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Voda – čo všetko v sebe skrýva?

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Agenda

- ISO methods for water analysis by Ion Chromatography
- Thermo Scientific Dionex Ion Chromatography systems and columns for water analysis
- Speciation analysis of water by IC-ICP/MS
- Water analysis by IC-MS and IC-MS/MS

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ISO methods for water analysis by Ion Chromatography

Standardized IC-Methods for Water Analysis

- ISO 14911 - Water Quality
  - Determination of dissolved lithium, sodium, ammonium, potassium, manganese(II), calcium, magnesium, strontium and barium by ion chromatography - methods for water and wastewater
- ISO 10304-1 –Water Quality
  - Determination of dissolved anions by liquid chromatography of ions -- Part 1: Determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulfate
- ISO 10304-3 – Water Quality
  - Water quality - determination of dissolved anions by liquid chromatography (LC) - part 3: Determination of chromate, iodide, sulfite, thiocyanate and thiosulfate in wastewater

Standardized IC-Methods for Water Analysis

- ISO 10304-4 – Water Quality
  - Water quality - determination of dissolved anions by liquid chromatography (LC) - part 4: Determination of chlorate, chloride and chlorite in slightly polluted wastewater
- ISO 15061 – Water Quality
  - Determination of dissolved bromate in water

  Comment: Preconcentration or direct injection – 10 µg/L Bromate
- ISO/DIS 11206 - Water Quality
  - Determination of dissolved bromate — Method using ion chromatography (IC) and post column reaction (PCR)

Working Ranges of the Analytical Method - ISO 14911

Cation	Typical Working Ranges with 10 µL loop [mg/L] 1)		
Lithium	0,01	-	1
Sodium	0,10	-	10
Ammonium	0,10	-	10
Potassium	0,10	-	10
Manganese	0,50	-	50
Calcium	0,50	-	50
Magnesium	0,50	-	50
Strontium	0,50	-	50
Barium	1,00	-	100

1) The working range is limited by the ion-exchange capacity of the separator column. If necessary, the sample shall be diluted to meet the working range, or use a 100 µL loop for lower working ranges.

ISO 10304-1 – News

- This second edition of ISO 10304-1 cancels and replaces ISO 10304-1:1992 and ISO 10304-2:1995.
  - One method for water, e.g. drinking water, ground water, surface water, waste water, leachates and marine water.

- Isocratic AND Gradient Elution
- Carbonate/Bicarbonate AND Hydroxide Eluents (e.g. KOH)
- Only Examples for Suppressed Conductivity Compatible Eluents
- Mode of Calibration: Customer‘s Choice (Linear, Quadratic…)

- AND:
- Minimum Requirement for the Separation: R ≥ 1.3 for Neighboring Peaks

The User Decides on Application, Mode of Calibration, and Mode of Elution !!

Examined Working Range of the Analytical Method – ISO 10304-1

Anion	Examined Working Range mg/L		
Bromide	0,1 to 1	to	1 to 10
Chloride	0,5 to 5	to	5 to 50
Fluoride	0,02 to 0,2	to	0,5 to 5
Nitrate	0,5 to 5	to	10 to 100
Nitrite	0,1 to 1	to	1 to 10
Orthophosphate	0,5 to 5	to	10 to 100
Sulfate	1 to 10	to	10 to 100

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Thermo Scientific Dionex Ion Chromatography systems and columns for water analysis

The Thermo Scientific Dionex Ion Chromatography Systems

RFIC

HPIC

Dionex Aquion

Dionex Integrion

Dionex ICS-4000

Dionex ICS-6000

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IC Autosamplers

Thermo Scientific Dionex **AS-DV Autosampler**

Entry Level

- Carousel Type
- 50 x 5 mL PolyVials
- 50 x 0.5 mL PolyVials
- Filter Caps
- Full Loop, Concentrator
- Simultaneous Injection
- Optional 6-port/10-port Valve

Thermo Scientific Dionex **AS-HV Autosampler**

High Volume

- X0Z-Type
- 24 x 250 mL TCF
- 15 x 250 mL Bottles
- Full Loop Injection, Concentrator Loading
- Simultaneous Injection
- Peristaltic Pump for sample loading and Needle Port Rinse

Thermo Scientific Dionex **AS-AP Autosampler**

For IC, BioIC, and Cap IC

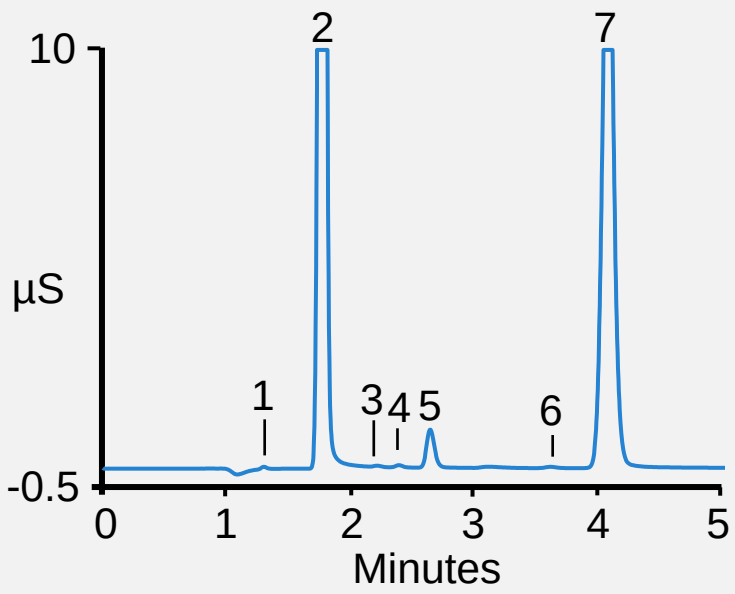
- Carousel-Type
- 81 x 10 mL Vials
- 120 x 1.5 mL or 0.3 mL Vials
- 3 x 96 Well Plates
- 3 x 384 Well Plates
- Full/Partial Loop, Limited Sample, Concentrator Loading
- Push and Pull Loop injection
- Tray Thermostat
- Optional Injection Valve
- Optional Diverter Valve
- Optional Fractionation valve
- Sequential Injection
- Simultaneous Injection
- Autodilution

Municipal Drinking Water Analysis

AB120

Municipal Drinking Water Analysis by Fast IC

Municipal Drinking Water



Conditions

Columns:	Dionex IonPac AG22-Fast-4µm Dionex IonPac AS22-Fast-4µm, 2 × 150 mm
Eluent:	4.5 mM Sodium Carbonate 1.4 mM Sodium Bicarbonate
Flow Rate:	0.5 mL/min
Inj. Volume:	2.5 µL
Column Temp.:	30 °C
Detection:	Suppressed conductivity, Dionex AERS 500 Carbonate, 2 mm 17 mA, recycle mode

Peaks:

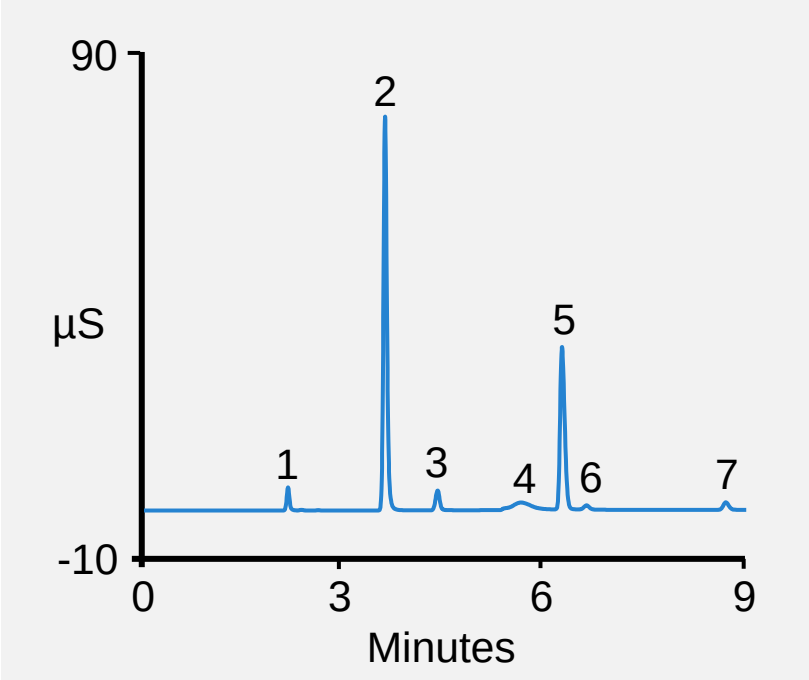
1. Fluoride	< 1	5. Nitrate	1.0	mg/L
2. Chloride	120	6. Phosphate	< 2	
3. Nitrite	< 1	7. Sulfate	56	
4. Bromide	< 1			

Water analysis

AN154 and Update with Dionex IonPac AS18-4µm column

Determination of Inorganic Anions in Environmental Waters Using a Hydroxide-Selective Column

Municipal Wastewater Sample



Conditions

Columns:	Dionex IonPac AG18-Fast-4µm Dionex IonPac AS18-Fast-4µm, 4 × 150 mm
KOH Gradient:	15–44 mM (0.2 to 6 min)
Eluent Source:	Dionex EGC 500 cartridge with Dionex CR-ATC 600 trap and Dionex high pressure degasser devices
Flow Rate:	1 mL/min
Inj. Volume:	10 µL
Column Temp.:	30 °C
Detection:	Suppressed conductivity, Dionex AERS 500, 4 mm, 109 mA, recycle
Sample Prep.:	5x dilution with deionized water

Peaks:

1. Fluoride	1.0	5. Sulfate	51.8	mg/L
2. Chloride	90.6	6. Nitrate	2.6	
3. Nitrite	1.0	7. Phosphate	0.36	
4. Carbonate	--			

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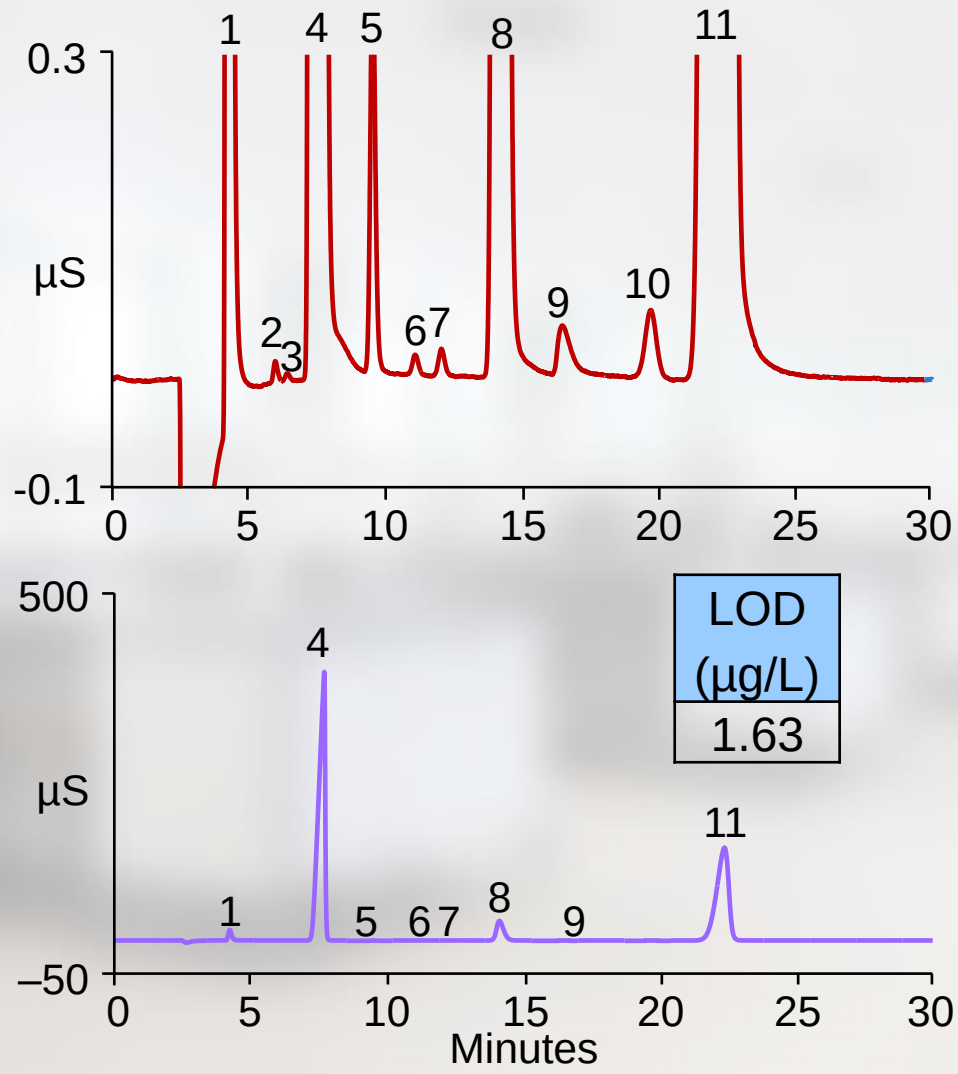
Determination of Trace Bromate Using IonPac AS23



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	

Recommended carbonate column for EPA Method 300.0 (B)

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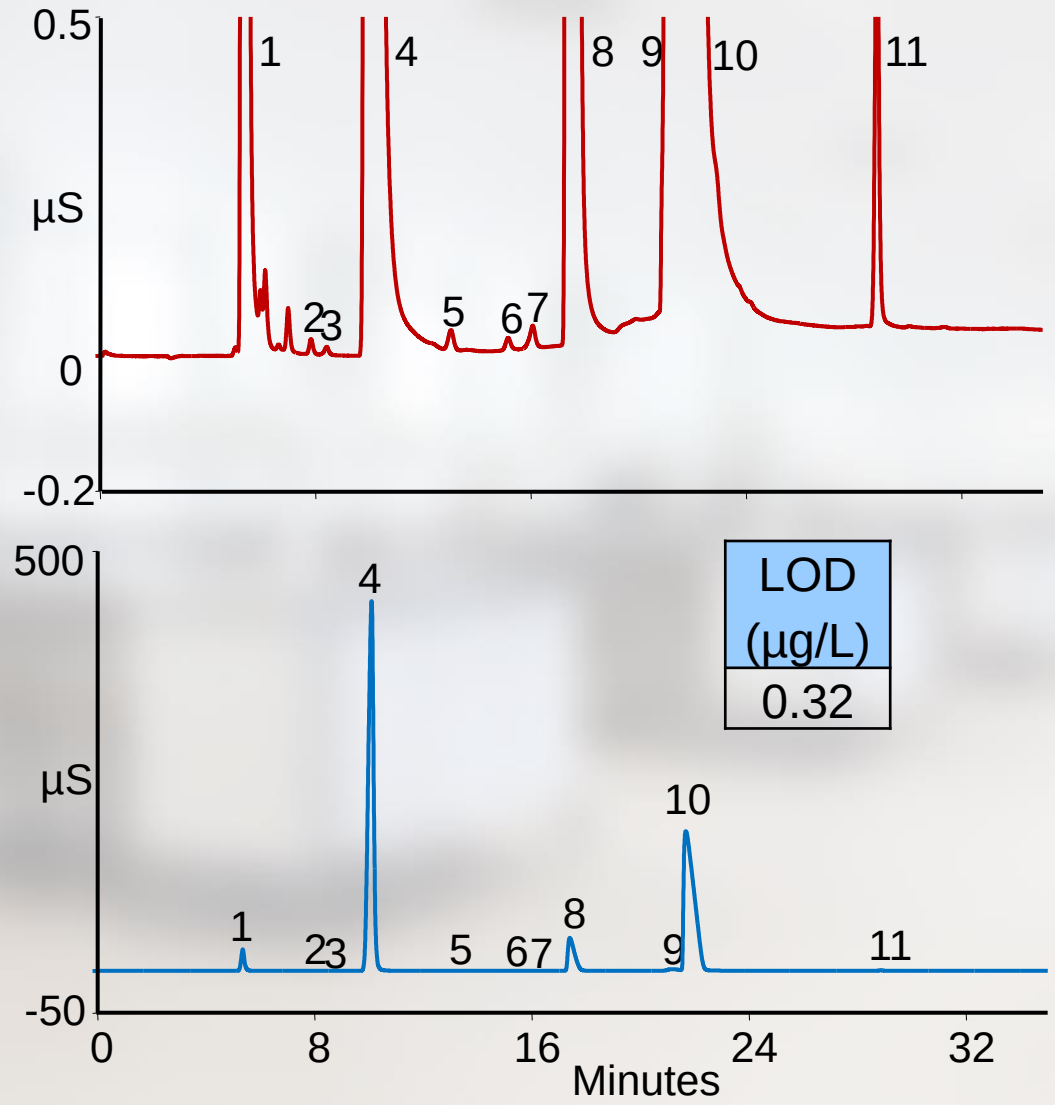
Determination of Trace Bromate Using IonPac AS19-4µm column



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	

Recommended hydroxide column for EPA Method 300.0 (B)

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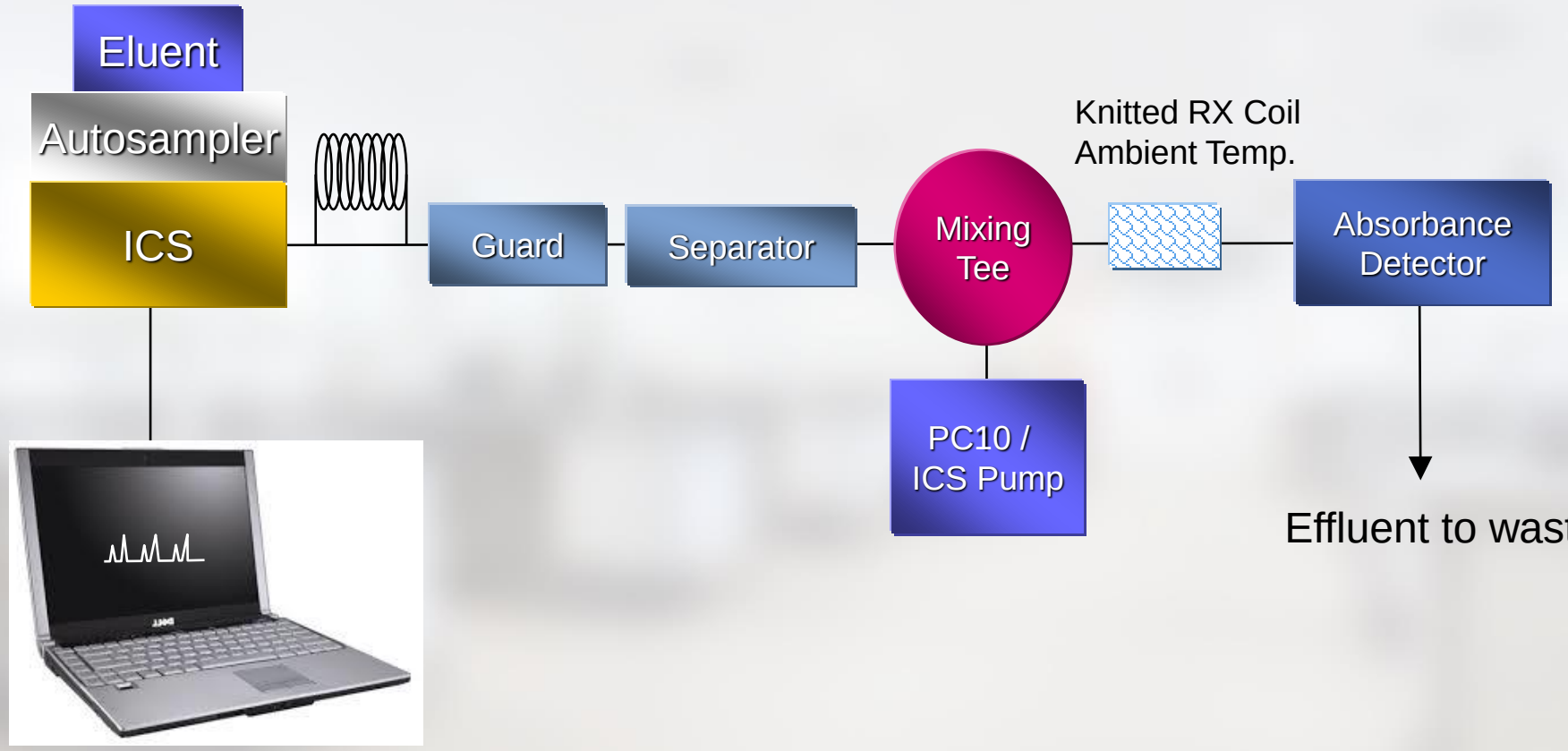
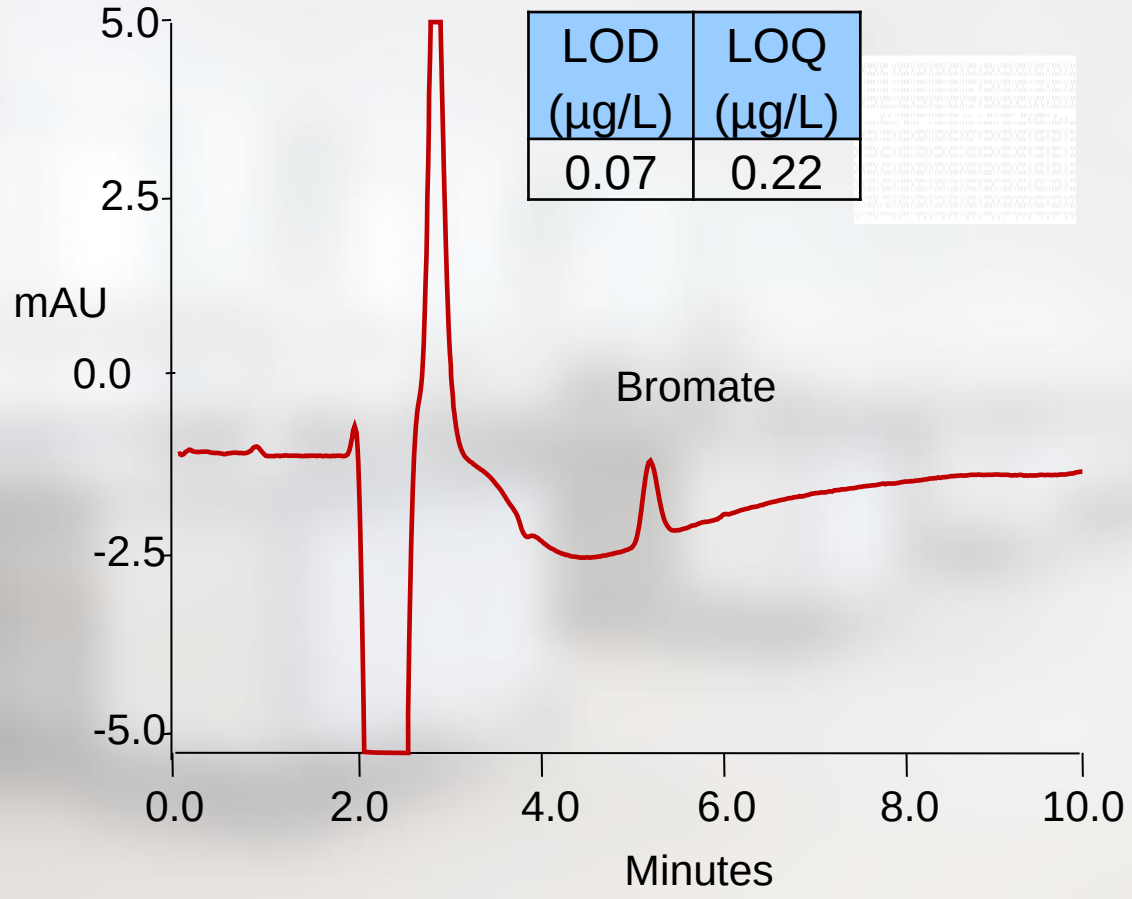
System Configuration - ISO 11206 for trace bromate analysis



Bromate Determination with Acidic Eluent - ISO 11206

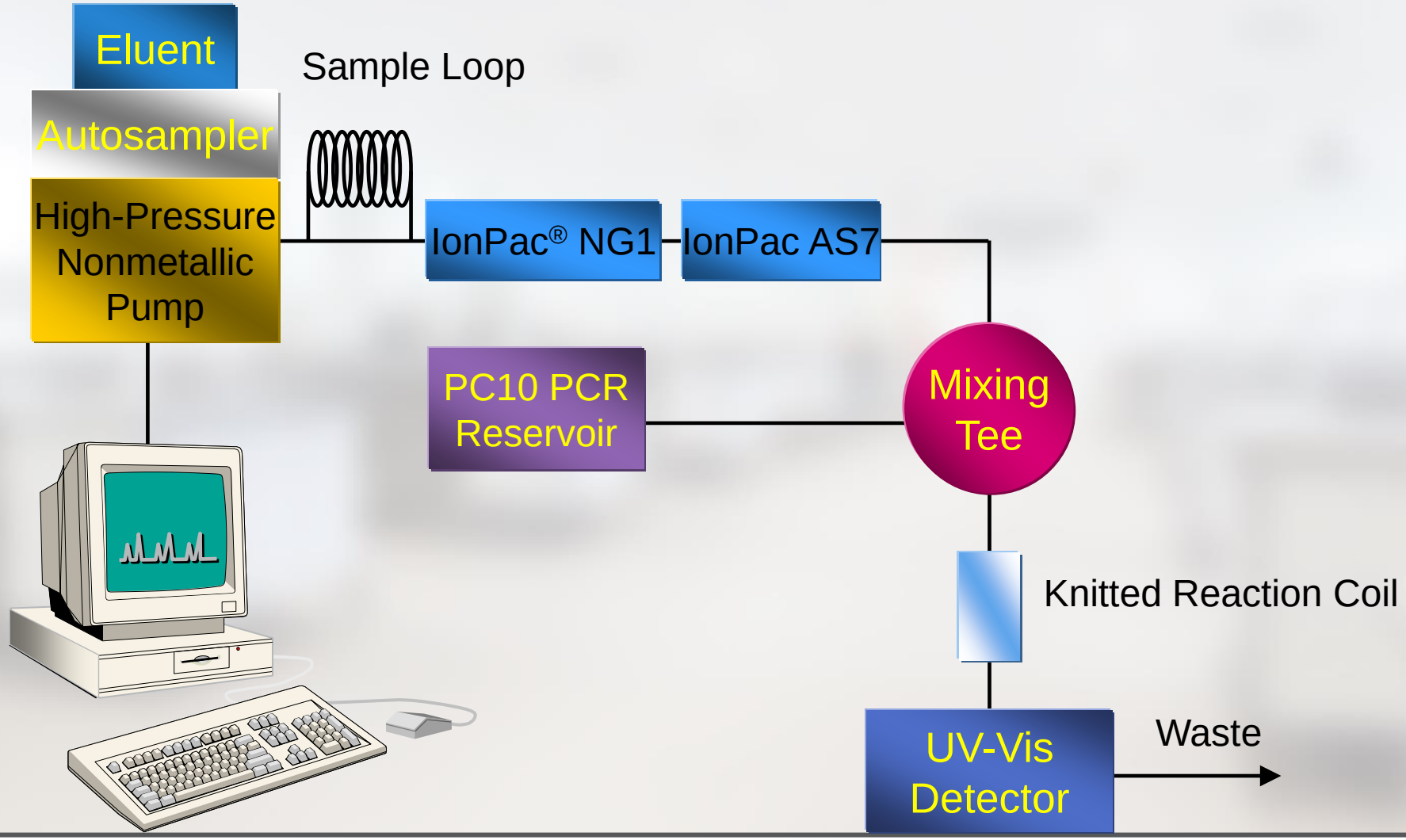


LOD (µg/L)	LOQ (µg/L)
0.07	0.22

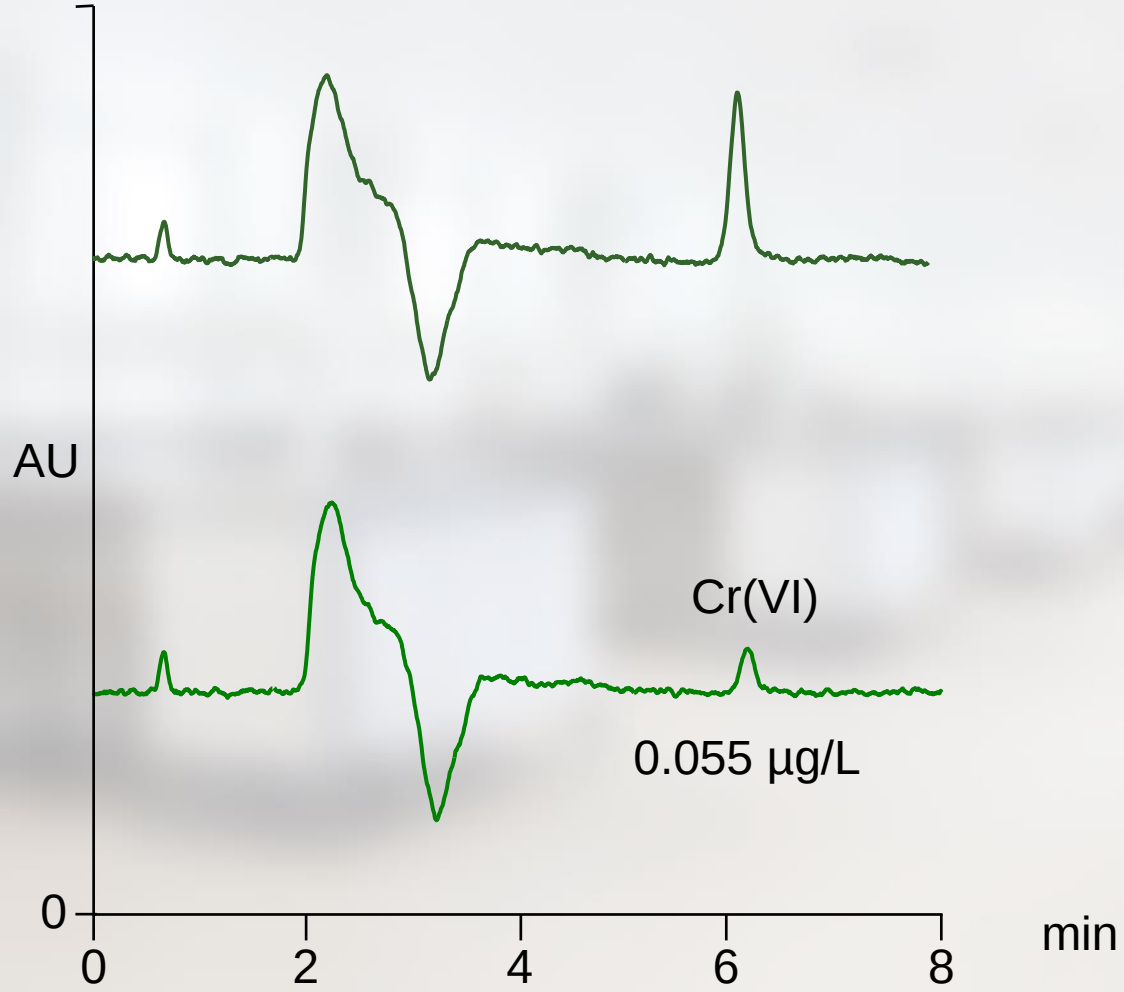
Column:	Thermo Scientific™ Dionex™ CarboPac™ PA1 (4 × 250 mm)
Eluent:	200 mmol/L MSA
Flow:	1 mL/min
Injection vol.:	500 µL
Detection:	UV 352 nm (after PCR)
Temperature:	30 °C
PCR:	
Solution A:	0.27 mol/L KI, 0.05 mmol/L $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$
Flow	0.3 mL/min
Reaction coil:	375 µL
Bromate	1.2 µg/L

Reaction at Ambient Temp., and no Interferences from Chlorite

System Configuration for Hexavalent Chromium by EPA Method 218.6



Determination of Cr(VI) in Drinking Water Using Optimized EPA Method 218.6



Column: IonPac® NG1, AS7

Eluent: 250 mM $(NH_4)_2 SO_4$
100 mM NH_4OH

Flow: 1.0 mL/min

Inj. Volume: 1000 mL

Postcolumn Reagent: 2 mM Diphenylcarbazide
10% CH_3OH
1N H_2SO_4
0.33 mL/min

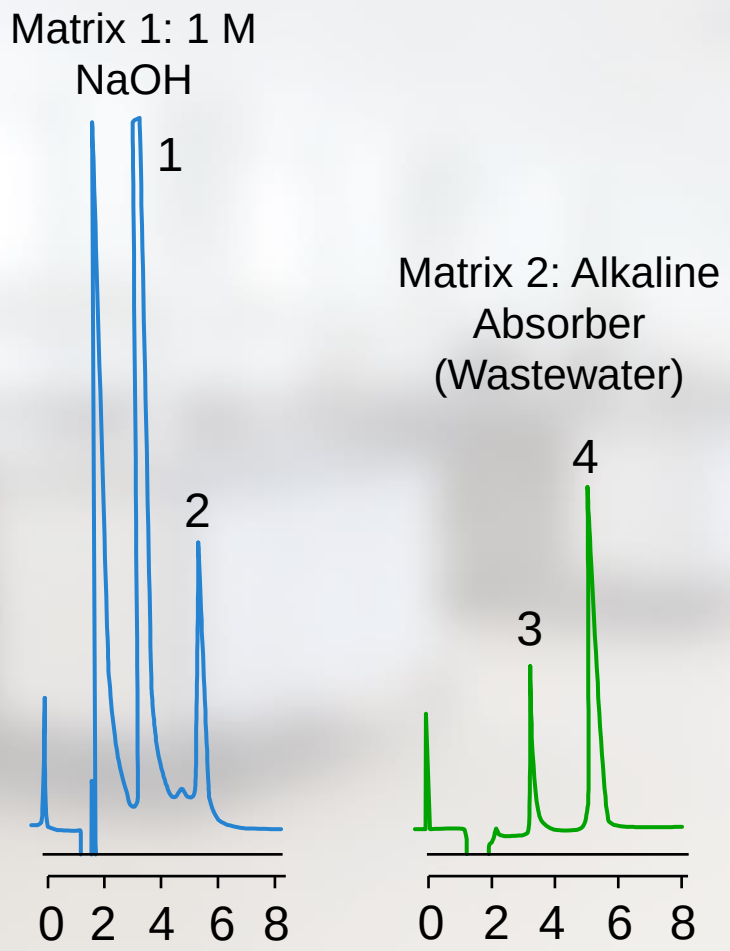
Reaction Coil: 750 mL

Detector: UV-Vis (530 nm)

Sample: Sunnyvale, CA tap water

MDL = 0.02 ppb

Determination of Cyanide and Sulfide in Sodium Hydroxide and Waste Water Samples Using the IonPac® AS7 Column with Amperometric Detection



Column: IonPac AS7

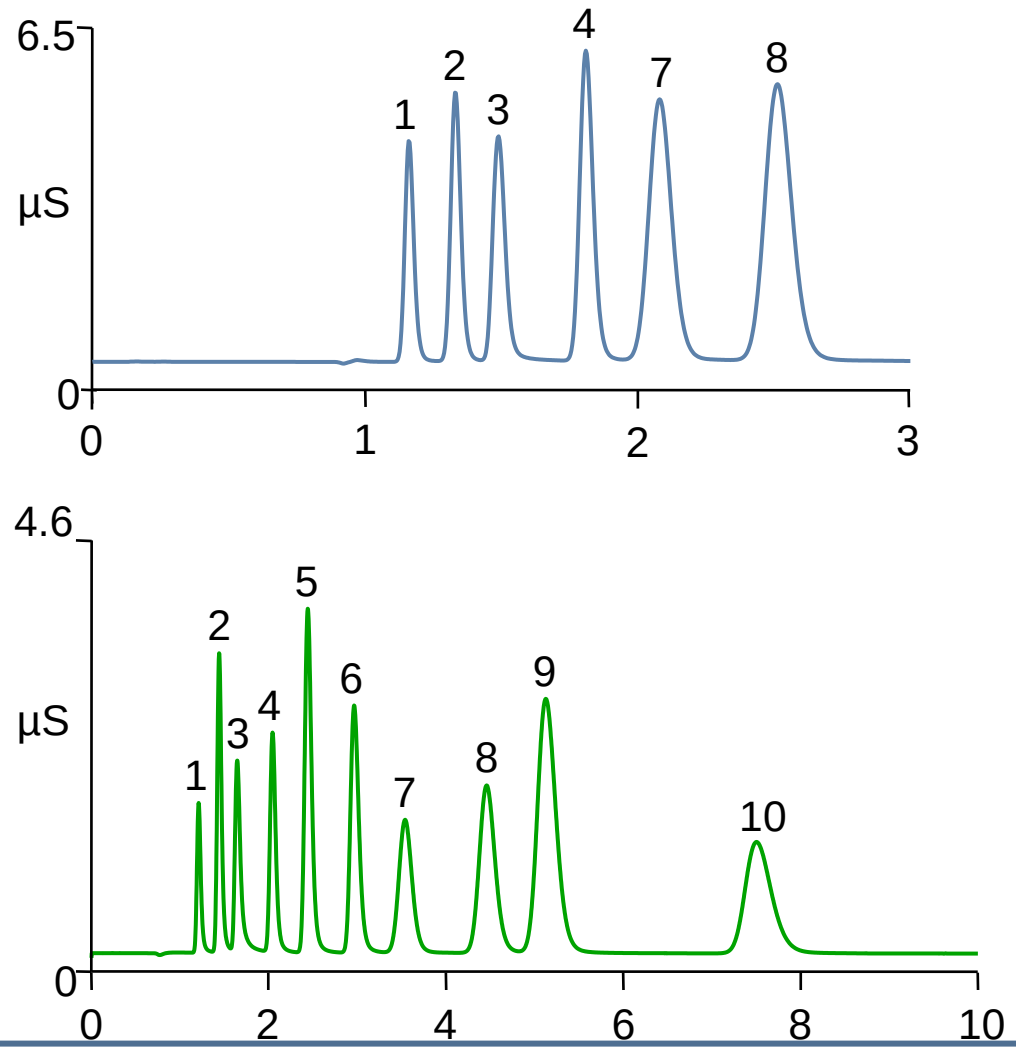
Eluent: 0.5 M Sodium acetate
0.1 M Sodium hydroxide
0.5 % (v/v) Ethylenediamine

Flow Rate:1 mL/min

Detector: ED40, silver working electrode,
0.00 V vs. Ag/AgCl reference

Peaks:	Matrix 1	Matrix 2
	1. S^{2-} 1000 ppb	3. S^{2-} 25ppb
	2. CN^- 100 ppb	4. CN^- 125 ppb

Fast Cation Separations with CS12A 5-µm 3 x 150 mm



Temperature: 30 °C

Eluent: A. 33 mM Methanesulfonic acid
B. 20 mM Methanesulfonic acid

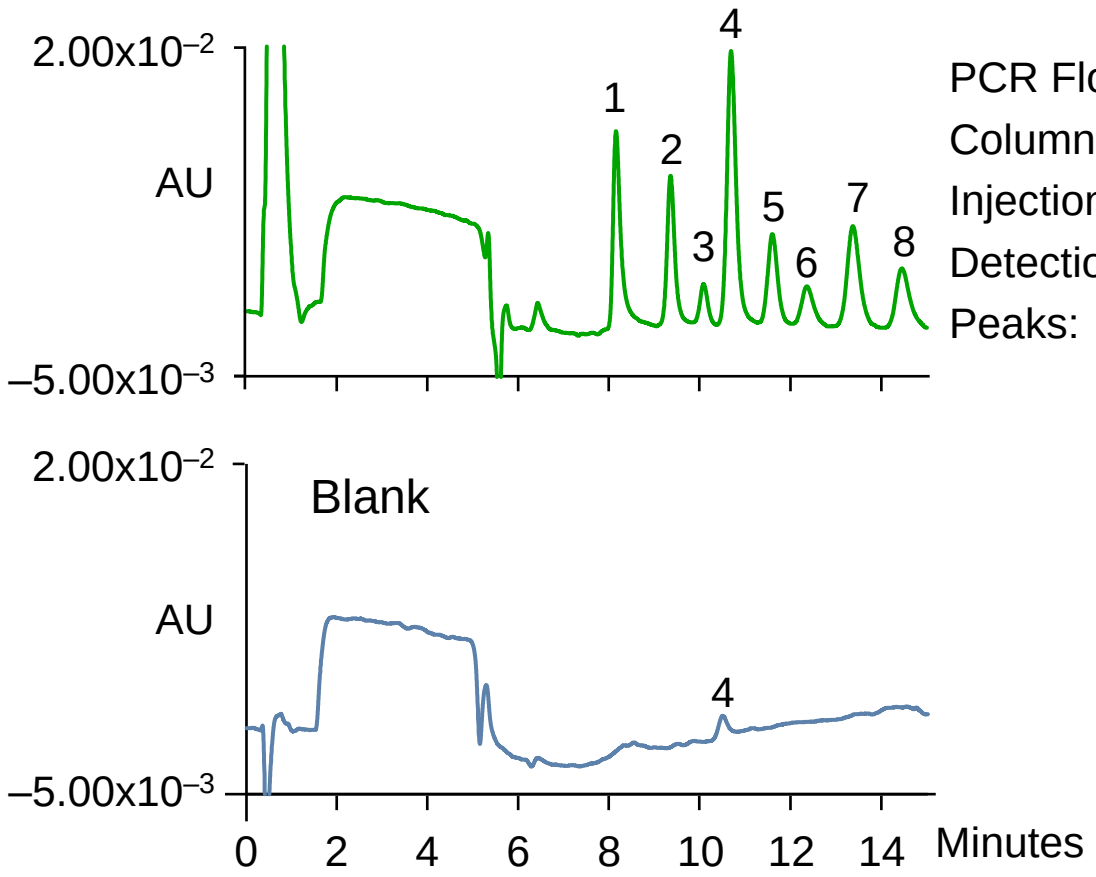
Flow Rate: A. 0.8 mL/min
B. 1.0 mL/min

Inj. Volume: 25 µL

Detection: Suppressed conductivity, CSRS® ULTRA 2 mm, AutoSuppression® recycle mode

Peaks:
1. Lithium
2. Sodium
3. Ammonium
4. Potassium
5. Rubidium
6. Cesium
7. Magnesium
8. Calcium
9. Strontium
10. Barium

Large Sample Loop Injection of µg/L Levels of Transition Metals in a 2-mm System with Pneumatic Postcolumn Delivery



Columns:	IonPac® CG5A, CS5A, 2mm
Eluent:	MetPac™ PDCA
Eluent Flow Rate:	0.3 mL/min
Post Column Reagent:	PAR in MetPac postcolumn reagent diluent
PCR Flow Rate:	0.15 mL/min
Column Temp:	30 °C
Injection Volume:	1000 µL
Detection:	530 nm, 10 mm cell

Peaks:

1. Iron	2	µg/L
2. Copper	1	
3. Nickel	2	
4. Zinc	>2	
5. Cobalt	1	
6. Cadmium	5	
7. Manganese	3	
8. Iron	2	

Advantages of Ion Chromatography in Water Analysis

- High Specificity & Selectivity
- Standardized Methods (ISO & Local Standards)
- Multiple Components
- High Degree of Automation
- Simple & Complex Matrices
- Easily Upgradable
- Multiple Option (Detectors, Columns, Iso/Grad)

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Speciation analysis of water by IC-ICP/MS

Speciation with IC-ICP-MS

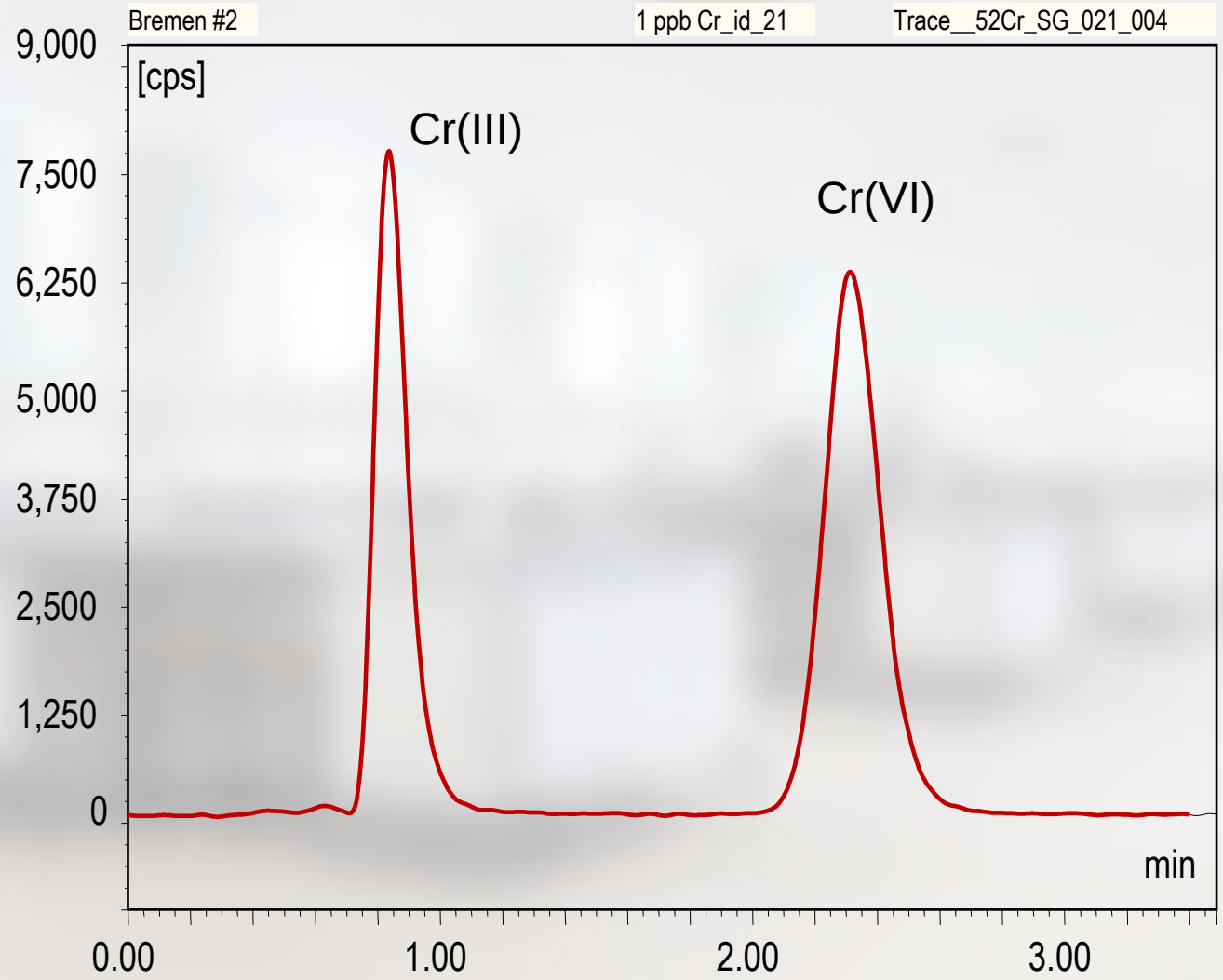
- IC-ICP-MS is the ideal choice for trace elemental speciation because:

- Very simple hardware connection:
  - Simple interchange between standard ICP-MS analysis and IC-ICP-MS
  - No need to turn off plasma
- Dionex IC systems are entirely metal-free (PEEK)
- Fully integrated systems with Chromeleon plug-in for Qtegra enables seamless control of both units
- Powerful separation chemistries with a wide selection of columns also for specialized applications
- Reagent-Free Ion Chromatography (RFIC) for ease of use

The IC-ICP-MS Bundles

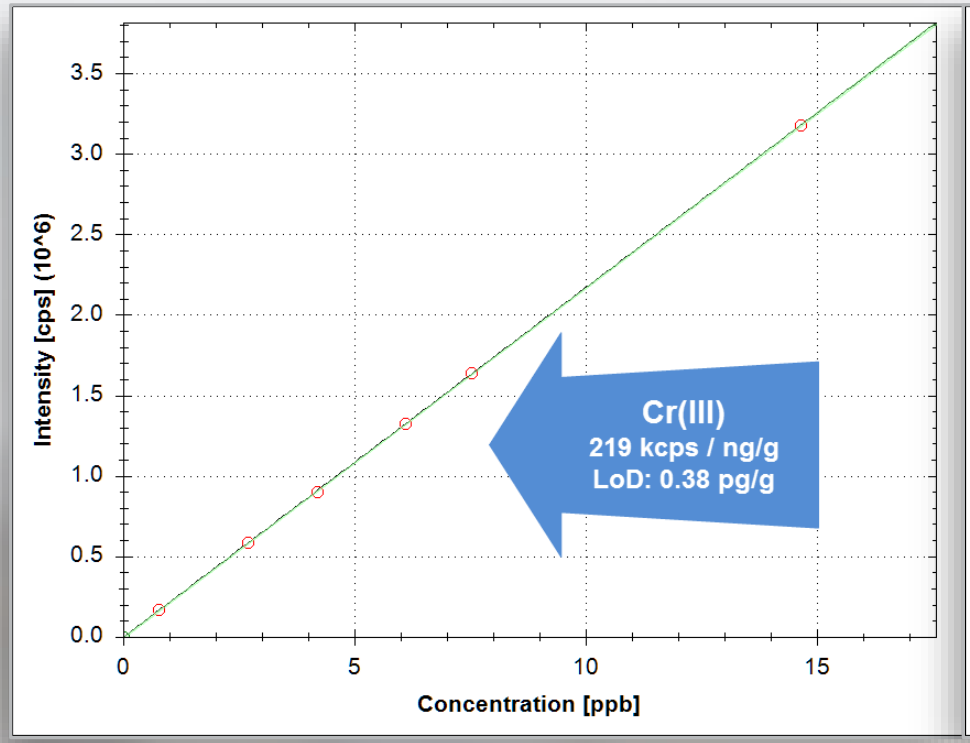
IC	Pump Channels	Autosampler	Column heater	RFIC	Elution possibilities	Applications
ICS-6000	Quaternary	AS-AP	✓	optional	Gradient - full flexibility	As, Br, Cr, Fe, Hg, I, Se, Sn

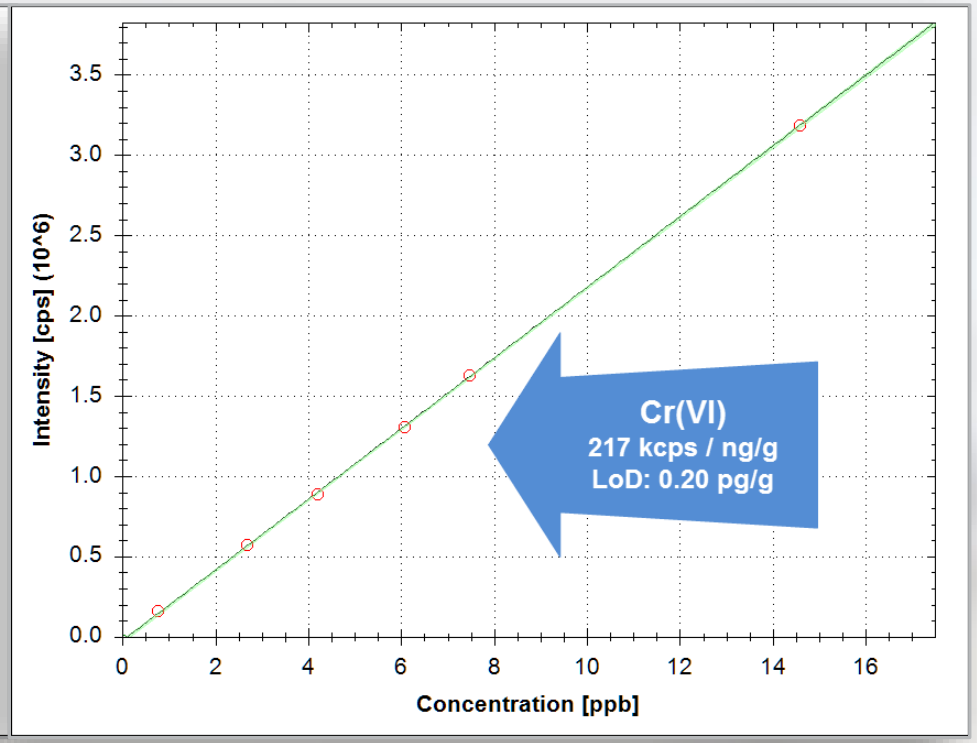
Cr-Species – Anion Exchange & ICP/MS



Column:	Thermo Scientific Dionex IonPac AG7, 2 x 50 mm
Eluent:	0.4 mL/min
Eluent:	60 mmol/L HNO_3, pH 2 with NH_4OH
Injection vol.:	100 µL
Runtime:	3.5 min
Analytes:	Cr(III) und Cr(VI) je 1 µg/L

IC-ICP-MS: Cr(III) and Cr(VI) Calibrations





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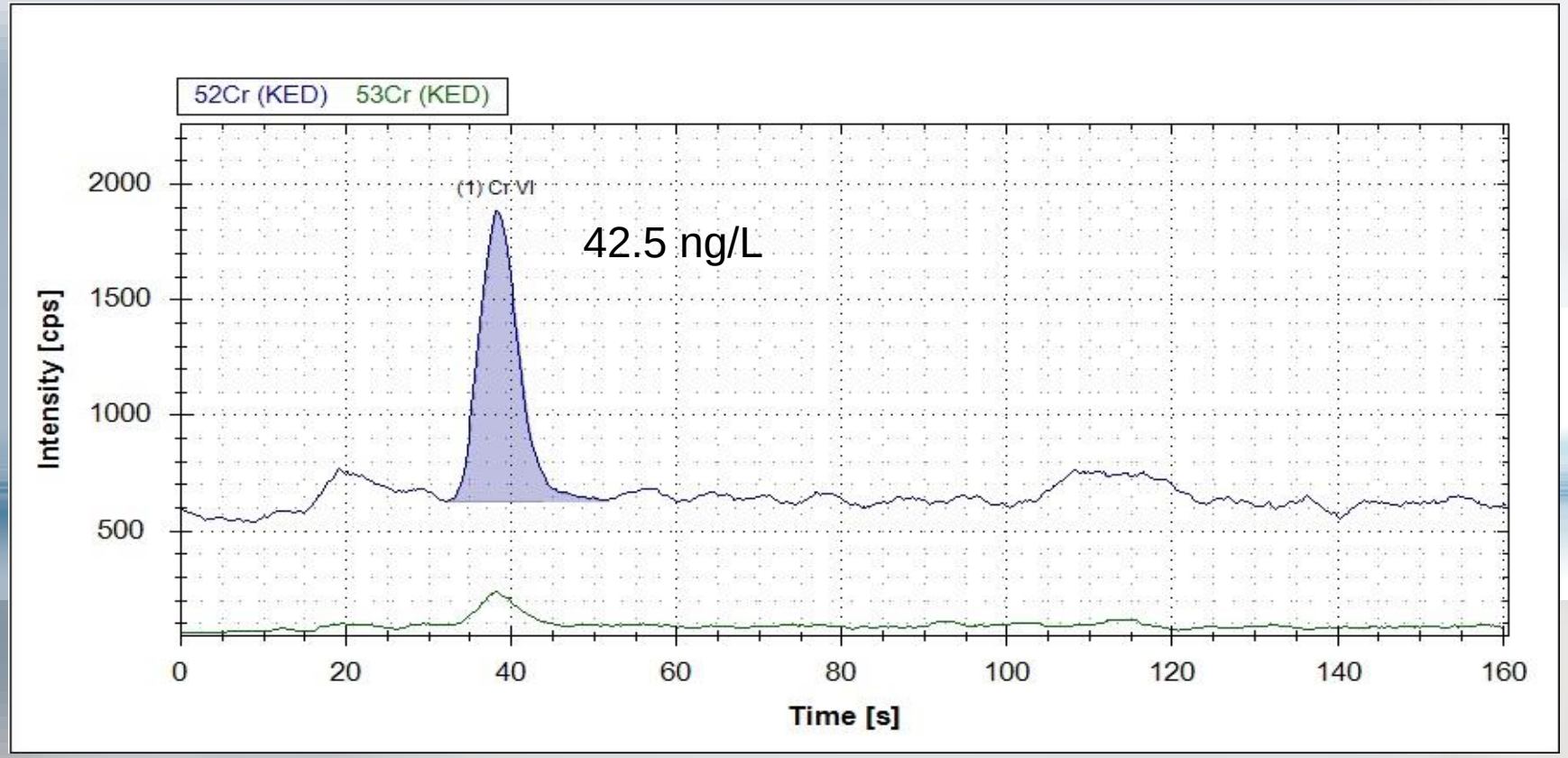
Cr in Drinking Water: Thermo Scientific AN 43098



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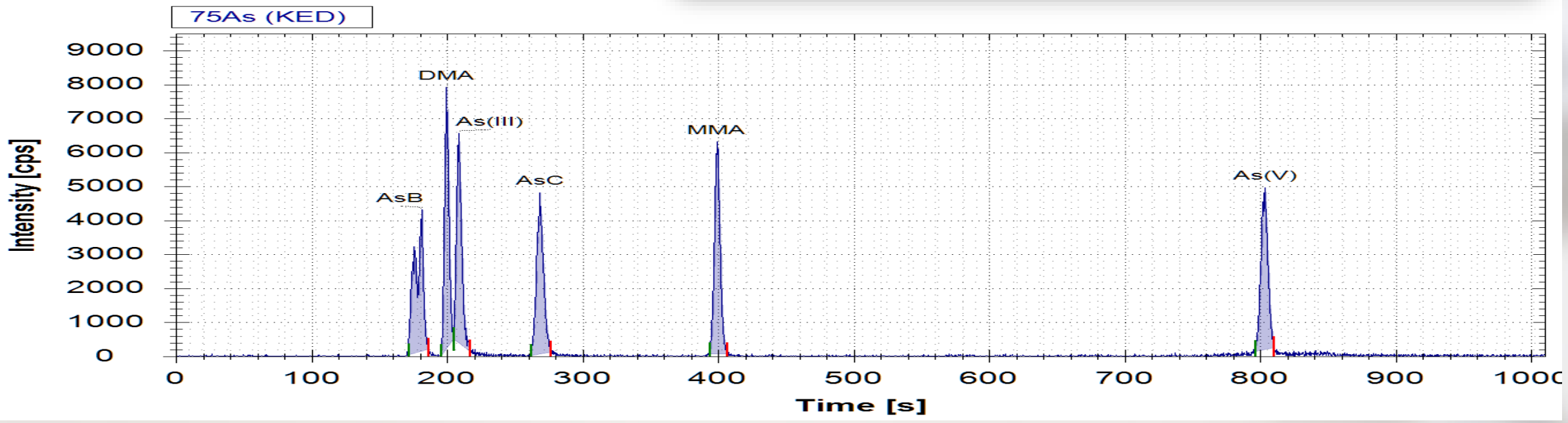
IC-ICP-MS for As Speciation

- 6 Species determined
- ~7000 cps / ppb
- ~15 Min. Runtime

- Anion Exchange:
  - Thermo Scientific Dionex IonPac AS7 (2x250mm)
  - Gradient-Elution
    - 20-200 mmol/L Ammonium carbonate
  - Flow: 0.3 mL·min^{-1}
  - Injectionvol.: 20 µL



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Water Analysis by IC-MS and IC-MS/MS

Analysis of Halo Acetic Acids (HAAs) by IC-MS/MS and IC-MS

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IC-MS/MS for HAAs diagram

High-Pressure Nonmetallic Pump

Eluent Generator (OH^-)

CR-TC

Waste

Sample Inject (Autosampler)

Separator Column IonPac AS 31

Electrolytic Eluent Suppressor

Conductivity Detector

Makeup Pump (MeCN or IPA)

MD Valve

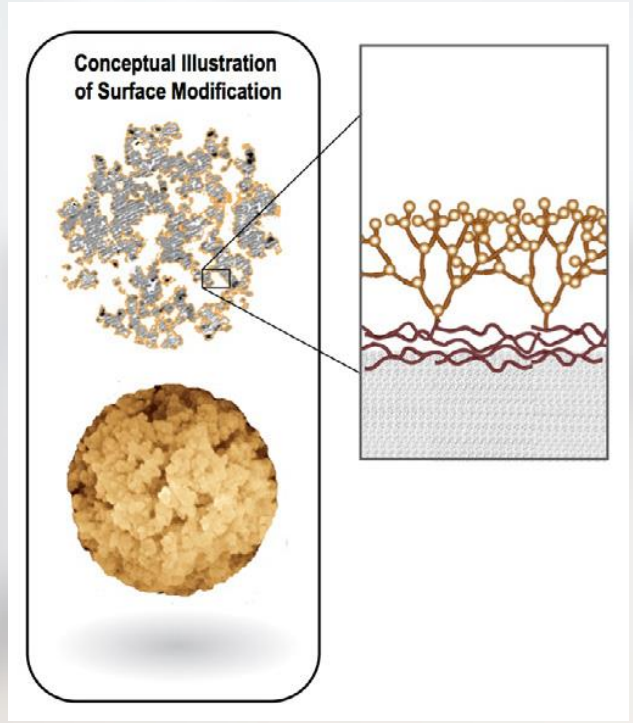
Waste

0.31 µS

TSQ MS

Data Management

Analysis of Haloacetic Acids in Municipal Drinking Water on Dionex IonPac AS31

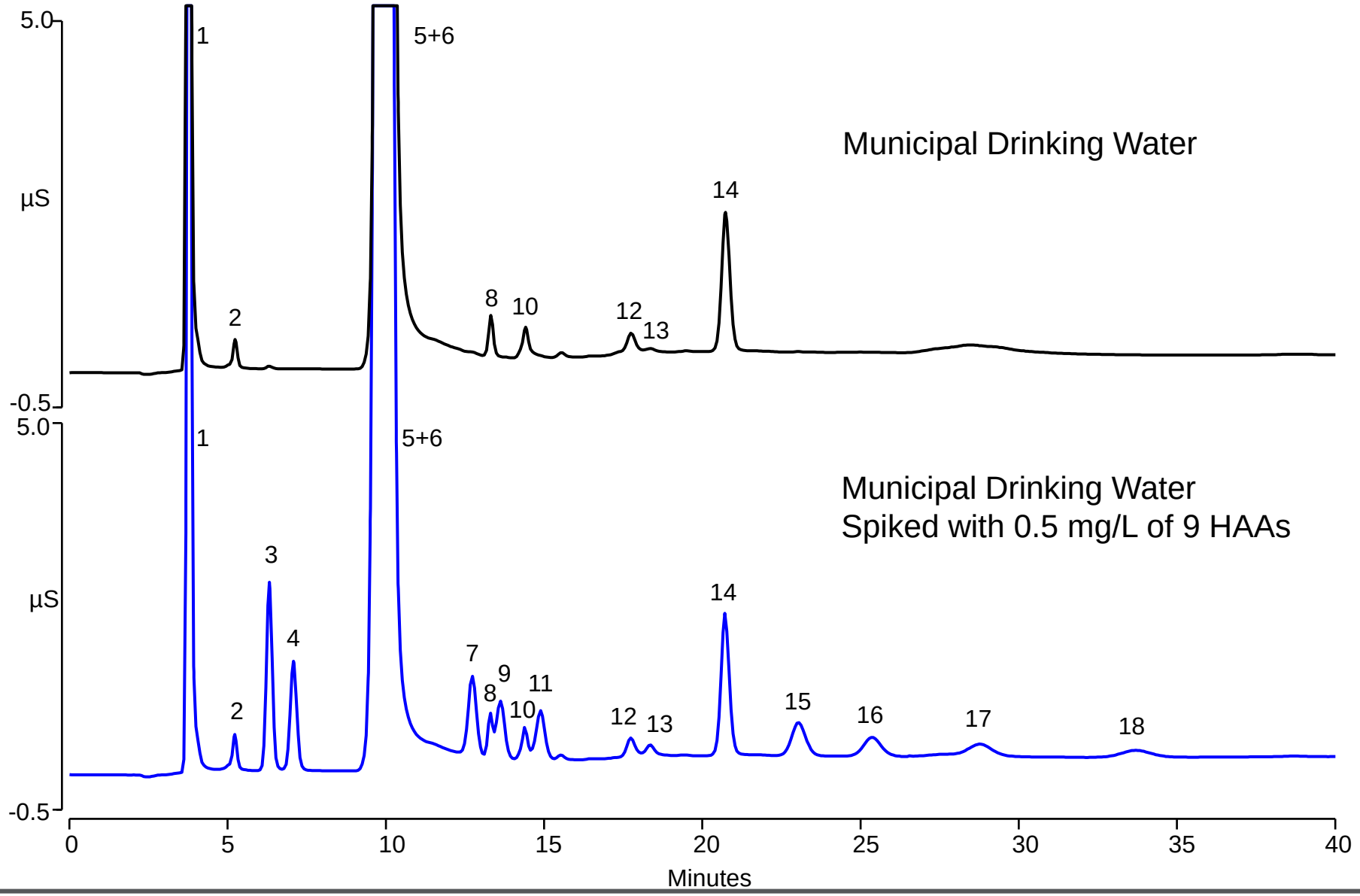


Column:	**Dionex IonPac AG31/AS31, 2mm**
Temperature:	15 ˚C
Eluent:	KOH (EG)
Gradient	17 mmol/L from 0 to 7 min, 17–85 mmol/L from 7 to 18 min, 85 mmol/L from 18 to 35 min
Flow rate:	0.30 mL/min
Inj. volume:	100 µL
Detection:	Suppressed conductivity, AutoSuppression, recycle mode
Sample	Municipal Drinking Water Spiked with 9HAAs

Peaks (Standard): in mg/L		
	1. Fluoride	NQ
	2. Unknown	NQ
	3. Monochloroacetate	0.5
	4. Monobromoacetate	0.5
	5. Chloride	NQ
	6. Sulfate+carbonate	NQ
	7. Dichloroacetate	0.5
	8. Unknown	NQ
	9. Bromochloroacetate	0.5
	10. Unknown	NQ
	11. Dibromoacetate	0.5
	12. Chlorate	NQ
	13. Bromide	NQ
	14. Nitrate	NQ
	15. Trichloroacetate	0.5
	16. Bromodichloroacetate	0.5
	17. Chlorodibromoacetate	0.5
	18. Tribromoacetate	0.5

NQ: Not Quantified

Analysis of Haloacetic Acids in Municipal Drinking Water on Dionex IonPac AS31



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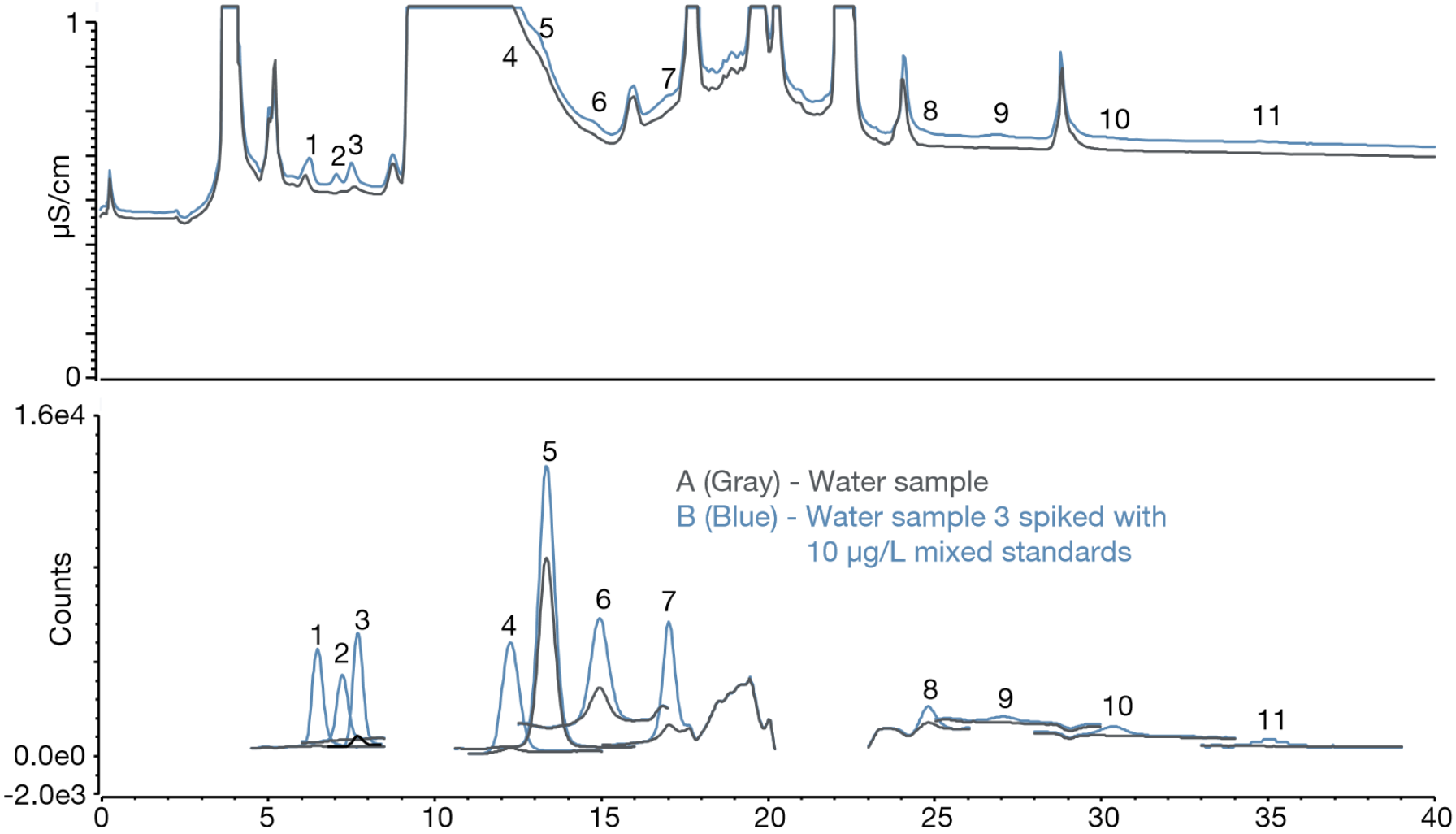
Water sample with and without spiking with 10 µg/L of 9 HAAs, Bromate and DALAPON



No.	Peak	RT (min)	Conc. (µg/L) A	Conc. (µg/L) B
1	MCAA	6.5	ND	10.7
2	MBAA	7.2	ND	11.1
3	Bromate	7.7	0.33	12.3
4	Dalapon	12.3	ND	10.4
5	DCAA	13.4	21.8	33.7
6	BCAA	15.0	4.9	14.7
7	DBAA	17.1	0.4	9.5
8	TCAA	24.8	4.7	16.5
9	BDCAA	27.0	ND	9.9
10	CDBAA	30.4	ND	10.3
11	TBAA	35.1	ND	8.8

A (Gray): Water sample 3
B (Blue): Water sample 3 spiked with 10 µg/L mixed standards

ND: Not detectable

Detection Limits for HAAs, Bromate & DALAPON

				IC – ESI MS/MS			
MDL (µg/L, n=7)	Abbreviation	EPA 557 Calculated DL	GC-ECD	AS24 Calculated DL	AS31 Calculated DL	IC X IC (2D IC)	IC-MS
Monochloroacetic acid	MCAA	0.2	0.273	0.105	0.19	0.085	0.1
Monobromoacetic acid	MBAA	0.064	0.204	0.104	0.021	0.1	0.03
Bromate	Bromate	0.02	N.D	0.059	0.014		0.12
Dalapon	Dalapon	0.038	N.D	0.05	0.079		0.12
Dichloroacetic acid	DCAA	0.055	0.242	0.044	0.019	0.41	0.033
Bromochloroacetic acid	BCAA	0.11	0.251	0.059	0.086	0.3	0.16
Dibromoacetic acid	DBAA	0.015	0.066	0.021	0.009	0.09	0.16
Trichloroacetic acid (163/119)	TCAA	0.09	0.079	0.033	0.073	0.26	0.67
Bromodichloroacetic acid	BDCAA	0.05	0.091	0.141	0.087	0.29	2.79
Chlorodibromoacetic acid	DBCAA	0.041	0.468	0.214	0.19	0.055	1.04
Tribromoacetic acid	TBAA	0.067	0.82	0.159	0.067	0.28	4.55

IC-MS/MS Method for HAAs

Suppressed ion chromatography with 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%

Determination of HAAs, Bromate and Dalapon in Drinking Water using IC-MS with IonPac AS31, 2 mm

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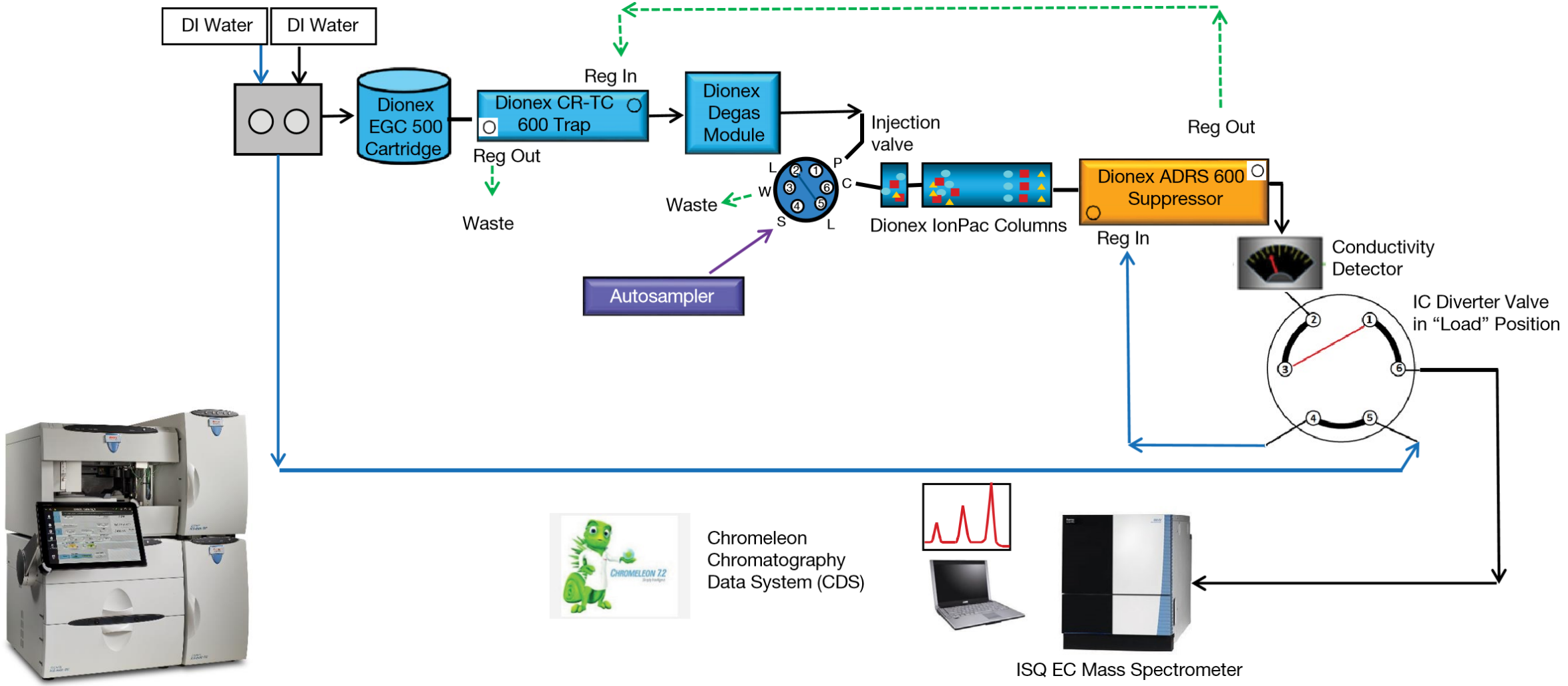
IC-MS Schematics



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Summary of method performance and comparison with MDL to U.S. EPA Method 557

Abbreviation	Retention Time	US EPA 557 DL	MDL	Calibration Range (µg/L)	r2-value
MCAA *	6.5	0.2	0.1	0.1–100	0.999
MBAA *	7.2	0.06	0.03	0.1–100	0.998
Bromate	7.7	0.02	0.12	0.5–100	0.998
Dalapon	12.3	0.04	0.12	0.5–100	0.999
DCAA *	13.4	0.06	0.03	0.1–100	0.998
BCAA	15	0.11	0.16	0.5–100	0.998
DBAA *	17.1	0.02	0.16	0.5–100	0.999
TCAA *	24.8	0.09	0.67	1–100	0.999
BDCAA	27	0.05	2.79	4–100	0.998
DBCAA	30.4	0.04	1.04	4–100	1
TBAA	35.1	0.07	4.55	10–100	1

Summary of IC-MS method for the determination of HAAs

- IC-MS method is fast (40 min vs. 60 min in U.S. EPA Method 557)

  and linear for 11 analytes with an r2 value range of 0.998 to 1.

- The method meets the sensitivity for the determination of U.S. EPA regulated HAA5,

  but its not regulated yet.

- Typically, the method is sensitive for the determination of not yet regulated HAAs

  (BCAA, BDCAA, CDBAA, TBAA).

Thank You – Any Questions?