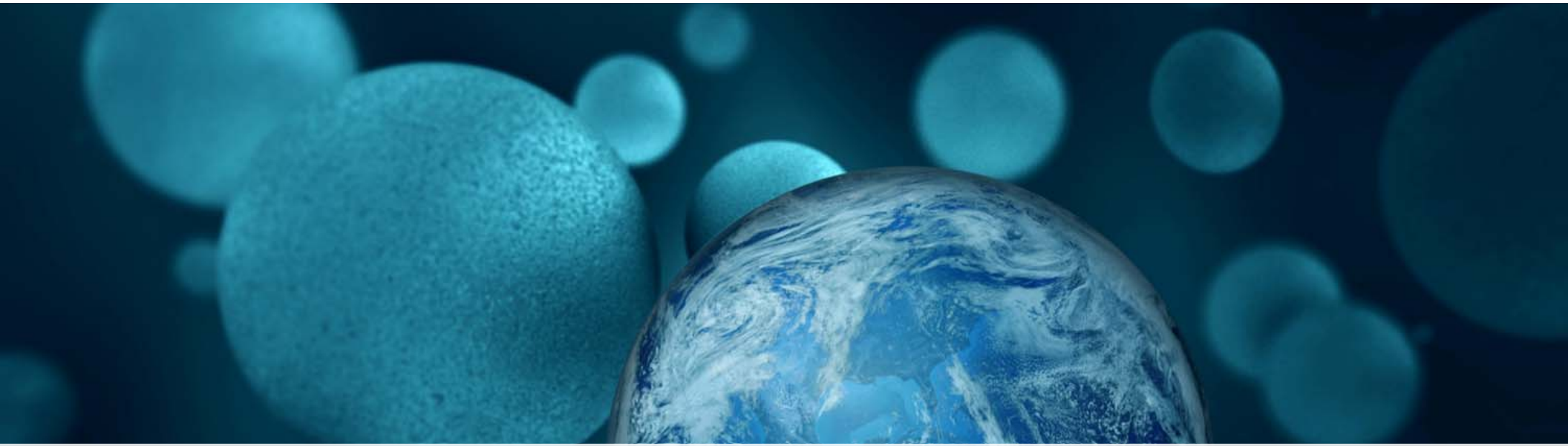

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Fast Analysis of Haloacetic Acids, Bromate and Dalapon Using Ion Chromatography Coupled with Mass Spectrometry

Richard Jack, Charanjit Saini, Chris Pohl, and Yan Liu

Disinfection Byproducts 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

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

Haloacetic Acids (HAA5 and HAA9)

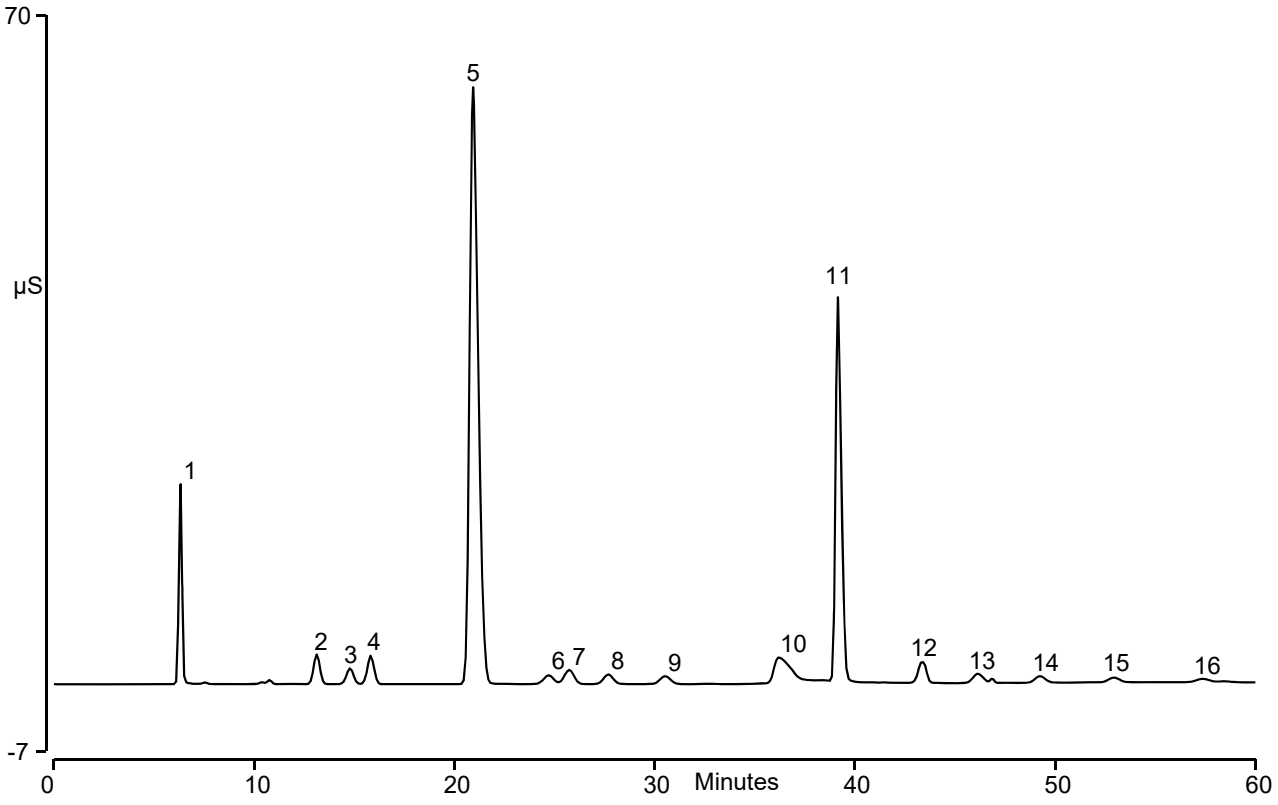
Acid	HAA	Formula	pK_a	Boiling Point (°C)
Monochloroacetic Acid	MCAA*	$ClCH_2CO_2H$	2.86	187.8
Dichloroacetic Acid	DCAA *	Cl_2CHCO_2H	1.25	194
Trichloroacetic Acid	TCAA *	Cl_3CCO_2H	0.63	197.5
Monobromoacetic Acid	MBAA *	$BrCH_2CO_2H$	2.87	208
Dibromoacetic Acid	DBAA *	Br_2CHCO_2H	1.47	195
Tribromoacetic Acid	TBAA**	Br_3CCO_2H	0.66	245
Bromochloroacetic Acid	BCAA**	$BrClCHCO_2H$	1.39	193.5
Chlorodibromoacetic Acid	CDBAA**	Br_2ClCCO_2H	1.09	NA
Bromodichloroacetic Acid	BDCAA**	Cl_2ClCCO_2H	1.09	NA

*HAA5; **HAA9

Summary of EPA Methods for HAAs (& Bromate, Dalapron)

Technique	EPA Method	Thermo Scientific™ 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	Thermo Scientific™ Dionex™ IonPac™ AG24 precolumn + Thermo Scientific™ 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)	557.1	First dimension: Dionex IonPac AG24A precolumn + Dionex IonPac AS24A separation column (4 mm i.d.)	Mono: 0.17–0.45
			Di: 0.06–0.13
		Second dimension: Thermo Scientific™ Dionex™ IonPac™ AG26 precolumn + Thermo Scientific™ Dionex™ IonPac™ AS26 separation column(0.4 mm i.d.)	Tri: 0.08–0.27

Separation of Haloacetic Acids, Dalapon, and Bromate in a Drinking Water Sample Obtained Using an IonPac AS24 Column



Column:	Dionex™ IonPac™ AG24/AS24
Eluent :	7mM from 0 to 16.8 min 7mM to 18mM KOH from 16.8 to 34.2 min 18mM to 60mM from 34.2 to 51.2 min
Eluent Source:	Dionex™ EGC-500 KOH cartridge
Flow Rate:	0.30mL/min
Inj. Volume:	100µL
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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METHOD 557: Determination of 9 HAAs, Bromate and Dalapon in Drinking Water by IC with Electrospray Ionization Tandem Mass Spectrometry (IC-ESI-MS/MS)

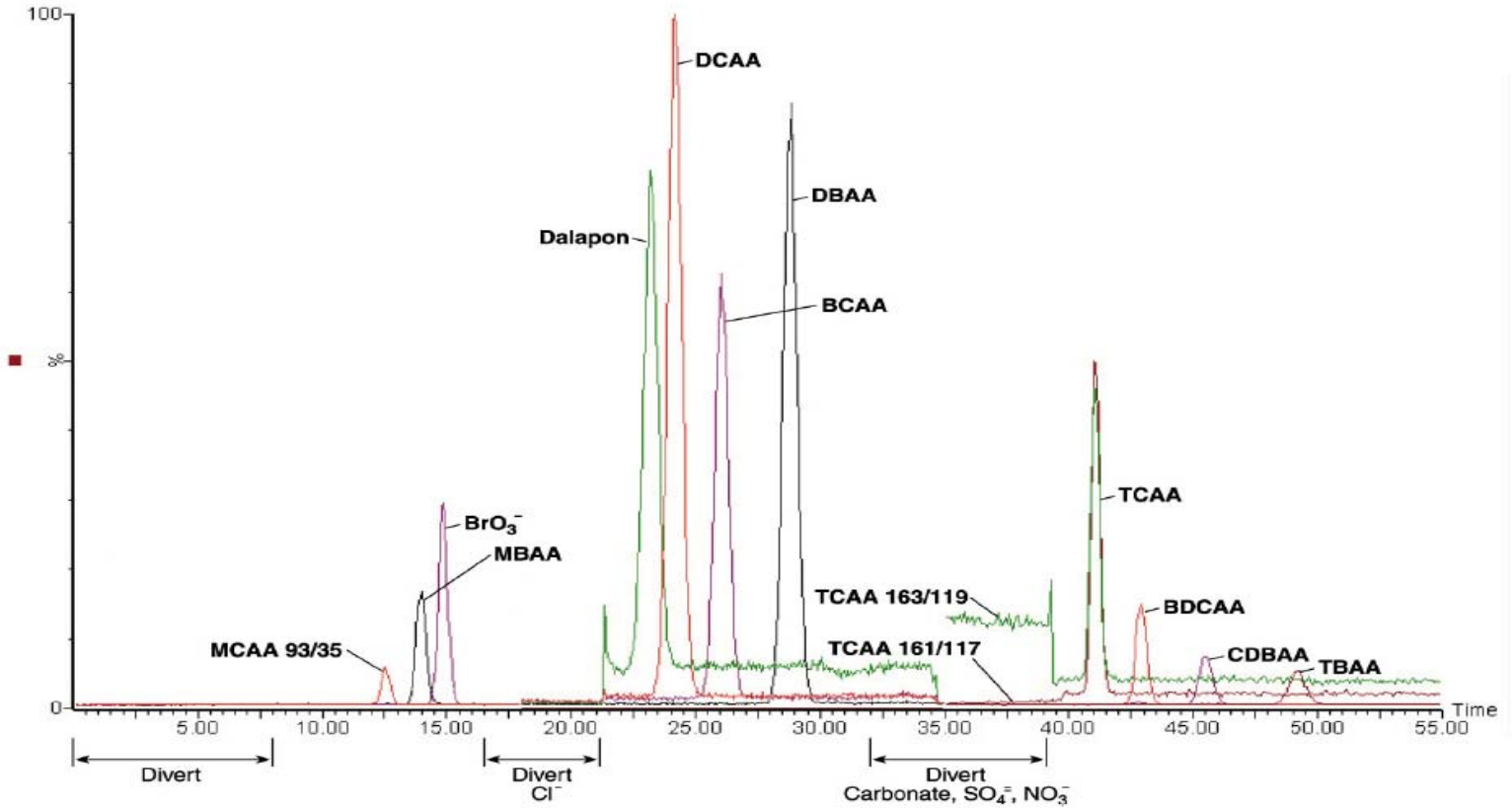

Figure 2. Dionex AS24 column: procedural calibration standard (5 µg/L).

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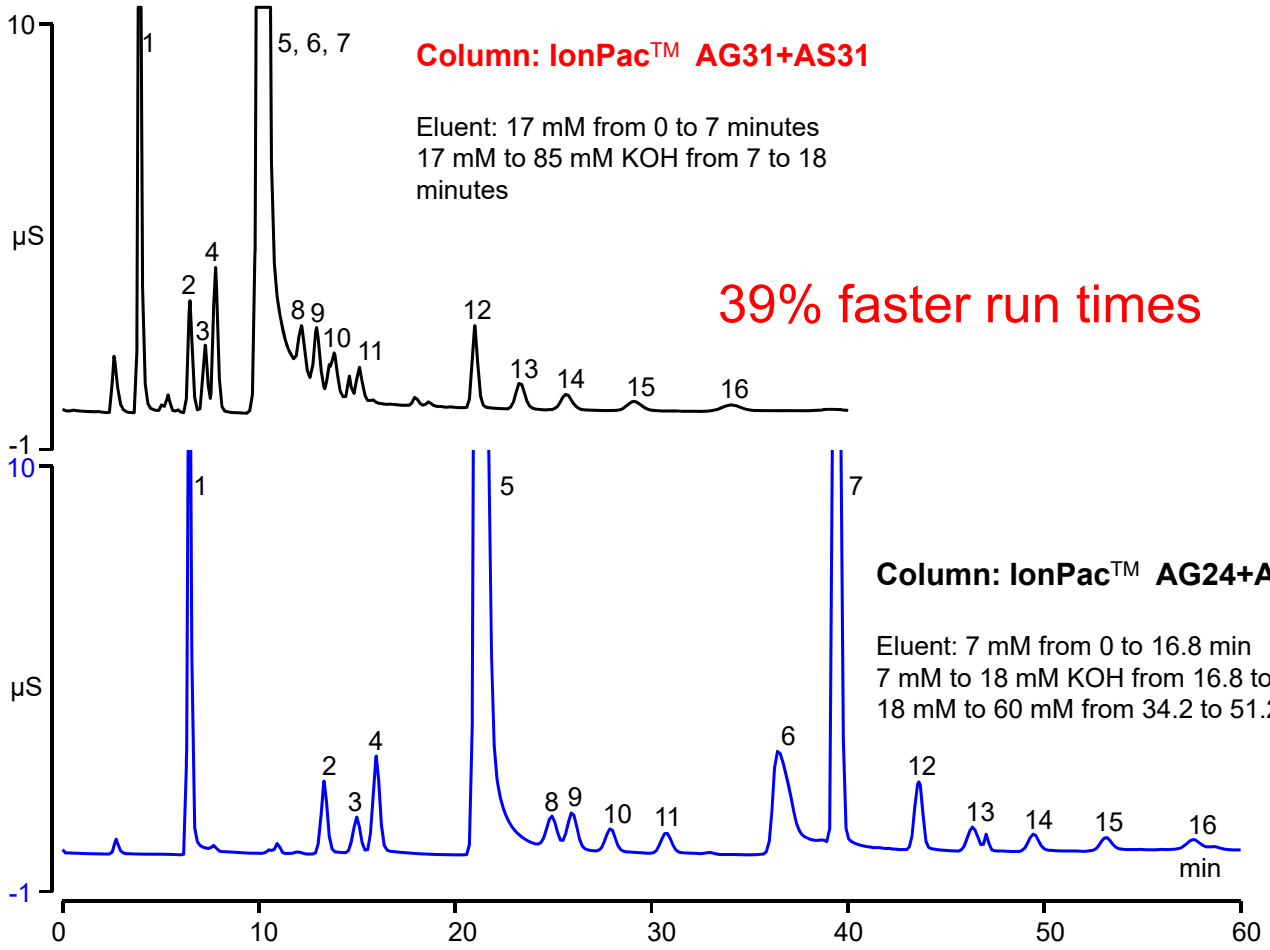
Separation of Haloacetic Acids, Dalapon, and Bromate in a Drinking Water Sample



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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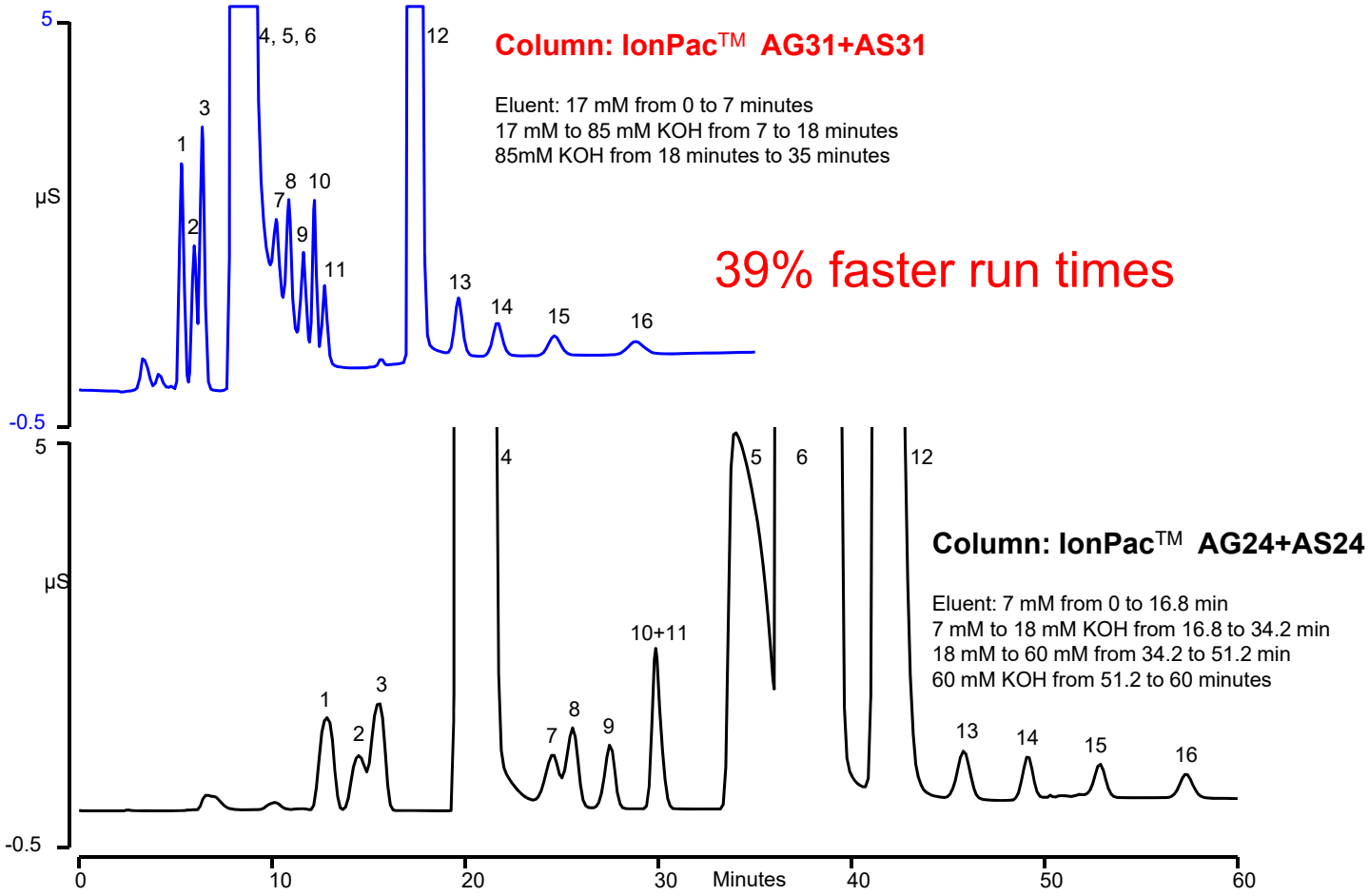
Separation of Haloacetic Acids, Dalapon, and Bromate in EPA Method 557 LSSM Matrix



Column: IonPac™ AG31+AS31

Eluent: 17 mM from 0 to 7 minutes
17 mM to 85 mM KOH from 7 to 18 minutes
85mM KOH from 18 minutes to 35 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
60 mM KOH from 51.2 to 60 minutes

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 2-mm AutoSuppression, recycle mode

Peaks (Standard):	mg/L
1. Monochloroacetate	1.0
2. Monobromoacetate	1.0
3. Bromate	1.0
4. Chloride	316
5. Sulfate	250
6. Carbonate	150
7. Dalapon	1.0
8. Dichloroacetate	1.0
9. Bromochloroacetate	1.0
10. Nitrite	0.25
11. Dibromoacetate	1.0
12. Nitrate	20.0
13. Trichloroacetate	1.0
14. Bromodichloroacetate	1.0
15. Chlorodibromoacetate	1.0
16. Tribromoacetate	1.0

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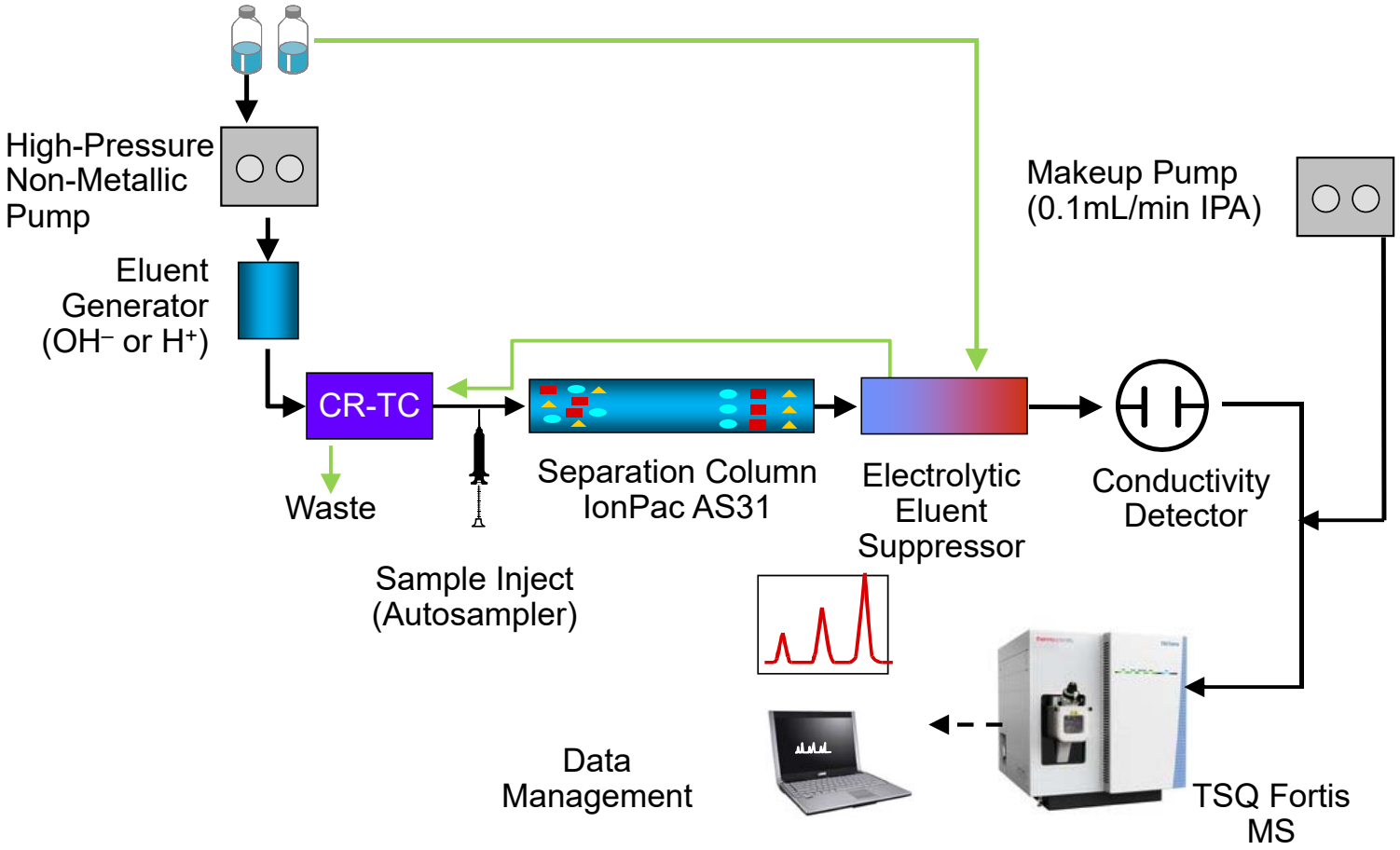
Laboratory Fortified Matrix

- Sulfate in drinking water currently has a secondary maximum contaminant level (SMCL) of 250 mg/L, based on aesthetic effects (i.e., taste and odor); this regulation is not a Federally-enforceable standard, but is provided as a guideline for states and public water systems;
- Chloride 250 mg/L
- Carbonate 150 mg/L
- Nitrate 20 mg/L
- Ammonium chloride 100 mg/L (chlorine scavenger)

IC-MS System Setup Using a Dionex™ IonPac™ AS31 Column



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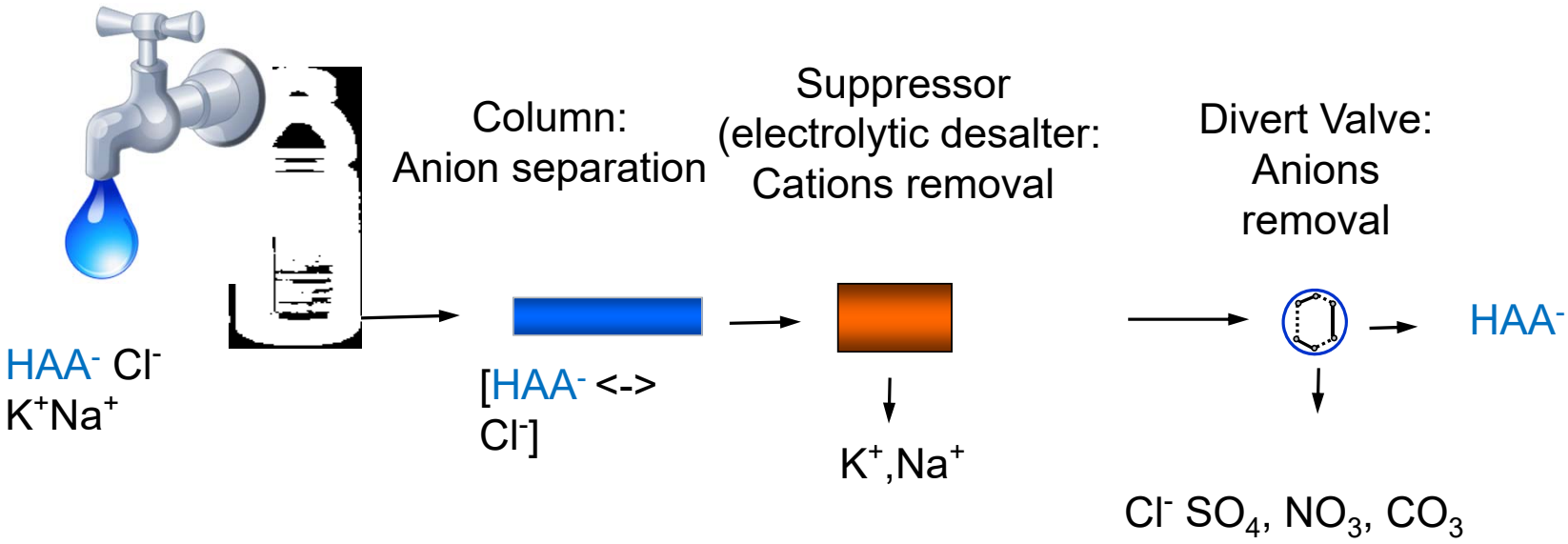
Matrix Elimination of Anions and Cations by Ion Exchange Chromatography



Strategy to eliminate signal suppression in the MS

IC-MS System Operating Conditions Using a Dionex™ IonPac™ AS31Column

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

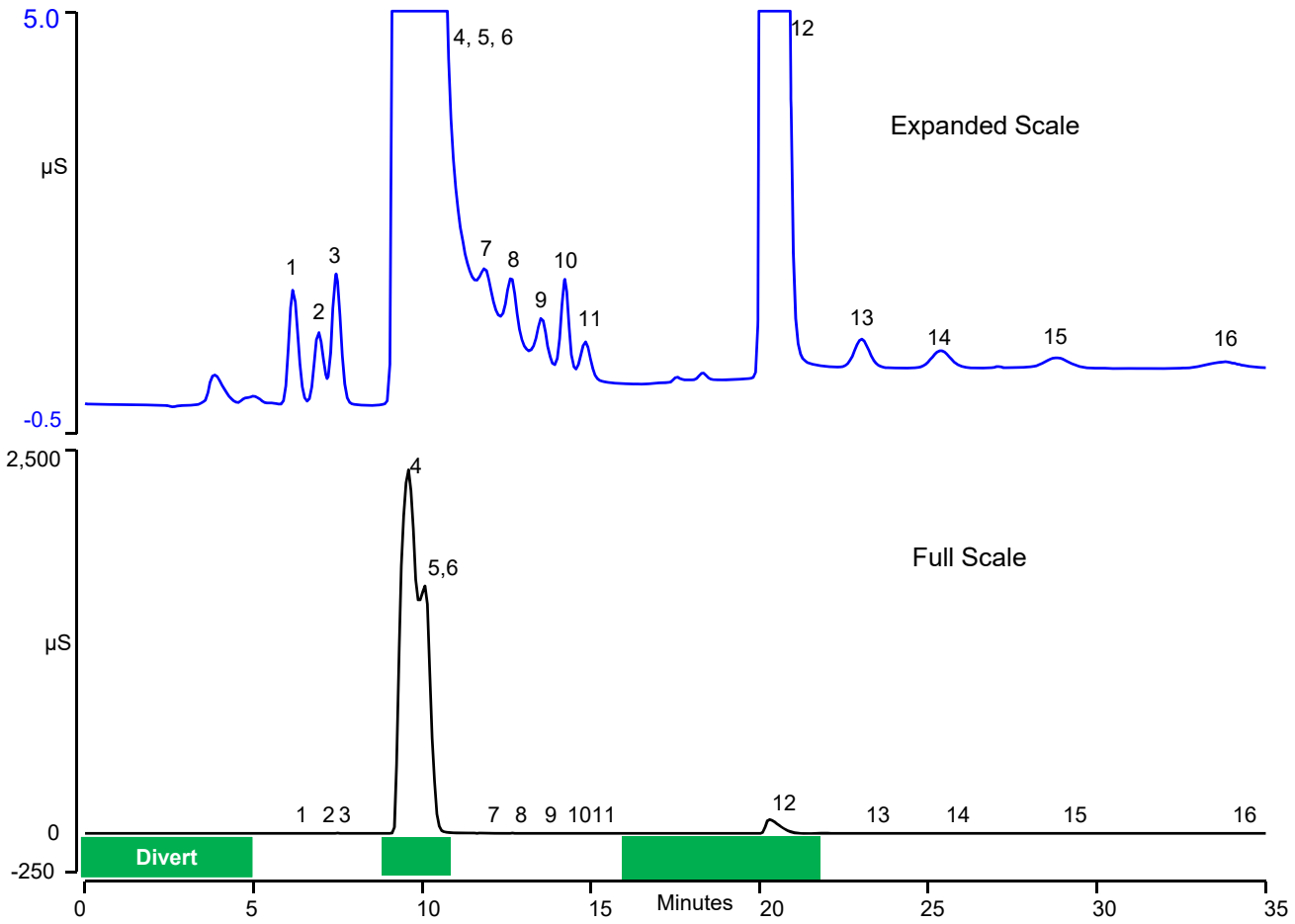
TSQ Fortis Tune Parameters:

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		

Separation of 9 HAAs, Dalapon, and Bromate in EPA Method 557 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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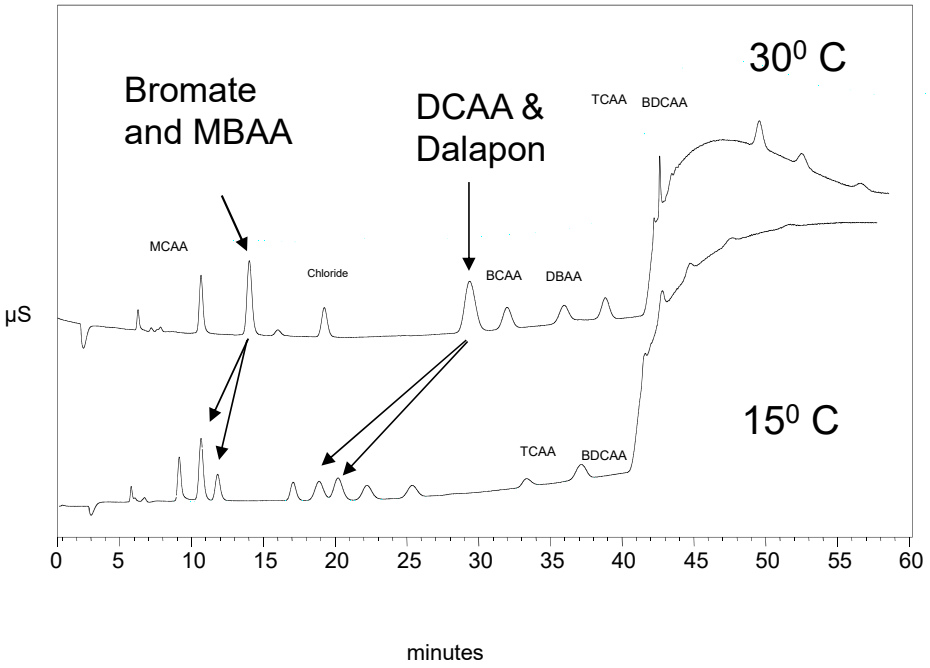
Separation at 15^0C versus 30^0C



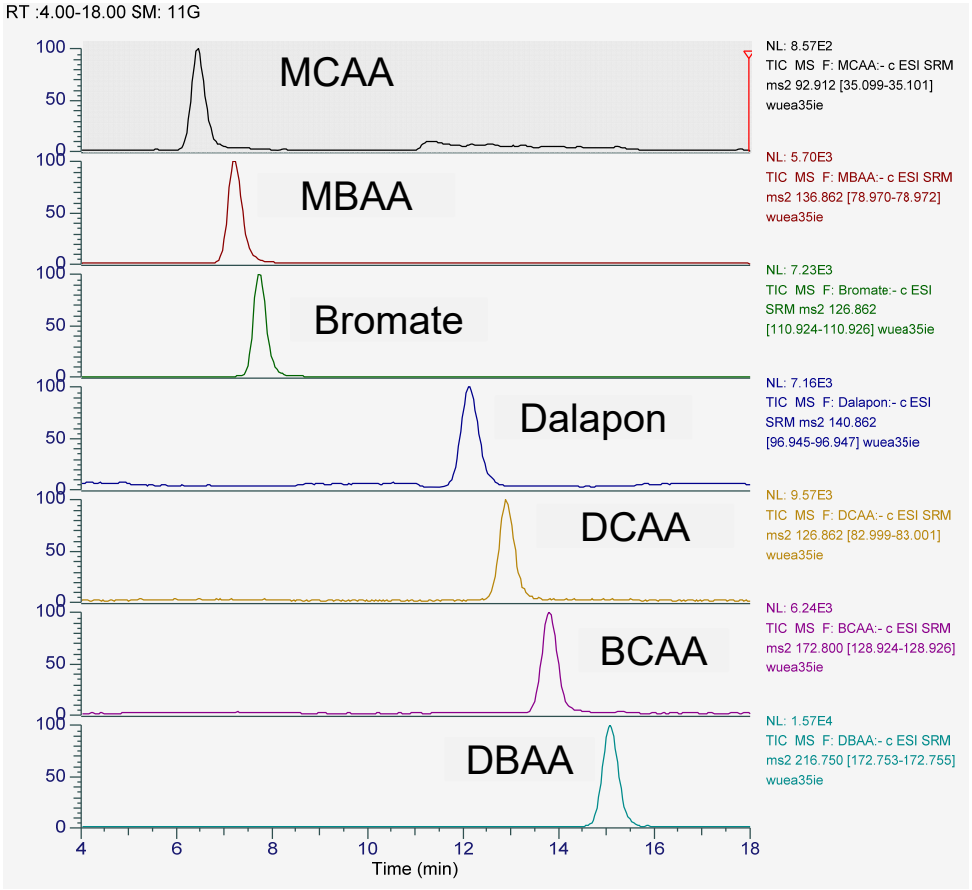
Higher Temperature

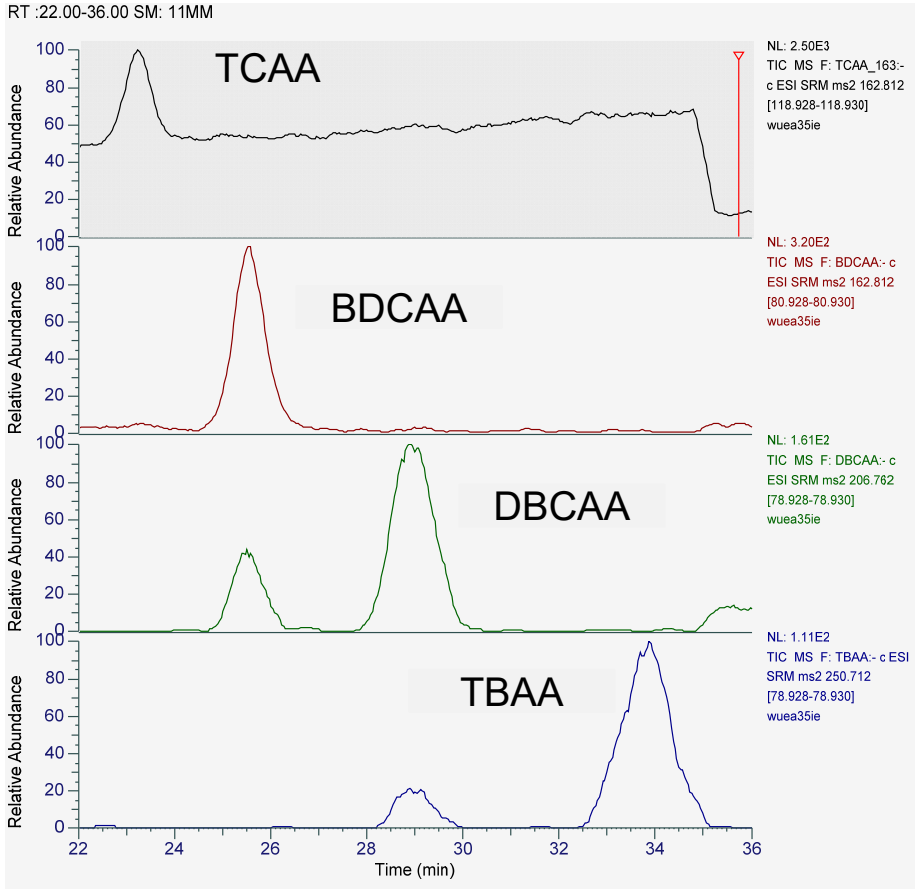
- Co-elution
- Higher MDLs

Lower temperature

- Better separation of bromate and MBAA
- Better Separation of Dalapon and DCAA
- Significantly lower degradation rate of unstable analytes
  - Lower MDLs of unstable analytes
- Faster separations

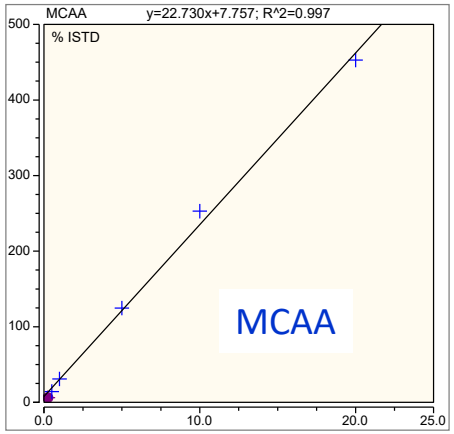
IC-MS Results for 9 HAAs, Dalapon and Bromate

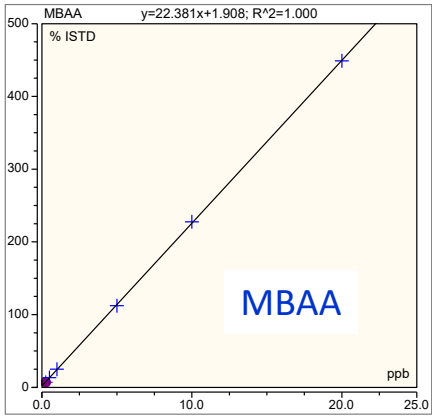


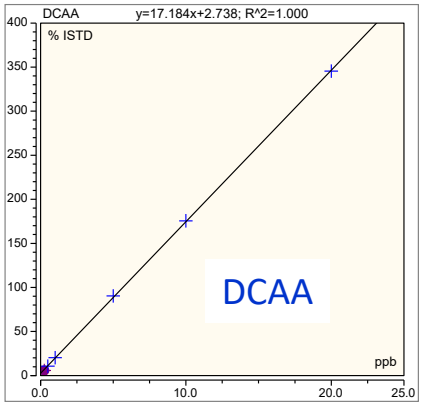


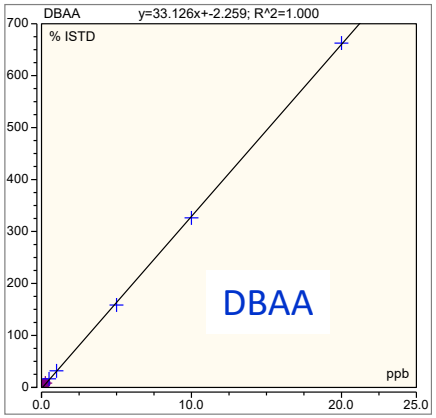
Concentrations of 9 HAAs, Dalapon and Bromate are 5 ppb in 100 mg/L NH_4Cl

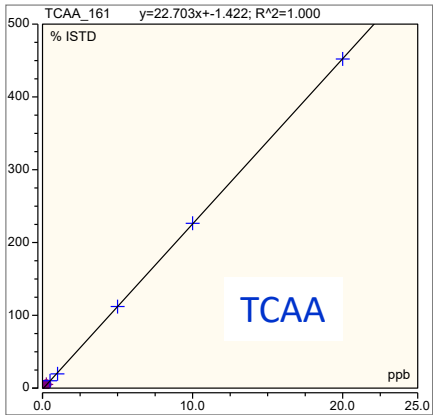
Calibration Curves: Five Regulated HAAs, Bromate, and Dalapon

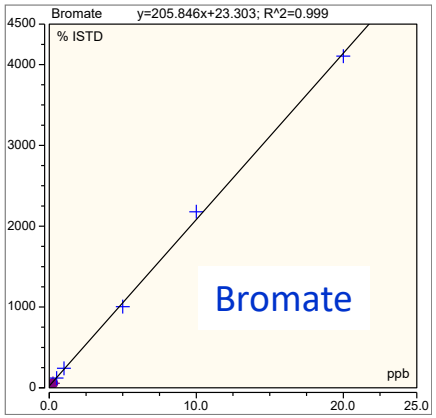


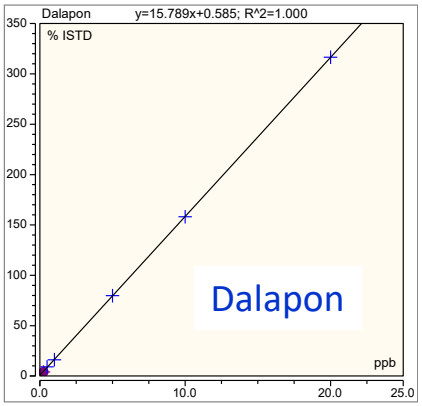












Linear curves obtained from 0.25-20 ppb with all R^2>0.99 for five regulated HAAs, Bromate and Dalapon

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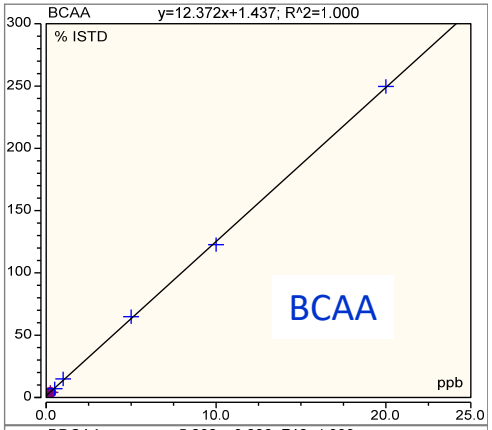
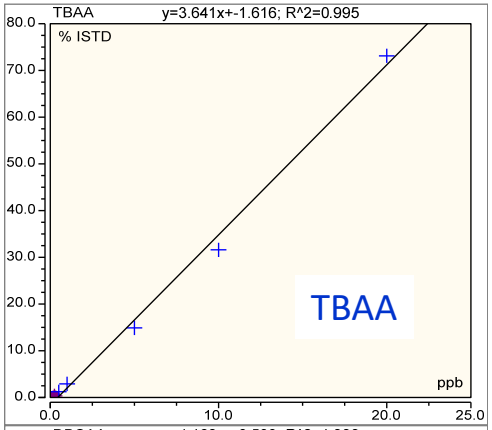
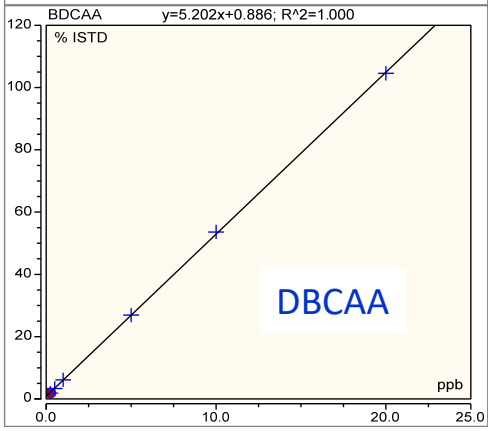
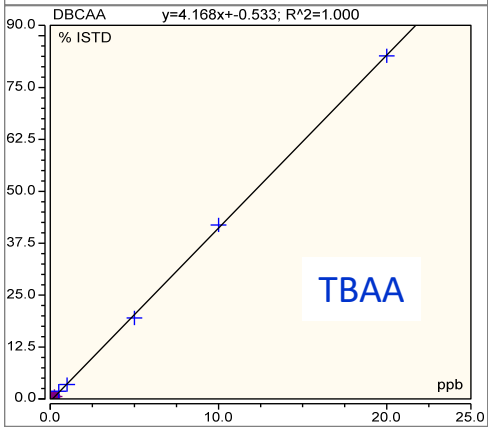
Calibration Curves : BCAA, BDCCA, DBCAA, and TBAA









Linear curves obtained from 0.25-20 ppb with all R^2>0.99 for the other 4 unregulated HAAs

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Recovery of 2µg/L HAAs, Delapon and Bromate Spiked 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

Recovery of 2µg/L HAAs, Delapon and Bromate in a City Tap Water Sample

Analytes	City Tap Water		City S water spiked 2µg/L	
	Conc.	%RSD	REC (%)	RSD (%)
MCAA	2.706	2.0	107.6	5.1
MBAA	0.078	4.9	104.2	4.0
Bromate	0.084	5.4	99.0	4.5
Dalapon	0.288	5.0	102.8	4.0
DCAA	12.36	0.8	107.0	2.0
BCAA	2.431	3.2	93.6	3.2
DBAA	0.339	0.4	94.8	2.2
TCAA_163	4.484	0.5	98.1	5.4
BDCAA	1.107	10	104.2	7.0
DBCAA	--	--	108.1	5.7
TBAA	--	--	102.7	5.7
AVG			102.0	4.4

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

IC-MS Method Detection Limits Obtained Using Dionex™ IonPac™ AS31Columns

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

EPA 557 Scope

- Sample Preservation
  - Ammonium Chloride (100 ppb) added to prevent HAA formation.
  - All standards are prepared in Ammonium Chloride.
- Sample prep cannot be changed
  - No pre-concentration or matrix cleanup
- QC requirements cannot be altered
- Laboratory Synthetic Sample Matrix
  - with NH_4Cl preservative

Compound	Conc. LSSM (mg/L)
Nitrate anion	20
Bicarbonate anion	150
Chloride anion	320
Sulfate anion	250

- Requires chromatographic resolution from common anions in DW
- 4 internal standards must be used.

EPA 557 Method aspects

- Analysis batch cannot exceed 24 hrs.
- Must use MS/MS, not MS
- Determination of the cut window
- Calibration acceptance criteria…

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

Summary

- Thermo Scientific™ Dionex™ IonPac™ AS31 columns are packed with a novel anion exchange resin developed specifically for faster analysis of haloacetic acids (HAAs), bromate, and dalapon.
- AS31 columns have high ion exchange capacity and allow large loop injections for trace analysis (µg/L) without sample pre-treatment.
- AS31 columns operates at 15 °C and about 3200 psi, so a Thermo Scientific Dionex ICS-5000+ or ICS-6000 HPIC system is required.
- AS31 columns can meet or exceed the performance requirements of EPA Method 557.
- AS31 columns deliver 39% faster run times relative to IonPac AS24 columns, reducing the EPA Method 557 run time from 57 minutes to 35 minutes

Thank You!

Questions?