

ThermoFisher
S C I E N T I F I C

Analysis of Disinfection Byproducts by Ion Chromatography

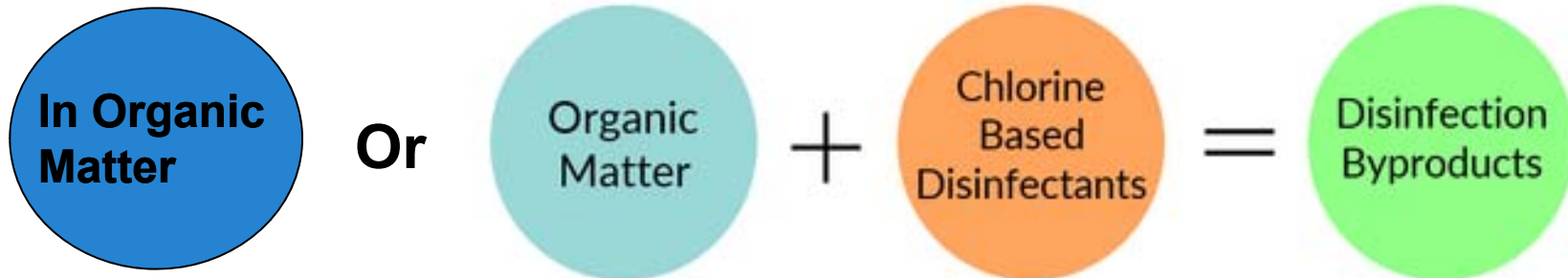
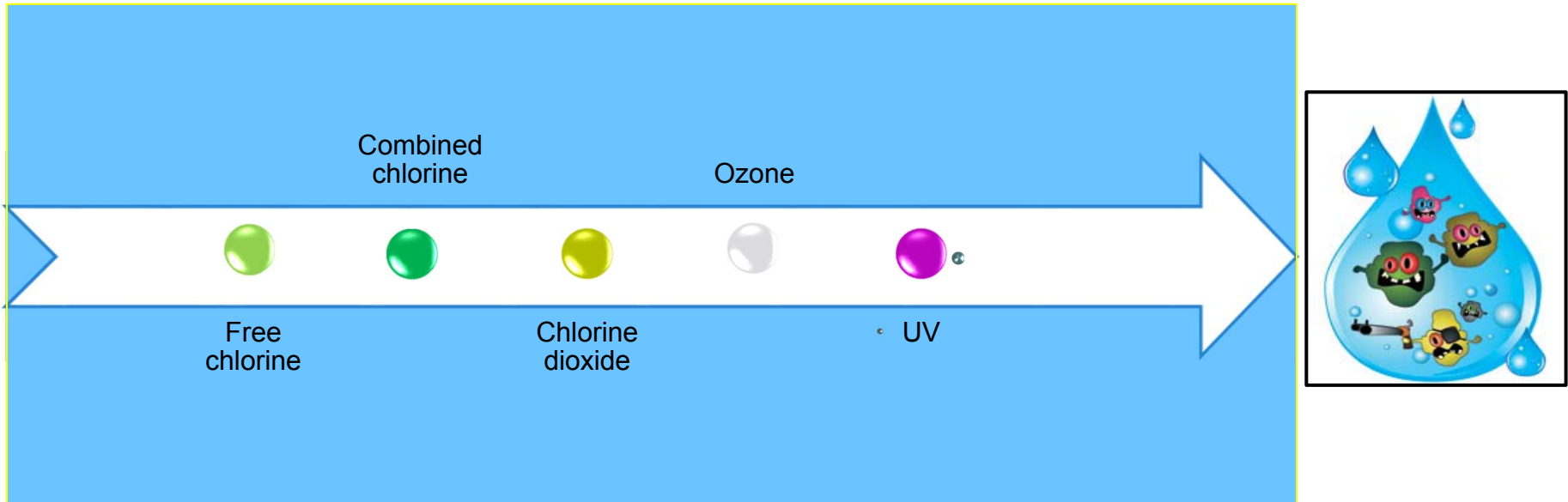
Elsamoul Hamdnalla
Thermo Fisher Scientific

The world leader in serving science

Objectives:

- Provide a better understanding of the simplicity of current IC technology, operation and main applications for disinfection byproducts
- Disinfection byproduct analysis by
 - Single channel IC
 - Two-Dimensional IC
 - IC-Mass Spectrometry
 - Bromate, Chlorite and chlorate
 - HAAS

Common Drinking Water Disinfectants



Toxic Disinfection Byproducts (DBPs)

Highly regulated due to associated health issues



Disinfection Byproducts in Drinking Water

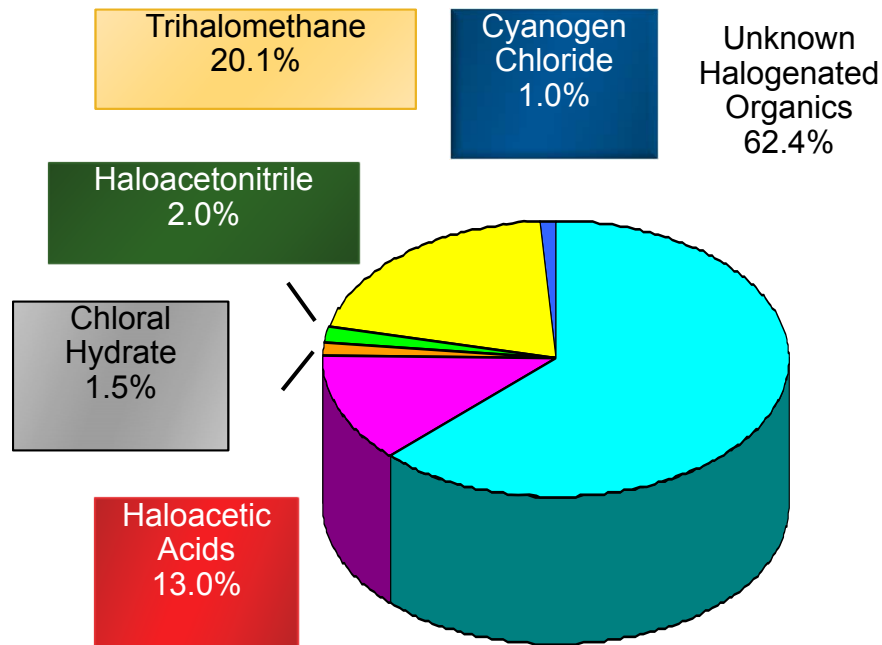
- Disinfection treatment is essential to eliminate waterborne disease-causing microorganisms
- Ozonation – bromate
- Chlorination (chlorine, Chlorine dioxide or chloramine)
 - Bromate, Chlorite, chlorate and perchlorate
 - Trihalomethanes (THM) and haloacetic acids (HAAs)
- Highly regulated due to associated 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 in the U.S. under the Safe Drinking Water Act
- EPA promulgated to the states



Disinfection Byproducts in Drinking Water

Occurrence of Disinfectant Byproducts

The WHO Guideline Parameters



The WHO guideline for inorganic Disinfection byproducts in $\mu\text{g/ml}$.

Residual Cl_2 < 0.50

Residual ClO_2 < 0.80

BrO_3^- < 0.010

ClO_2^- < 0.700

ClO_3^- < 0.700

THM's : The sum of the ratio of the concentration of each to its respective guideline value should not exceeded 1.0

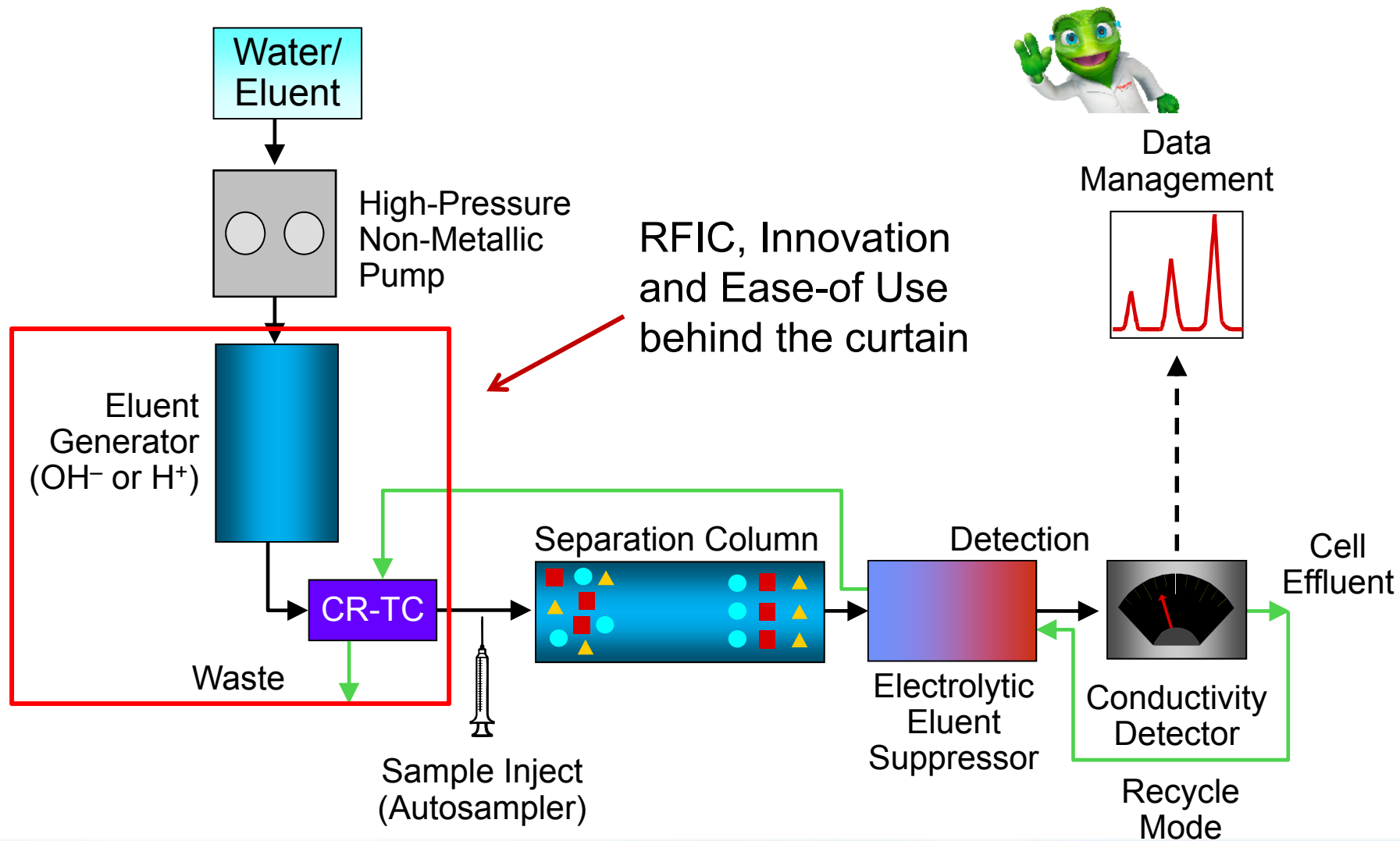
Disinfectant Byproduct (DBP) Regulations

- 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

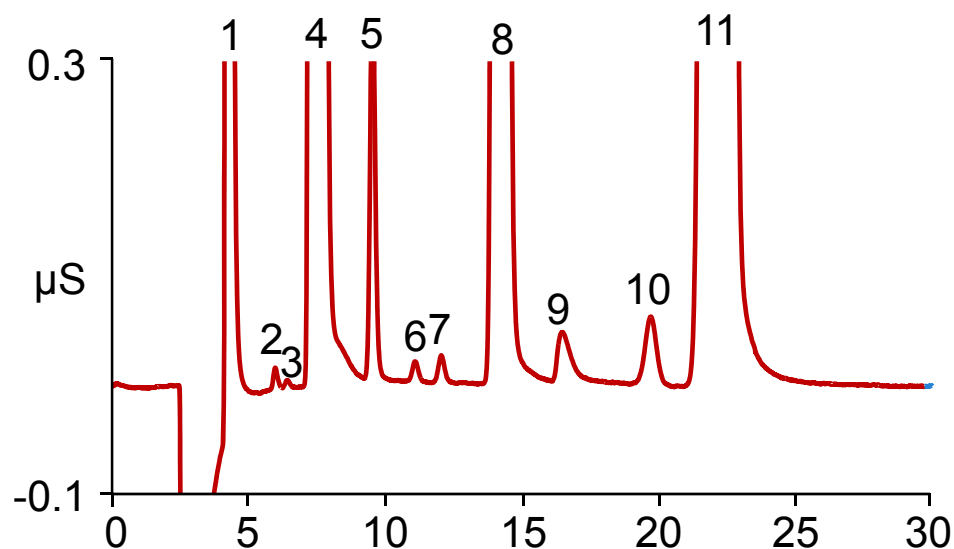
Bromate Method Summary

IC Technique	EPA Method	Dionex IonPac Columns	Eluent	Thermo Scientific Application	MDL (ppb)
Suppressed Cond.	300.0 (B)	Dionex IonPac AS9-HC or Dionex IonPac AS23 column	Carbonate	AN167	CD 5.0, 1.63
		Dionex IonPac AS19 column	Hydroxide	AN184	0.32
Suppressed Cond.	300.1	Dionex IonPac AS9-HC or Dionex IonPac AS23 column	Carbonate	AN167	5.0, 1.63
		Dionex IonPac AS19 column	Hydroxide	AN184	0.32
2D-IC Suppressed Cond.	302.0	4 mm Dionex IonPac AS19 to 2 mm Dionex IonPac AS24 column	Hydroxide	AN187	0.036
		4 mm Dionex IonPac AS19 to 0.4 mm Dionex IonPac AS20 column	Hydroxide	AN187	0.20
Suppressed Cond. + Postcolumn ODA	317.0	Dionex IonPac AS9-HC column	Carbonate	AN168	UV/vis
		Dionex IonPac AS19 column	Hydroxide	AN168	0.14
Suppressed Cond. + Postcolumn acidified KI	326.1	Dionex IonPac AS9-HC column	Carbonate	AN171	5.0, 1.63
		Dionex IonPac AS19 column	Hydroxide	---	0.17
IC-ICP/MS	321.8	Thermo Scientific™ Dionex™ IonPac™ AS19 column	Hydroxide	AN43227	MS 0.014

Reagent-Free IC System (RFIC™)



Determination of Trace Concentrations of Bromate Using Prepared Eluents (Isocratic)



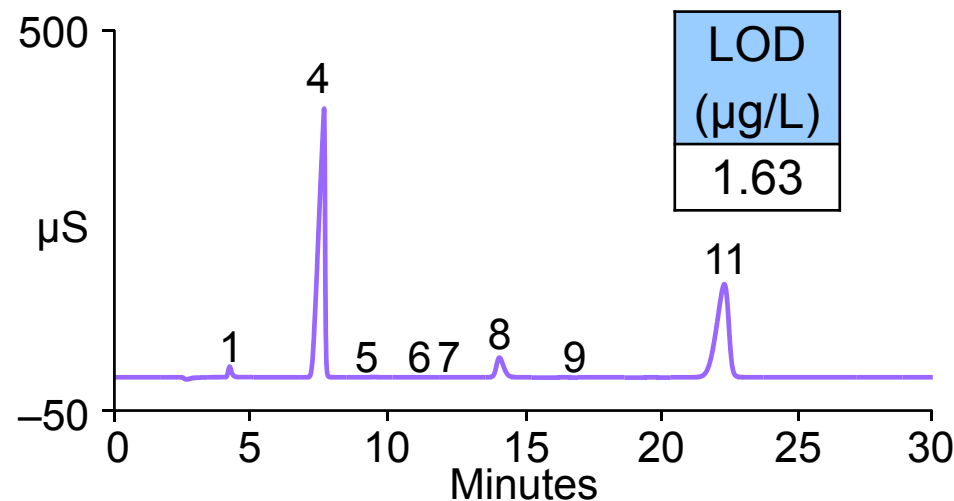
Columns: Dionex IonPac AG23, AS23, 4 mm
 Eluents: 4.5 mM Sodium carbonate/
 0.8 mM Sodium bicarbonate

Temperature: 30 °C

Flow Rate: 1.0 mL/min

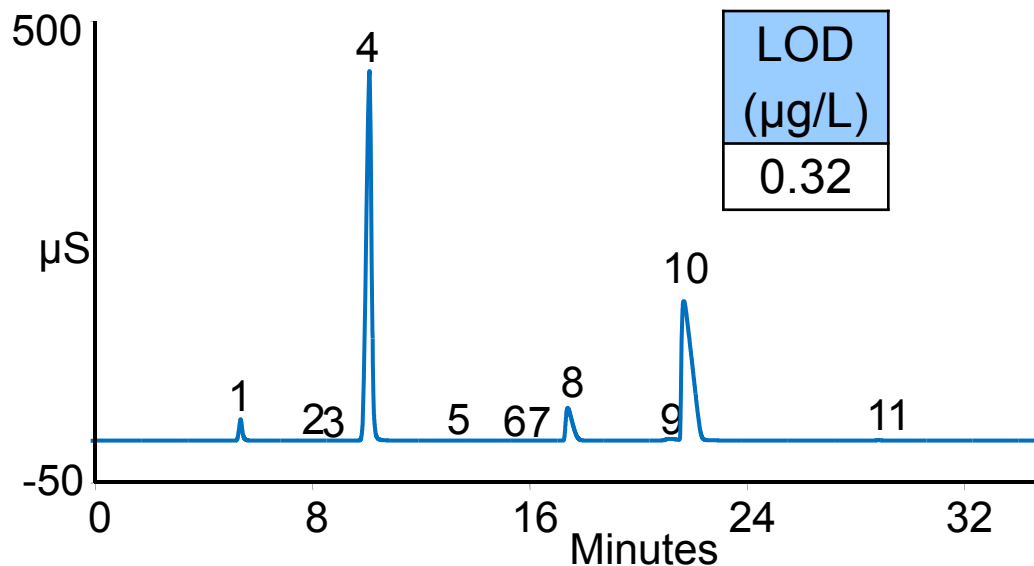
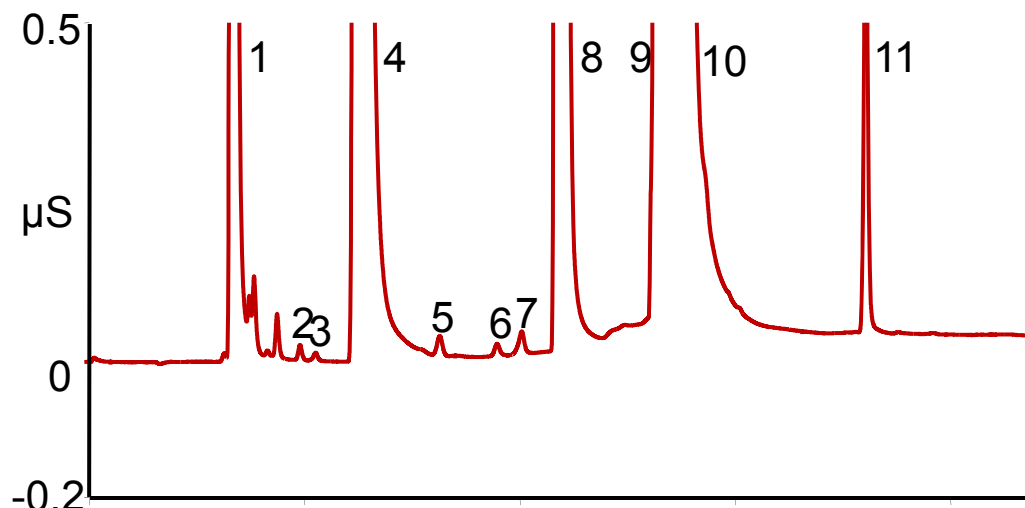
Inj. Volume: 200 µL

Detection: Suppressed conductivity,
 Dionex ASRS, 4 mm,
 AutoSuppression™,
 external water mode



Peaks:	Concentration	Unit
1. Fluoride	1.0	mg/L (ppm)
2. Chlorite	0.01	
3. Bromate	0.005	
4. Chloride	50	
5. Nitrite	0.1	
6. Chlorate	0.01	
7. Bromide	0.01	
8. Nitrate	10	
9. Carbonate	50	
10. Phosphate	0.1	
11. Sulfate	50	

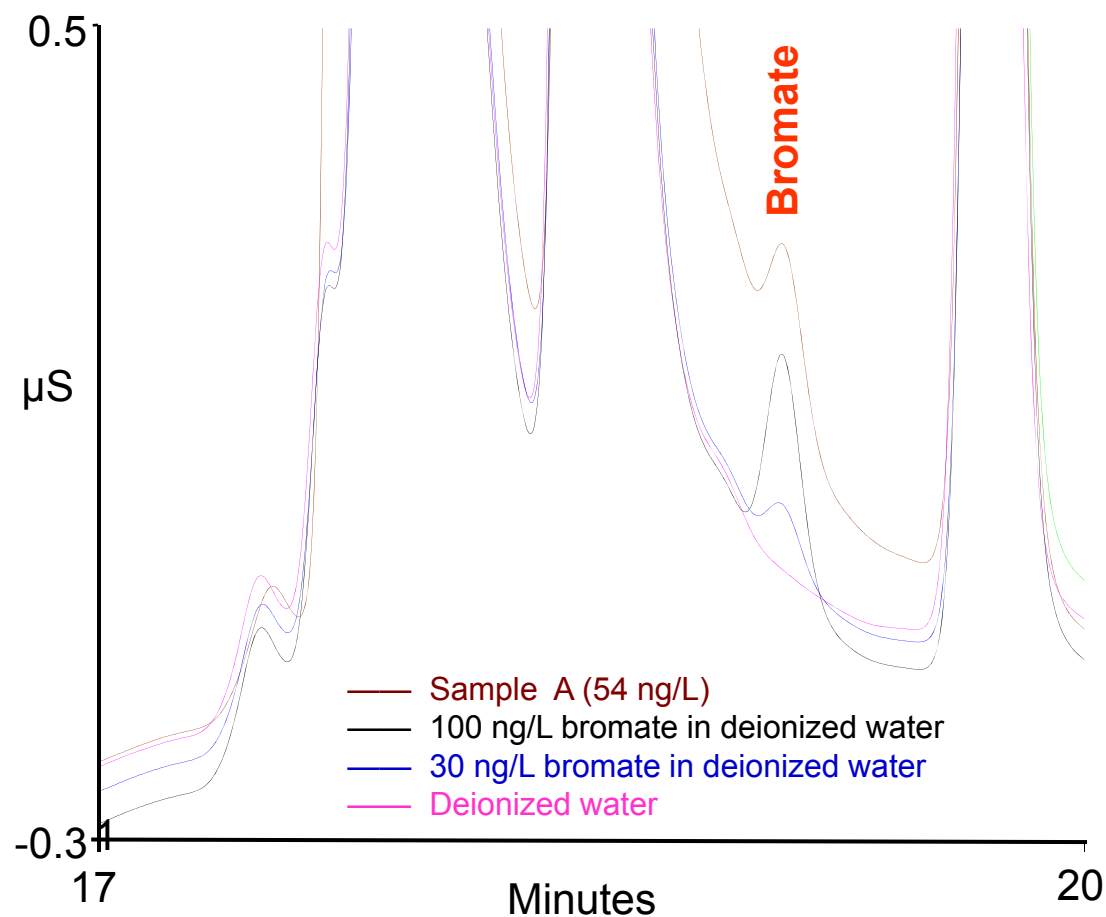
Bromate in Simulated Drinking Water



System: Thermo Scientific™ Dionex™ ICS-5000+ HPIC system
 Column: Thermo Scientific™ Dionex™ IonPac™ AS19-4µm + guard (4 × 250 mm)
 Eluent : 10 mM KOH from 0 to 10 min, 10–45 mM KOH from 10 to 25 min
 Eluent Source: Thermo Scientific™ Dionex™ EGC 500 KOH Cartridge
 Flow Rate: 1.0 mL/min
 Inj. Volume: 200 µL
 Temperature: 30 °C
 Detection: Suppressed Conductivity, Thermo Scientific™ Dionex™ AERS™ 500 suppressor, 4 mm AutoSuppression, recycle mode
 Sample: Simulated Drinking Water

Peaks:	Concentration	Unit
1. Fluoride	1.0	mg/L
2. Chlorite	0.005	
3. Bromate	0.005	
4. Chloride	50.0	
5. Nitrite	0.005	
6. Chlorate	0.005	
7. Bromide	0.005	
8. Nitrate	10.0	
9. Carbonate	25.0	
10. Sulfate	50.0	
11. Phosphate	0.20	

Trace Analysis of Bromate in Bottled Water by 2-D IC



A. 1st Dimension

Column: Dionex IonPac AG19, AS19,
4 mm
Flow rate: 1 mL/min
Eluent: 10-60 mmol/L KOH (EG)
Suppressor: Thermo Scientific™ Dionex™
SRS 300 (4 mm)
Inj. volume: 1000 µL
Temperature: 30 °C

B. 2nd Dimension

Column: Thermo Scientific™ Dionex™
IonPac™ AS20 (0.4 mm)
Flow rate: 10 µL/min
Eluent: 35 mmol/L KOH (EG)
Suppressor: Thermo Scientific™ Dionex™
ACES™ 300
Temperature: 30 °C
Concentrator: Capillary concentrator,
2500 µL of the suppressed
effluent from the 1st dimension
(7.5–10 min)

Haloacetic Acids (HAA5, HAA6Br, and HAA9)

Acid	HAA	Formula	pK _a
Monochloroacetic Acid	MCAA	ClCH ₂ CO ₂ H	2.86
Dichloroacetic Acid	DCAA	Cl ₂ CHCO ₂ H	1.25
Trichloroacetic Acid	TCAA	Cl ₃ CCO ₂ H	0.63
Monobromoacetic Acid	MBAA	BrCH ₂ CO ₂ H	2.87
Dibromoacetic Acid	DBAA	Br ₂ CHCO ₂ H	1.47
Tribromoacetic Acid	TBAA	Br ₃ CCO ₂ H	0.66
Bromochloroacetic Acid	BCAA	BrClCHCO ₂ H	1.39
Chlorodibromoacetic Acid	CDBAA	Br ₂ ClCCO ₂ H	1.09
Bromodichloroacetic Acid	BDCAA	Cl ₂ BrCCO ₂ H	1.09

HAA5

HAA6Br

HAA9

UCMR* 4 (2017-2021, 30 contaminants)

Regulated (EPA)

**Unregulated Contaminant Monitoring Rule*

Summary of EPA Methods for HAAs

Technique	EPA Method	Dionex IonPac Columns	MDL (ppb)
1) Liquid/Liquid Extraction 2) Derivatization 3) GC-ECD	552.2	GC-ECD	Mono: 0.13–0.20
	552.3		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
2-D IC Suppressed Cond. (direct)	Pending (current 2-D IC methods: 302.0, 314)	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: Dionex IonPac AG26 precolumn + Dionex IonPac AS26 separation column(0.4 mm i.d.)	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)
 - Derivatization: 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
 - Multi-step process with potential procedural errors
 - Analytes are temperature sensitive

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

*HAA5; **HAA9

U.S. EPA Method 557

Suppressed ion chromatography with MS or MS-MS detection

- **Advantages**

- Direct injection method with matrix diversion
- Eliminates liquid-liquid extraction, derivatization and separation
- Eliminates co-elution issues because MS is a selective detector
- MS/MS provides confirmation information
- Fully automated
- Recovery > 90%

- **Limitations**

- Investment in MS
- Analytes are temperature sensitive

Matrix Elimination Ion Chromatography (2-D IC)

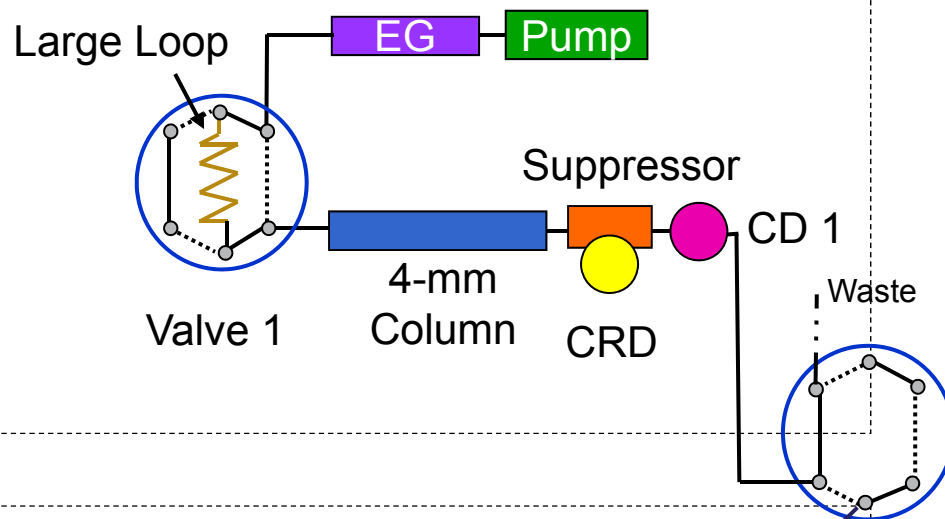
- First Dimension: Allows for large-loop loading of sample
- Concentrator and Second Dimension
 - Focuses the ions of interest onto a concentrator column
 - Resolves the analytes on a smaller diameter column
- Combined Effect
 - Enhanced sensitivity proportional to the column radius (r)² or flow rate
 - Enhanced selectivity by using different column chemistries
 - Convenience of using only one system designed with greater temperature control -- Dionex ICS-6000+ HPIC system
- Regulatory Acceptance
 - Approved for bromate (EPA 302) and perchlorate (314.2)
 - Pending approval for HAAs and hexavalent chromium

2-D IC: Increased Sensitivity with Capillary IC

1st Dimension

Large Loop injection

- Partially resolve analyte from matrix



Intermediate Step

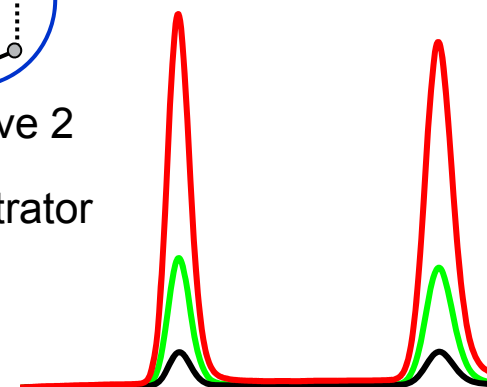
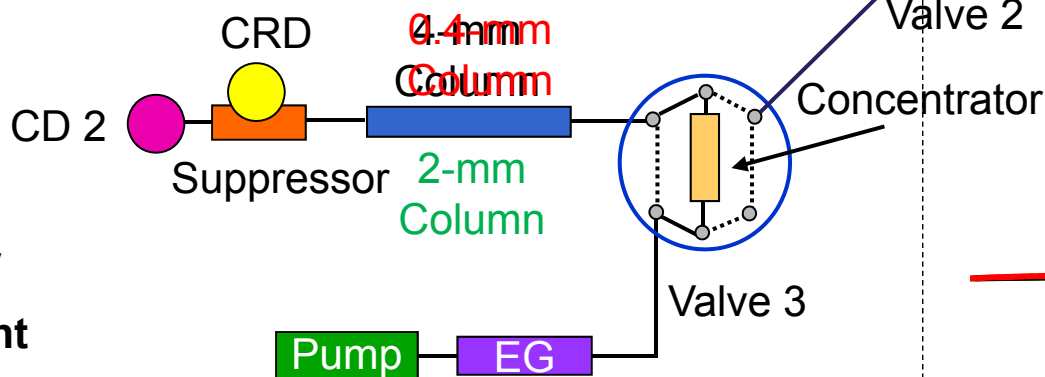
Transfer cut volume

- Trap and focus ions of interest

2nd Dimension

Separate on smaller ID column

- Different **selectivity**
- Signal **enhancement**



Introducing the ICS-6000 HPIC System: What's New

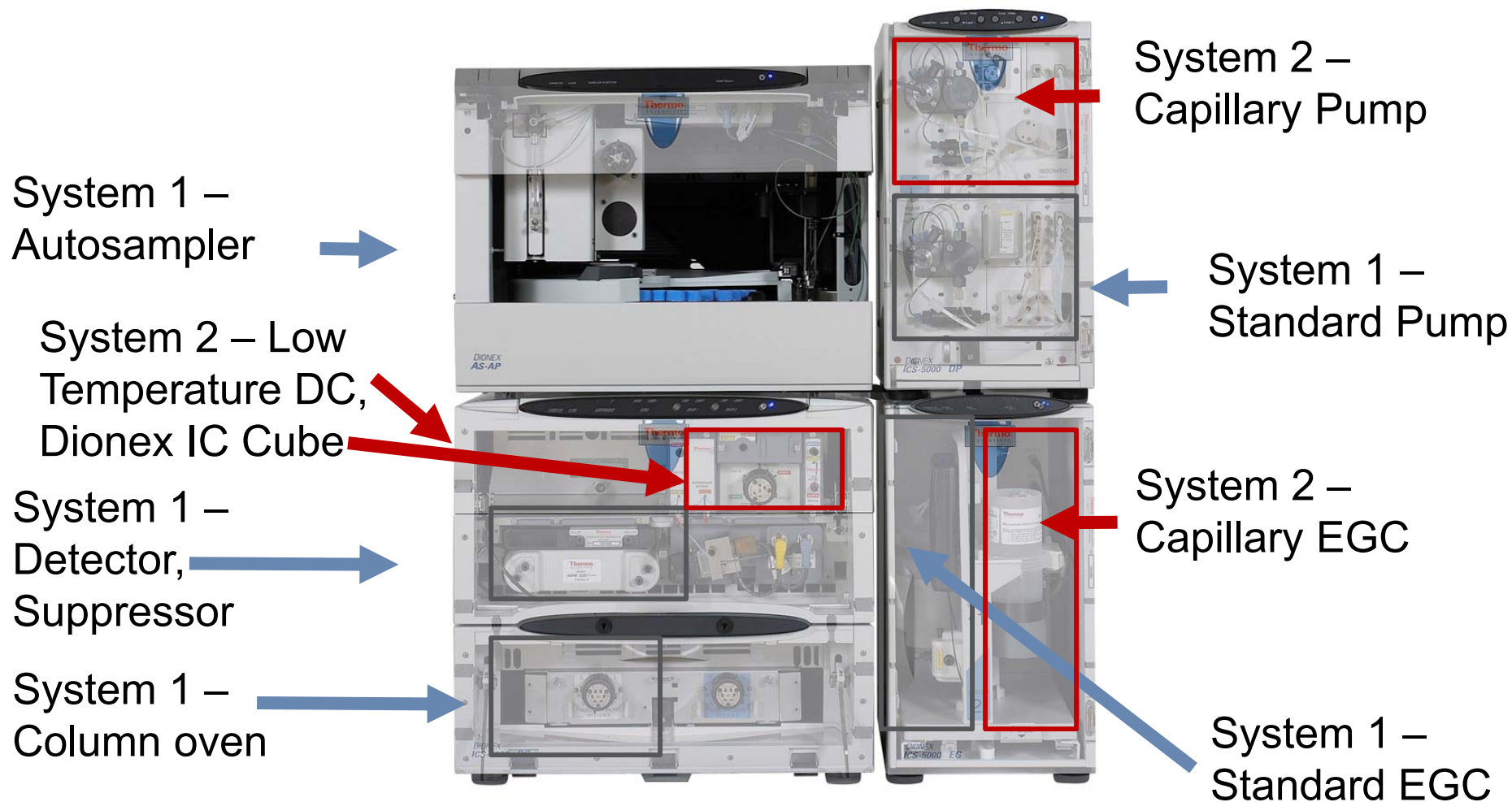
Thermo Scientific™ Dionex™ ICS-6000 HPIC System



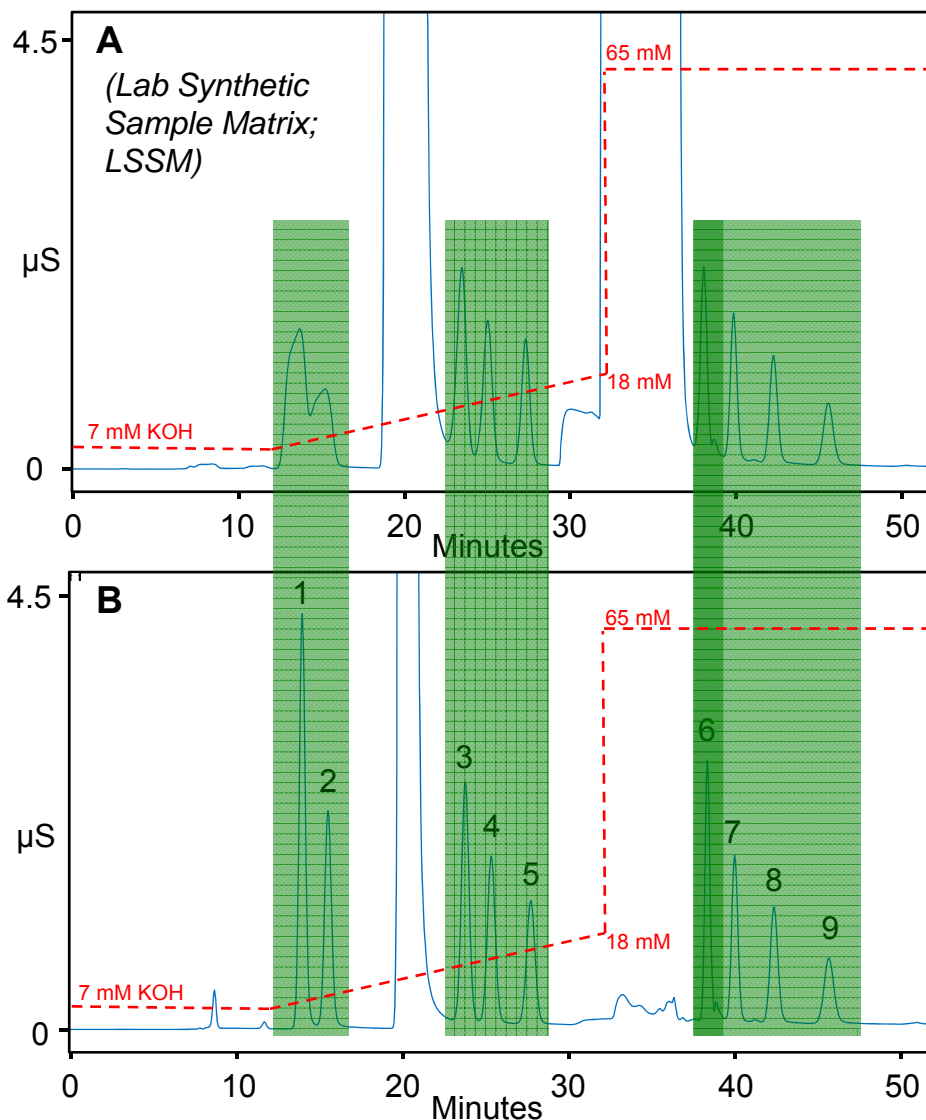
- Single or dual channel configurations
- IC PEEK Viper Fittings **NEW**
- Consumables Device Monitor **NEW**
- Unity™ Remote Services **NEW**
- Tablet control of the IC system **NEW**
- HPIC capable up to 5000 psi
- Automated Eluent Generation (RFIC-EG)
- Always ready system operation with Capillary IC

HPIC - High Resolution, Fast Analyses

Simplifying on a single IC: First Dimension – System 1



First Dimension Cuts: Dionex IonPac AS24A Column



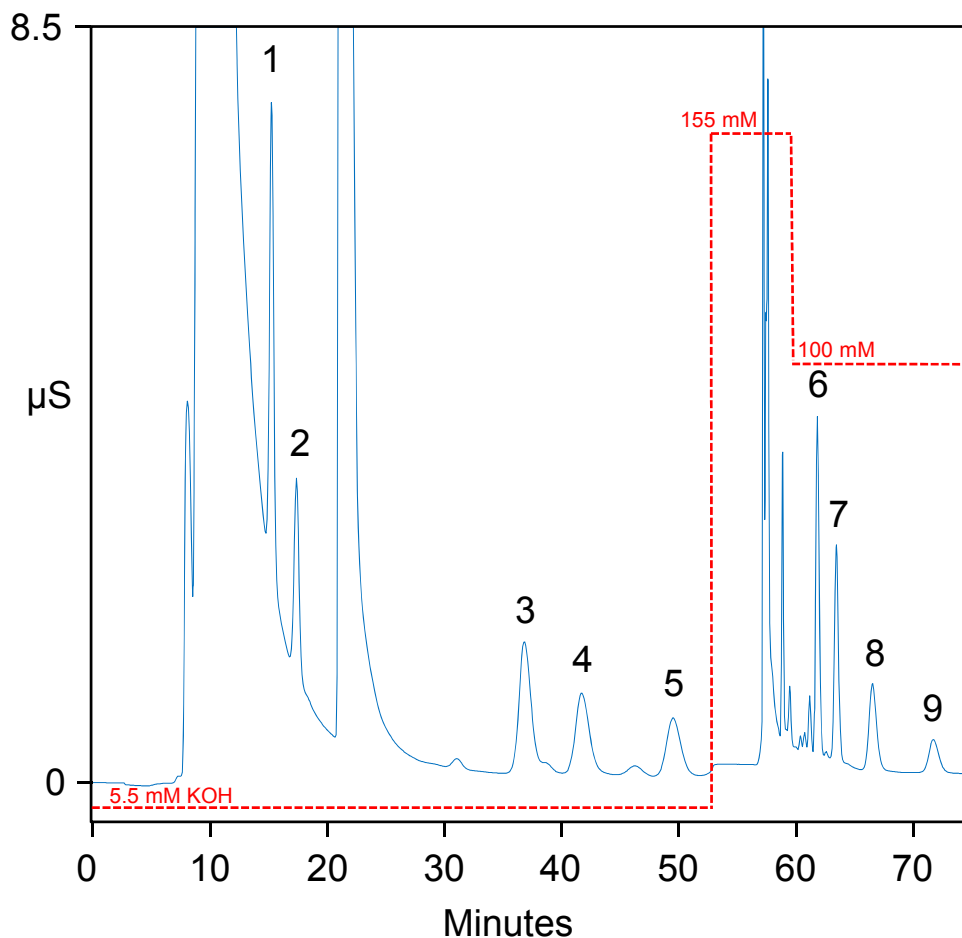
Columns: Dionex IonPac AG24A/AS24A, 4 mm
 Flow Rate: 1.0 mL/min
 Eluent: KOH: 7 mM KOH (0–12 min),
 7 to 18 mM (12–32 min),
 Step to 65 mM at 32.1 min
 Eluent Source: Thermo Scientific™ Dionex™ EGC-500
 KOH cartridge
 Detection: Suppressed conductivity,
 Thermo Scientific™ Dionex™ AERS 500
 Suppressor, 4 mm, 161 mA
 Inj. Volume: 500 µL
 Temp.: 15 °C
 Sample: 1 mg/L HAA9 in
 A. LSSM* B. 100 ppm NH₄Cl

Peaks:

12-17 min	1. MCAA	6. TCAA	37-39 min (HAA5)
	2. MBAA	7. BDCAA	
22-29 min	3. DCAA	8. CDBAA	37-48 min (HAA9)
	4. BCAA	9. TBAA	
	5. DBAA		

* LSSM = 250 ppm Cl, 250 ppm SO₄, 150 ppm HCO₃,
 10 ppm NO₃, 100 ppm NH₄Cl

Second Dimension: Dionex IonPac AS26 Column



Columns: Dionex IonPac AG26/AS26, 0.4 mm
Flow Rate: 0.012 mL/min
Eluent: KOH: 5.5 mM (0–50 min)
Step to 155 mM at 53 min
Step to 100 mM at 60 min
Eluent Source: Thermo Scientific 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.: 15 °C
Sample: 20 µg/L HAA9 in 100 ppm NH₄Cl

Peaks:

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

2-D IC: LCMRL Results Vs. U.S. EPA Method 557

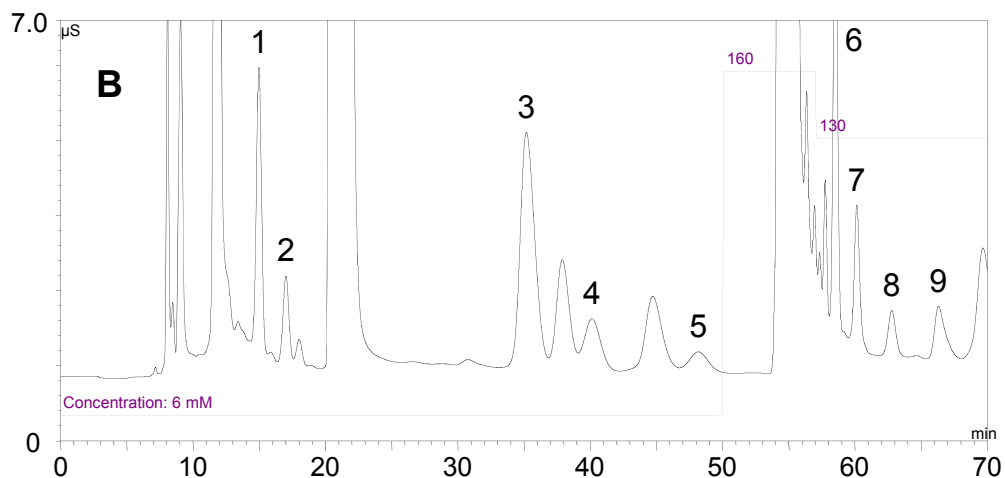
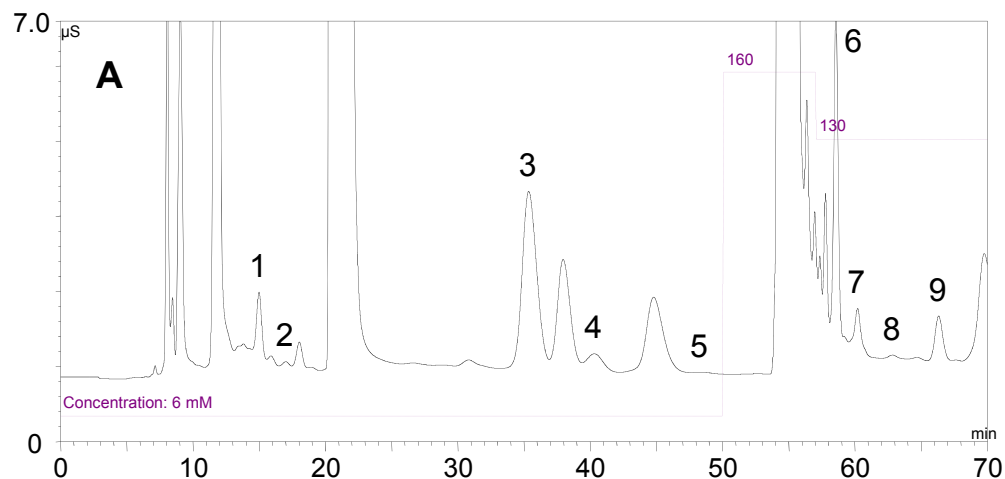
LCMRLs*
 • 8 HAA9 standards
 (0.05-2 µg/L)
 • 4 replicates each

HAA	Calculated LCMRL* (µg/L)	U.S. EPA Method 557 (µg/L)
MCAA	0.085	0.58
DCAA	0.41	0.13
TCAA	0.26	0.25
MBAA	0.10	0.19
DBAA	0.090	0.062
TBAA	0.28	0.27
BCAA	0.30	0.16
CDBAA	0.055	0.080
BDCAA	0.29	0.19

*Lowest Concentration Minimum Reporting Level

2-D IC LCMRLs comparable to U.S. EPA Method 557

Determination of HAA9 in Drinking Water from a Surface Water Source



First Dimension

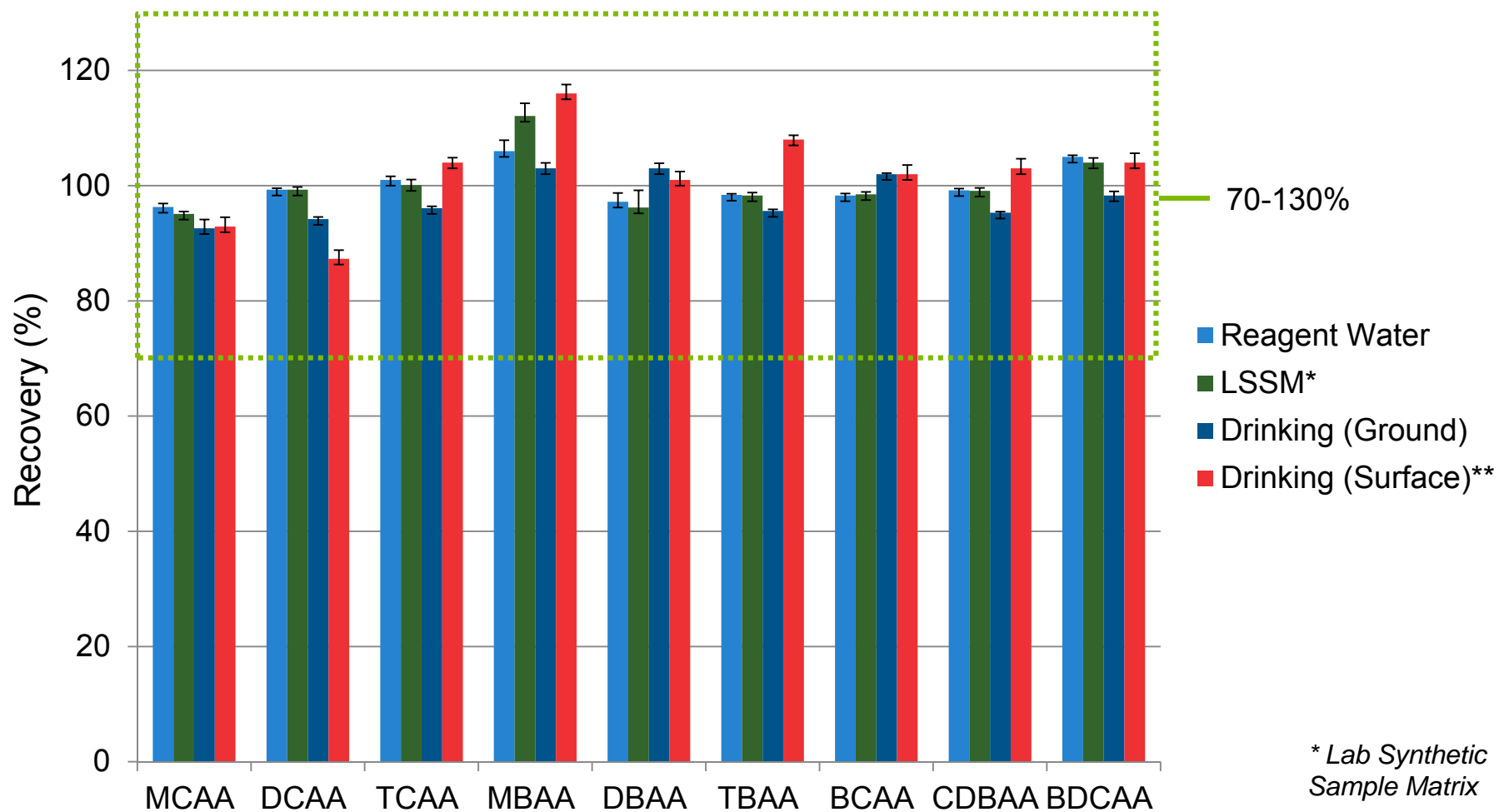
Columns: Dionex IonPac AG24A, AS24A, 4 mm
 Flow Rate: 1.0 mL/min
 Eluent: 7 mM KOH (0–12 min),
 7–18 mM (12–32 min), 65 mM (32.1 min)
 Eluent Source: Dionex EGC-500 KOH cartridge
 Detection: Suppressed conductivity,
 Dionex ASRS 300, 4 mm, 161 mA
 Inj. Volume: 500 μL
 Temp.: 15 °C
 Sample: A: Surface water
 B: Sample A + 10 $\mu\text{g/L}$ 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 | 6. TCAA |
| 2. MBAA | 7. BDCAA |
| 3. DCAA | 8. CDBAA |
| 4. BCAA | 9. TBAA |
| 5. DBAA | |

2-D IC Accuracy (% Recovery) and Precision



* Lab Synthetic Sample Matrix

** 5-fold dilution

~ 100% recovery in all waters (87–112%); ~0.5% RSD

Comparing the 2-D IC Results to EPA Method 552.3

Surface Water	Method 552.3	2-D 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	2-D 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

Conclusion

The 2-D 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
- Method has been submitted for regulatory approval
- Similar to other 2-D IC methods that have regulatory acceptance
- Simplified and less costly using a single system
 - Dionex ICS-6000+ HPIC system with its dual system capabilities and enhanced temperature control

Thank you!



ThermoFisher
S C I E N T I F I C

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