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Applications of Ion Chromatography for the Analysis of Water-Based Products in the Food Industry

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Outline

- Conventional water analysis of common inorganic anions and cations
- Analysis of disinfection by-products
  - Bromate analysis
  - Haloacetic acid analysis
- Cyanide analysis
- Hexavalent chromium analysis
  - Chromium speciation
- Conclusions

CONVENTIONAL WATER ANALYSIS OF COMMON INORGANIC ANIONS AND CATIONS

IC Regulatory Methods in the European Union for Water Analysis

ISO 10304-01

Water quality – Determination of dissolved fluoride, chloride, nitrite, orthophosphate, bromide, nitrate and sulfate ions, using liquid chromatography of ions – Part 1 Method for water with low contamination.

ISO 10304-03

Water quality – Determination of dissolved anions by liquid chromatography of ions – Part 3: Determination of chromate, iodide, sulfite, thiocyanate and thiosulfate.

ISO 10304-04

Water quality – Determination of dissolved anions by liquid chromatography of ions – Part 4: Determination of chlorate, chloride and chlorite in water with low contamination

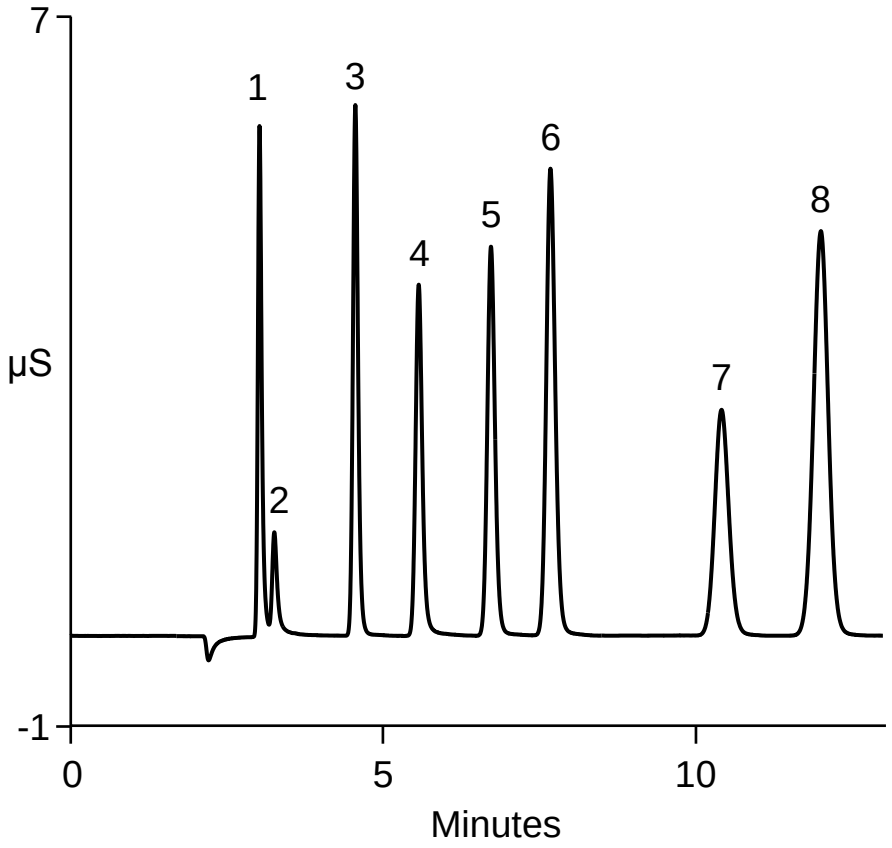
ISO 14911

Determination of dissolved Li^+, Na^+, NH_4^+, K^+, Mn^{2+}, Ca^{2+}, Mg^{2+}, Sr^{2+}, and Ba^{2+} using ion chromatography – Method for water and wastewater.

Carbonate Chemistry Using Dionex IonPac AS22

- Universal purpose carbonate-based anion exchange column for anion analysis in diverse water sample matrices
- Improved performance in comparison with older columns
  - Improved peak shape and efficiencies
  - Improved selectivity
  - Carbonate (from dissolved bicarbonate) resolved from inorganic anions
- High anion exchange capacity
  - 210 µequiv/column for 250 mm × 4 mm i. d., super-macroporous

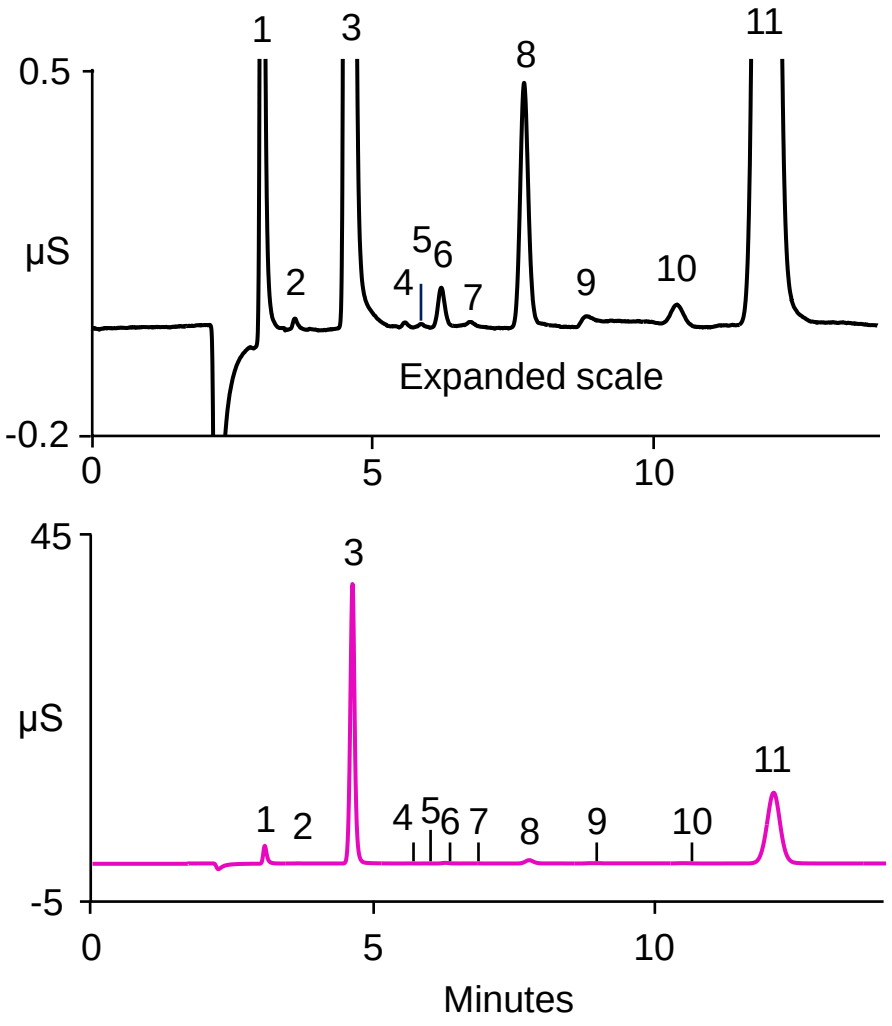
Separation of Common Anions on a Dionex IonPac AS22 Hyperbranched Anion Exchanger



Column:	Dionex IonPac AS22 with guard
Dimensions:	250 mm × 4 mm i. d.
Temperature:	30 °C
Eluent:	4.5 mmol/L Na_2CO_3 / 1.4 mmol/L $NaHCO_3$
Flow rate:	1.2 mL/min
Inj. volume:	10 µL
Detection:	Suppressed conductivity, AutoSuppression, recycle mode

Peaks		
1. Fluoride	5	mg/L
2. Acetate	20	
3. Chloride	10	
4. Nitrite	15	
5. Bromide	25	
6. Nitrate	25	
7. Orthophosphate	40	
8. Sulfate	30	

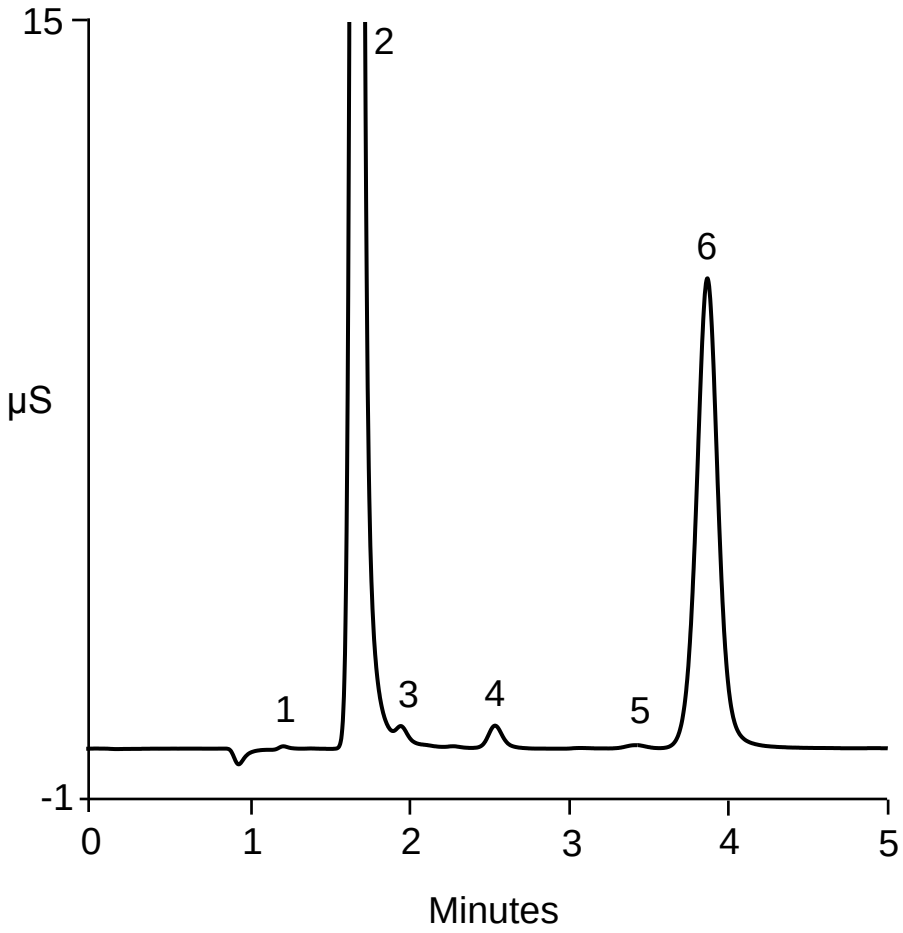
Determination of Common Anions in Municipal Drinking Water



Column:	Dionex IonPac AS22 with guard
Dimensions:	250 mm × 4 mm i. d.
Temperature:	30 ºC
Eluent:	4.5 mmol/L Na_2CO_3 / 1.4 mmol/L $NaHCO_3$
Flow rate:	1.2 mL/min
Inj. volume:	25 µL
Detection:	Suppressed conductivity, AutoSuppression, recycle mode

Peaks			
	1. Fluoride	0.84	mg/L
	2. Formate	0.03	
	3. Chloride	15.59	
	4. Nitrite	0.01	
	5. Unknown	–	
	6. Chlorate	0.18	
	7. Bromide	0.02	
	8. Nitrate	0.89	
	9. Carbonate	–	
	10. Orthophosphate	0.22	
	11. Sulfate	0.45	

Fast Determinations of Anions in a Municipal Drinking Water Sample



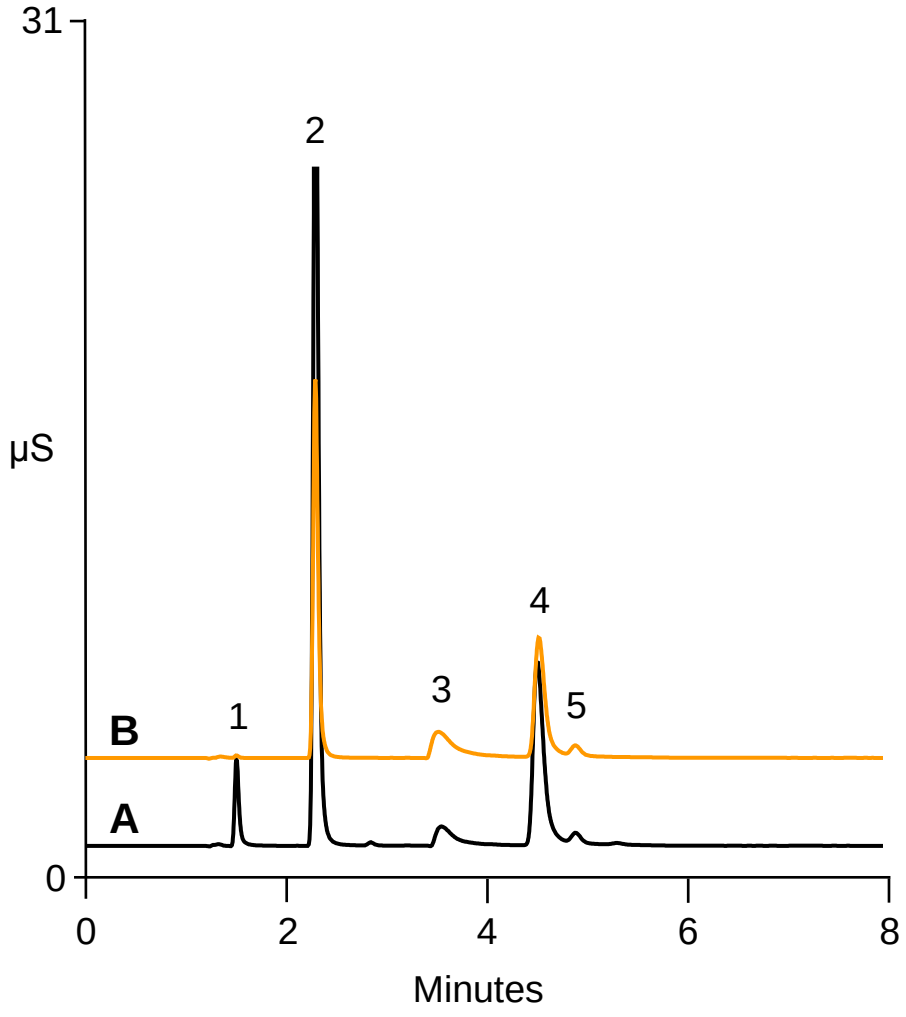
Column:	Dionex IonPac AS22-Fast with guard
Dimensions:	150 mm × 2 mm i. d.
Temperature:	30 ºC
Eluent:	4.5 mmol/L Na_2CO_3 / 1.4 mmol/L $NaHCO_3$
Flow rate:	0.5 mL/min
Inj. volume:	2.5 µL
Detection:	Suppressed conductivity, AutoSuppression, recycle mode

Peaks:			
	1. Fluoride	0.4	mg/L
	2. Chloride	99.5	
	3. Nitrite	2.7	
	4. Nitrate	4.3	
	5. Orthophosphate	8.9	
	6. Sulfate	51.8	

Hydroxide Chemistry Using Dionex IonPac AS18-4µm

- Universal purpose hydroxide-selective anion exchanger column for anion analysis
- Moderate capacity (45 µequiv/column)
- Separation of standard anions and acetate in less than eight minutes
- Complies with ISO and EPA Methods
- Highest performance in isocratic mode (ideal with Eluent Generation)

High-Pressure IC of Inorganic Anions in Municipal Drinking Water Samples

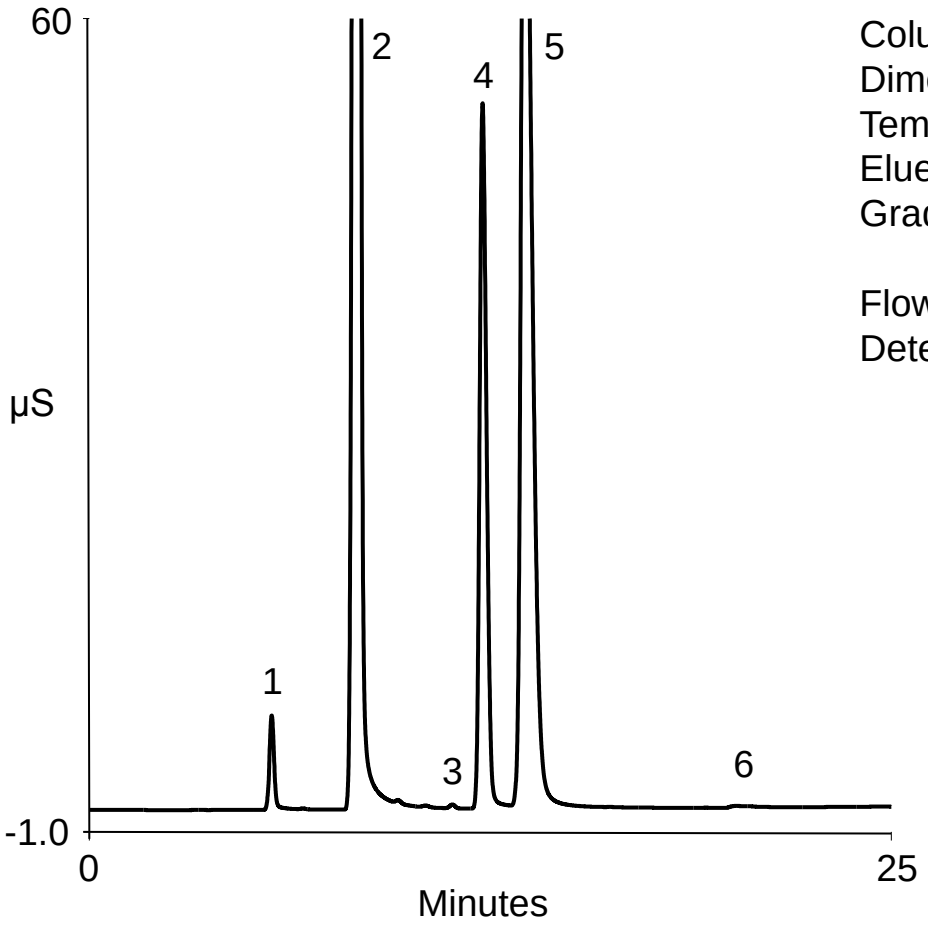


Column:	Dionex IonPac AS18-4µm with guard
Dimensions:	150 mm × 2 mm i. d.
Temperature:	30 °C
Eluent:	23 mmol/L KOH (EG)
Flow rate:	0.38 mL/min
Inj. Volume:	5 µL
Detection:	Suppressed conductivity, AutoSuppression, recycle mode
Samples:	A. City 1 Drinking Water B. City 2 Drinking Water
Dilutions:	A: Undiluted B: 5-fold dilution

Peaks (mg/L):

	A	B
1. Fluoride	0.86	0.11
2. Chloride	18.0	36.0
3. Carbonate	--	--
4. Sulfate	12.0	38.0
5. Nitrate	0.57	2.90

Anion Analysis in a Treated Wastewater

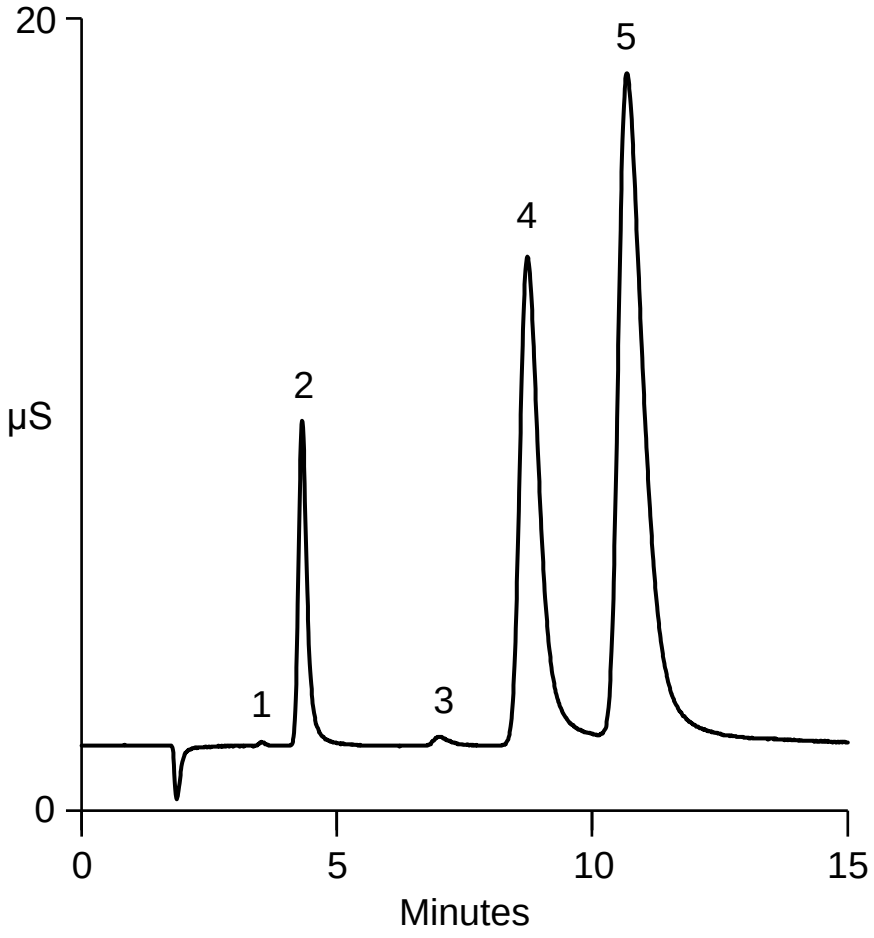


Column:	IonPac AS19
Dimensions:	250 mm × 0.4 mm i. d.
Temperature:	30°C
Eluent:	KOH (EG)
Gradient:	10 bis 25 mmol/L (0-10 min), 25 to 70 mmol/L (10-20 min)
Flow rate:	10 µL/min
Detection:	Suppressed conductivity, ACES 300 AutoSuppression, recycle mode

Concentration, mg/L

Peak	Cap IC	ICS-2100
1. Fluoride	1.76	1.69
2. Chloride	180.24	179.48
3. Bromide	0.42	0.51
4. Nitrate	11.84	11.92
5. Sulfate	96.89	96.79
6. Orthophosphate	0.94	1.25

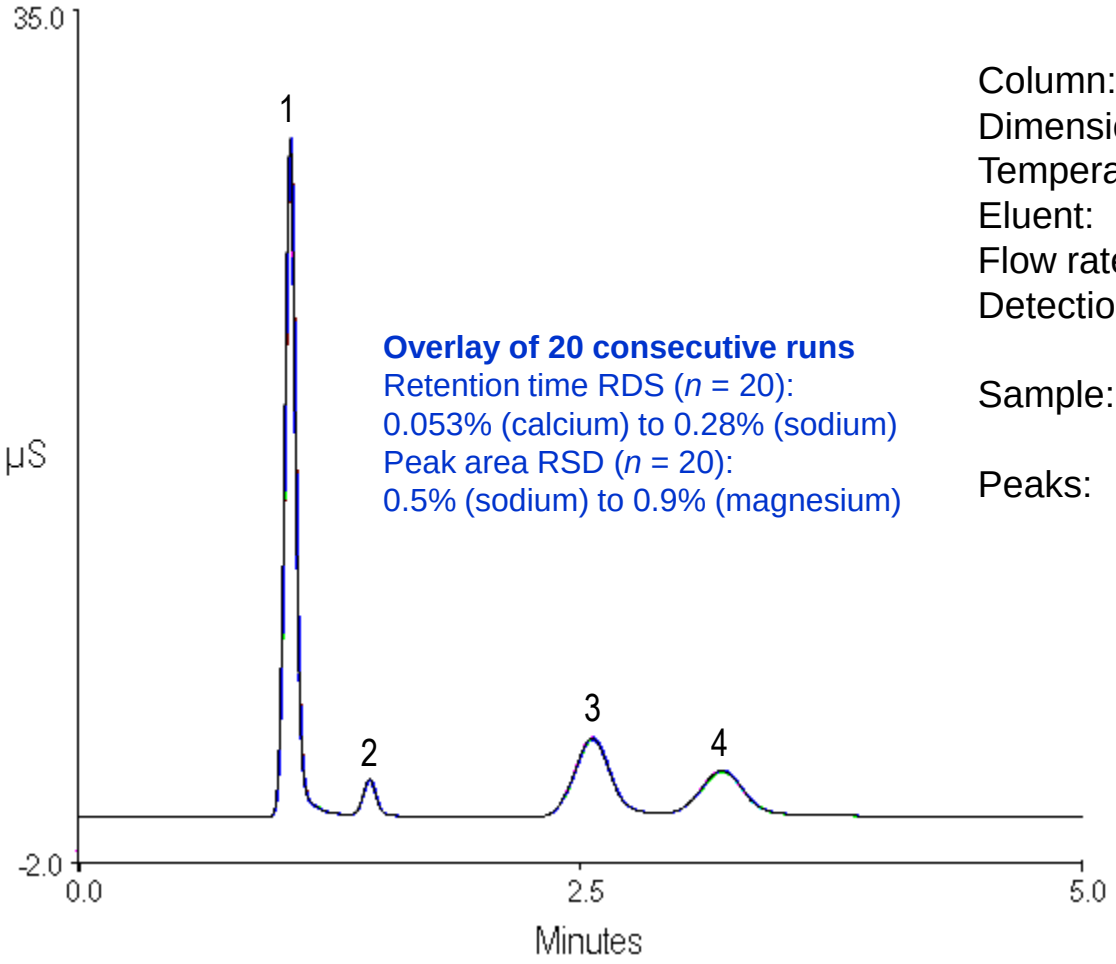
Cation Analysis of Municipal Drinking Water



Column:	Dionex IonPac CS12A with guard
Dimensions:	250 mm × 4 mm i. d.
Temperature:	30 ºC
Eluent:	18 mmol/L MSA
Flow rate:	1 mL/min
Detection:	Suppressed conductivity, AutoSuppression, recycle mode
Inj. volume:	25 µL
Sample:	Tap water, acidified to pH 3

Peaks:
1. Lithium
2. Sodium
3. Potassium
4. Magnesium
5. Calcium

Rapid Determination of Cations - Treated Wastewater

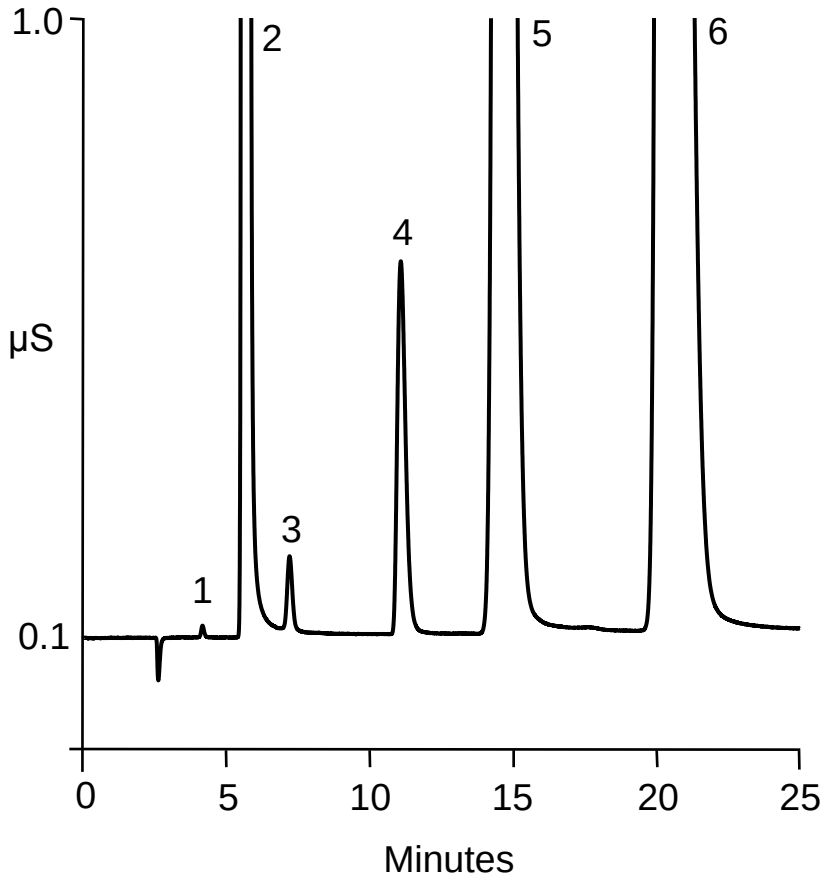


Overlay of 20 consecutive runs
Retention time RDS (*n* = 20):
0.053% (calcium) to 0.28% (sodium)
Peak area RSD (*n* = 20):
0.5% (sodium) to 0.9% (magnesium)

Column:	CS12A-5m column
Dimensions:	150 mm × **0.4** mm i. d.
Temperature:	30°C
Eluent:	28 mmol/L MSA (EG)
Flow rate:	18 µL/min
Detection:	Suppressed conductivity, CCES 300
Sample:	Treated wastewater (1:10 diluted)

Peaks:		
	1. Sodium	19.6 mg/L
	2. Potassium	0.8
	3. Magnesium	3.5
	4. Calcium	3.1

Municipal Drinking Water Analysis Utilizing a High-Capacity Cation Exchange Column



Column:	Dionex IonPac CS16		
Dimensions:	250 mm × 5 mm i. d.		
Temperature:	40 °C		
Eluent:	30 mmol/L MSA		
Flow rate:	1 mL/min		
Inj. volume:	25 µL		
Detection:	Suppressed conductivity, AutoSuppression, recycle mode		
Peaks:	1. Lithium	0.01	mg/L
	2. Sodium	19.73	
	3. Ammonium	0.07	
	4. Potassium	0.99	
	5. Magnesium	7.21	
	6. Calcium	18.54	

ANALYSIS OF DISINFECTION BY-PRODUCTS

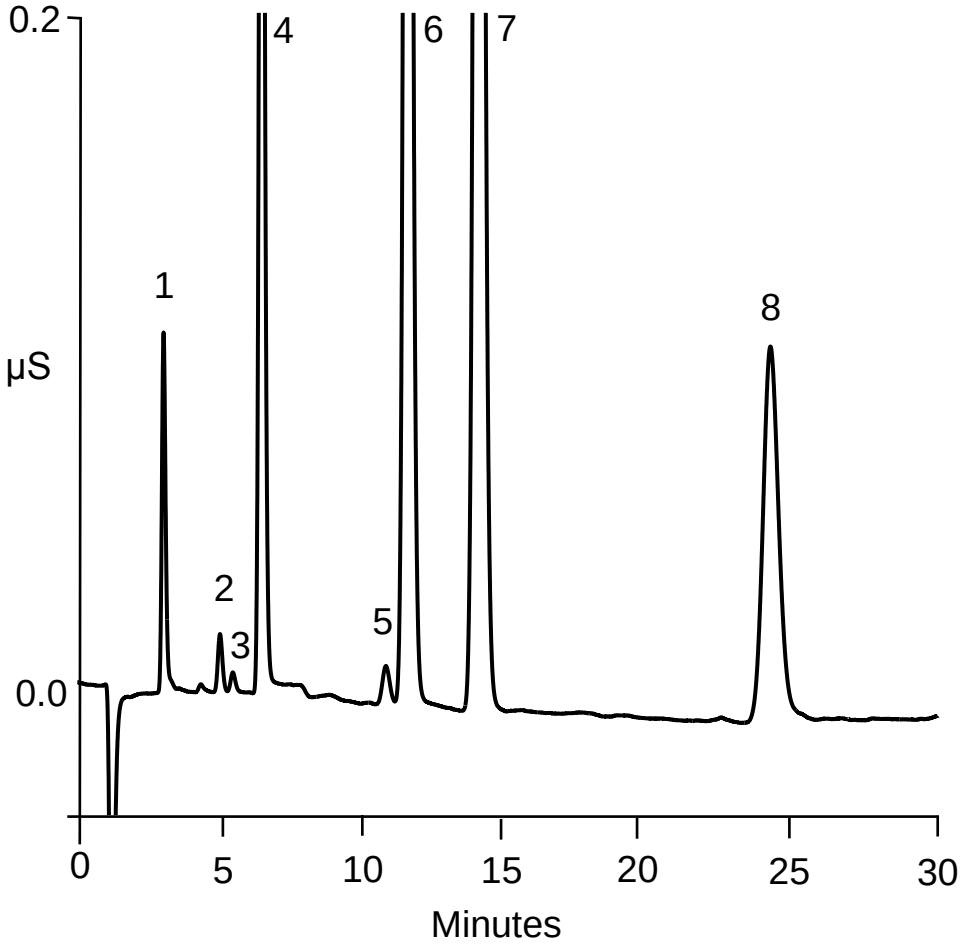
Requirements for Trace Analysis of Bromate in Drinking and Bottled Water

- High resolution between analyte ions
  - Minimal interferences by matrix ions
  - Suitable for different concentrations of matrix ions
- Sensitive detection – preferably in the low µg/L range – with suppressed conductivity detection
- Simple and direct injection technique
- Automation
  - Avoid labor-intensive SPE methods
  - Inline method

Current IC Methods for Bromate Analysis

Technique	EPA Method	Column	Eluent	MDL (µg/L)
IC-Suppressed Cond.	300.0 (B)	Dionex IonPac AS9-HC or AS23 Dionex IonPac AS19	Carbonate Hydroxide	CD 5.0, 1.63 0.32
IC-Suppressed Cond.	300.1	AS9-HC or AS23 AS19	Carbonate Hydroxide	5.0, 1.63 0.32
2D-IC Suppressed Conductivity	302.0	Dionex IonPac AS19, 4 mm to AS24, 2 mm Dionex IonPac AS19, 4 mm to AS20, 0.4 mm	Hydroxide Hydroxide	0.036, ~ 0.004
IC – Suppressed Conductivity + Post-Column ODA	317.0	Dionex IonPac AS9-HC Dionex IonPac AS19	Carbonate Hydroxide	UV/vis 0.14
IC – Suppressed Conductivity + Post-Column acidified KI	326.1	Dionex IonPac AS9-HC Dionex IonPac AS19	Carbonate Hydroxide	0.17
IC-ICP/MS	321.8	CarboPac PA100	Nitric acid + ammonium nitrate	MS 0.010

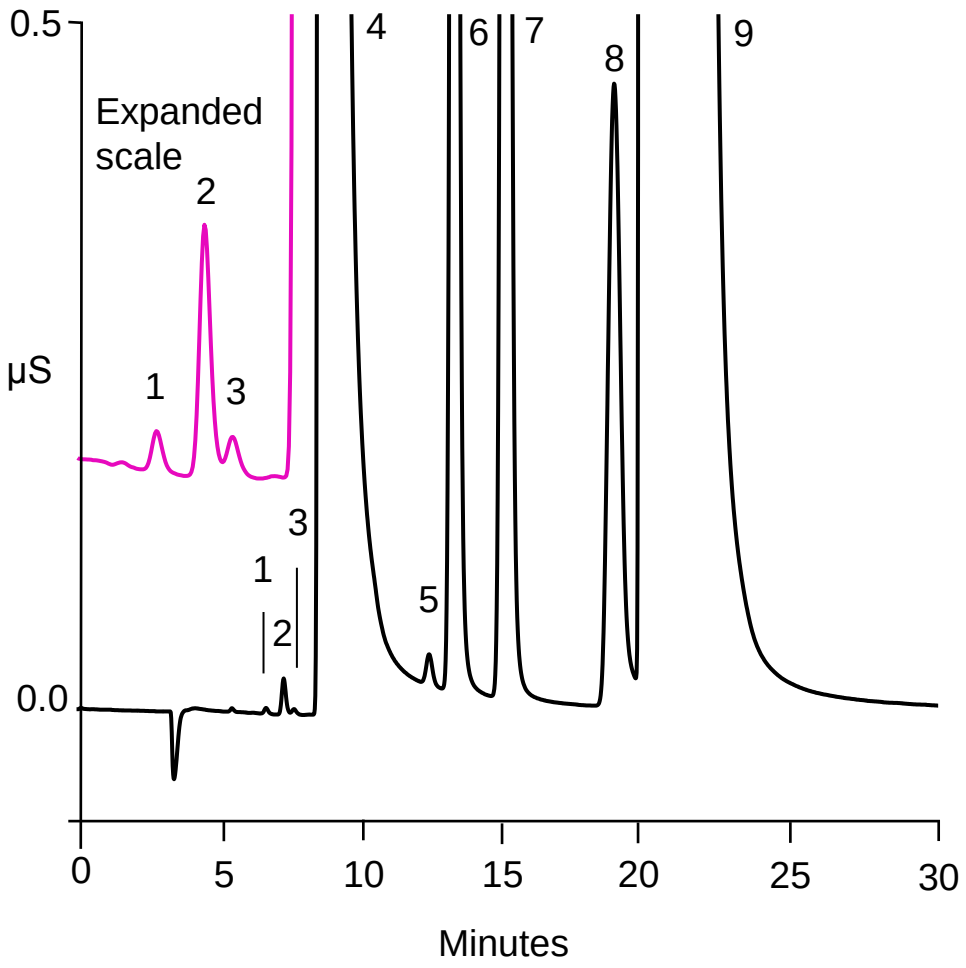
Conventional Trace Analysis of Bromate with Suppressed Conductivity Detection



Column:	Dionex IonPac AS23 with guard
Dimensions:	250 mm × 4 mm i. d.
Temperature:	30 °C
Eluent:	4.5 mmol/L Na_2CO_3 / 1.0 mmol/L $NaHCO_3$
Flow rate:	1 mL/min
Inj. volume:	100 µL
Detection:	Suppressed conductivity, Thermo Scientific Dionex CRD 300
Background:	< 1.0 µS
Scrubber:	0.5 mol/L KOH (Recycle mode)

Peaks:		
1. Fluoride	10	µg/L
2. Chlorite	10	
3. Bromate	5	
4. Chloride	100	
5. Chlorate	10	
6. Bromide	500	
7. Nitrate	500	
8. Sulfate	100	

Trace Analysis of Bromate with RFIC-EG

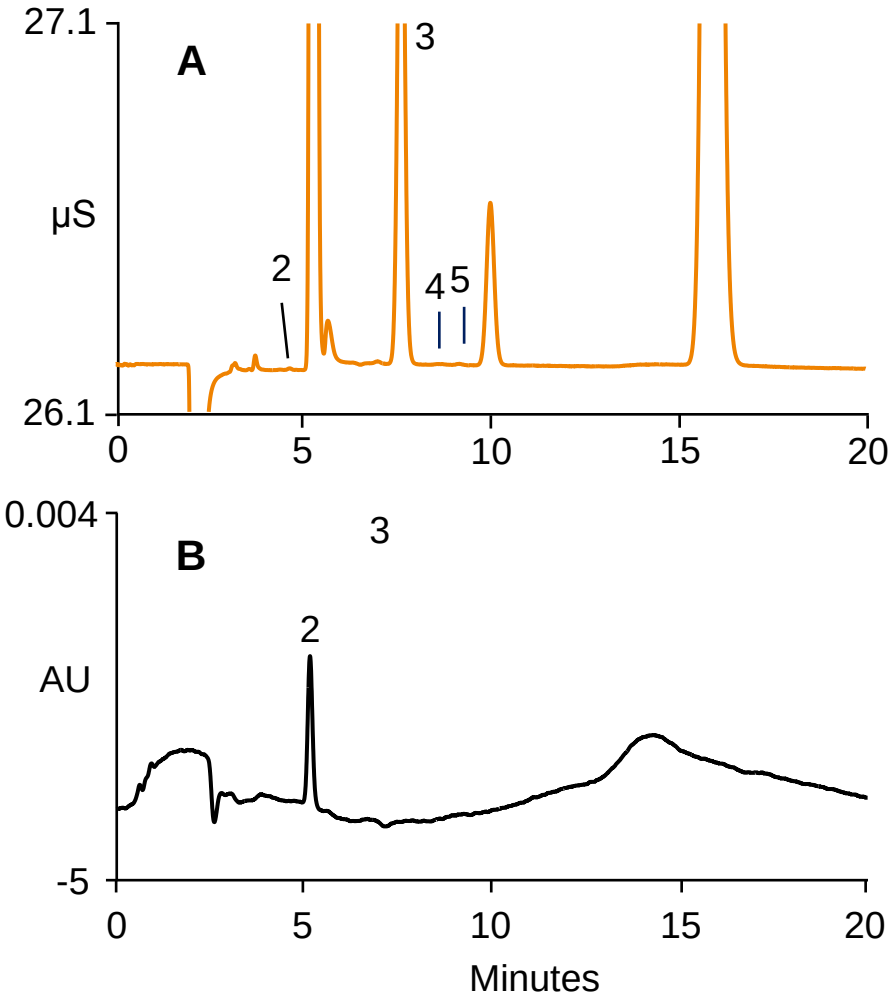


Column:	Dionex IonPac AS19 with guard
Dimensions:	250 mm × 4 mm i. d.
Temperature:	30 °C
Eluent:	20 mmol/L KOH (EG)
Flow rate:	0.75 mL/min
Inj. Volume:	100 µL
Detection:	Suppressed conductivity, external water mode

Peaks:

1. Fluoride		
2. Chlorite		
3. Bromate	5	µg/L
4. Chloride	100	mg/L
5. Chlorate		
6. Bromide		
7. Nitrate		
8. Carbonate		
9. Sulfate	100	mg/L

Analysis of Ozonated Bottled Water Using EPA Method 326.0



Column:	Dionex IonPac AS9-HC with guard
Eluent:	9 mmol/L Na_2CO_3
Temperature:	30 °C
Flow rate:	1.3 mL/min
Inj. volume:	225 µL
Detection:	A. Suppressed conductivity, External water mode B. UV, 352 nm
Post-column reagent:	Acidified KI
Post-column flow rate:	0.4 mL/min
Post-column heater:	80 °C

Peaks:		
	1. Chlorite	n.d. µg/L
	2. Bromate	1.52
	3. DCA*	
	4. Bromide	1.12
	5. Chlorate	1.08
	2. Bromate	1.84 µg/L

* DCA = Dichloroacetate
Quality control surrogate

Features of the IC × IC Technique

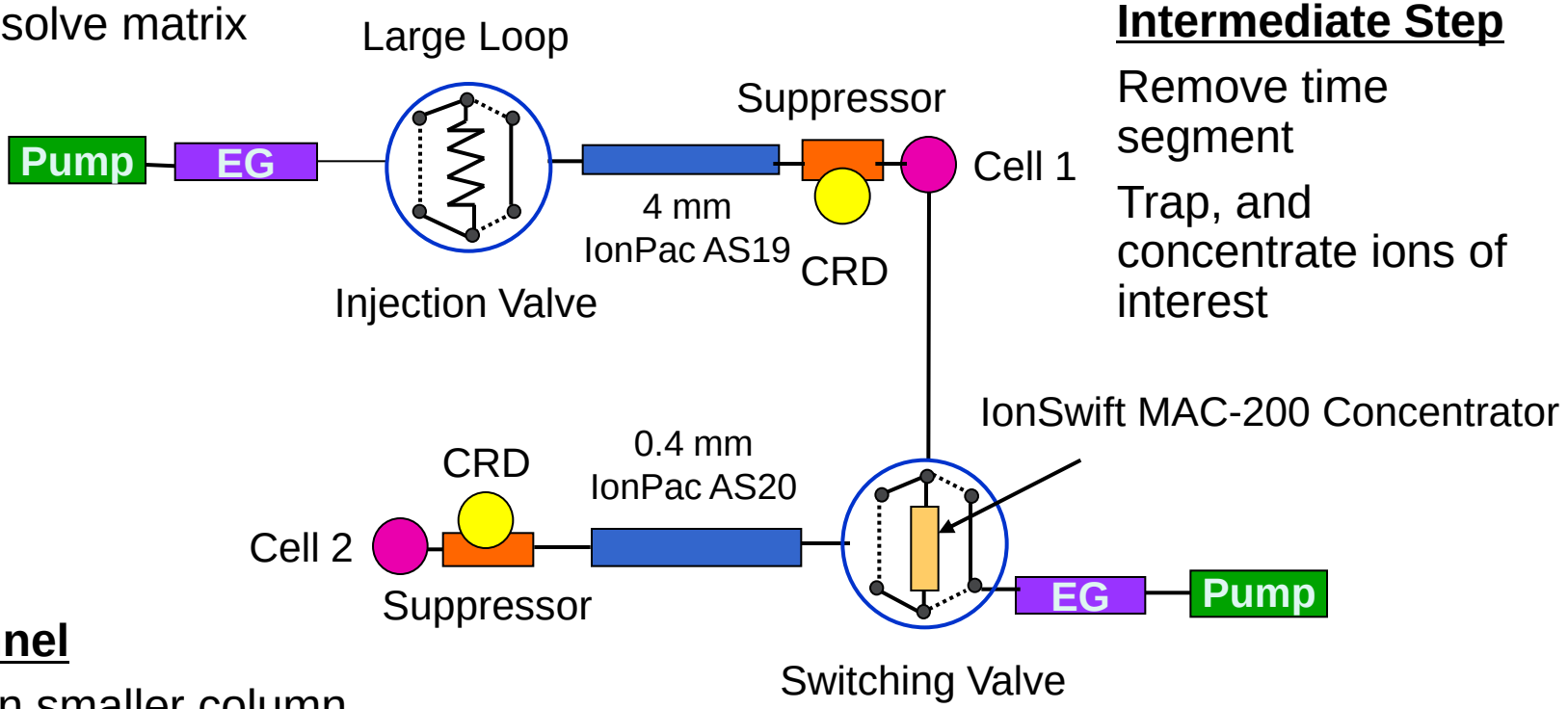
- Allows large-volume injection onto the first column (4 mm column)
  - **Possibility of large-volume injection** in comparison to the standard method, because capacity and selectivity of the first analytical column determines recovery; analyte analysis is carried out on the second column.
- Focuses the analytes in the concentrator column after suppression
  - Hydroxide eluent is converted to water, ideal for **focusing or pre-concentrating** analytes
- **Increased sensitivity** by using a 0.4 mm column with the lower flow rate as the second column
- Possibility of using separator columns with different selectivity as second columns
  - **Higher selectivity**
- **Easy implementation with a dual-channel ion chromatography system**

Instrumental Setup of IC × IC for Bromate Analysis

1st Channel

Large-loop injection

Partially resolve matrix



Intermediate Step

Remove time segment

Trap, and concentrate ions of interest

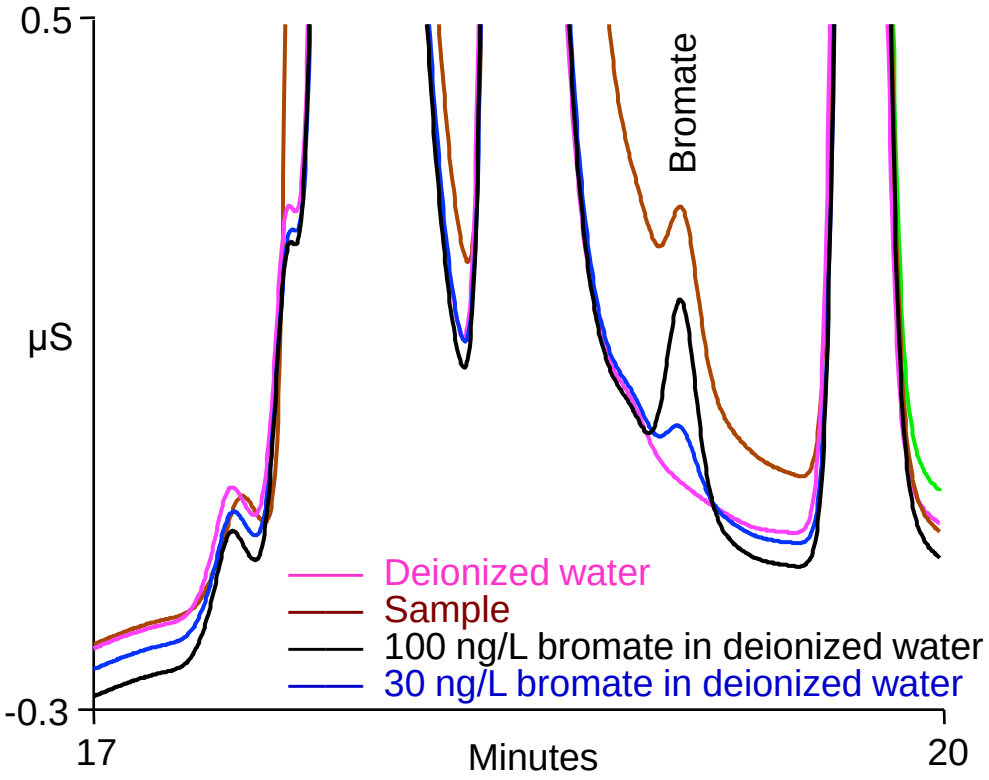
2nd Channel

Resolve on smaller column

Sensitivity enhancement

Different selectivity optional

Trace Analysis of Bromate on a Capillary IonPac AS20 Column with IC × IC



A. Channel 1

Column:	Dionex IonPac AS19 with guard
Dimensions:	250 mm × 4 mm i. d.
Temperature:	30 ºC
Eluent:	10 mmol/L KOH (0 to 12 min), 65 mmol/L KOH (12 to 35 min), 10 mmol/L KOH (35 to 40 min)
Flow rate:	1 mL/min
Inj. volume:	1000 µL
Detection:	Suppressed conductivity

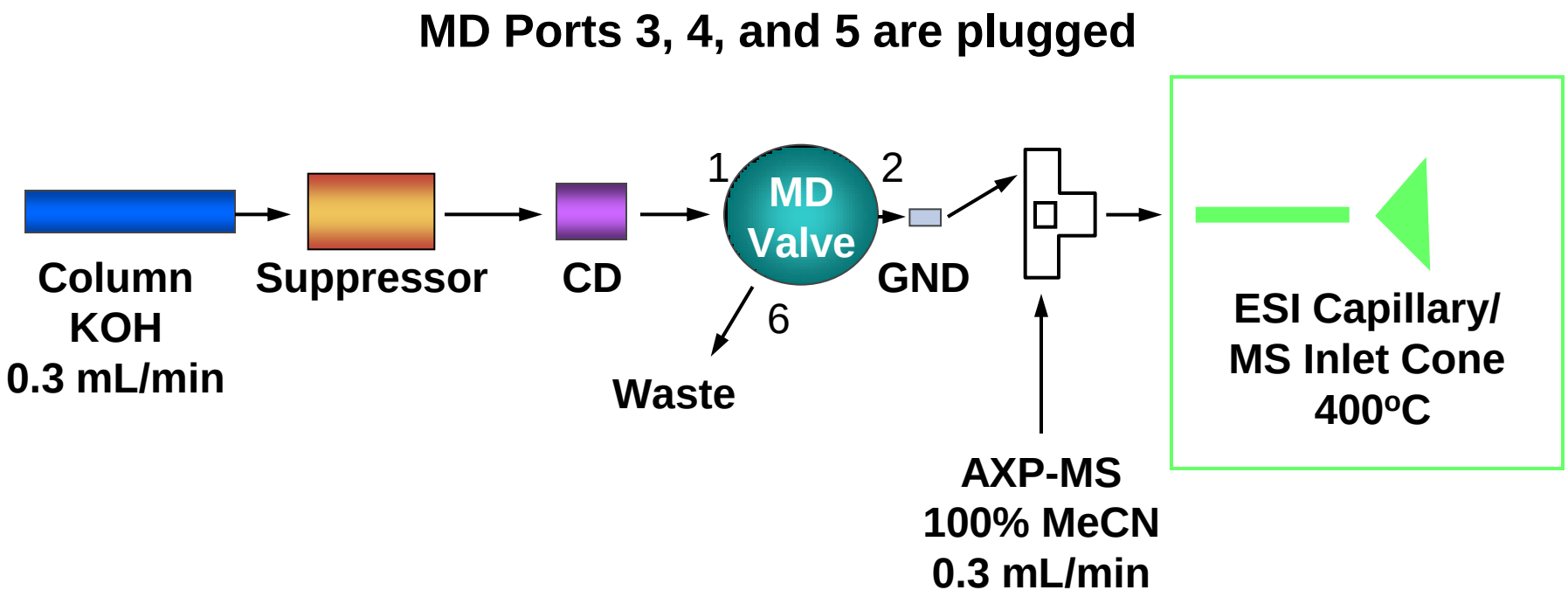
B. Channel 2

Column:	Thermo Scientific Dionex IonPac AS20
Dimensions:	250 mm × 0.4 mm i. d.
Temperature:	30 ºC
Eluent:	8 mmol/L KOH (0 to 12 min), 8-65 mmol/L KOH (12 to 35 min) and 8 mmol/L KOH (35 to 40 min)
Flow rate:	10 µL/min
Detection:	Suppressed conductivity
Concentrator:	IonSwift MAC-200
Dimensions:	80 mm × 0.75 mm i. d. 2500 µL from channel 1 (7.5–10 min)

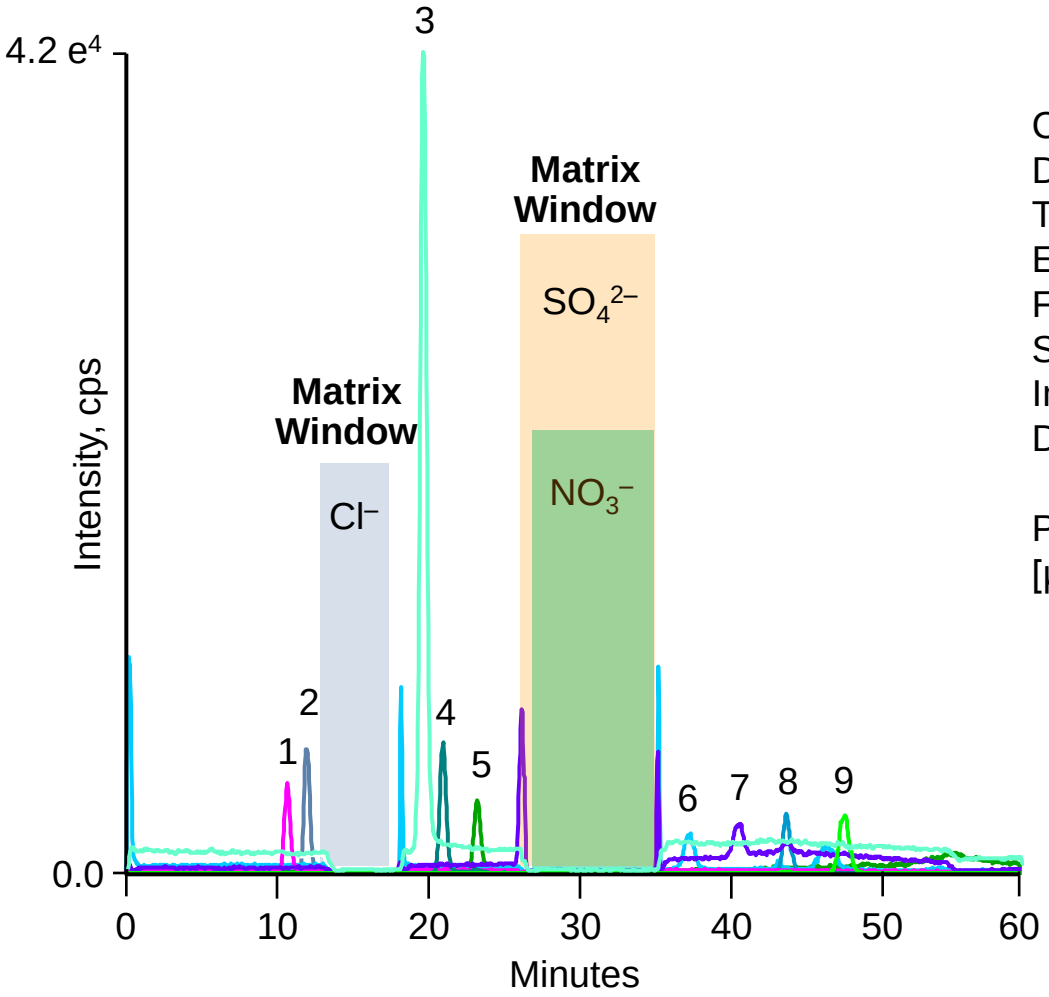
U.S. EPA Regulation for Haloacetic Acids

- Current: Stage 1 DBPR
  - Monitor of HAA5 at all plants that disinfect with chlorine
    - Total MCAA, MBAA, DCAA, DBAA, and TCAA
    - Maximum Contamination Level (MCL) = 60 µg/L
  - Maximum Contamination Level Goal (MCLG)
    - DCAA should not be present
    - TCAA less than 30 µg/L
- Future
  - MCL less than 30 µg/L for HAA5 proposed in Stage 2 DBPR

Flow Diagram with Matrix Diversion



Trace Analysis of Haloacetic Acids on Dionex IonPac AS24



Column:	Dionex IonPac AS24
Dimensions:	250 mm × 2 mm i.d.
Temperature:	30 °C
Eluent:	KOH gradient (EG)
Flow rate:	0.3 mL/min
Solvent:	0.3 mL/min MeCN
Inj. volume:	100 µL
Detector:	-ESI-MS/MS, SRM mode

Peaks: [µg/L]		
	1. Chloroacetic acid	6
	2. Bromoacetic acid	4
	3. Dichloroacetic acid	6
	4. Bromochloroacetic acid	4
	5. Dibromoacetic acid	2
	6. Trichloroacetic acid	2
	7. Bromodichloroacetic acid	2
	8. Chlorodibromoacetic acid	10
	9. Tribromoacetic acid	20

Simulated matrix: sulfate 250 mg/L; chloride 250 mg/L; nitrate 20 mg/L; NH_4Cl 100 mg/L

MDLs for HAAs and Bromate in Deionized Water and Simulated Matrix

Analyte (m/z)	DI H_2O		*Simulated Matrix	
	MDL *n* = 7 ng/L	%RSD	MDL *n* = 7 ng/L	%RSD
MCAA (93)	110	6.4	192	5.3
DCAA (127)	88	6.2	207	9.8
Bromate (127)	119	6.6	282	12.4
MBAA (137)	271	14.5	352	16.3
TCAA (161)	307	15.6	397	23.2
BCAA (173)	210	9.8	259	8.5
DBAA (216.8)	177	10.1	262	9.3
DCBAA (206.8)	762	17.5	783	18.2
DBCAA (206.8)	837	18.3	844	12.2
TBAA (251)	894	21.1	952	31.5

***** Simulated matrix: sulfate 250 mg/L; chloride 250 mg/L; nitrate 20 mg/L; NH_4Cl 100 mg/L

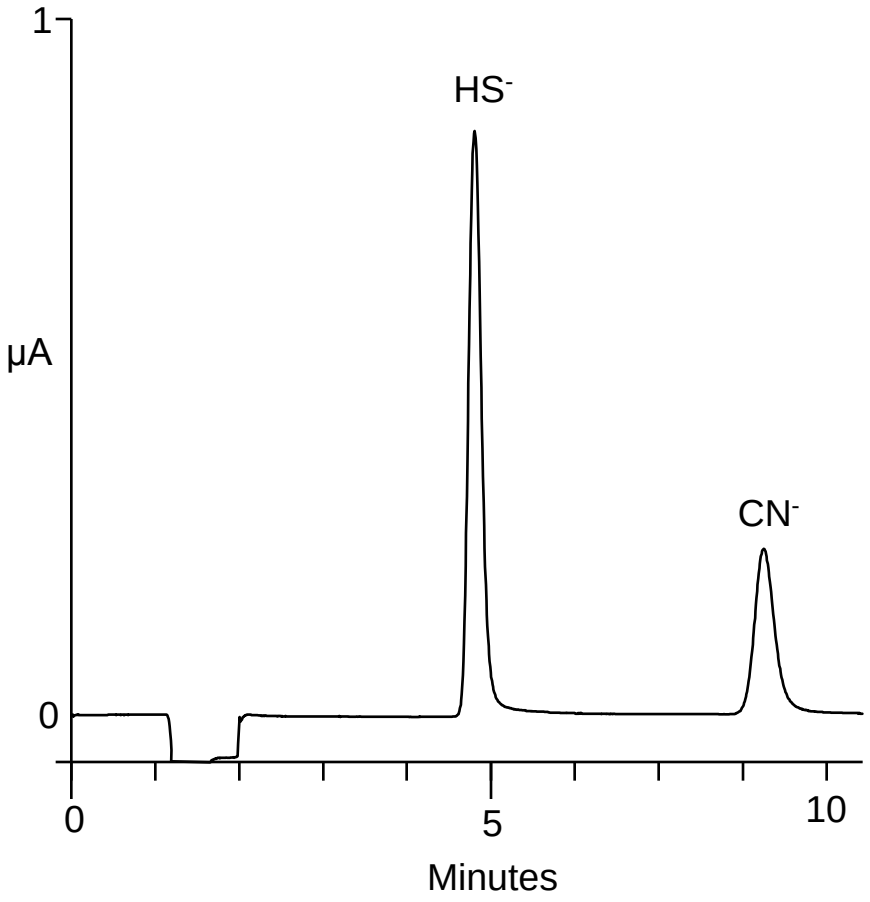
Recovery Rates

Analyte	% Recovery			
	500 ppt	750 ppt	1000 ppt	2000 ppt
MCAA	97.3	98.2	96.8	99.9
DCAA	93.2	97.6	97.4	101.4
Bromate	101.0	97.3	98.5	105.2
MBAA	90.7	91.2	96.5	97.8
TCAA	92.6	94.7	98.1	102.2
BCAA	94.8	97.2	103.7	98.4
DBAA	93.1	95.2	97.6	103.5
DCBAA	n. n.	n. n.	93.5	107.2
DBCAA	n. n.	n. n.	109.7	97.9
TBAA	n. n.	n. n.	88.4	93.5

Recovery rates for the simulated matrix with 250 mg/L Cl^-, 250 mg/L SO_4^{2-} and 20 mg/L NO_3^- were determined in comparison to deionized water.

CYANIDE ANALYSIS

Analysis of Sulfide and Cyanide



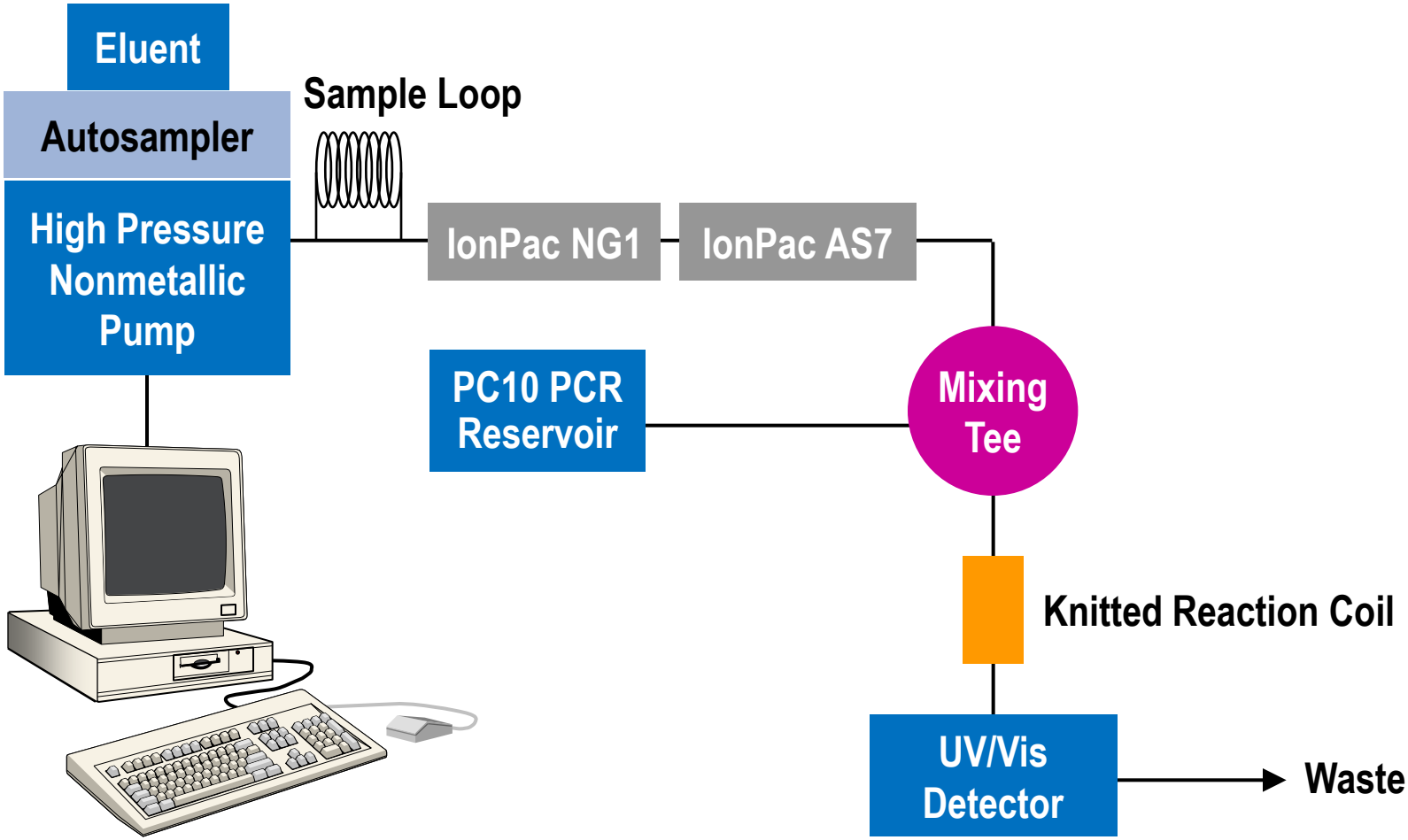
Column:	CarboPac PA1 with Guard
Eluent:	0.1 mol/L NaOH + 0.5 mol/L NaOAc + 0.5 % (v/v) ethylenediamine
Flow rate:	1 mL/min
Detection:	DC Amperometry, Ag electrode, 0 V
Inj. volume:	50 µL
Sample preparation:	Samples have been acidified, distilled acc. DIN 38 405 D13 and absorbed in 0.1-1 mol/L NaOH.

HEXAVALENT CHROMIUM ANALYSIS BY IC AND CHROMIUM SPECIATION BY IC-ICP

Hexavalent Chromium Analysis with Post-Column Derivatization and UV/Vis Detection

- Health concerns
  - Trivalent chromium is nontoxic
  - Hexavalent chromium is very toxic
- Traditional analysis method
  - EPA Method 218.4 – chelation extraction, atomic absorption
  - Positive interference from some metals
  - Cumbersome – not automated
  - Modest detection limits (~5 ppb)
- IC analysis method
  - EPA Method 218.6 (ASTM Method D5257-03) – IC separation of chromium VI coupled with post-column reaction (diphenylcarbizide) – UV/Vis detection (530 nm)

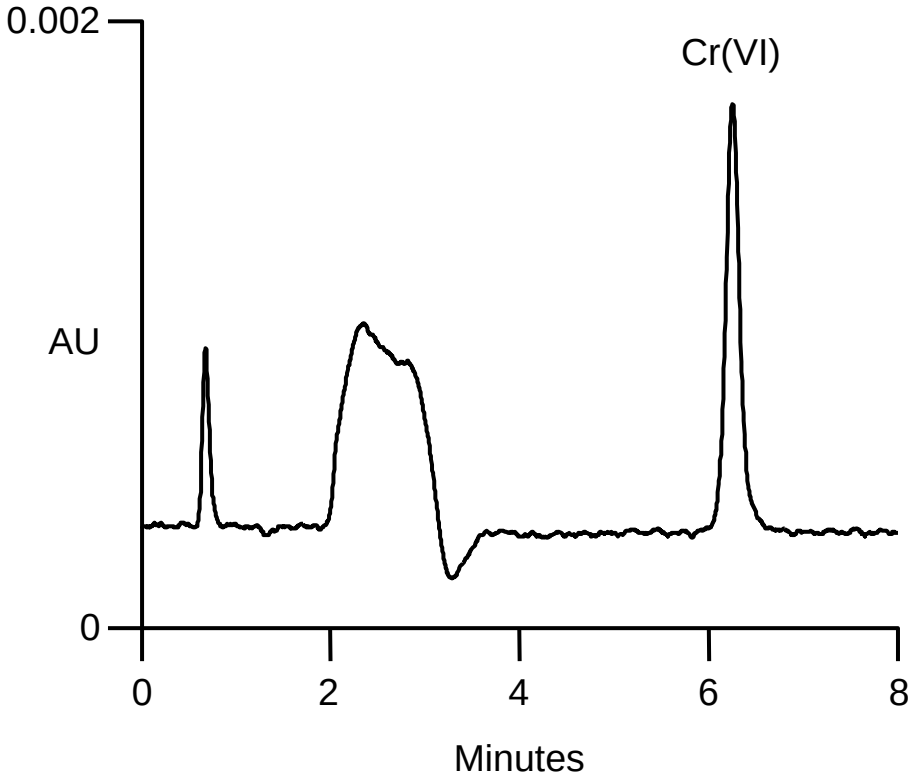
System Configuration for Hexavalent Chromium by EPA Method 218.6



Summary of Modifications to EPA Method 218.6

- Use a lower-sulfate buffer to adjust sample pH
- Increase sample size to 1000 µL
- Reduce eluent flow rate to 1 mL/min
- Reduce PCR flow rate to 0.33 mL/min
- Increase post-column reaction coil to 750 µL
- New MDL in reagent water is 0.018 µg/L – 15x lower than in Method 218.6

Determination of Hexavalent Chromium Using Optimized EPA Method 218.6



Columns:	IonPac NG1, AS7
Eluent:	250 mmol/L $(NH_4)_2$ SO_4 100 mmol/L NH_4OH
Flow rate:	1.0 mL/min
Inj. volume:	1000 µL
Post-column reagent:	2 mmol/L diphenylcarbizide 10 % MeOH, 0.5 mol/L H_2SO_4 0.33 mL/min
Reaction coil:	750 µL
Detection:	UV/Vis, 530 nm
Sample:	1.0 µg/L Cr(VI)

Method Detection Limits for Chromate

Based on a 1000-µL Injection			
Chromate Conc. [µg/L]	**Std. Dev. [µg/L]**	**RSD [%]**	**MDL* [µg/L]**
0.1	0.0060	6.986	0.018
0.2	0.0056	3.193	0.018

* MDL = (Std. Dev.) x ($t_{s,\,99}$), where $t_{s,99}$ = 3.14 for *n* = 7

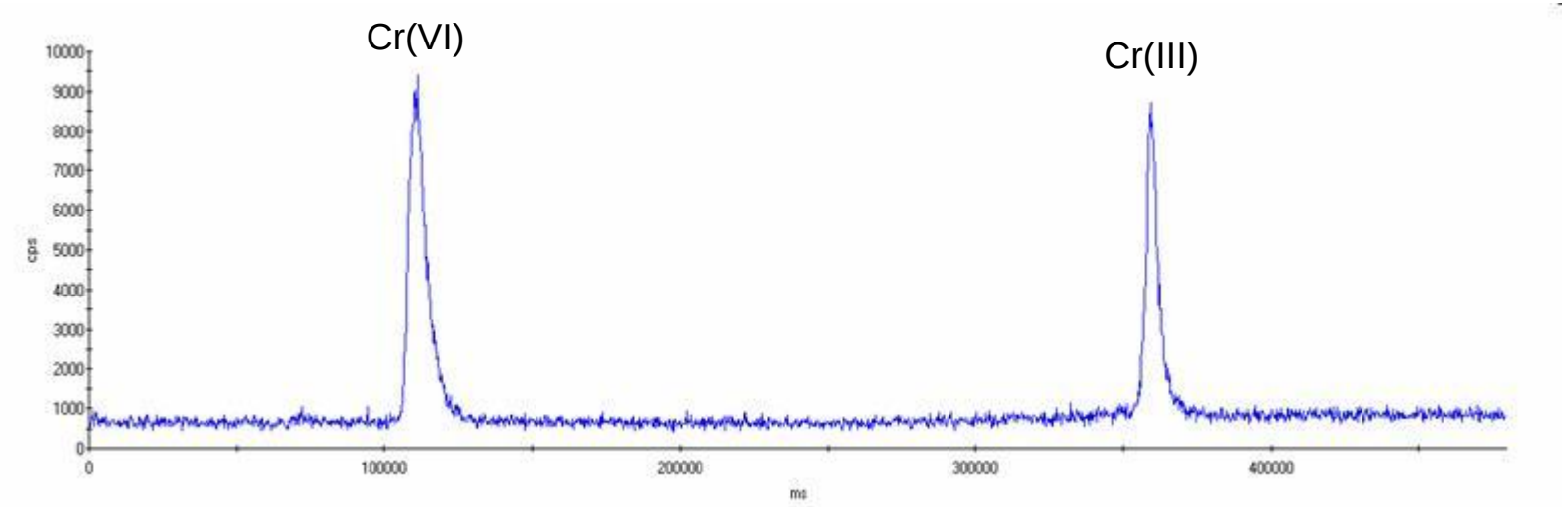
Speciation of Chromium with IC/ICP-MS

Powell et al. **D**irect **I**njection **N**ebulization, DIN

- Band spreading minimized due to the absence of a nebulizer chamber
- Sampling via an injection valve
- With another switching valve the sample can be directed either to a micro column for separating chromium(III)/(VI) or directly into the plasma
- Chromium is measured via m/z 52, since Cr^{52} yields larger signals than Cr^{53}
- MDLs for total chromium, chromium(III), and chromium(VI) are 30, 60, and 180 ng/L, respectively (one order of magnitude lower than photometry after derivatization with 1,5-DPC)

Speciation of Chromium Using IC-ICP-MS

- Commercial standards prepared in deionised water
- 100 µL injection volume, 2 ng/mL standard
- IonPac CS5A (250 mm × 2 mm i. D.) plus guard column
- Gradient elution (0.3-1 mol/L nitric acid, 0.5 mL/min)
- X Series ICP-MS conditions
- Peltier cooled spray chamber, PlasmaScreen and Xt interface



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Speciation of Chromium Using IC-ICP-MS

- Commercial standards prepared in deionised water
- 100 µL injection volume, 2 ng/mL standard
- IonPac CS5A (250 mm x 2 mm ID) plus guard column
- Gradient elution (0.3-1 mol/L nitric acid, 0.5 mL/min)
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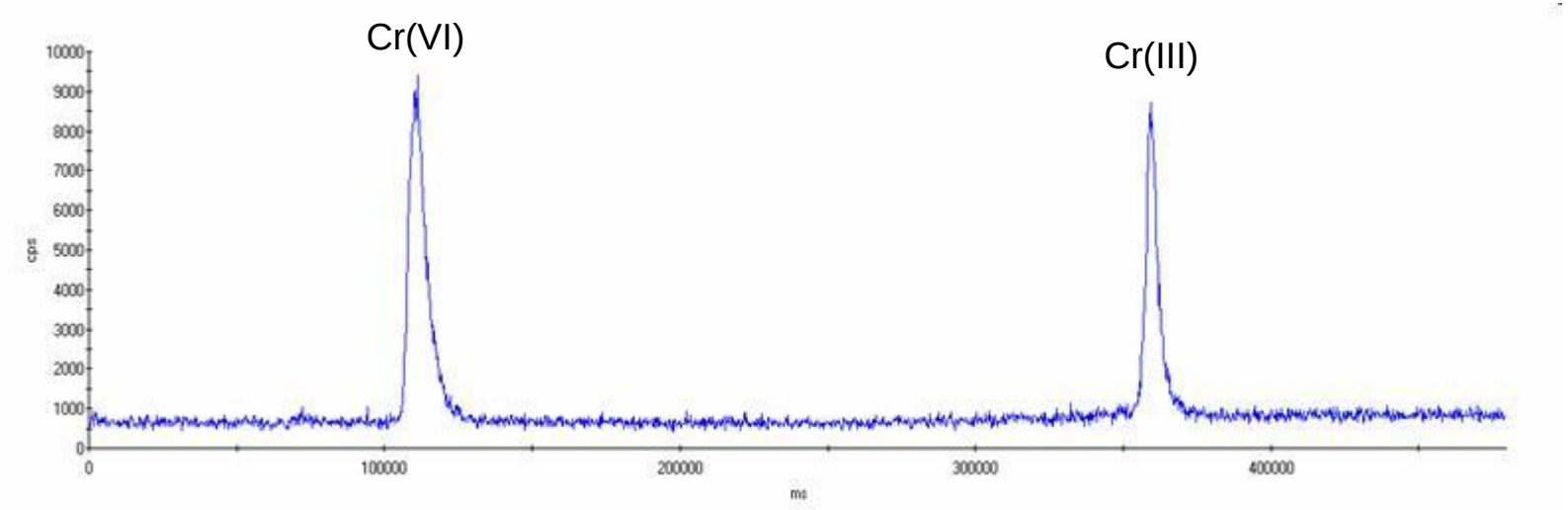

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Conclusions

- EPA Method 300.0(A) column selection:
  - IonPac AS22 is suited for conventional water analysis using carbonate-based eluents
  - IonPac AS18 is suited for conventional water analysis using hydroxide eluents with improved linearity and MDLs as well as an improved separation between fluoride and short-chain organic acids
- EPA Method 300.1 specified for bromate analysis:
  - IonPac AS23 for conventional bromate analysis using carbonate-based eluents
  - IonPac AS19 for bromate analysis with RFIC-EG
- EPA Method 326.0 specified for trace bromate analysis:
  - Post-column derivatization with KI under acid conditions is necessary for sub-µg/L concentrations of bromate
- IC × IC using a capillary column in the 2nd channel can easily achieve low-ng/L concentrations of bromate and perchlorate in low to high salt matrices

Thank you for your kind attention!

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