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The use of 2-D IC for the determination of Haloacetic Acids in Drinking Water

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Notes page

- **NEMC Topics in Drinking Water (Continued)**

- 1:30 — 5:00

- Columbia B

- Session Chairs: Andy Eaton, MWH Laboratories and ?

- 1:30 *Ozone-based Treatment of Emerging Contaminants in Water*
  - Rominder Suri, Temple University
- **2:00 *The Use of 2-D IC for the Determination of Haloacetic Acids in Drinking Water***
  - **Brian Deborba, Thermo Fisher Scientific**
- 2:30 *High Resolution LC-MS for Screening and Quantitative Analysis of Antibiotics in Drinking Water Using an Orbitrap and Online Sample Preparation*
  - Jonathan Beck, Thermo Fisher Scientific
- 3:30 *Using Root Cause Analysis to Determine the Source of Total Coliform Contamination*
  - Elizabeth Turner, North Texas Municipal Water District
- 4:00 *EPA's Water Contaminant Information Tool - A Practical Tool for Prevention of and Response to Water Contamination*
  - Adrian Hanley, US EPA OW
- 4:30 *EPA Full-Scale Exercises Increase Preparedness to Provide Laboratory Support to Large-Scale Contamination Incidents*
  - Adrian Hanley, US EPA OW

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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**

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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_2ClCCO_2H	1.09	NA

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

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Drinking Water Disinfection: Treatment and Byproducts

Disinfection Treatment	Major Disinfection Byproducts
Chlorine	Trihalomethanes **Haloacetic Acids** Chlorate
Chlorine Dioxide	Chlorite Chlorate
Chloramine	Chlorate
Ozone	Bromate

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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

Cyanogen Chloride 1.0%

Trihalomethane 20.1%

Haloacetonitrile 2.0%

Unknown Halogenated Organics 62.4%

Chloral Hydrate 1.5%

Haloacetic Acids 13.0%

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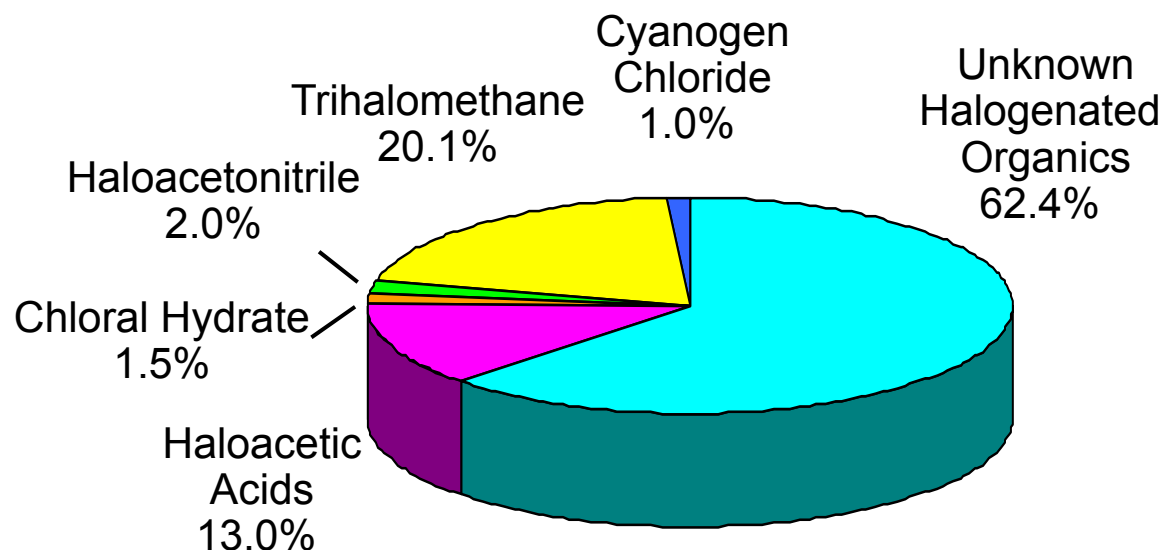
Why a Disinfectants and Disinfection Byproducts Rule?

- **Trihalomethanes (THM)** can cause liver, kidney, or central nervous system problems; increased risk of cancer

- **Haloacetic Acids (HAAs)** can cause increased risk of cancer

- **Bromate** can cause increased risk of cancer

- **Chlorite** can cause anemia in infants and young children; nervous system effects

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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
    - Total MCAA, MBAA, DCAA, DBAA, and TCAA
  - Maximum Contamination Level (MCL) = 60 µg/L
    - Annual average (calculated for each monitoring location in the distribution system)
  - Maximum Contamination Level Goal (MCLG)
    - DCAA should not be present
    - TCAA less than 0.30 mg/L
- 2006 U.S. EPA Stage 2 D/DBP Rule
  - Maximum Contamination Level Goal (MCLG)
    - MCAA less than 0.07 mg/L
    - DCAA should not be present
    - TCAA less than 0.02 mg/L

Current EPA Methods for HAA Analysis

- U.S. EPA Method 552.1 552.2 and 552.3 (1992)

  Liquid-Liquid Microextraction, Derivatization, and Gas Chromatography with Electron Capture Detection

- U.S. EPA Method 557 (2009)

  Suppressed Ion Chromatography with MS or MS-MS Detection

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U.S. EPA Method 552.3

- Summary
  - Adjust sample (*40 mL*) pH to 0.5
  - Extract either with methyl *tert*-butyl ether (MTBE) or *tert*-amyl methyl ether (TAME)
  - Convert HAA to their methyl esters by adding acidic methanol and heating 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
- Sample Handling
  - Granular ammonium chloride is added to sample (Conc. of 100 mg/L in the sample)
    - Convert free chlorine residual to combined chlorine

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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

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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 derivatization
  - Fully automated
  - Recovery >90%

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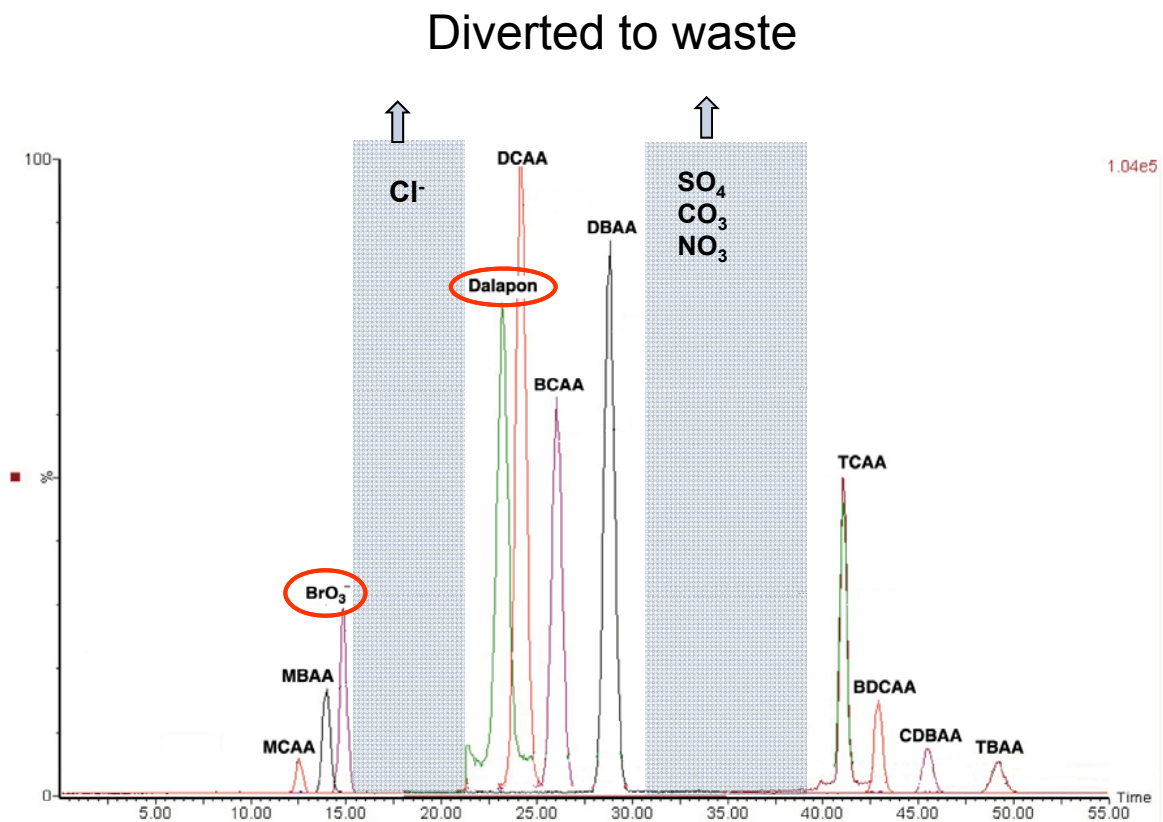
2-D IC for Haloacetic Acids

- 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*
- Perchlorate
  - *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

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Possible Anions in Drinking Water

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

    Chloride

    Bicarbonate

    Sulfate

    Nitrogen (Nitrate)

- ## Oxyhalide
  - Chlorite, bromate, chlorate

- ## Organic Acids
  - Acetate, formate, benzoate, etc.

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Early Separations with existing columns

Peaks

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

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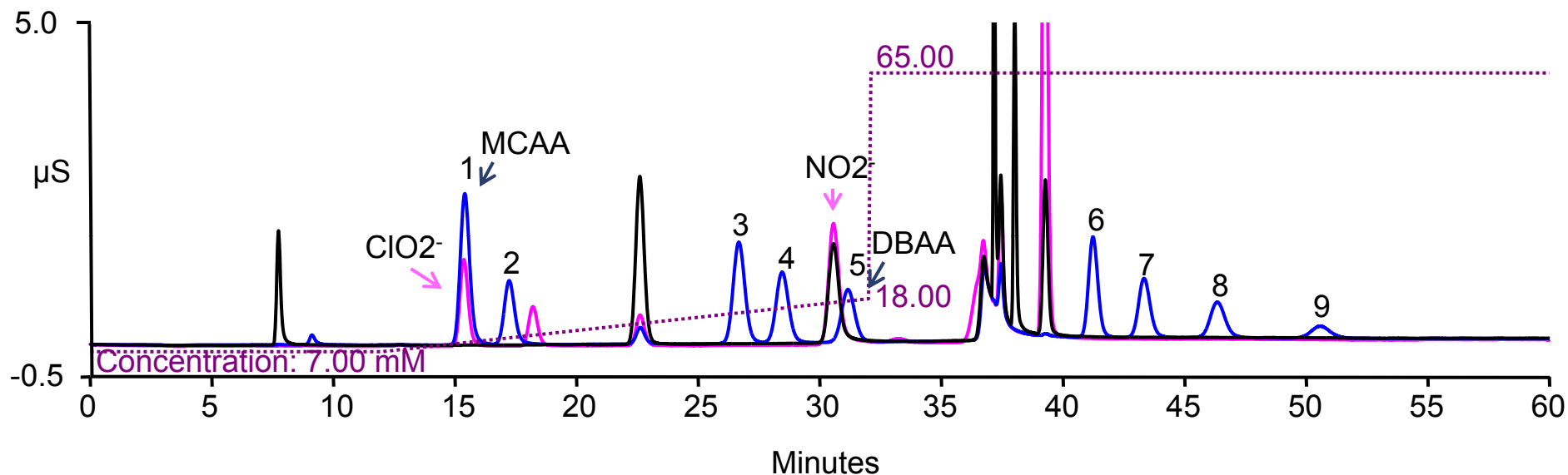
Selectivity Optimization
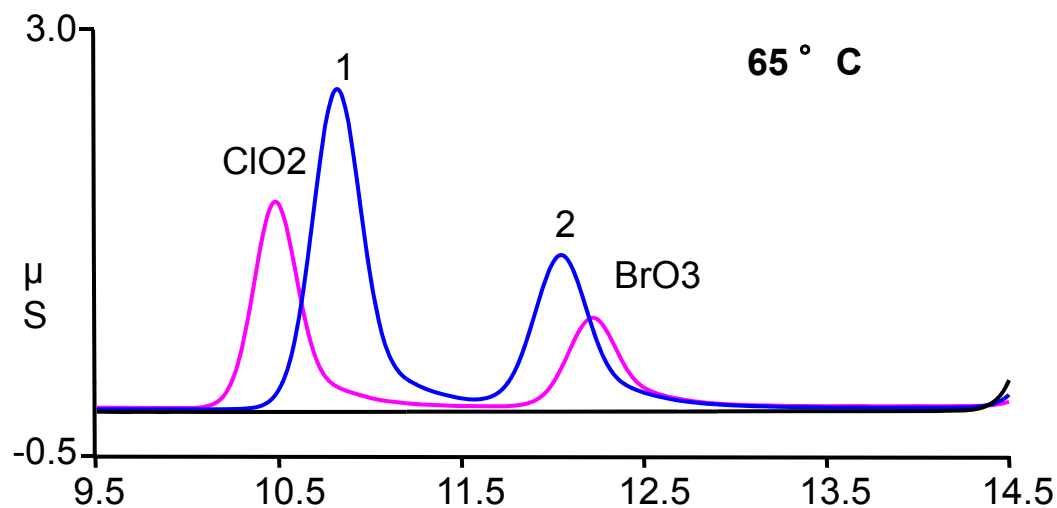
Column: Prototype
Flow Rate: 0.25 mL/min
Eluent: KOH Gradient
Suppressor: ASRS 300, 2 mm
Current: 45 mA (recycle)
Column Temp.:   15 ° C
Loop: 250 µL

Peaks: 1. MCAA 100 ppb
                       2. MBAA 100 ppb

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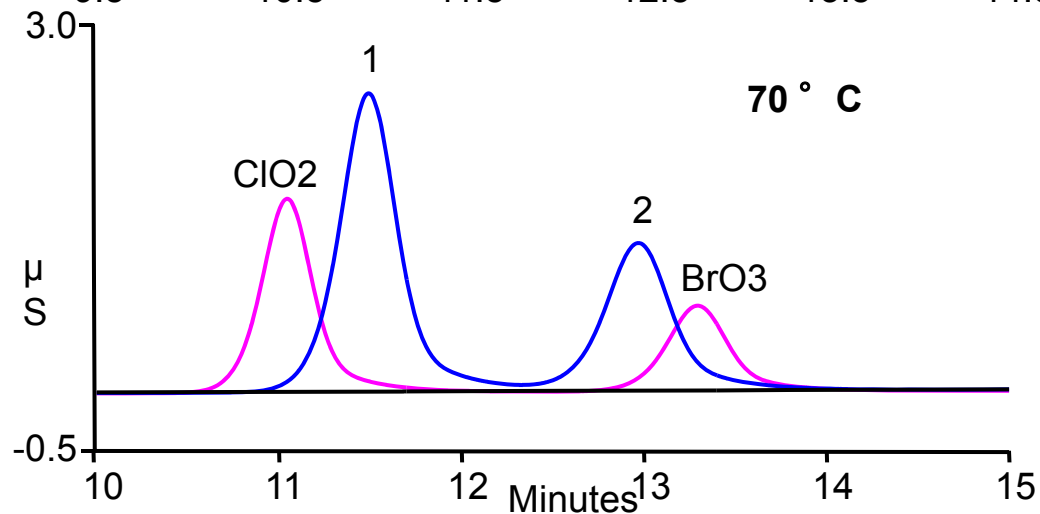
HAA9 Separation with New IonPac AS26 Column (Optimized Synthesis)
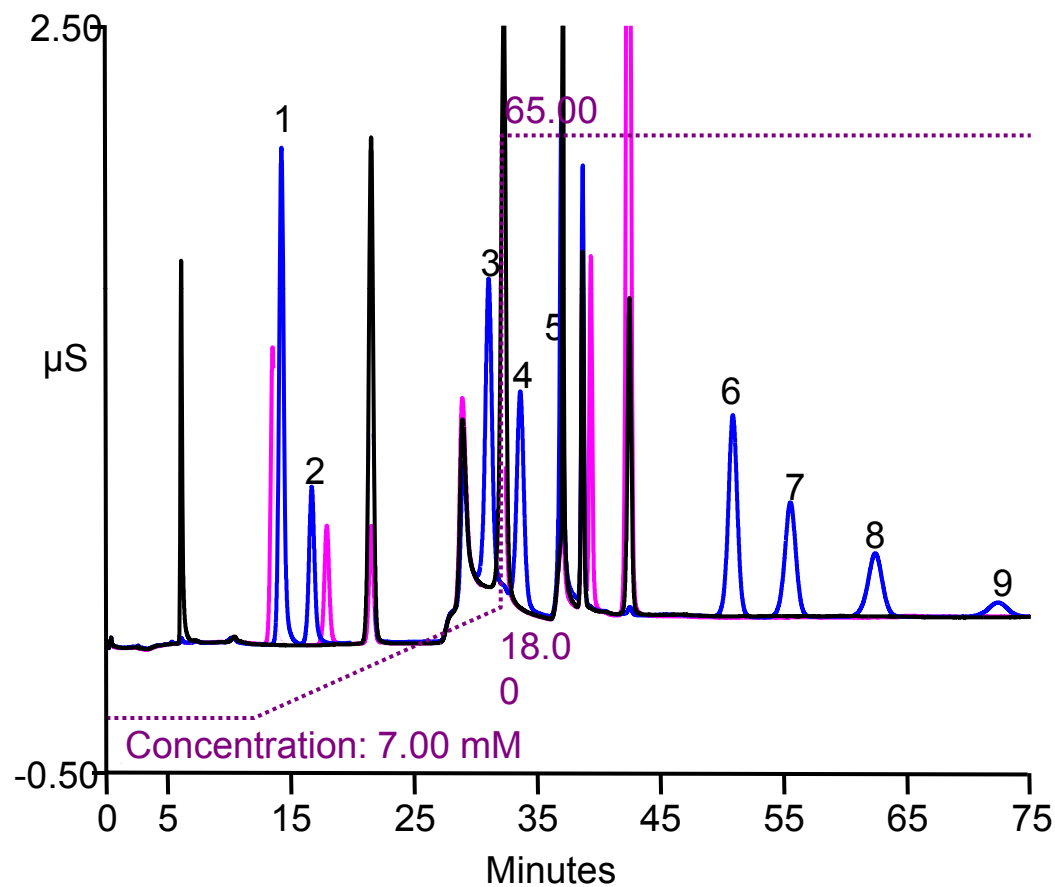
Column: IonPac® AS26 2 mm
Flow Rate: 0.25 mL/min
Eluent: KOH Gradient
Suppressor: ASRS 300 2 mm
Current: 45 mA (Recycle)
Column Temp: 15° C
Loop: 250 μL

Peaks:

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

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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

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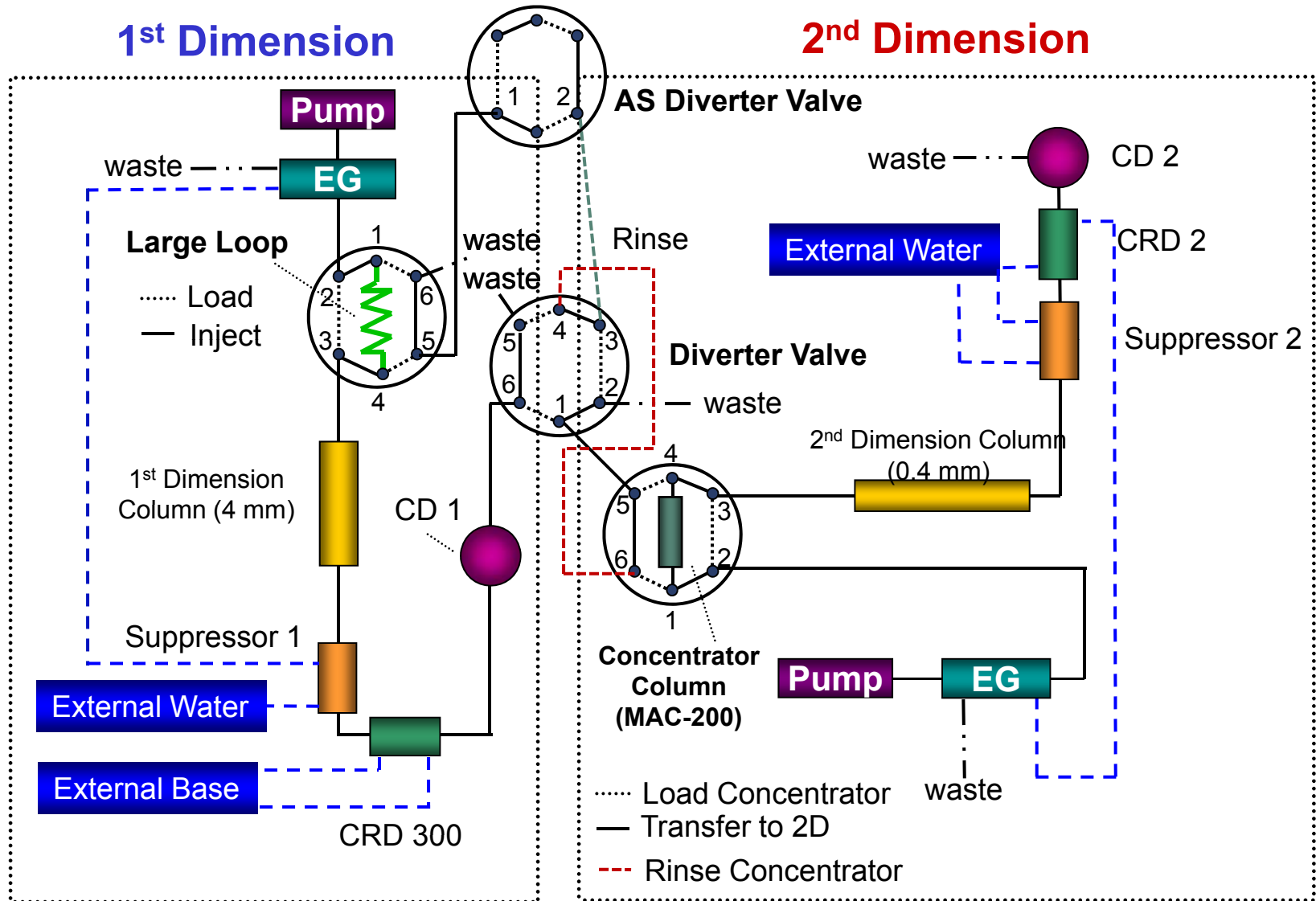
2D-IC Analysis of HAAs in a Fortified Matrix
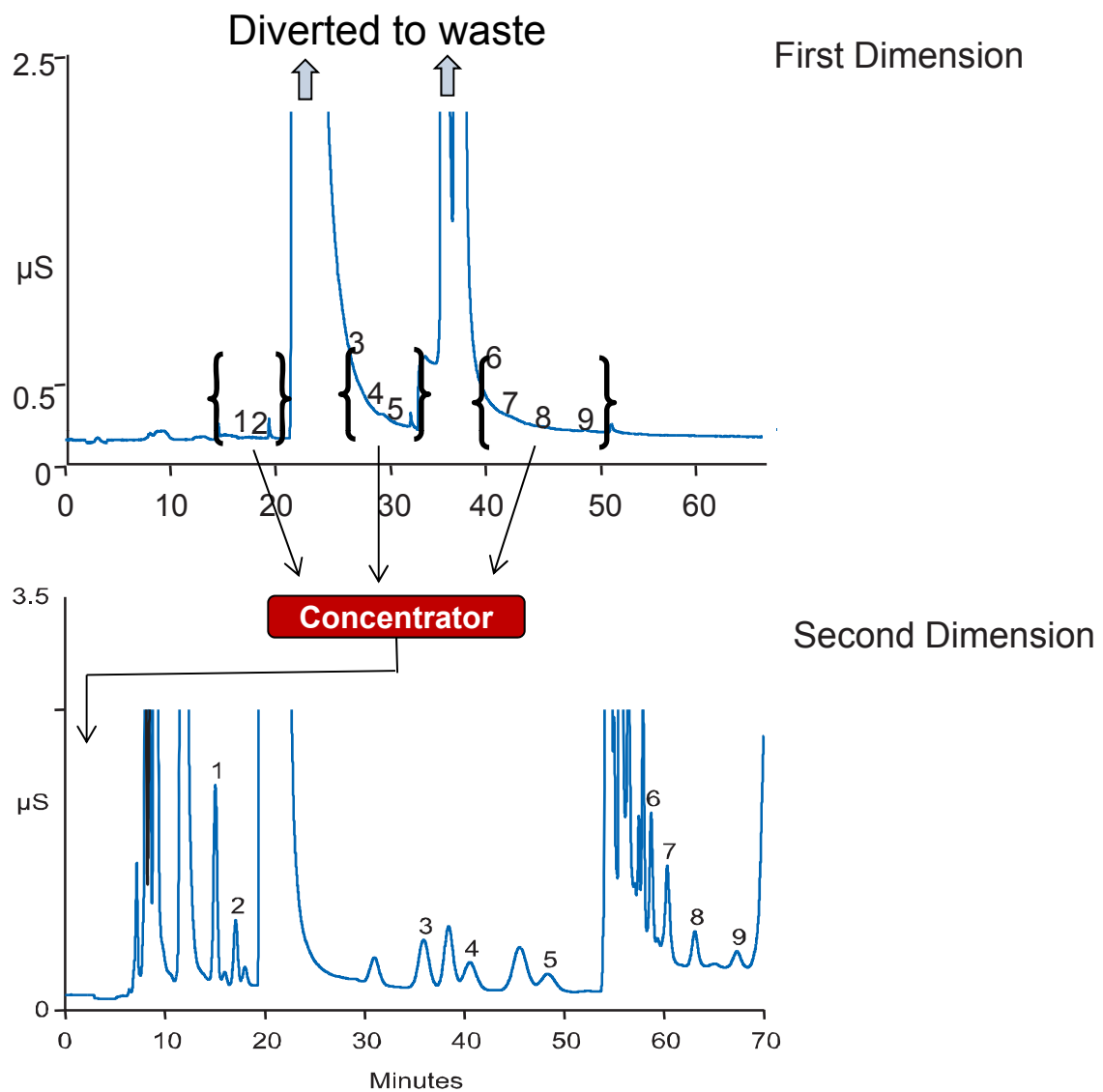
2D-IC Analysis of HAAs in Simulated Samples Using the Dionex IonPac AS24A and AS26 Columns

First Dimension

Second Dimension
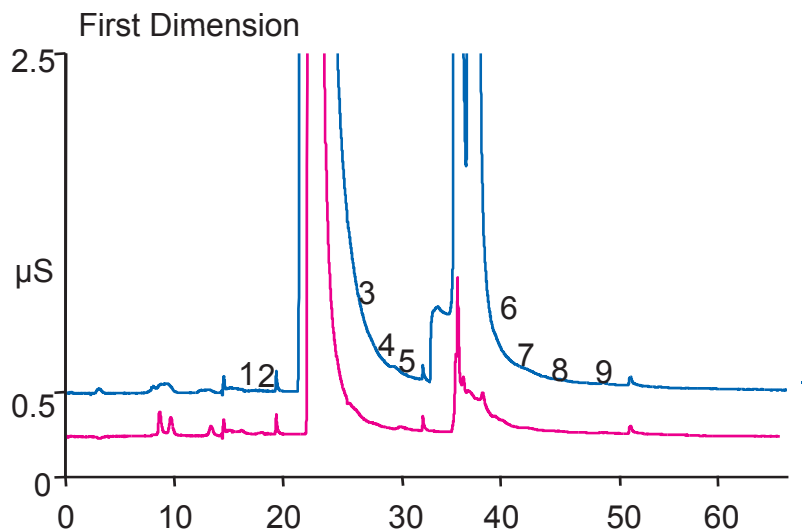
First Dimension Conditions

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
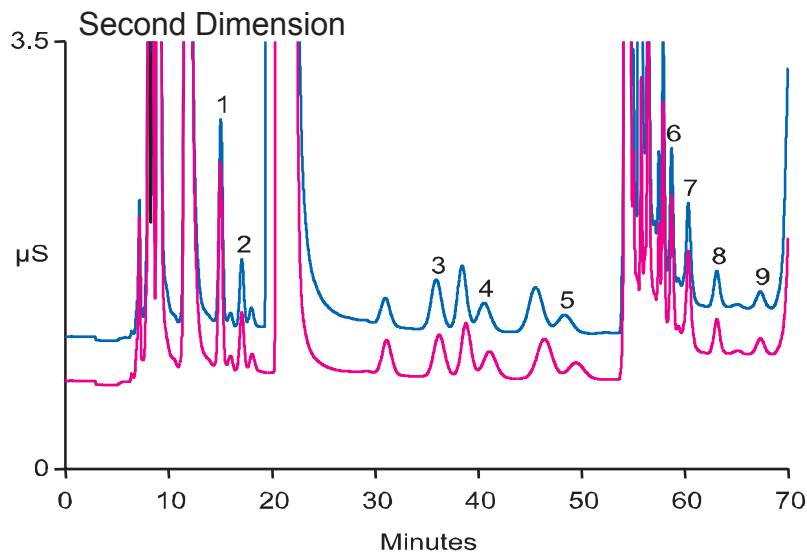
Second Dimension Conditions:

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)
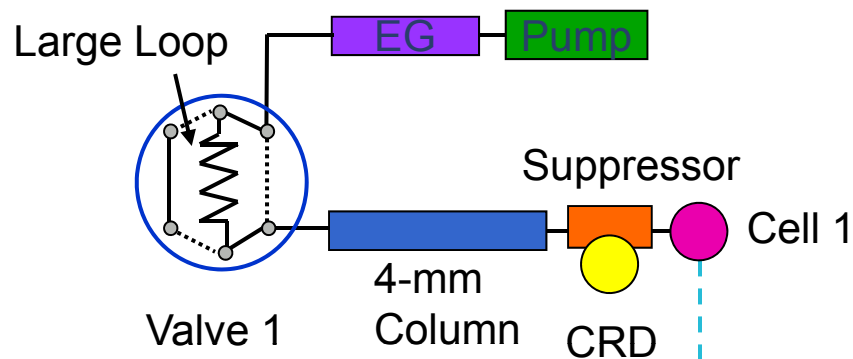
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Sensitivity Improvement increased with Capillary IC

1st Dimension

Large Loop injection

Partially resolve analyte from matrix

.... Load
— Inject

Large Loop

EG — Pump

Suppressor

Cell 1

4-mm Column

CRD

Valve 1

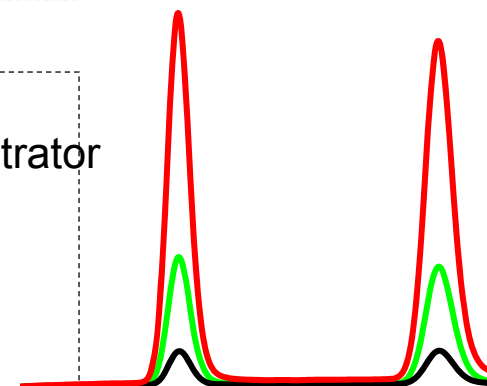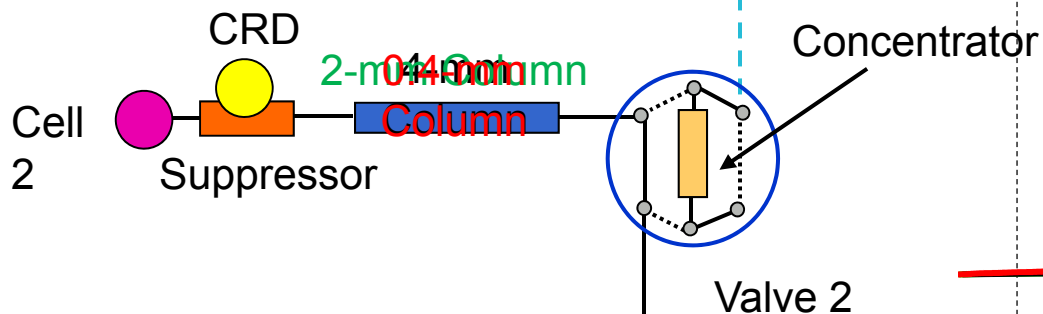**Intermediate Step**

Transfer cut volume

Trap and focus ions of interest

2nd Dimension
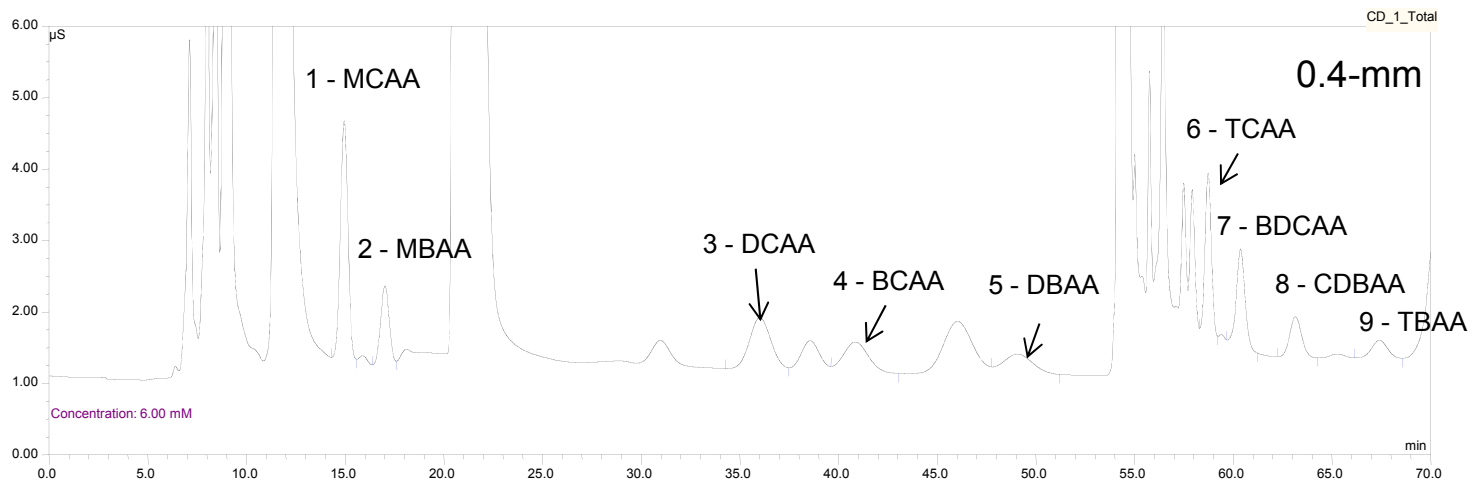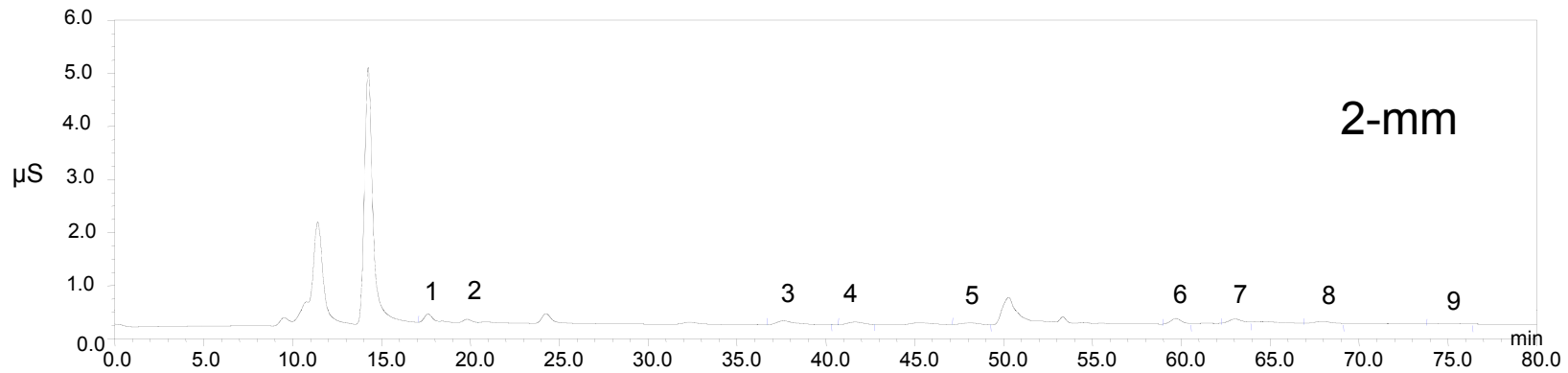
Separate on smaller ID column

Different Selectivity

Signal Enhancement

– – Transfer to 2-D
— Load Concentrator

CRD

2-mm Column / 4-mm Column

Cell 2

Suppressor

Concentrator

Valve 2

Pump — EG

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

10 ppb of each HAA9 injected

LCMRL for HAA9

Analyte	LCMRL Fortification Levels (µg/L)	Calculated LCMRL (µg/L) using 2mm column in 2nd Dimension
Monochloroacetic acid	0.3, 0.5, 1.0, 2.0, 5.0, 8.0, 15.0	0.47
Monobromoacetic acid	0.3, 0.5, 1.0, 2.0, 5.0, 8.0, 15.0	0.49
Dichloroacetic acid	0.3, 0.5, 1.0, 2.0, 5.0, 8.0, 15.0	0.94
Bromochloroacetic acid	0.3, 0.5, 1.0, 2.0, 5.0, 8.0, 15.0	1.7
Dibromoacetic acid	0.3, 0.5, 1.0, 2.0, 5.0, 8.0, 15.0	**2.2**
Trichloroacetic acid	0.3, 0.5, 1.0, 2.0, 5.0, 8.0, 15.0	**1.3**
Bromodichloroacetic acid	0.3, 0.5, 1.0, 2.0, 5.0, 8.0, 15.0	**1.9**
Chlorodibromoacetic acid	0.3, 0.5, 1.0, 2.0, 5.0, 8.0, 15.0	0.74
Tribromoacetic acid	0.3, 0.5, 1.0, 2.0, 5.0, 8.0, 15.0	**2.7**

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LCMRL for EPA IC-MS/MS and 2-D IC capillary

Analyte	LCMRL (EPA 557)	Expected LCMRL (Capillary)
Monochloroacetic acid	0.58	0.019
Monobromoacetic acid	0.19	0.020
Dichloroacetic acid	0.13	0.038
Bromochloroacetic acid	0.16	0.068
Dibromoacetic acid	0.062	0.088
Trichloroacetic acid	0.25	0.052
Bromodichloroacetic acid	0.19	0.076
Chlorodibromoacetic acid	0.080	0.030
Tribromoacetic acid	0.27	0.11

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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

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Calibration Standards

- CONTINUING CALIBRATION CHECK standard (CCC) – A standard containing the method analytes at the MRL, mid- and high-level of the calibration curve which are analyzed at the start, during and at the end of each analysis batch to verify the accuracy of the existing calibration.

- LABORATORY SYNTHETIC SAMPLE MATRIX CONTINUING CALIBRATION CHECK STANDARD (LSSM CCC) – A standard containing the method analytes at the MRL, mid- and high-level of the calibration curve which are analyzed at the start, during and at the end of each analysis batch to confirm that the 1-D heart cutting procedure has acceptable recovery in high inorganic matrices.

- SECOND SOURCE QUALITY CONTROL SAMPLE (QCS) – A solution containing the method analytes at a known concentration, which is obtained from a source different from the source of calibration standards. The purpose of the QCS is to verify the accuracy of the Primary calibration standards.

- CALIBRATION ACCEPTANCE CRITERIA – Validate the initial calibration by calculating the concentration of the 5 regulated HAA's for each of the concentrations used to generate the calibration curve by use of the regression equations using peak areas verses concentration. Calibration points that are ≤MRL must calculate to be within +30% of their true value. All other calibration points must calculate to be within +20% of their true value. All 5 regulated HAA's MUST have acceptable calibrations, with R^2 values of 0.999^+.

- 4 matrices; RW, LSSM, ground water and surface water. This will involve analyzing 3 native samples and seven individually prepared replicates

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Conclusions

- A new column IonPac® AS26 was developed by optimizing amine epoxide reaction conditions

- Excellent resolution of 9 HAAs was achieved in the presence of inorganic matrix ions

- Preliminary studies with the 2-D IC methodology allowed analysis of HAA9 in the presence of matrix ions with suppressed conductivity detection

    - Matrix diversion and selective concentration of HAA species in the first dimension

    - Separation and enhanced detection by suppressed conductivity detection in the second dimension

- Method can be shortened for only the regulated HAA5

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Thank You!

Special
Thanks to:
Chris Pohl
Kannan
Srinivasan
Sheetal
Bhardwaj
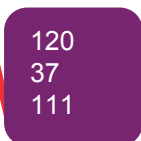Asavari Kale
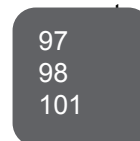Rahmat Ullah

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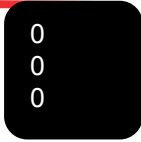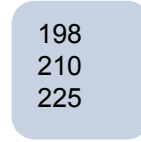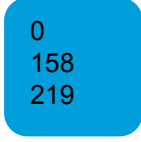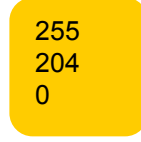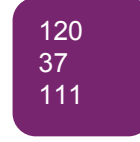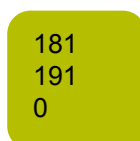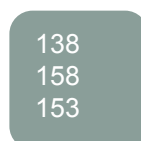
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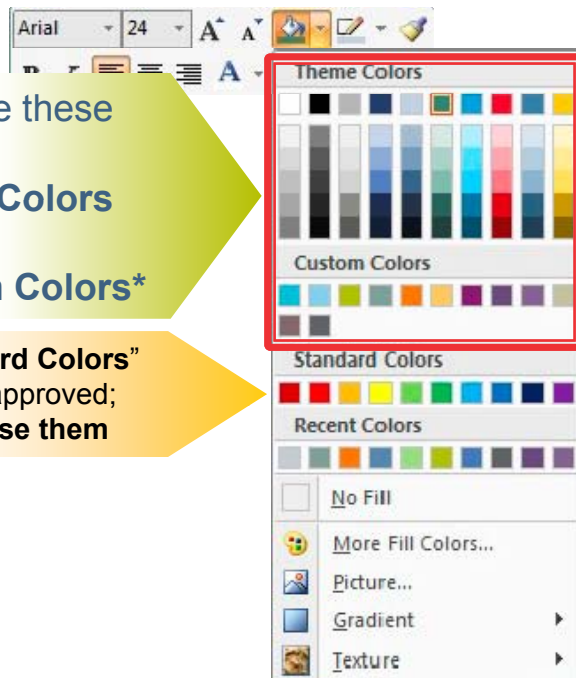
Pickup object style tool

Apply object style tool

Object fill

Line fill

Text fill

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0 158 219 **Accent 3**	238 49 52 **Accent 4**	83 129 172 **Accent 5**	255 204 0 **Accent 6**	38 188 215 **Hyperlink**	120 37 111 **Followed Hyperlink**
38 188 215 **Cyan accent**	158 206 235 **lt blue**	181 191 0 **Green**	138 158 153 **grey-green**	239 130 0 **orange**	242 203 101 **lt orange**
120 37 111 **magenta accent**	98 77 125 **dk blue-magenta**	122 102 145 **lt blue-magenta**	196 193 160 **putty accent**	126 105 109 **brown accent**	97 98 101 **moss accent**

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