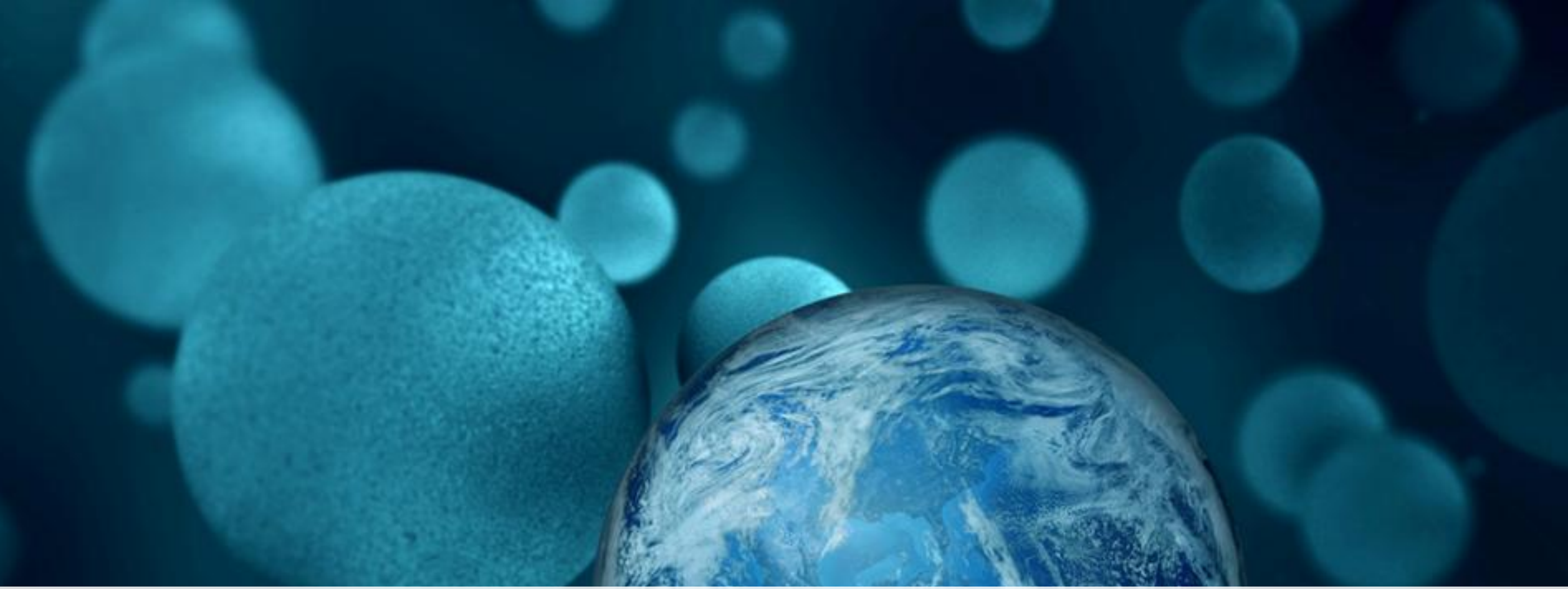


ThermoFisher
SCIENTIFIC

Analysis of Disinfection Byproducts by Ion Chromatography

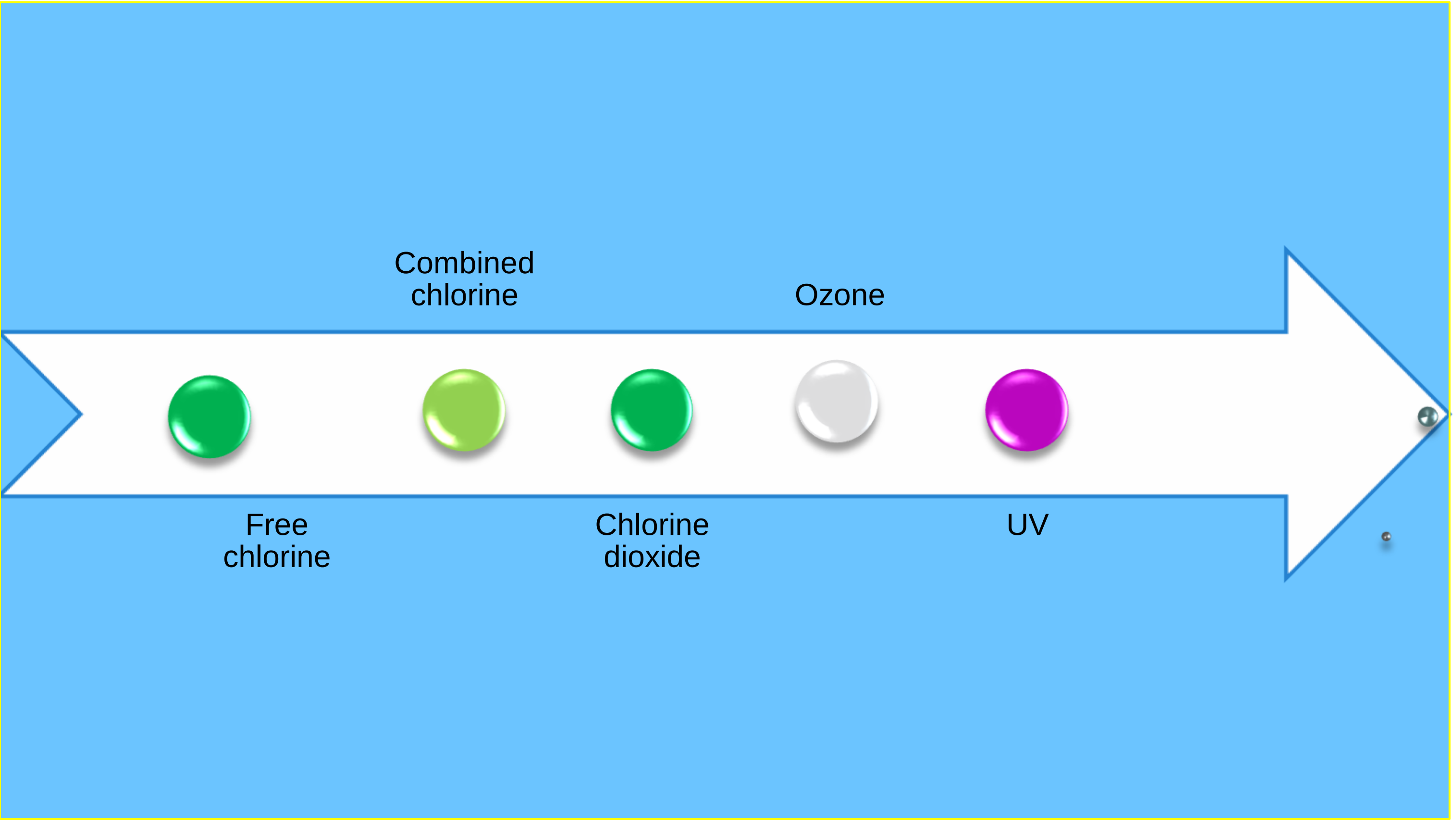
Elsamoul Hamdnalla
Thermo Fisher Scientific

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



Combined chlorine

Ozone

Free chlorine

Chlorine dioxide

UV

Toxic Disinfection Byproducts (DBPs)

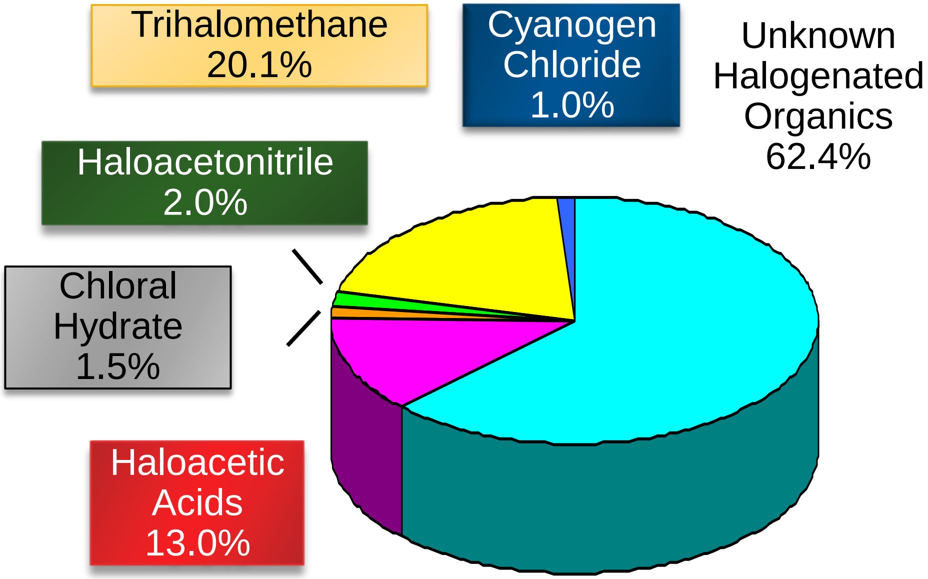
Highly regulated due to associated health issues

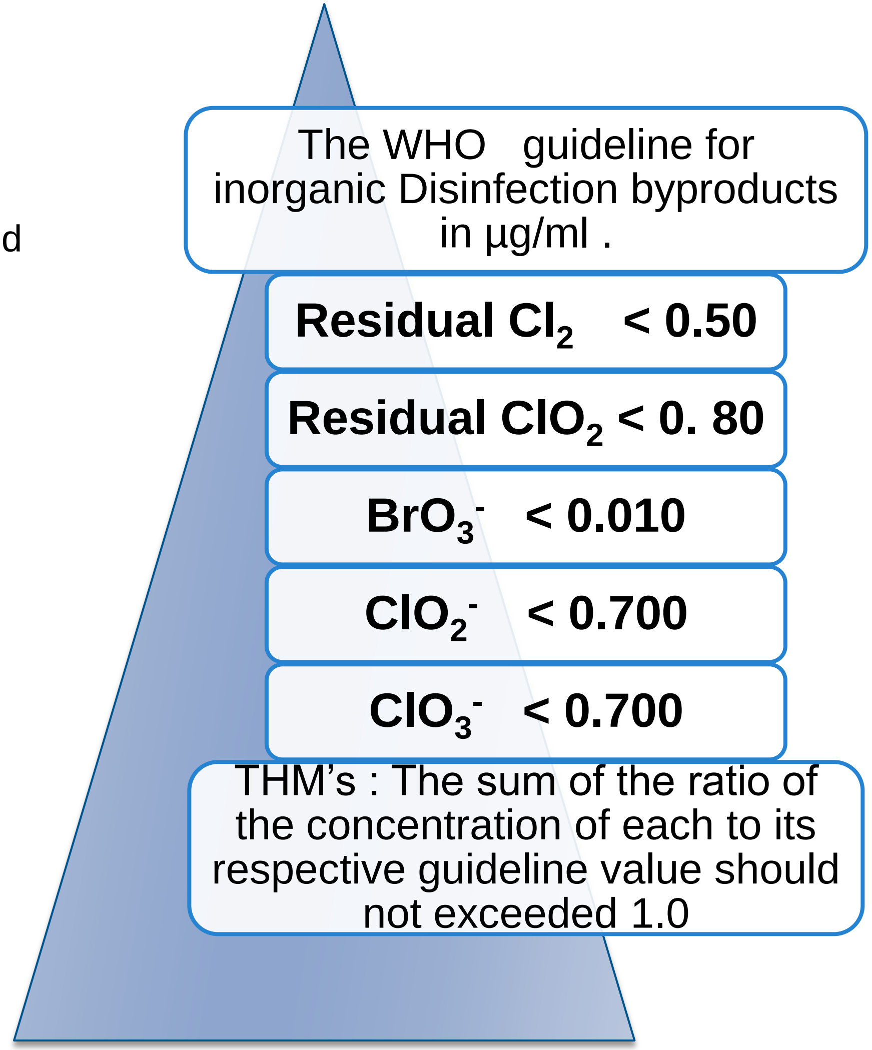
Disinfection Byproducts in Drinking Water

- 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

WHO Guideline Parameters

Occurrence of Disinfectant Byproducts





The WHO guideline for inorganic Disinfection byproducts in µg/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

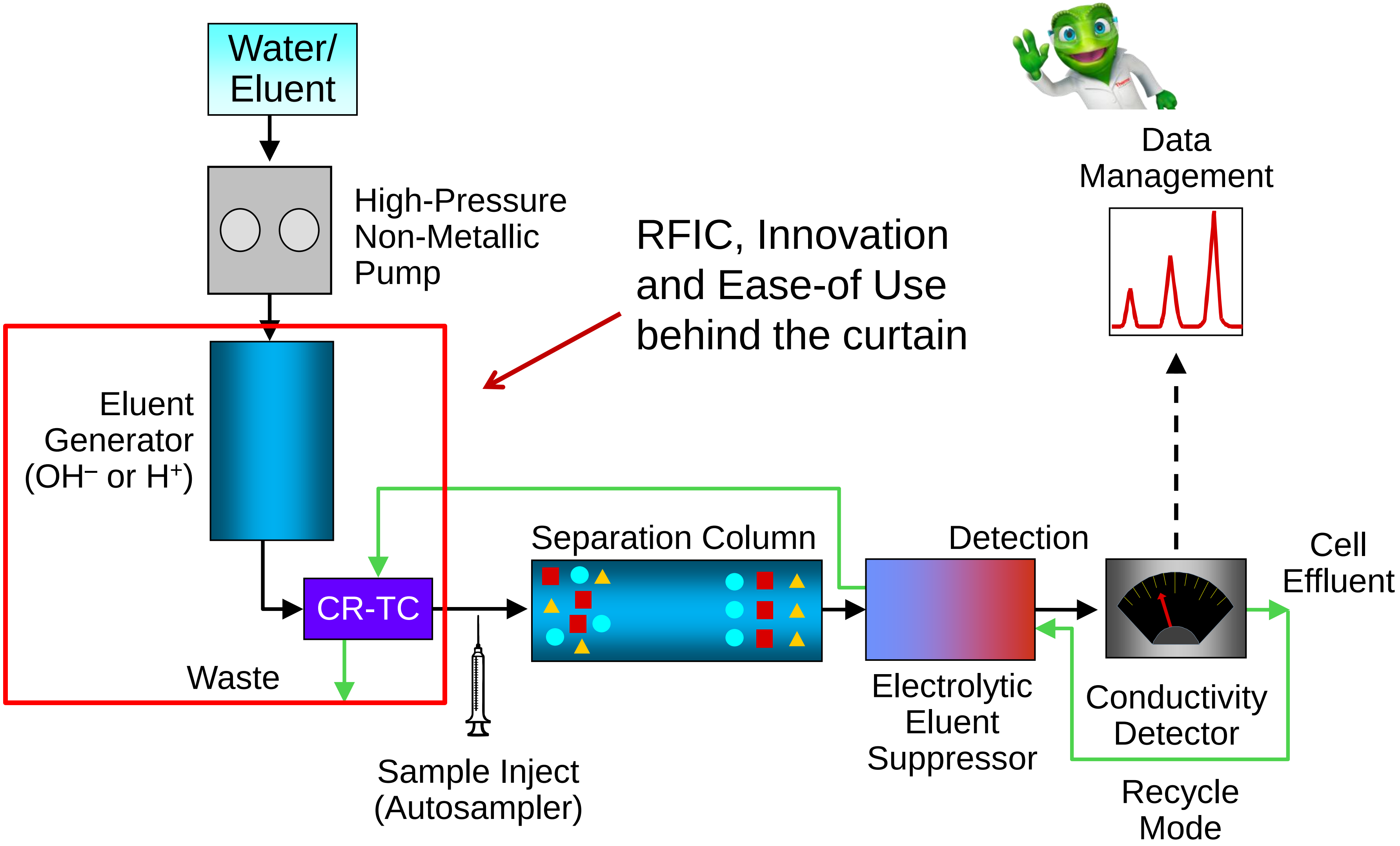
- Total Trihalomethanes (TTHMs) in 1970s
- 1998 U.S. EPA Stage 1 Disinfectants/Disinfection Byproducts (D/DBP) Rule:
  - Seven new regulations, including HAA5 and bromate
  - Monitoring of HAA5 at all plants that disinfect with chlorine
  - Report total MCAA, MBAA, DCAA, DBAA, and TCAA
  - Maximum Contamination 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

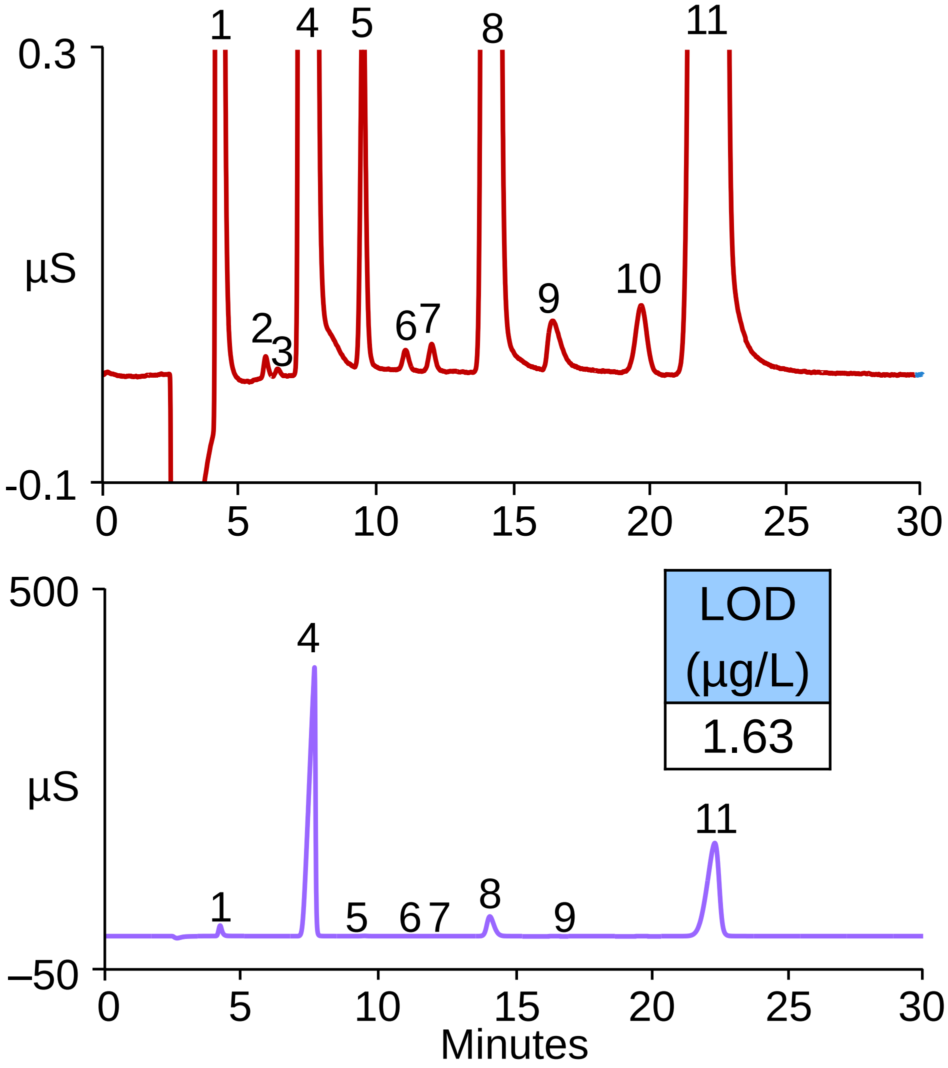
IC Technique	EPA Method	Thermo Scientific™ Dionex IonPac Columns	Eluent	Thermo Scientific Application	MDL (ppb)
Suppressed Cond.	300.0 (B)	Dionex IonPac AS9-HC or Dionex IonPac AS23 column	Carbonate	AN167	CD 5.0, 1.63
		Dionex IonPac AS19 column	Hydroxide	AN184	0.32
Suppressed Cond.	300.1	Dionex IonPac 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 0.14
		Dionex IonPac AS19 column	Hydroxide	AN168	
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	Dionex IonPac™ AS19 column	Hydroxide	AN43227	MS 0.014

Reagent-Free IC System (RFIC™)



RFIC, Innovation and Ease-of Use behind the curtain

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

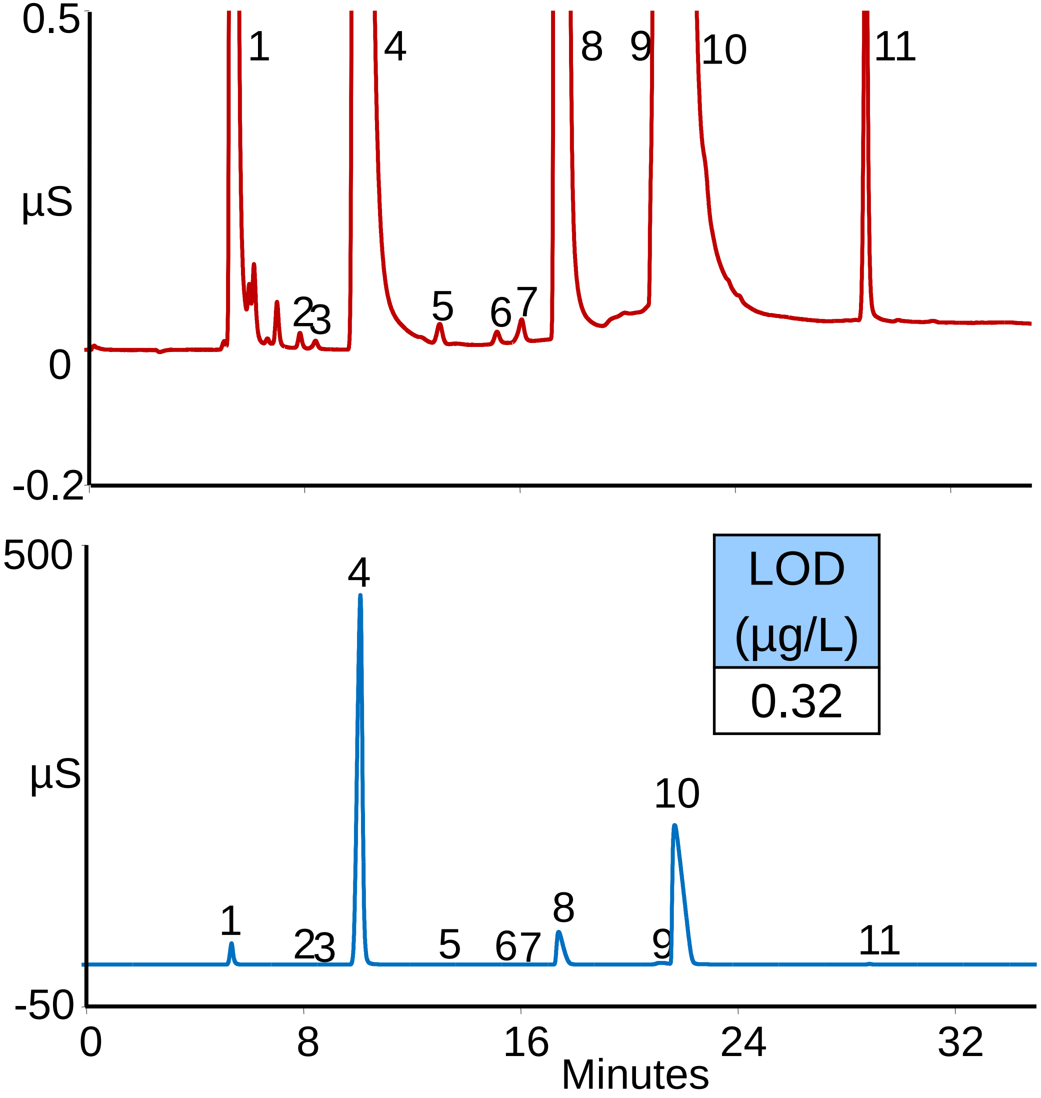


LOD (µg/L)
1.63

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:			
	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

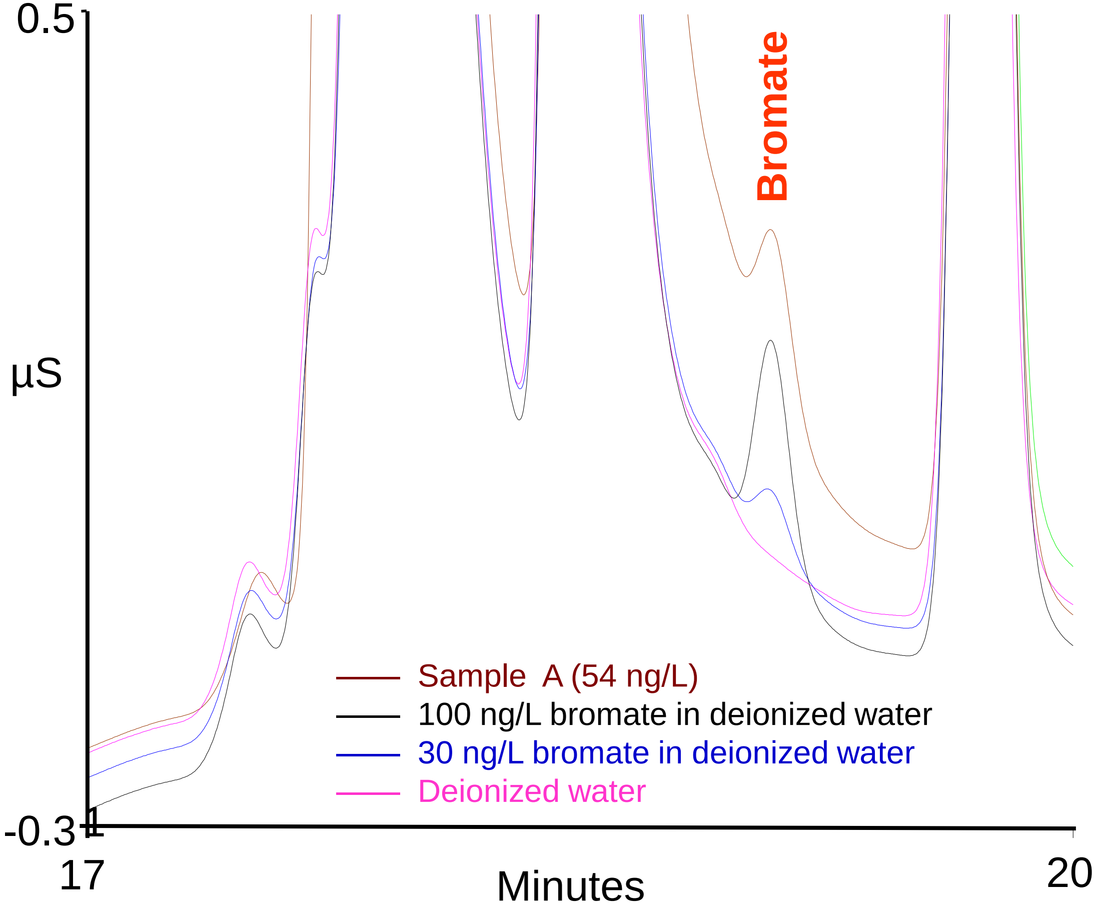


LOD (µg/L)
0.32

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:		
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



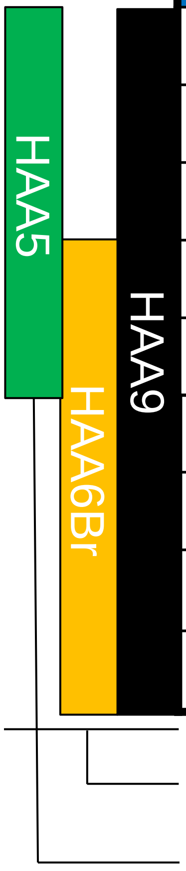
A. 1st Dimension

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	$ClCH_2CO_2H$	2.86
Dichloroacetic Acid	DCAA	Cl_2CHCO_2H	1.25
Trichloroacetic Acid	TCAA	Cl_3CCO_2H	0.63
Monobromoacetic Acid	MBAA	$BrCH_2CO_2H$	2.87
Dibromoacetic Acid	DBAA	Br_2CHCO_2H	1.47
Tribromoacetic Acid	TBAA	Br_3CCO_2H	0.66
Bromochloroacetic Acid	BCAA	$BrClCHCO_2H$	1.39
Chlorodibromoacetic Acid	CDBAA	Br_2ClCCO_2H	1.09
Bromodichloroacetic Acid	BDCAA	Cl_2BrCCO_2H	1.09

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) 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
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)
  - 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 hDone***

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)

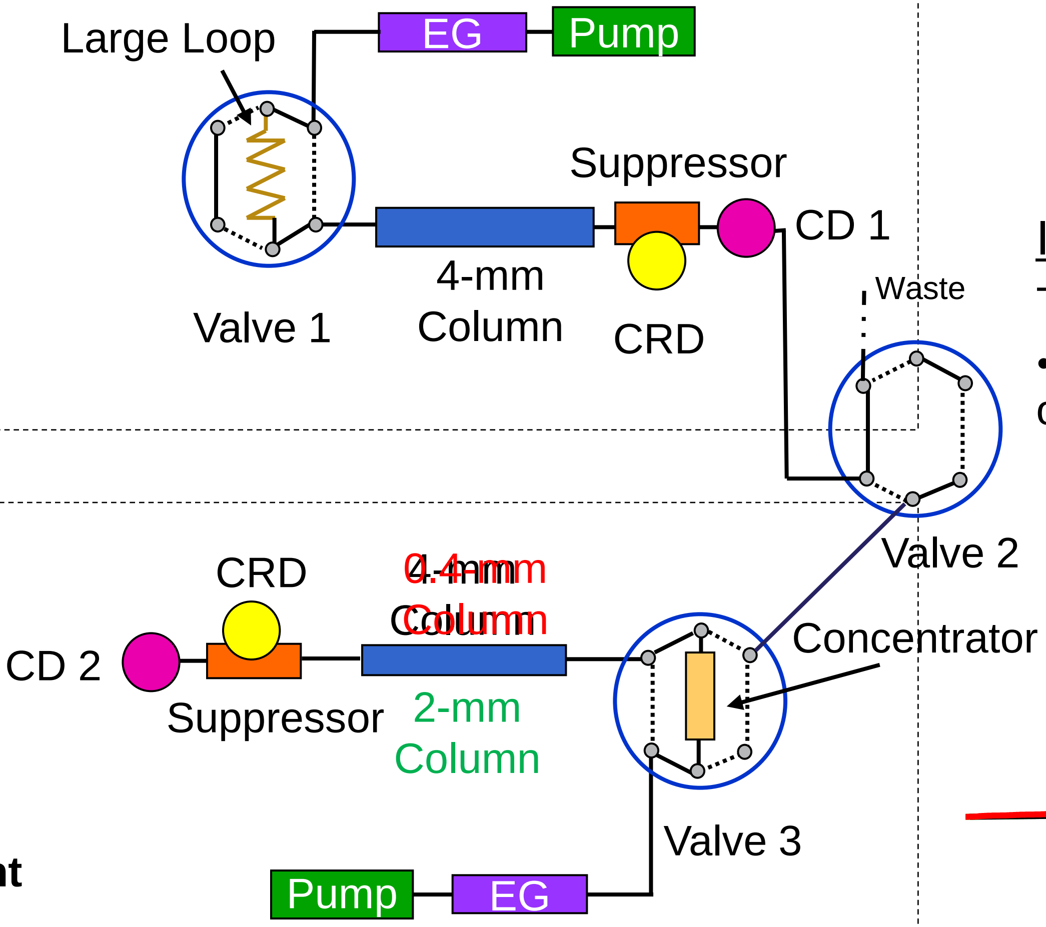
- First Dimension: Allows for large-loop loading of sample
- Concentrator and Second Dimension
  - Focuses the ions of interest onto a concentrator column
  - Resolves the analytes on a smaller diameter column
- Combined Effect
  - Enhanced sensitivity proportional to the column radius $(r)^2$ or flow rate
  - Enhanced selectivity by using different column chemistries
  - Convenience of using only one system designed with greater temperature control -- Dionex ICS-5000$^+$ 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

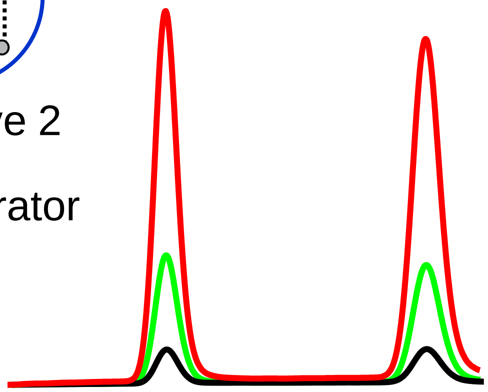
- Partially resolve analyte from matrix



Intermediate Step

Transfer cut volume

- Trap and focus ions of interest



2nd Dimension

Separate on smaller ID column

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

Thermo Scientific™ Dionex ICS-5000+ HPIC System

The Dionex ICS-5000+ is a universal HPIC system

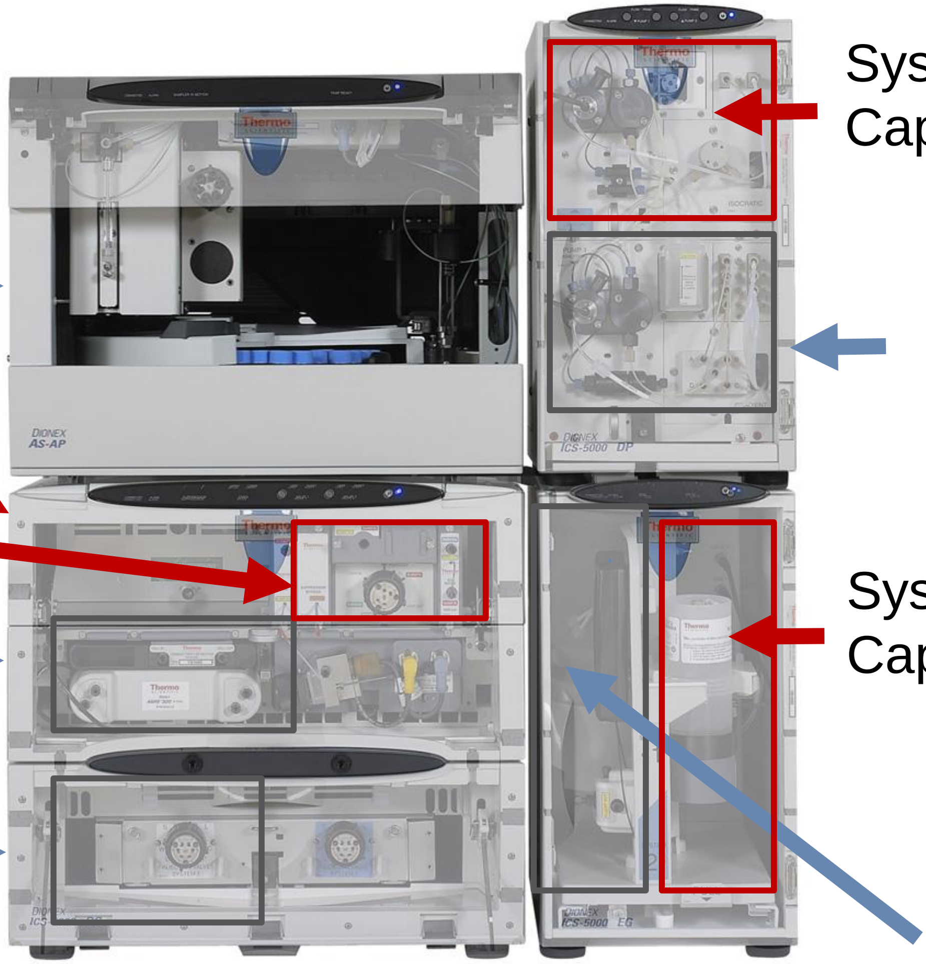
High-Pressure Ion Chromatography

- 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
- Low temperature version DC module has 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 2 – Low Temperature DC, Dionex IC Cube

System 1 – Detector, Suppressor

System 1 – Column oven

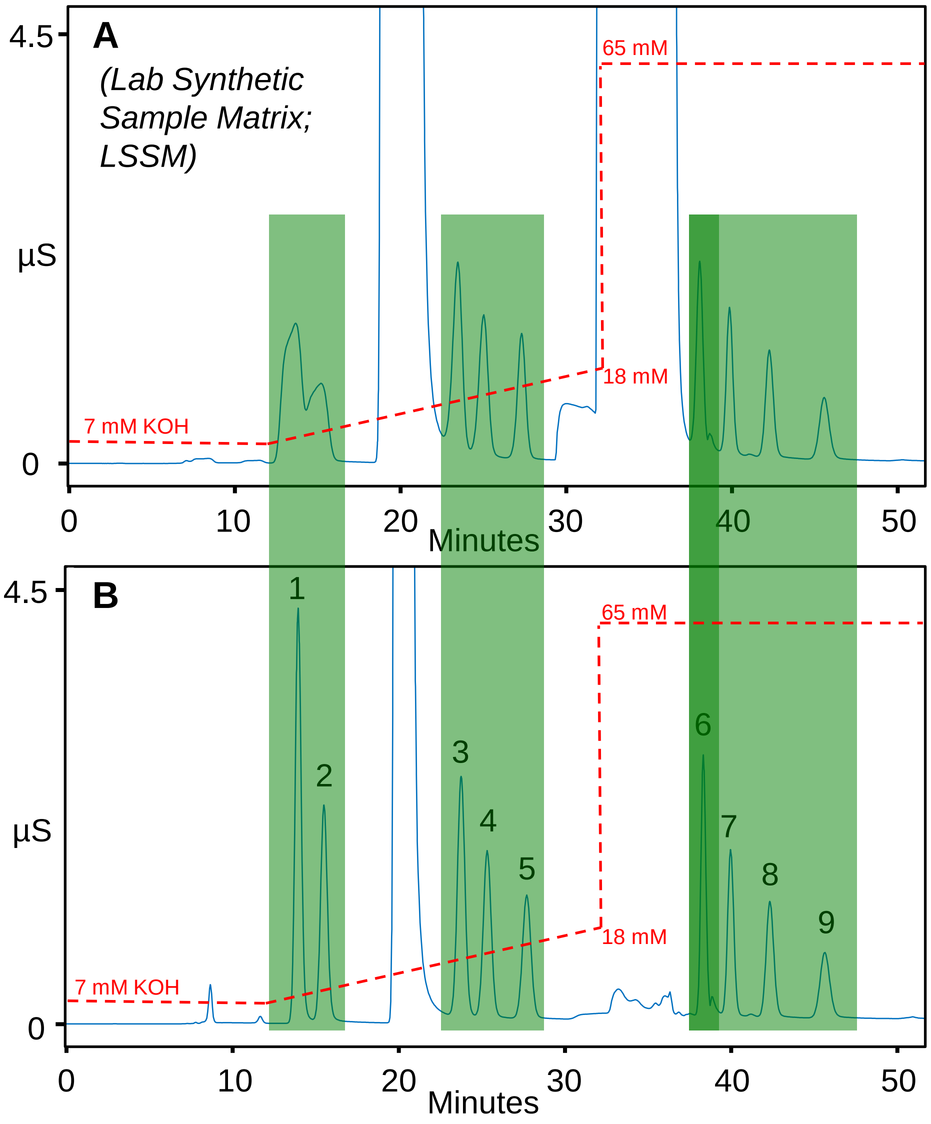
System 2 – Capillary Pump

System 1 – Standard Pump

System 2 – Capillary EGC

System 1 – Standard EGC

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 NH_4Cl

Peaks:

12-17 min
1. MCAA
2. MBAA

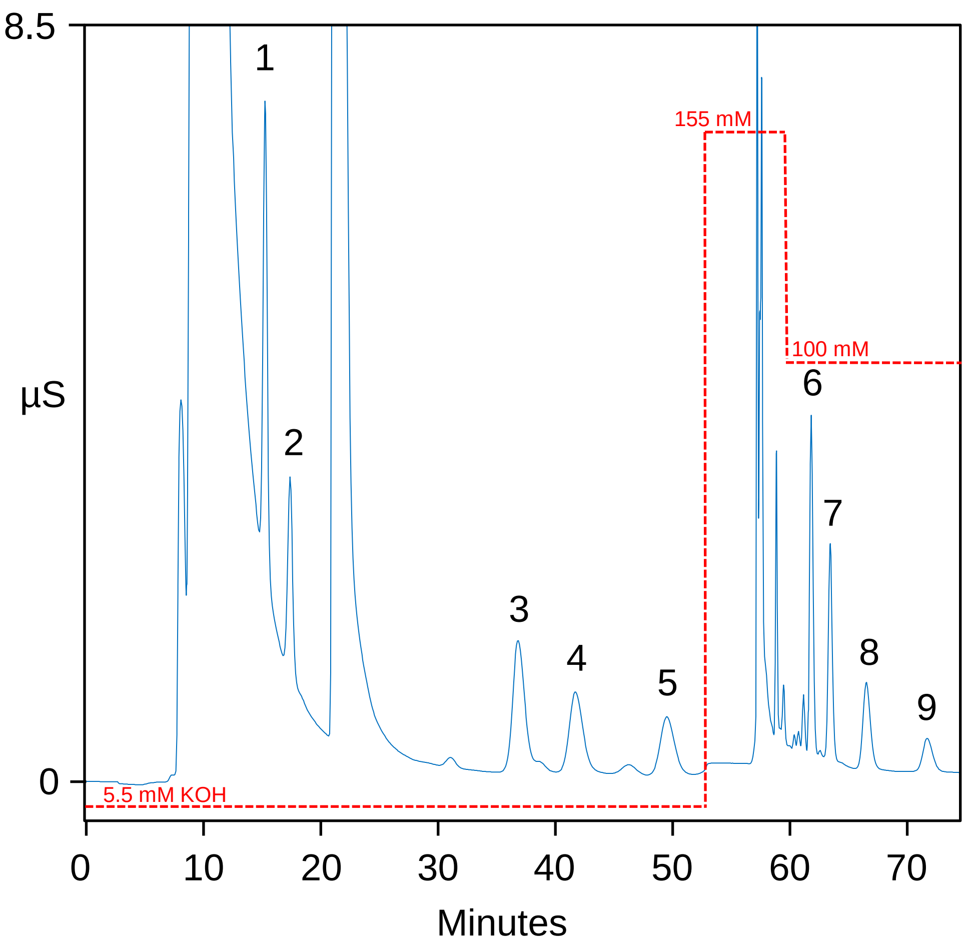
22-29 min
3. DCAA
4. BCAA
5. DBAA

37-39 min (HAA5)
6. TCAA

37-48 min (HAA9)
7. BDCAA
8. CDBAA
9. TBAA

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

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 NH_4Cl

Peaks:

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

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

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

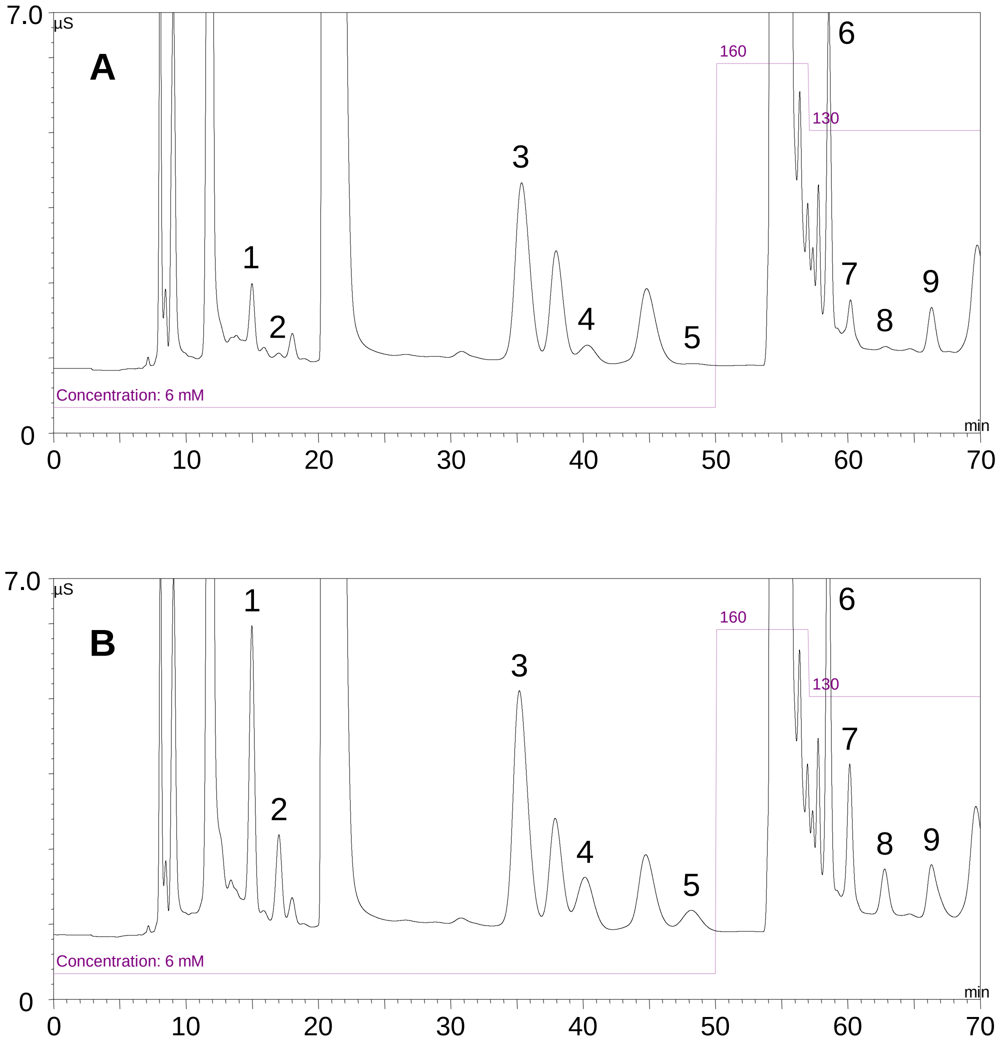
*Lowest Concentration Minimum Reporting Level

LCMRLs*

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

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

Determination of HAA9 in Drinking Water from a Surface Water Source

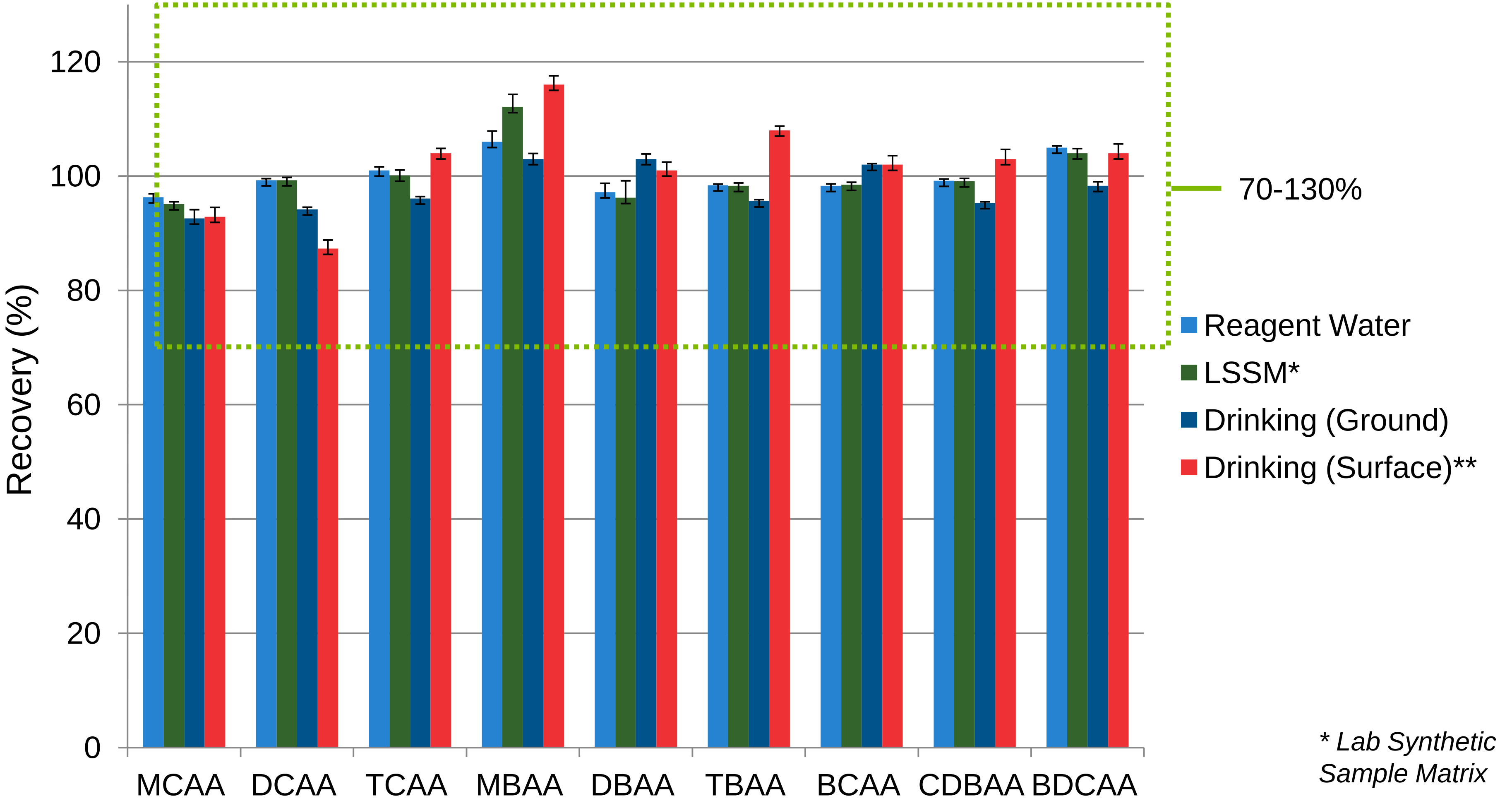


First Dimension	
Columns:	Dionex IonPac AG24A, AS24A, 4 mm
Flow Rate:	1.0 mL/min
Eluent:	7 mM KOH (0–12 min), 7–18 mM (12–32 min), 65 mM (32.1 min)
Eluent Source:	Dionex EGC-500 KOH cartridge
Detection:	Suppressed conductivity, Dionex ASRS 300, 4 mm, 161 mA
Inj. Volume:	500 µL
Temp.:	15 °C
Sample:	A: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

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

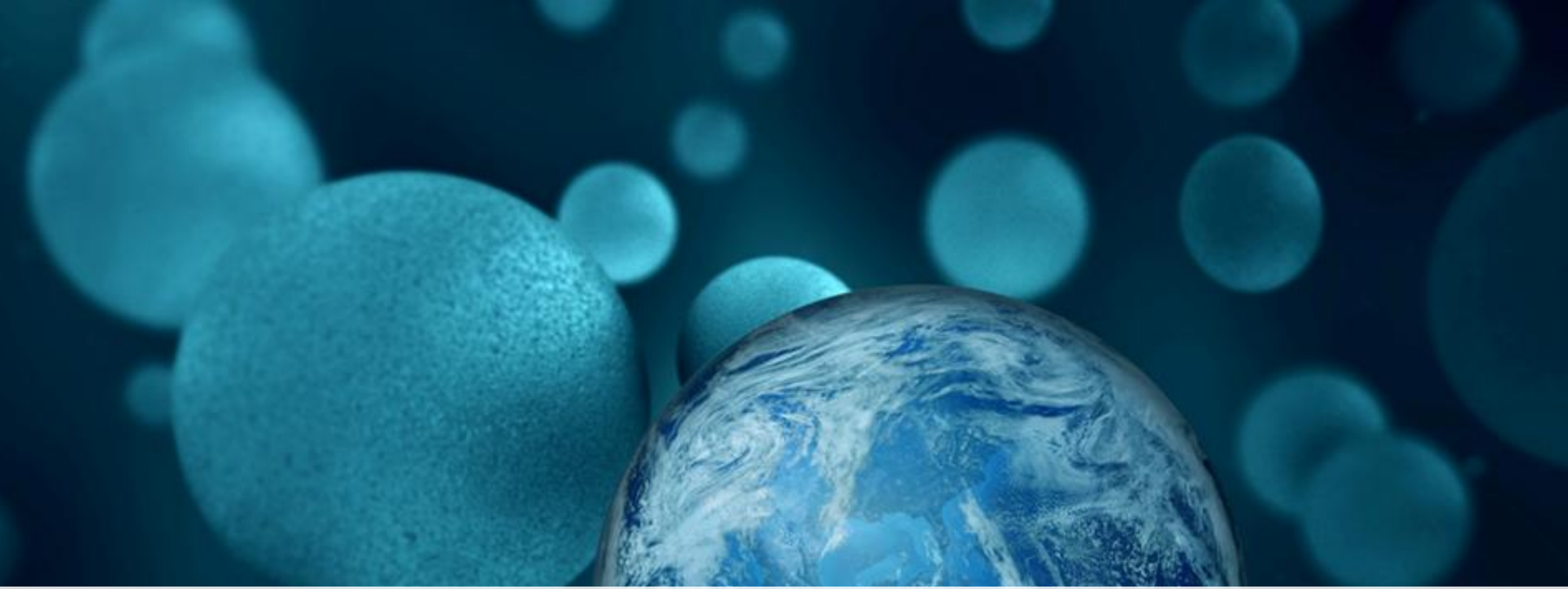
Ground Water	Method 552.3	2-D IC HAA
MCAA*	0.33	0.28
DCAA*	1.20	1.43
TCAA*	0.30	0.33
MBAA*	Not Reported	0.53
DBAA*	1.75	1.05
BCAA**	1.67	1.28

*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-5000^{+} HPIC system with its dual system capabilities and enhanced temperature control



ThermoFisher
SCIENTIFIC

Thank you!

elsamoul.hamdnalla@thermofisher.com