</u>

Separate on smaller ID column

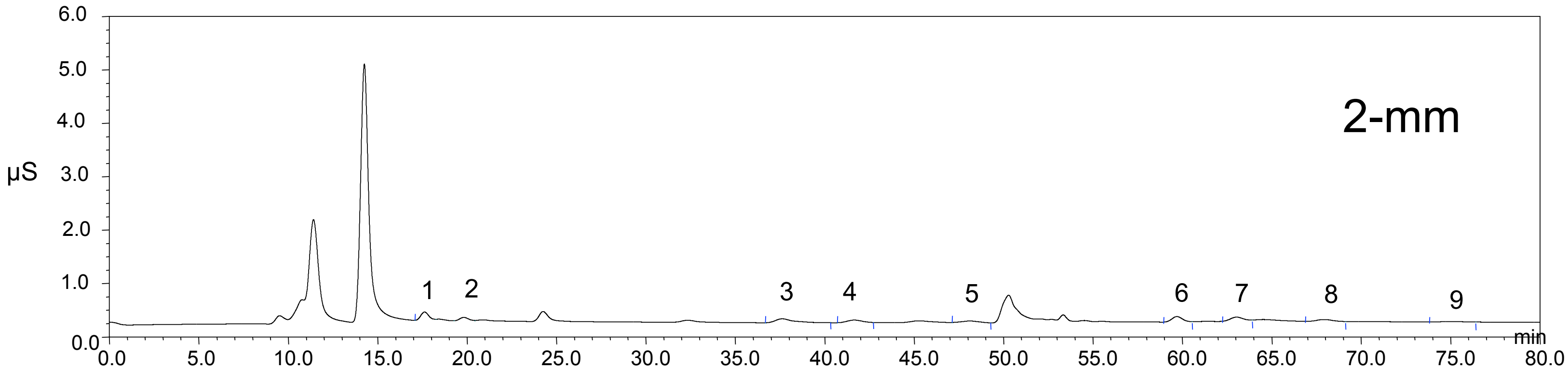
Different Selectivity

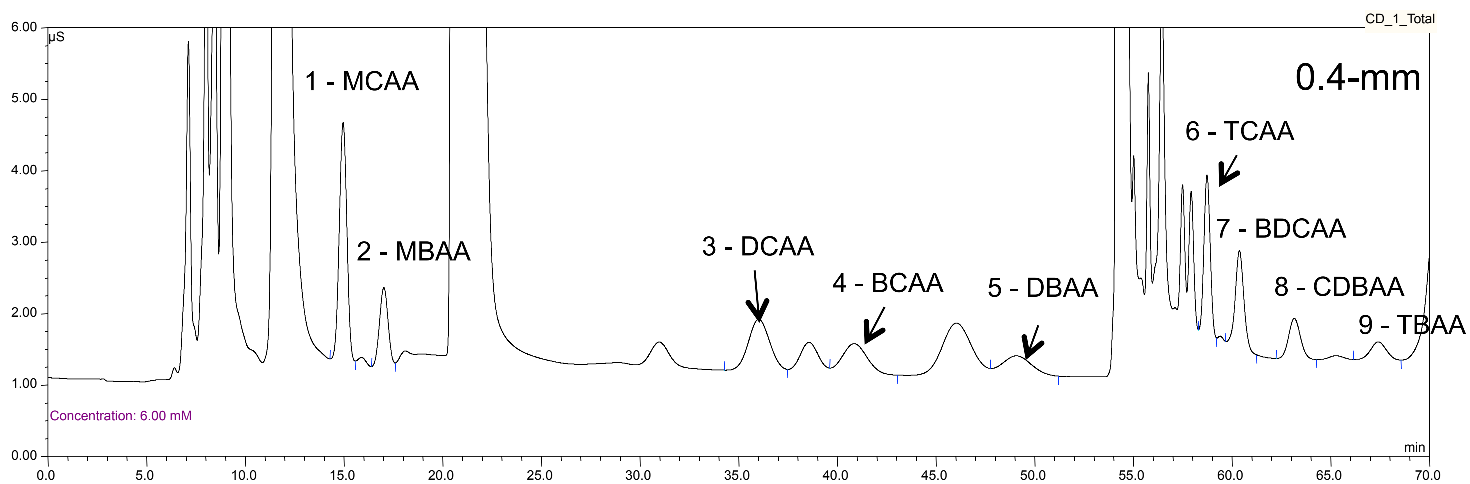
Signal Enhancement



Second Dimension separation of Haloacetic Acids on 2mm vs. 0.4 mm IonPac® AS 26

10 ppb of each HAA9 injected





Sensitivity Improvement

- RFIC™ system uses hydroxide eluents which are suppressed to water, resulting in lower backgrounds and higher sensitivity

- Using an RFIC system in 2-D IC method
  - From 4 to 2 mm enhances sensitivity 4x
  - From 4 to 0.4 mm format enhances sensitivity 100x

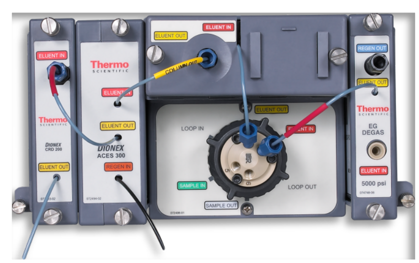
Dimension	Sensitivity	Flow rate (mL/min)
First (4 mm)	1	1
Second (2 mm)	4	0.25
Second (0.4 mm)	100	0.01

Thermo Scientific Dionex ICS-5000$^+$ HPIC System

The Dionex ICS-5000$^+$ is a universal HPIC system

High-Pressure Ion Chromatography

- Continuous operation up to 5000 psi
- High pressure capable with both standard bore and capillary systems
- Increased productivity with fast run times
- Improved separations and higher resolution with 4 µm particle columns
- Enhanced temperature control for HAAs



Thermo Scientific™ Dionex™ IC Cube™

HPIC - High Resolution, Fast Analyses

Simplifying on a single IC: First Dimension – System 1

System 1 –
Autosampler

System 1 –
Detector,
Suppressor

System 1 –
Column oven

System 1 –
Standard Pump

System 1 –
Standard EGC

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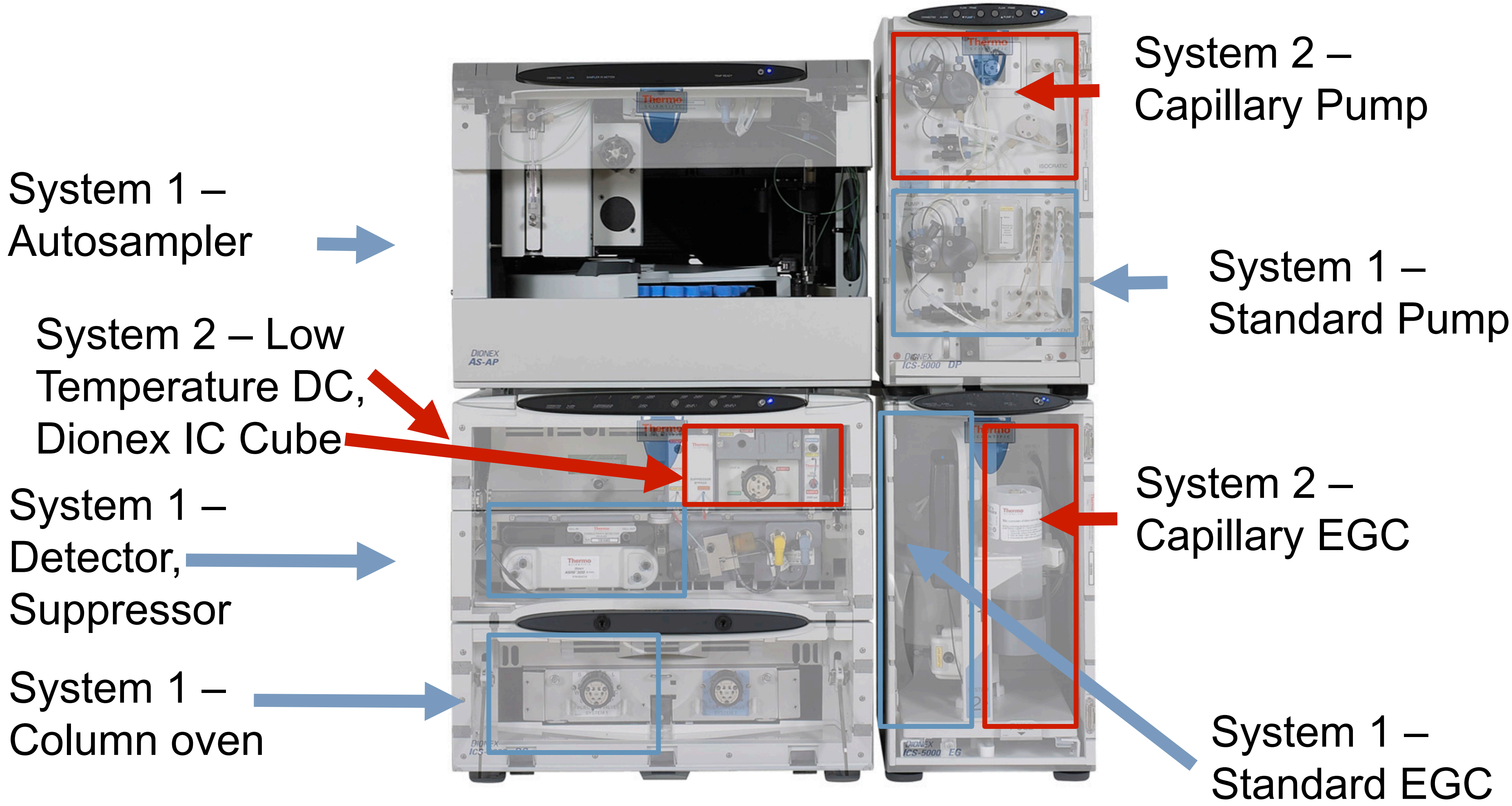
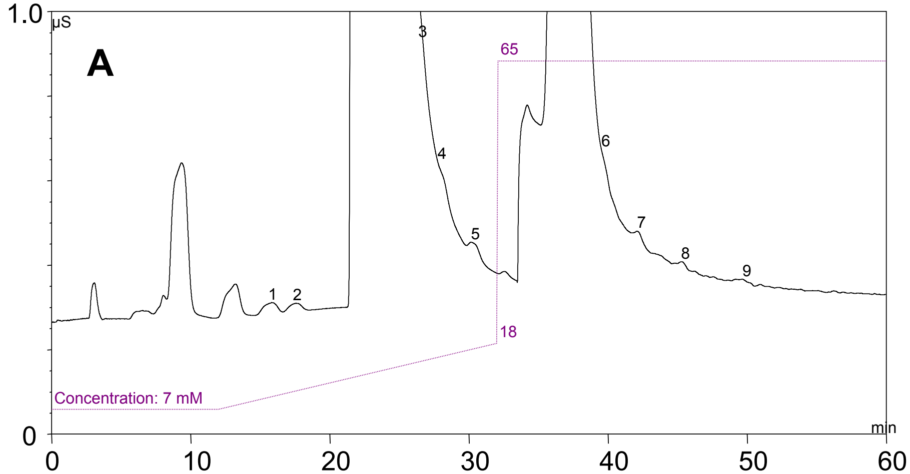
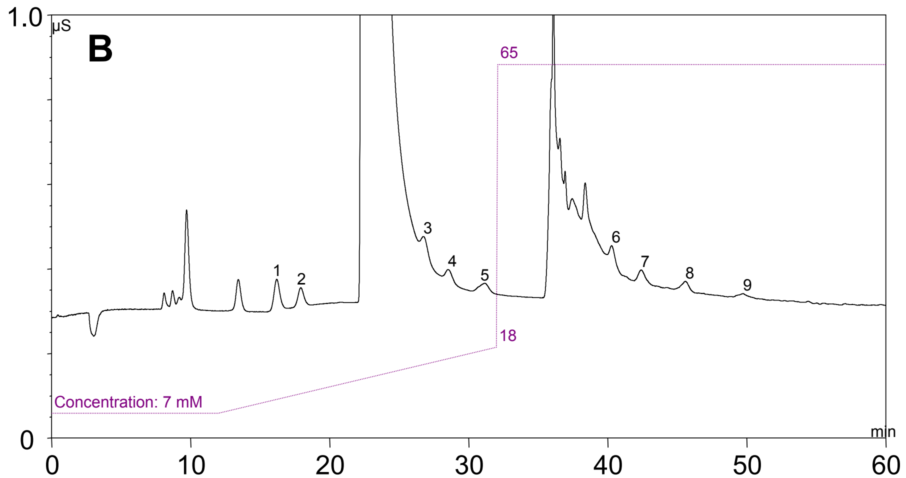
Simplifying on a single IC: First Dimension – System 1



First Dimension with Dionex IonPac AS24A Column





Columns:	Dionex IonPac AG24A,/AS24A, 4 mm
Flow Rate:	1.0 mL/min
Eluent:	KOH: 7 mM KOH (0–12 min), 7 to 18 mM (12–32 min), Step to 65 mM at 32.1 min
Eluent Source:	Dionex EGC-500 KOH cartridge
Detection:	Suppressed conductivity, Dionex ASRS 300 suppressor, 4 mm, 161 mA
Inj. Volume:	500 µL
Temp.:	15 °C
Sample:	**20 ppb HAA9 in** **A. HIW* B. 100 ppm NH_4Cl**
Peaks:	

1. MCAA	6. TCAA
2. MBAA	7. BDCAA
3. DCAA	8. CDBAA
4. BCAA	9. TBAA
5. DBAA	

* HIW = 250 ppm Cl, 250 ppm, SO_4,150 ppm HCO_3, 10 ppm NO_3, 100 ppm NH_4Cl

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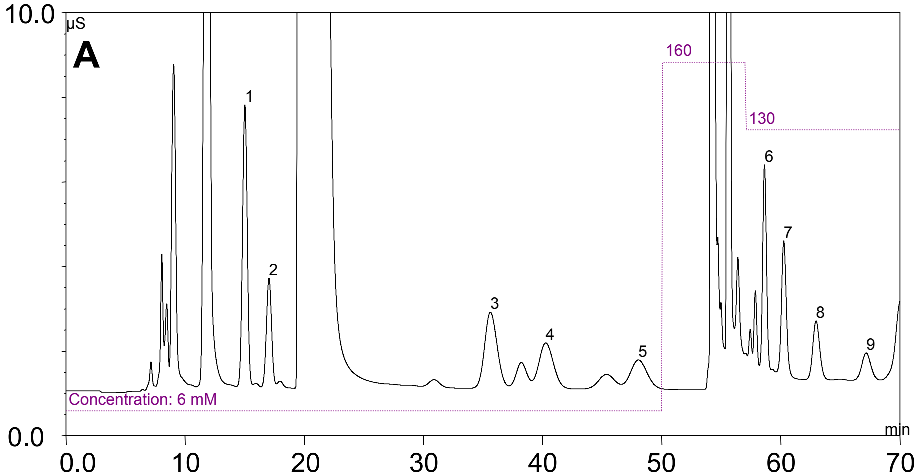
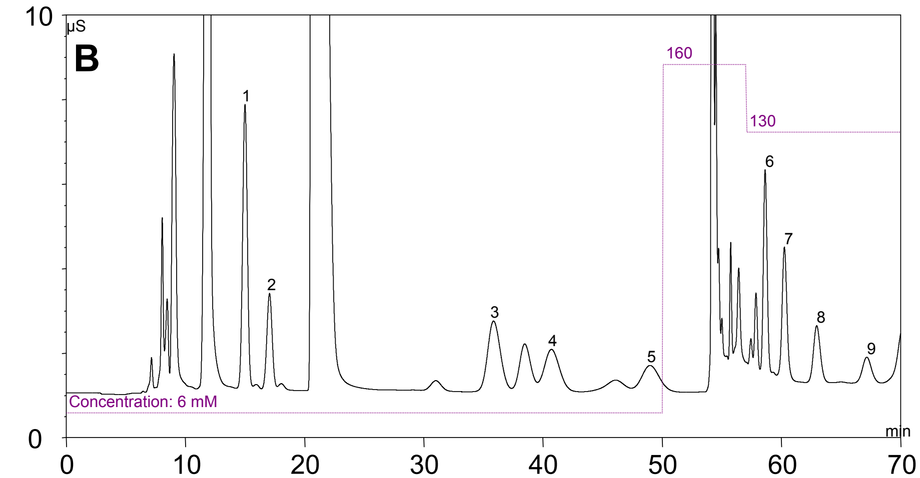
Second Dimension with Dionex IonPac AS26 Column





Columns: Dionex IonPac AG26,/AS26, 0.4 mm
Flow Rate: 0.012 mL/min
Eluent: KOH: 6 mM (0–50 min)
Step to 160 mM at 50 min
Step to 130 mM at 57 min
Eluent Source: Dionex EGC KOH capillary cartridge
Detection: Suppressed conductivity, Thermo Scientific™ Dionex™ ACES™ Anion Capillary Electrolytic Suppressor, 25 mA
Concentrator: Thermo Scientific™ Dionex™ IonSwift ™ MAC-200 column
Temp.: 14 °C

Sample: **20 ppb HAA9 in**
A. HIW* B. 100 ppm NH_4Cl

Peaks:

1. MCAA	6. TCAA
2. MBAA	7. BDCAA
3. DCAA	8. CDBAA
4. BCAA	9. TBAA
5. DBAA	

* HIW = 250 ppm Cl, 250 ppm, SO_4,150 ppm HCO_3, 10 ppm NO_3, 100 ppm NH_4Cl

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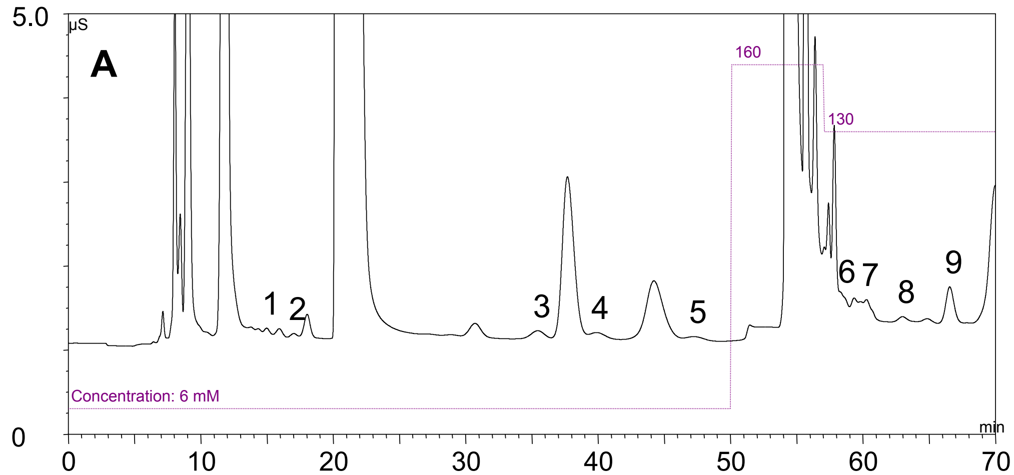
2D-IC LCMRL Results Compared to Method 557

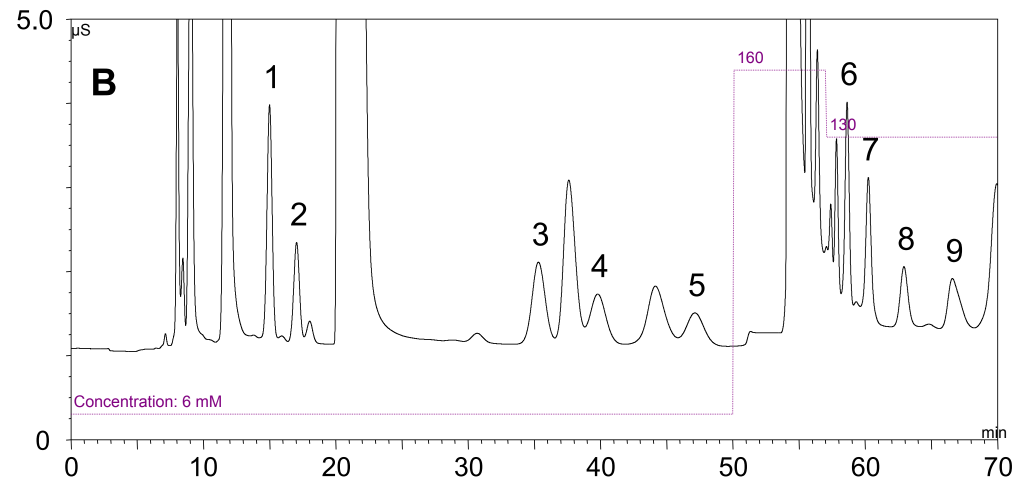
	HAA	Calculated LCMRL (µg/L)	Method 557 (µg/L)
MCAA*	Monochloroacetic acid	0.17	0.58
DCAA*	Dichloroacetic acid	0.15	0.13
TCAA*	Trichloroacetic acid	0.32	0.25
MBAA*	Monobromoacetic acid	0.45	0.19
DBAA*	Dibromoacetic acid	0.32	0.062
TBAA**	Tribromoacetic acid	0.39	0.27
BCAA**	Bromochloroacetic acid	0.21	0.16
CDBAA**	Chlorodibromoacetic acid	0.17	0.080
BDCAA**	Bromodichloroacetic acid	0.47	0.19

+ Lowest concentration method reportable level

*HAA5; **HAA9

Determinations of HAA9 in Ground Water





First Dimension

Columns:	Dionex IonPac AG24A,/AS24A, 4 mm
Flow Rate:	1.0 mL/min
Eluent:	7 mM KOH (0–12 min), 7–18 mM (12–32 min), 65 mM (32.1 min)
Eluent Source:	Dionex EGC-500 KOH cartridge
Detection:	Suppressed conductivity, Dionex ASRS 300 suppressor, 4 mm, 161 mA
Inj. Volume:	500 µL
Temp.:	15 °C
Sample:	**A: Ground water** **B: Sample A + 10 µg/L HAA9**

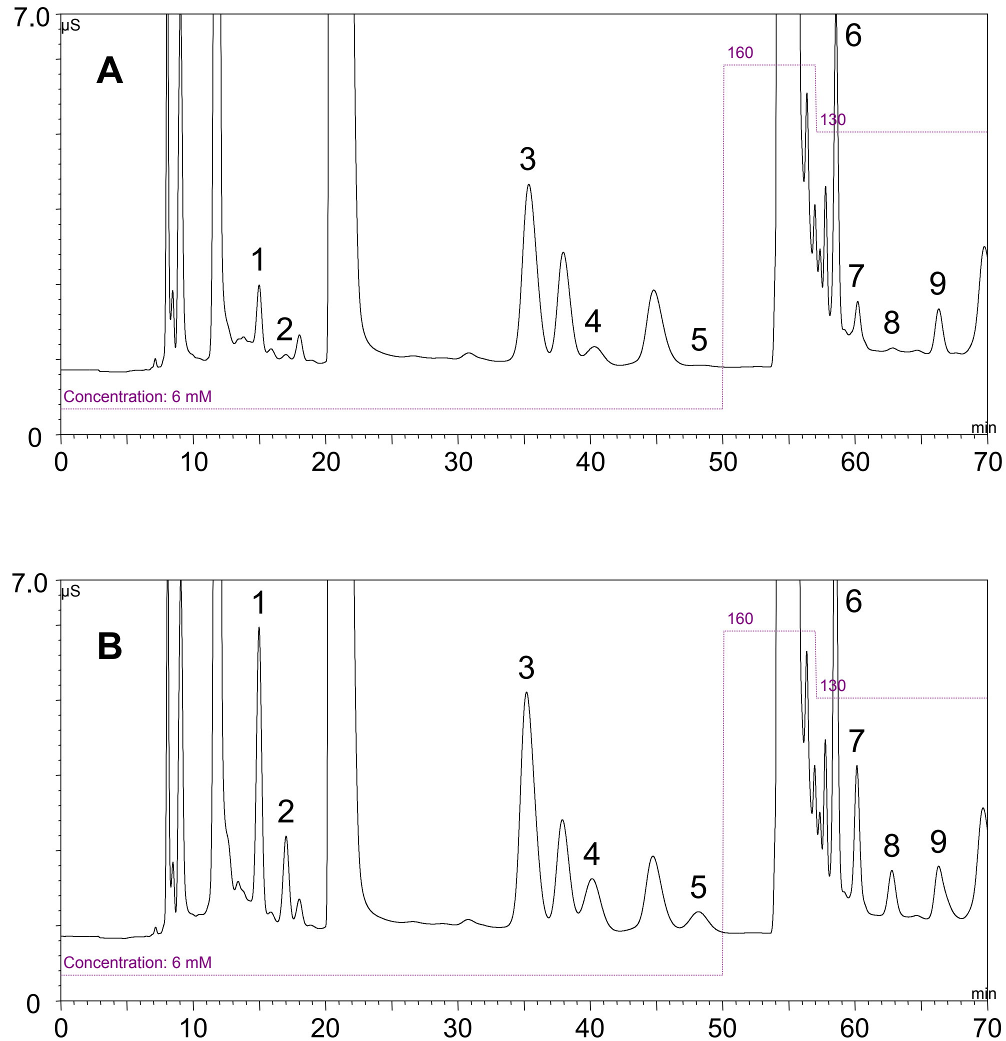
Second Dimension

Columns:	Dionex IonPac AG26/AS26, 0.4 mm
Flow Rate:	0.012 mL/min
Eluent:	6 mM KOH (0–50 min), 160 mM (50 min) 130 mM (57 min)
Eluent Source:	Dionex EGC KOH capillary cartridge
Detection:	Suppressed conductivity, Dionex ACES suppressor, 25 mA
Concentrator:	Dionex IonSwift MAC-200 column
Temp.:	14 °C

Peaks:

1. MCAA
2. MBAA
3. DCAA
4. BCAA
5. DBAA
6. TCAA
7. BDCAA
8. CDBAA
9. TBAA

Determinations of HAA9 in Surface Water



First Dimension

Columns:	Dionex IonPac AG24A, AS24A, 4 mm
Flow Rate:	1.0 mL/min
Eluent:	7 mM KOH (0–12 min), 7–18 mM (12–32 min), 65 mM (32.1 min)
Eluent Source:	Dionex EGC-500 KOH cartridge
Detection:	Suppressed conductivity, Dionex ASRS 300, 4 mm, 161 mA
Inj. Volume:	500 µL
Temp.:	15 °C
Sample:	**A: Surface water** **B: Sample A + 10 µg/L HAA9**

Second Dimension

Columns:	Dionex IonPac AG26, AS26, 0.4 mm
Flow Rate:	0.012 mL/min
Eluent:	6 mM KOH (0–50 min), 160 mM (50 min) 130 mM (57 min)
Eluent Source:	Dionex EGC KOH capillary cartridge
Detection:	Suppressed conductivity, Dionex ACES suppressor, 25 mA
Concentrator:	Dionex IonSwift MAC-200
Temp.:	14 °C

Peaks:

1. MCAA
2. MBAA
3. DCAA
4. BCAA
5. DBAA
6. TCAA
7. BDCAA
8. CDBAA
9. TBAA

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Recovery Results

HAA5	Spiked Levels (µg/L)	Surface Water	Drinking Water
Monochloroacetic acid	10	85.4%	107%
Dichloroacetic acid	10	104%	75.6%
Trichloroacetic acid	10	101%	82.0%
Monobromoacetic acid	10	102%	123%
Dibromoacetic acid	10	115%	120%

Comparing the 2D-IC Results to EPA Method 552.3

Surface Water	Method 552.3	2D-IC HAA
MCAA*	3.13 µg/L	3.21 µg/L
DCAA*	32.5	31.2
TCAA*	26.6	21.4
MBAA*	Not Reported	0.90
DBAA*	0.88	1.76
BCAA**	5.89	5.74

Ground Water	Method 552.3	2D-IC HAA
MCAA*	0.33	0.28
DCAA*	1.20	1.43
TCAA*	0.30	0.33
MBAA*	Not Reported	0.53
DBAA*	1.75	1.05
BCAA**	1.67	1.28

*HAA5; **HAA9

Method aspects

- Sample Preservation
  - Ammonium Chloride (100 ppb) added to prevent HAA formation.
  - All standards are prepared in Ammonium Chloride.
- Laboratory Synthetic Sample Matrix
  - Contains NH_4Cl preservative

Compound	Conc. LSSM (mg/L)
Nitrate anion	20
Bicarbonate anion	150
Chloride anion	250
Sulfate anion	250

- Analysis batch cannot exceed 24 hrs.
- Wash cycle for concentrator after each injection
- Concentrator column concentrates approx.15 mL of sample from the 1st Dimension.
- Determination of the cut window
- Calibration acceptance criteria

Conclusion

The 2D-IC method for HAAs is a viable alternative to EPA methods 552.3 and 557

- HAAs are directly determined without multiple and lengthy derivitization steps as in EPA 552.3
- This method is selective and sensitive and designed to reduce matrix interference effects
- Regulatory acceptance is pending
- Similar to other 2D-IC methods that have regulatory acceptance
- Simplified and less costly using a single system; the Dionex ICS-5000^{+} HPIC system with its dual system capabilities and enhanced temperature controls

Thank you!

The world leader in serving science

OT71563-EN 0315S