Ion Chromatography – A Reliable, Accurate Way of Measuring Ionic Pollutants in Environmental Samples

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Outline

- Conventional water analysis
- Bromate analysis by conventional IC and RFIC
- Bromate analysis with post-column derivatization
- Two-dimensional analysis of bromate with suppressed conductivity detection
- Bromate and halocetic acid analysis by IC-MS
- Summary

Advantages of Ion Chromatography

- **High Sensitivity Detection**

  Allows sample to be diluted to reduce the concentration of matrix components

- **Specific Detection**

  Analytes can be detected at low levels in the presence of much higher levels of matrix components

- **Analyte Specific Separations**

  Column selectivities tailored to specific analyte classes

Conventional Water Analysis

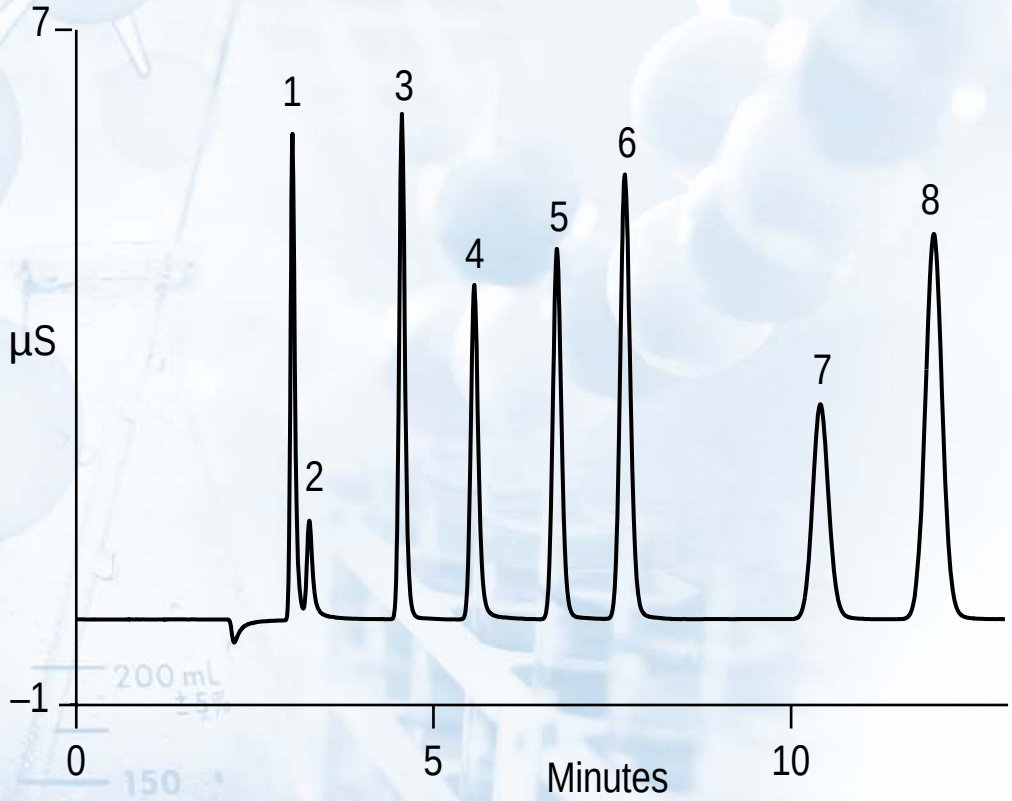
IonPac AS22 Column Features

- Carbonate-based anion exchanger for inorganic anions in diverse sample matrices
- Targeted for AS4A-SC, AS12A, AS14, and AS14A inorganic anion applications
- Improved performance compared to AS4A-SC, AS12A, AS14, and AS14A
  - Improved peak shape and efficiencies
  - Improved selectivity
  - Carbonate resolved from inorganic anions
- High capacity
  - 210 µequiv/column for 250 mm x 4 mm ID, super-macroporous
  - 6 µequiv/column for 50 mm x 4 mm ID, microporous

IonPac AS22 Column Features / cont.

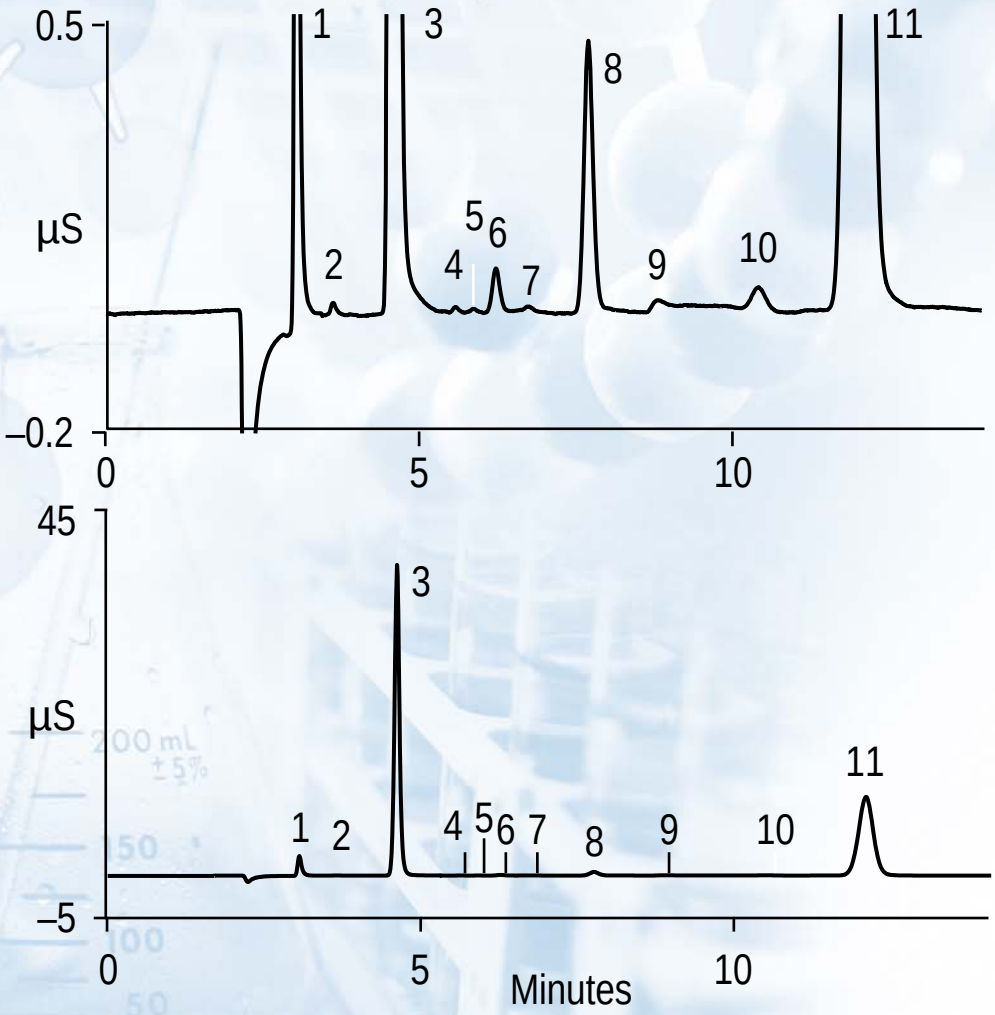
- Column selectivity optimized for 30°C
  - Ensures reproducible retention times
- Meets U.S. EPA Method 300.0 (A) and ISO performance requirements
- Compatible with ICS-2000 and ICS-3000 Systems
  - Generate carbonate/bicarbonate eluant with EGC- K_2CO_3 and EPM
- Compatible with ICS-90/1000/1500

Separation of Common Inorganic Anions and Acetate on IonPac AS22



Column:	IonPac AG22, AS22, 4 mm	
Eluant:	4.5 mmol/L Na_2CO_3/ 1.4 mmol/L $NaHCO_3$	
Temperature:	30°C	
Flow rate:	1.2 mL/min	
Inj. volume:	10 µL	
Detection:	Suppressed conductivity, ASRS ULTRA II 4 mm, 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. Phosphate	40
	8. Sulfate	30

Determination of Inorganic Anions in Municipal Drinking Water on IonPac AS22

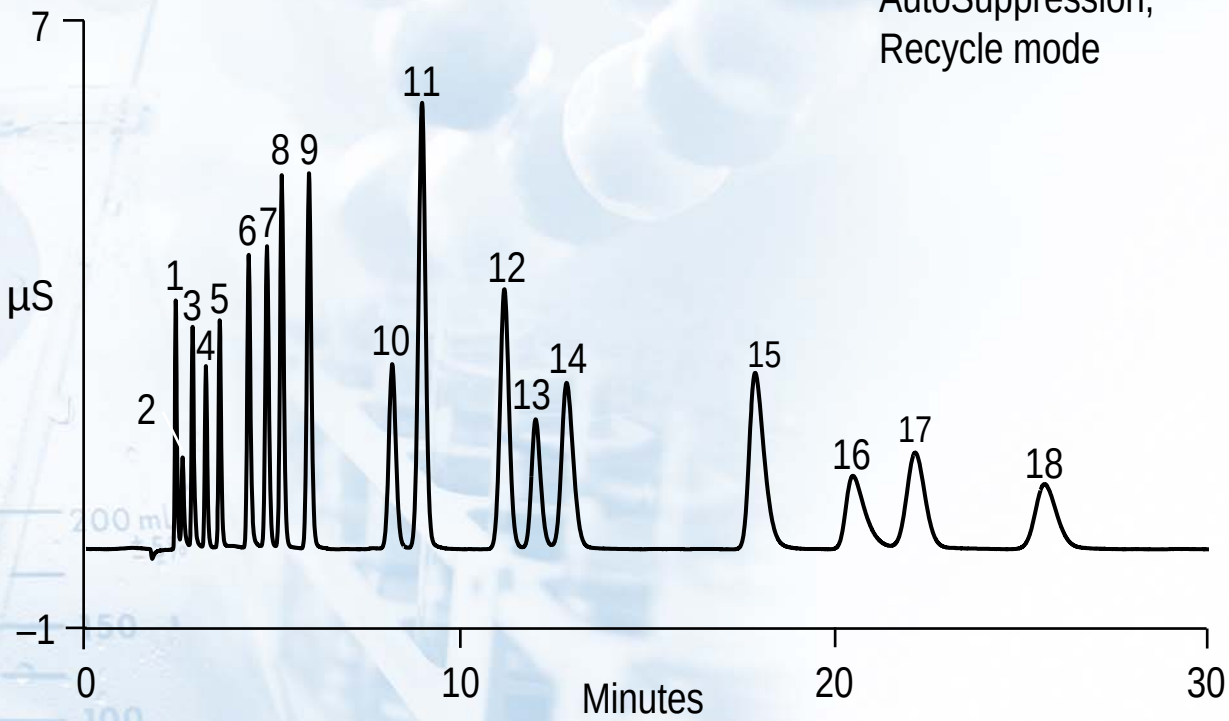


Column:	IonPac AG22, AS22 4 mm
Eluant:	4.5 mmol/L Na_2CO_3/ 1.4 mmol/L $NaHCO_3$
Temperature:	30°C
Flow rate:	1.2 mL/min
Inj. volume:	25 µL
Detection:	Suppressed conductivity, ASRS ULTRA II 4 mm, AutoSuppression, recycle mode

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. Phosphate	0.22	
11. Sulfate	20.45	

Separation of Environmental Anions on IonPac AS22

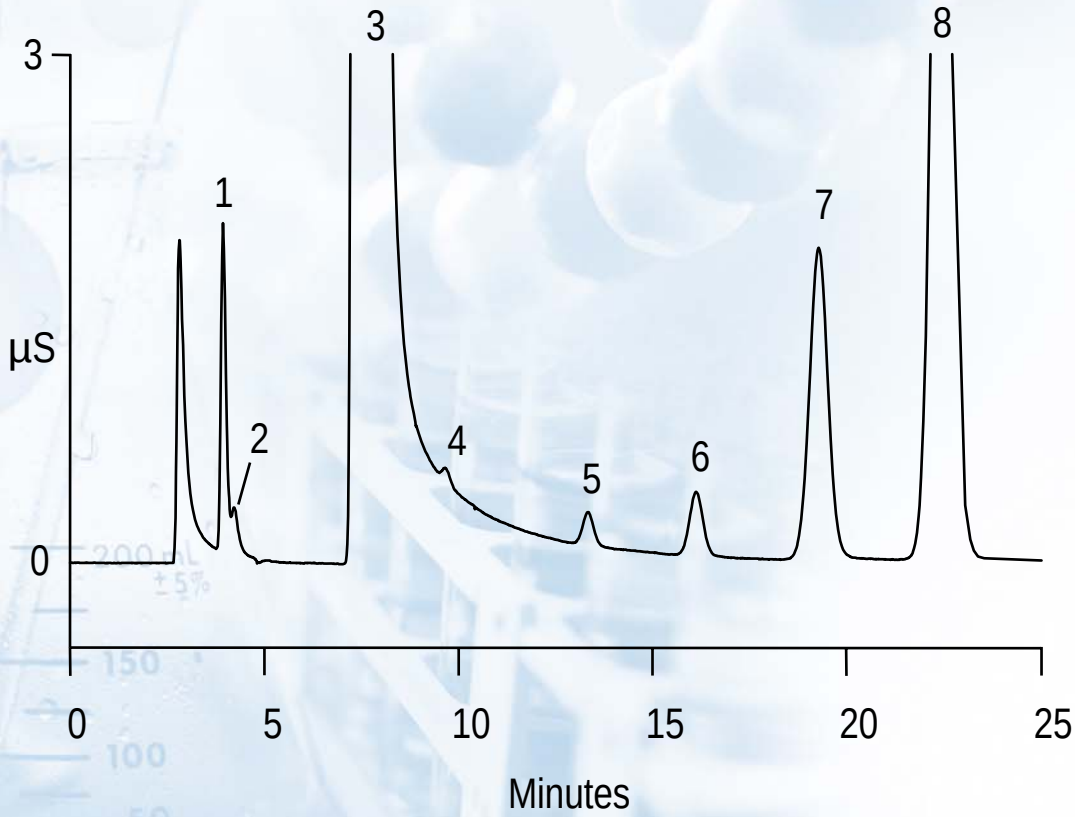
Column:	IonPac AG22, AS22, 4 mm
Eluant :	4.8 mmol/L Na_2CO_3/ 1.0 mmol/L $NaHCO_3$
Flow rate:	1.5 mL/min
Temperature:	30°C
Inj. volume:	10 µL
Detection:	Suppressed conductivity, ASRS ULTRA II, 4 mm, AutoSuppression, Recycle mode



Peaks:

1. Fluoride	3	mg/L
2. Acetate	20	
3. Formate	10	
4. Bromate	20	
5. Chloride	5	
6. Nitrite	15	
7. Chlorate	25	
8. Bromide	25	
9. Nitrate	25	
10. Phosphate	40	
11. Sulfate	30	
12. Selenate	30	
13. Iodide	40	
14. Arsenate	30	
15. Thiocyanate	40	
16. Perchlorate	40	
17. Thiosulfate	40	
18. Chromate	40	

Anion Analysis in High Chloride Wastewater with a High Capacity Anion Exchanger: Conductivity Detection



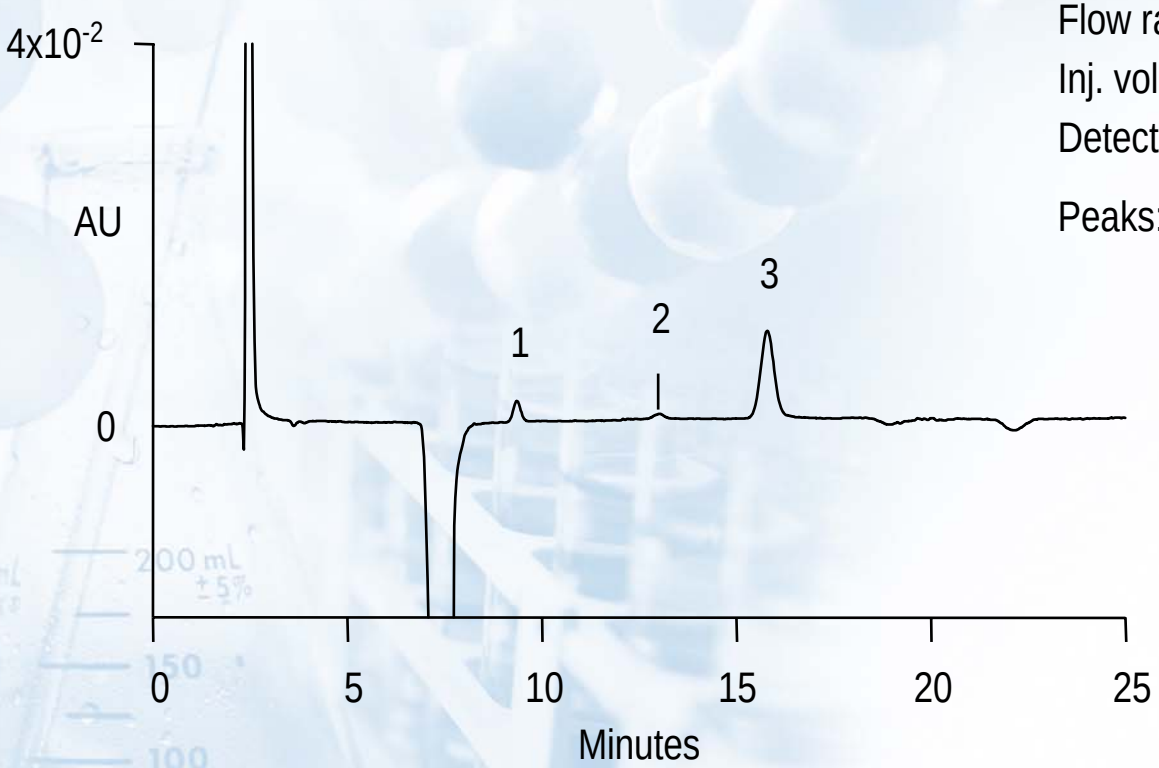
Column:	IonPac AG9-HC, AS9-HC
Eluant:	9 mmol/L Na_2CO_3
Flow rate:	1 mL/min
Inj. volume:	25 µL
Detection:	Suppressed conductivity, ASRS-ULTRA, Recycle Mode

Peaks:

1.	Fluoride	1.14	mg/L
2.	Acetate	–	
3.	Chloride	–	
4.	Nitrite	0.14	
5.	Bromide	0.82	
6.	Nitrate	1.47	
7.	Phosphate	21.1	
8.	Sulfate	30.3	

Sample: Synthetic wastewater containing 2 g/L chloride

Anion Analysis in High Chloride Wastewater with a High Capacity Anion Exchanger : UV Detection



Column:	IonPac AG9-HC, AS9-HC
Eluant:	9 mmol/L Na_2CO_3
Flow rate:	1 mL/min
Inj. volume:	25 µL
Detection:	UV at 214 nm

Peaks:			
	1. Nitrite	0.18	mg/L
	2. Bromide	0.79	
	3. Nitrate	1.58	

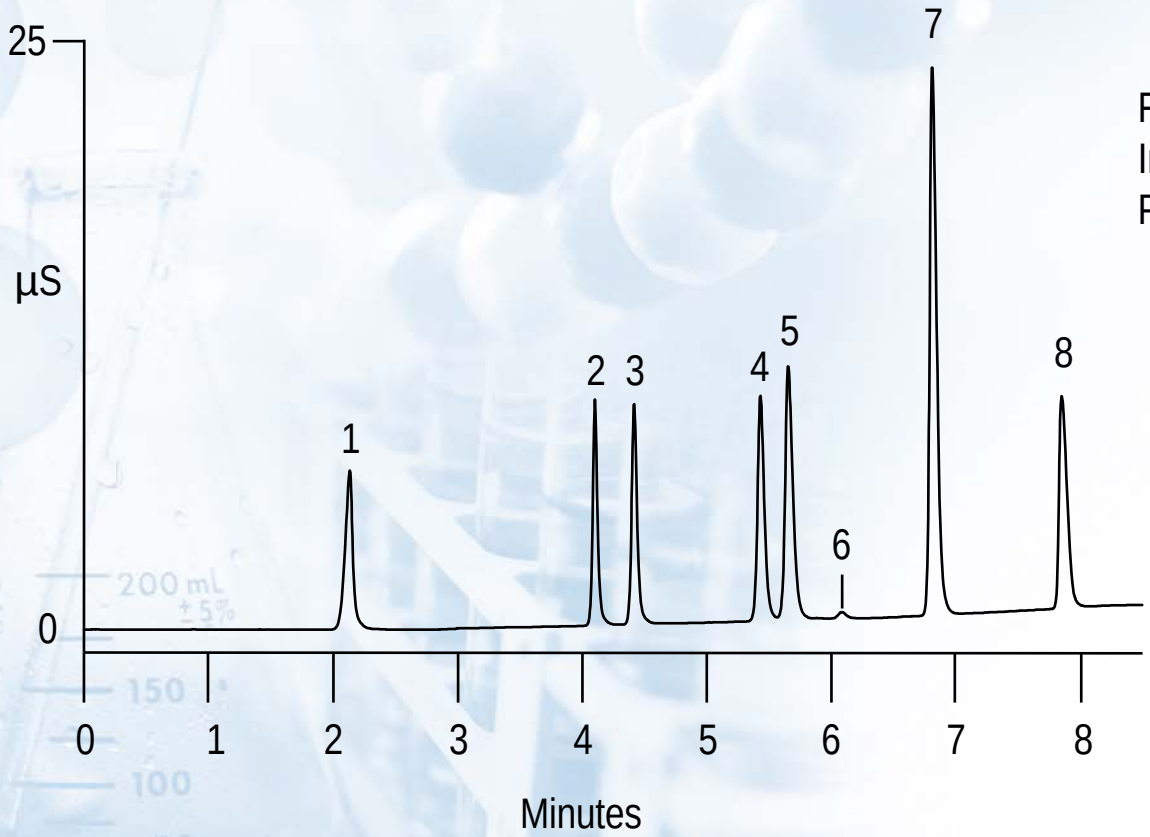
Sample: Synthetic wastewater containing 2 g/L chloride

Maximum $Cl:NO_2$ Ratios Applicable to IonPac AS9-HC[a]

Column / Detection Mode	$Cl : NO_2$	$Cl : NO_2$-N
AS9-HC / Conductivity	2000:0.2 mg/L (10,000:1)	2000:0.068 mg/L (32,850:1)
AS9-HC / UV (214 nm)	5000:0.045 mg/L (111,000:1)	5000:0.014 mg/L (365,000:1)

[a] Standard eluant conditions were used with a 25-µL injection volume

EPA Method 300.0 (A) with RFIC: IonPac AS17

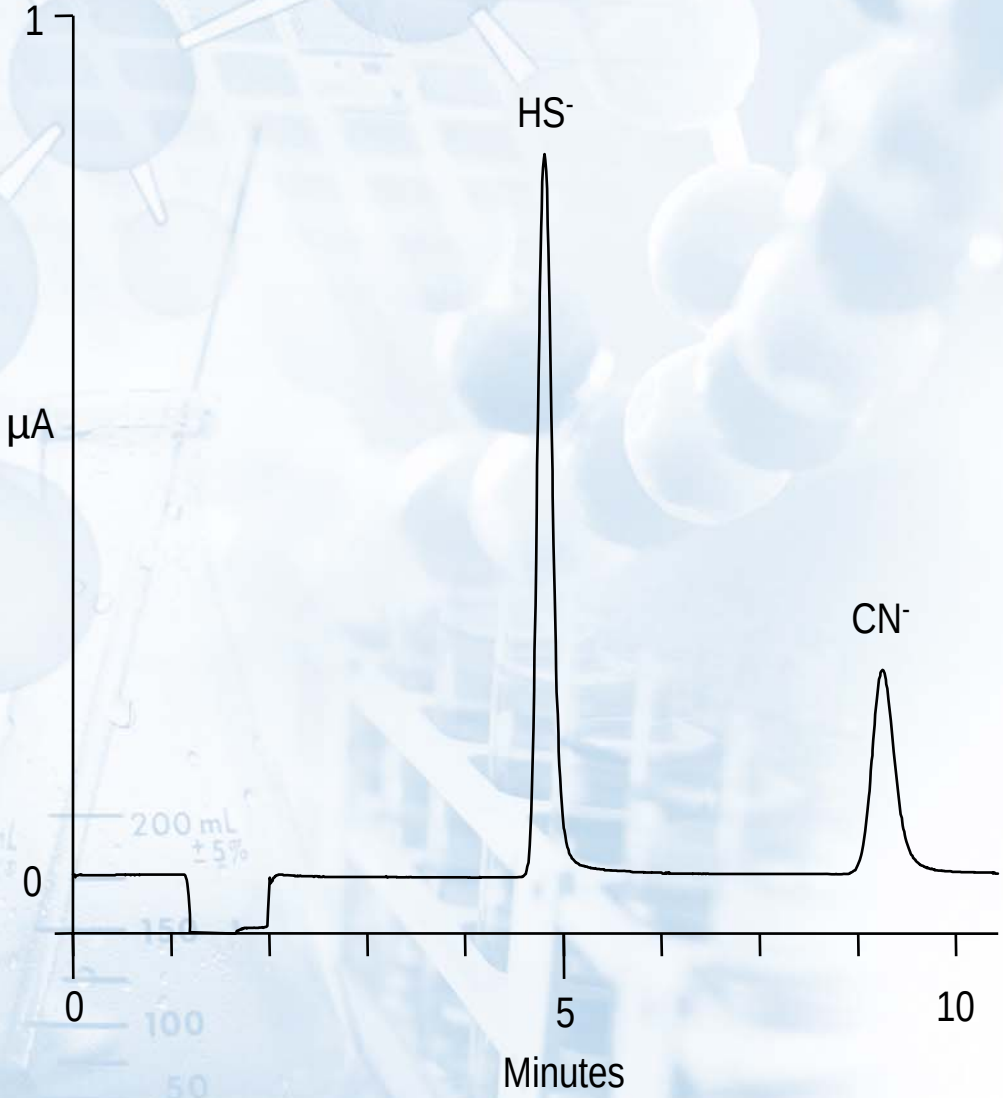


Column:	IonPac AG17, AS17
Eluant:	KOH (EG), 1 mmol/L for 1.5 min to 20 mmol/L in 3.5 min and from 20 mmol/L to 40 mmol/L in 2 min
Flow rate:	2 mL/min
Inj. volume:	25 µL

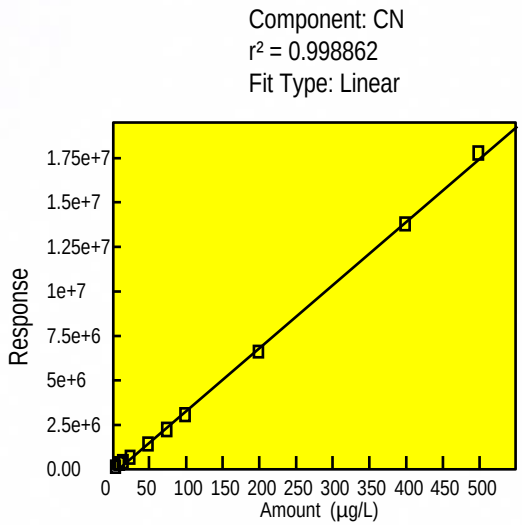
Peaks:

1.	Fluoride	2	mg/L
2.	Chloride	3	
3.	Nitrite	5	
4.	Bromide	10	
5.	Nitrate	10	
6.	Carbonate	—	
7.	Sulfate	15	
8.	Phosphate	15	

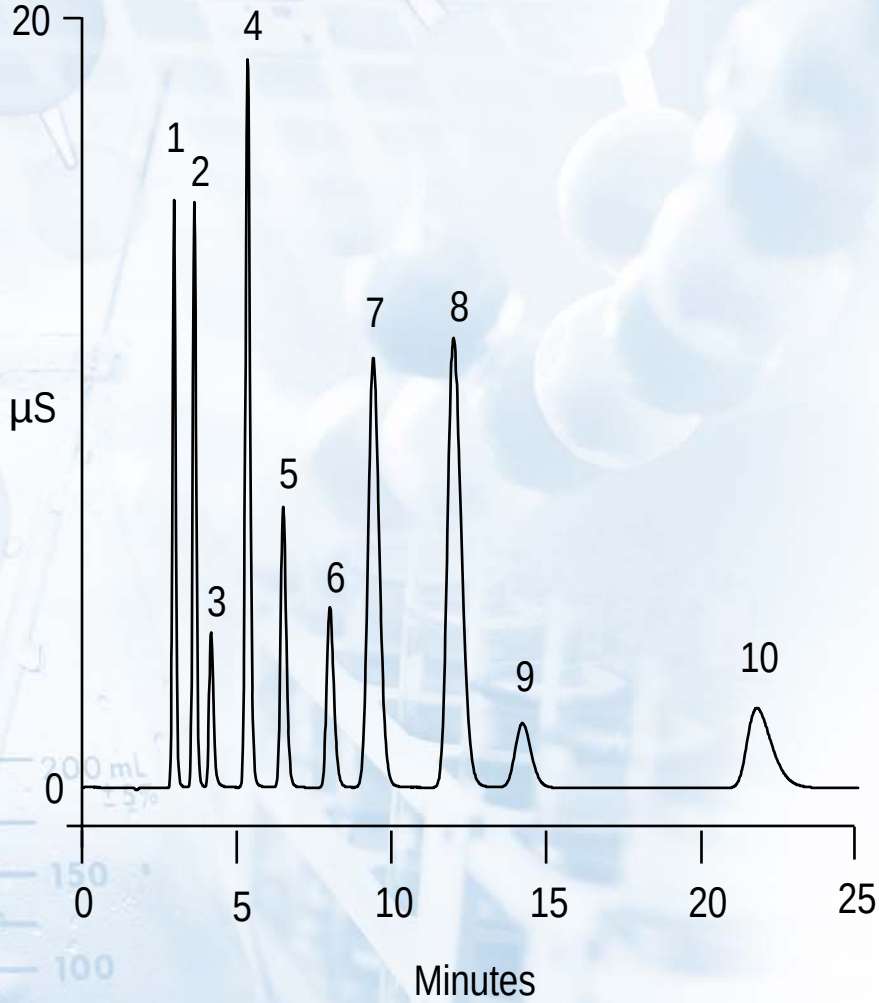
Analysis of Sulfide and Cyanide



Separator:	CarboPac PA1 with Guard
Eluant:	0.1 mol/L NaOH + 0.5 mol/L NaOAc + 0.5 % (v/v) ethylendiamine
Flow rate:	1 mL/min
Detection:	DC Amperometry, Ag electrode (0 V)
Inj. volume:	50 µL (250 µL)
Sample preparation:	Samples are acidified and distilled acc. to DIN 38 405 D13, and absorbed in 0.1-1 mol/L NaOH.



Separation of Alkali- and Alkaline-Earth Metals and Ammonium

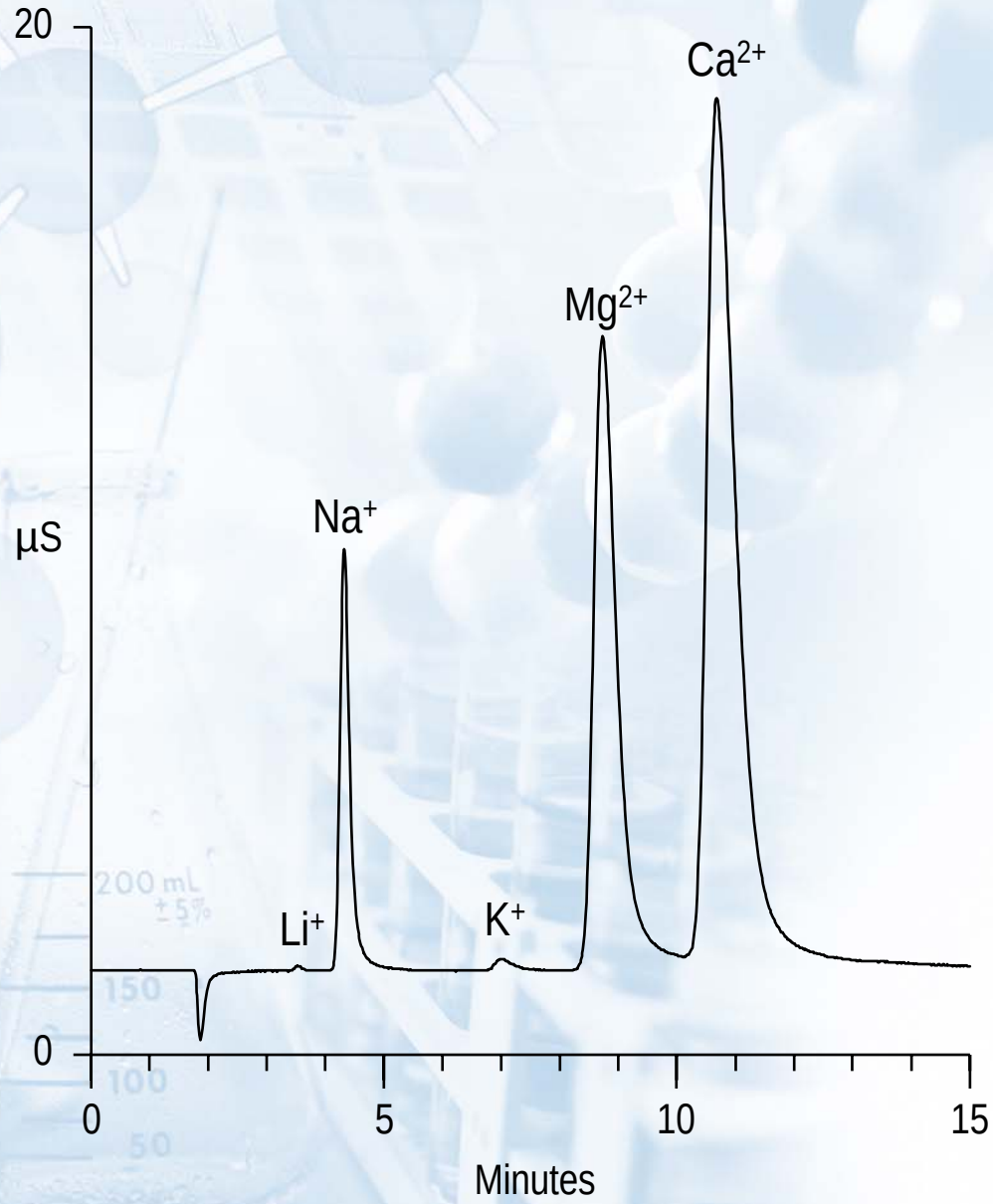


Separator:	IonPac CS12A
Eluant:	18 mmol/L MSA
Flow rate:	1 mL/min
Inj. volume:	25 µL
Detection:	Suppressed conductivity, Recycle Mode

Peaks:

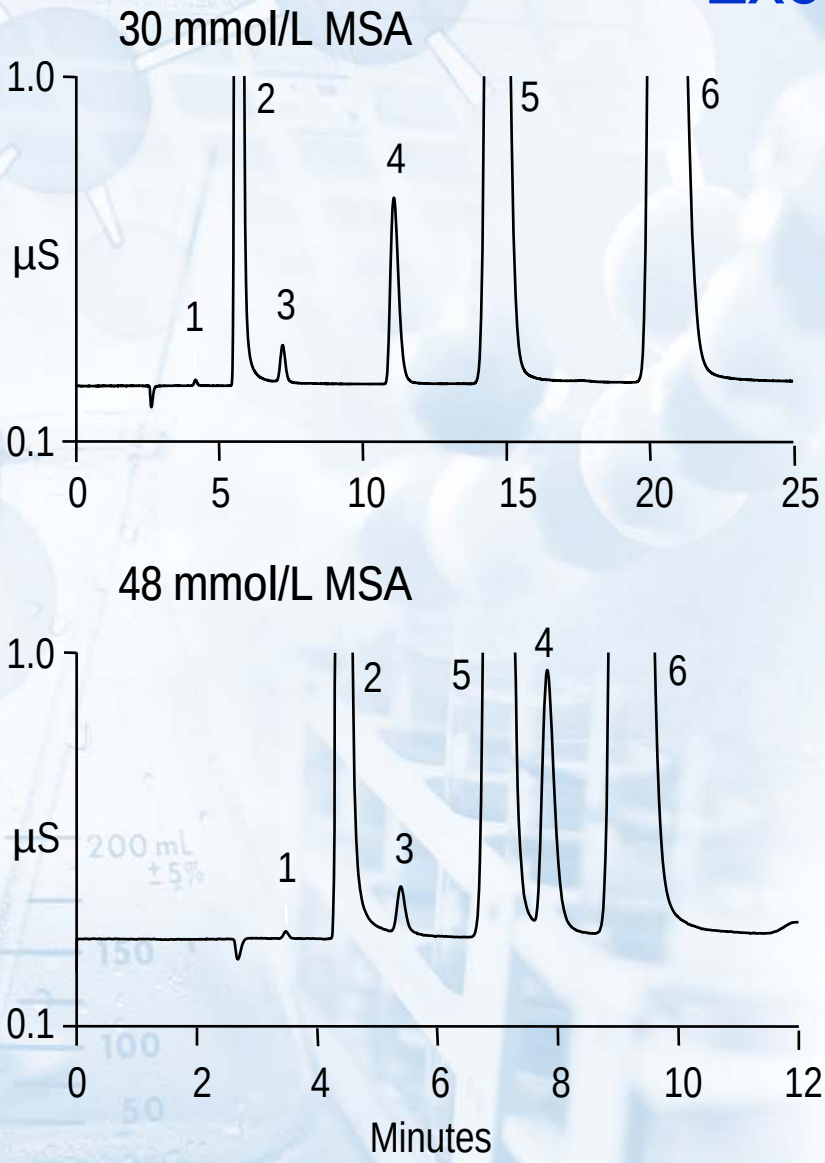
1. Lithium	1 mg/L
2. Sodium	4
3. Ammonium	5
4. Potassium	10
5. Rubidium	10
6. Cesium	10
7. Magnesium	5
8. Calcium	10
9. Strontium	10
10. Barium	10

Cation Analysis in Municipal Drinking Water



Separator:	IonPac CS12 / CG12
Eluant:	9 mmol/L H_2SO_4
Flow rate:	1 mL/min
Detection:	Suppressed conductivity
Inj. volume:	25 µL
Sample:	Tap water, acidified

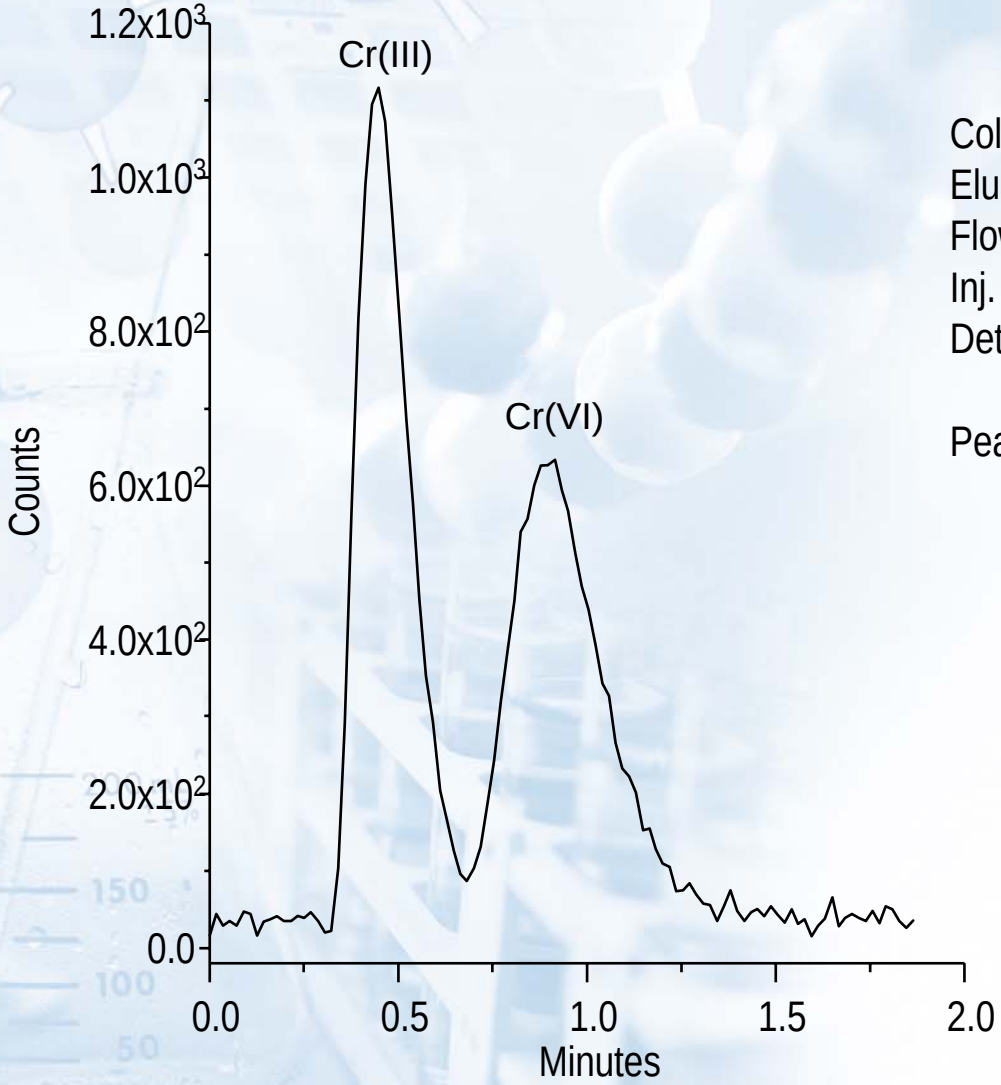
Tap Water Analysis Utilizing a High Capacity Cation Exchanger



Column:	IonPac CS16 (5 µm) (250 mm x 5 mm ID)
Flow rate:	1 mL/min
Temperature:	40°C
Inj. volume:	25 µL
Detection:	Suppressed conductivity, CSRS-ULTRA (4-mm), AutoSuppression, Recycle Mode

Peaks:		Calculated
1.	Lithium	0.002 mg/L
2.	Sodium	19.730
3.	Ammonium	0.065
4.	Potassium	0.987
5.	Magnesium	7.210
6.	Calcium	18.544

Separation of Chromium(III)/(VI) Utilizing Element-Specific Detection



Column:	OmniPac PAX100 Guard
Eluant:	0.1 mol/L HNO_3 (pH 2 with NH_4OH)
Flow rate:	2 mL/min
Inj. volume:	250 µL
Detection:	ICP-OES, 267.716 nm
Peaks:	1 mg/L Cr(III) and Cr(VI)

Bromate Analysis by Conventional IC

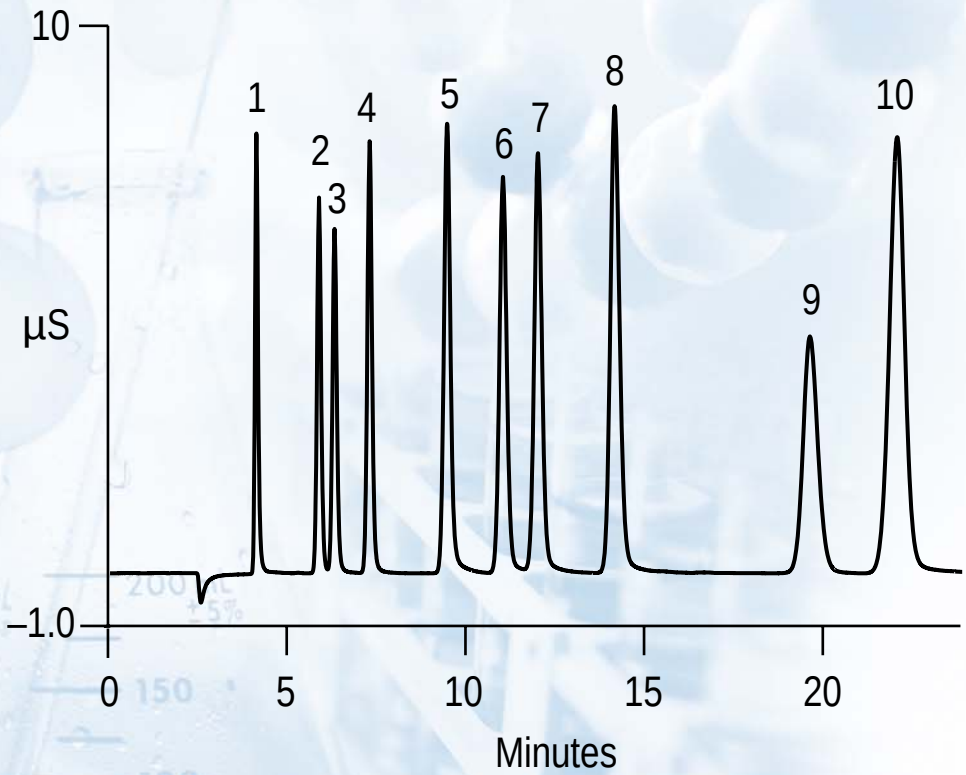
IonPac AS23 Column Features

- Carbonate-based anion exchange column for inorganic anions and oxyhalides
- Improved performance as compared to IonPac AS9-HC
  - Improved peak shape and efficiencies
  - Improved selectivity
  - Carbonate resolved from oxyhalides and inorganic anions
- High capacity
  - 320 µequiv/column for 250 mm x 4 mm ID, super-macroporous
  - 6 µequiv/column for 50 mm x 4 mm ID, microporous
  - Allows large loop injections
- Quantification of trace bromate in high ionic strength samples without sample pre-treatment or pre-concentration

IonPac AS23 Column Features / cont.

- Meets U.S. EPA Methods 300.0 (B) and 300.1 (A&B) and ISO performance requirements
- Compatible with ICS-2000 and ICS-3000 systems
  - Generate carbonate/bicarbonate eluant with EGC- K_2CO_3 and EPM
- Compatible with ICS-90/1000/1500

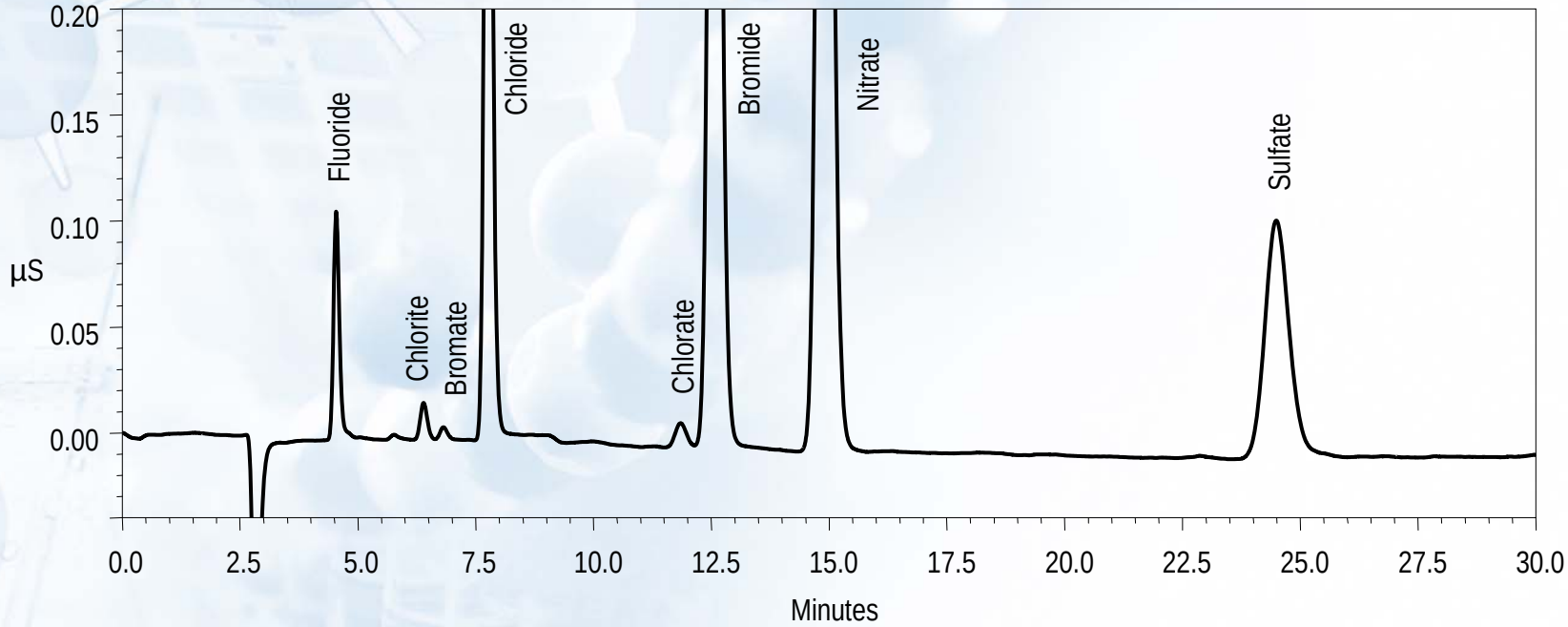
Determination of Oxyhalides and Inorganic Anions on IonPac AS23



Column:	IonPac AG23, AS23, 4 mm
Eluant:	4.5 mmol/L Na_2CO_3/ 0.8 mmol/L $NaHCO_3$
Temperature:	30°C
Flow rate:	1.0 mL/min
Inj. volume:	25 µL
Detection:	Suppressed conductivity, ASRS ULTRA II, 4 mm, AutoSuppression, recycle mode

Peaks			
	1. Fluoride	3	mg/L
	2. Chlorite	10	
	3. Bromate	20	
	4. Chloride	6	
	5. Nitrite	10	
	6 . Bromide	25	
	7. Chlorate	25	
	8. Nitrate	25	
	9. Phosphate	40	
	10. Sulfate	30	

Trace Analysis of Bromate with IonPac AS23/CRD and Suppressed Conductivity Detection



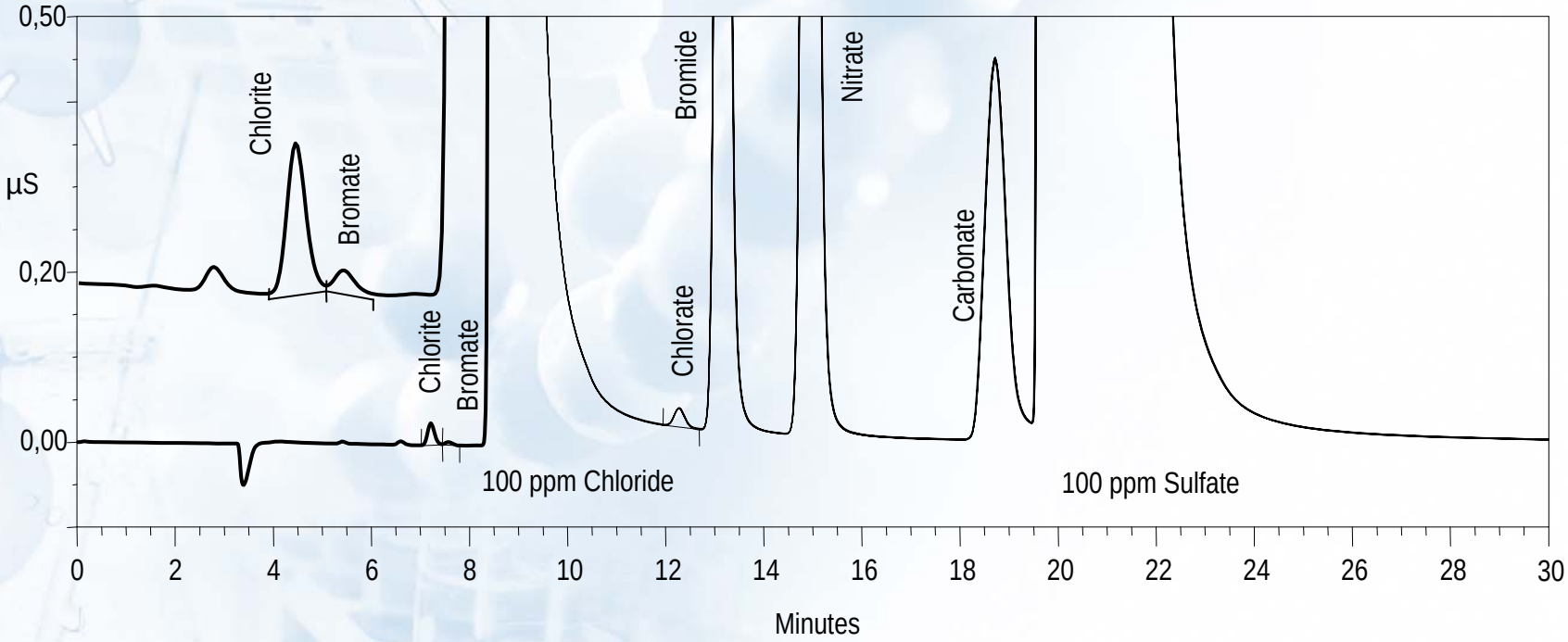
Column:	AS23, AG23
Eluant:	4.5 mmol/L Na_2CO_3
	1.0 mmol/L $NaHCO_3$
Flow rate:	1.0 mL/min
Detection:	Suppressed conductivity (Atlas + 2 CRD)
Scrubber:	0.5 mol/L KOH (Recycle Mode)
Background:	< 1.0 µS
Inj. volume:	100 µL

Peak	ppb
Fluoride	10
Chlorite	10
Bromate	5
Chloride	100
Chlorate	10
Bromide	500
Nitrate	500
Sulfate	100

IonPac AS19 Column Features

- Hydroxide-selective anion exchanger for trace analysis of bromate in drinking water
- Use of RFIC for an environmental key application
- High ion-exchange capacity
  - 240 µequiv/column for 250 mm x 4 mm ID, super-macroporous
  - 6 µequiv/column for 50 mm x 4 mm ID, microporous
  - Compatible with large-volume injection
- Quantitation of bromate at trace level in samples with high ionic strength without sample preparation or pre-concentration

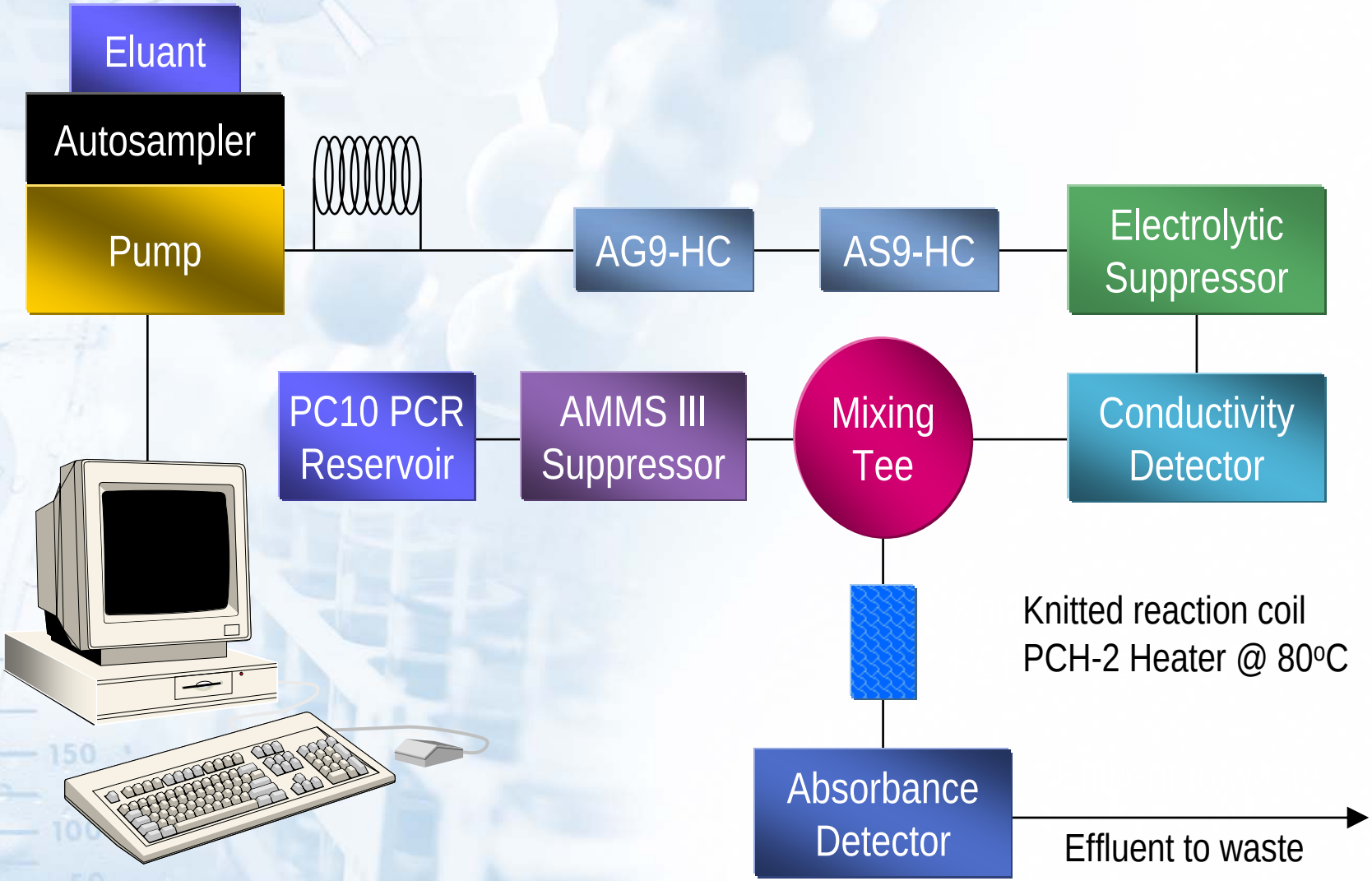
Trace Analysis of Bromate on IonPac AS19 with RFIC



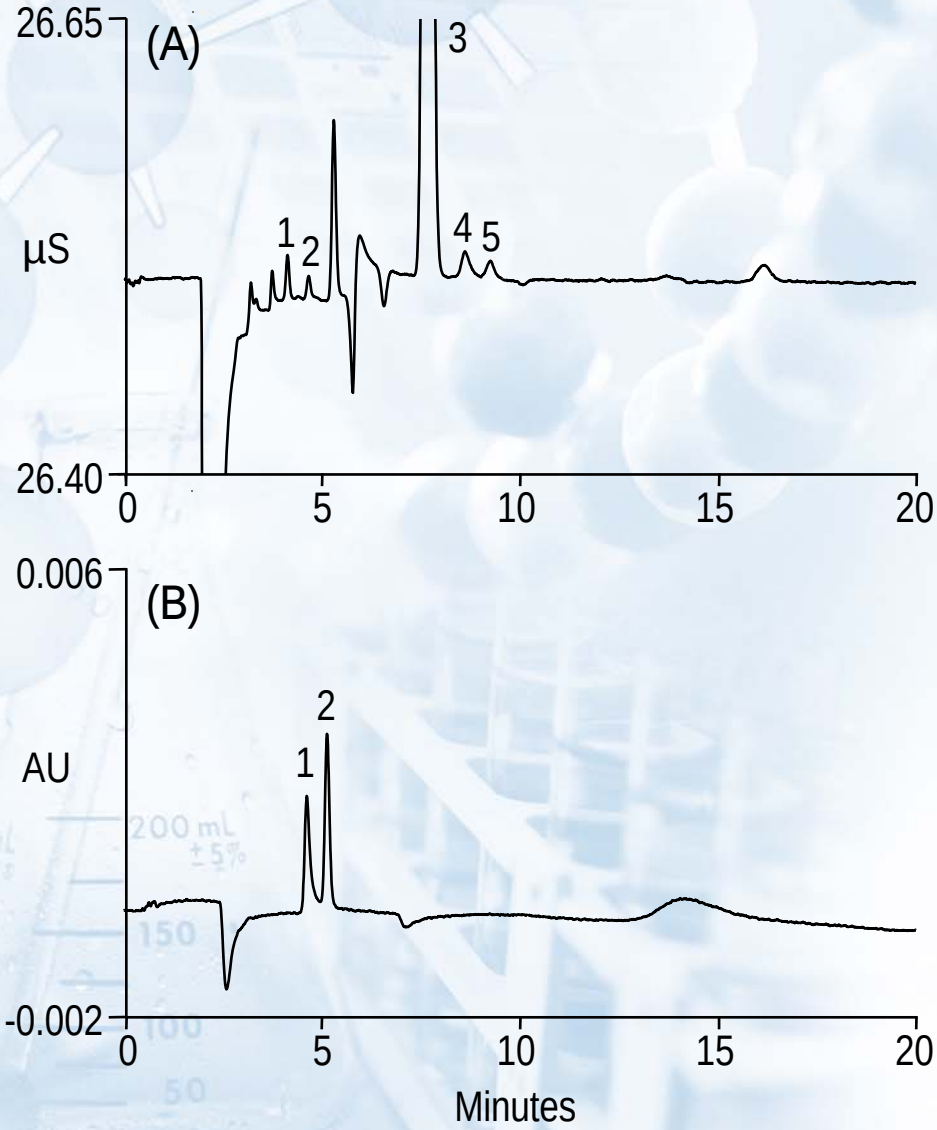
Column:	Ion Pac AG19/AS19 (4-mm)
Flow rate:	0.75 mL/min
Eluant:	20 mmol/L KOH (EG)
Detection:	Suppressed conductivity / External Water Mode
Inj. volume:	100uL
Sample:	2 ppb bromate in 100 ppm chloride and sulfate

Bromate Analysis with Post-column Derivatization

System Configuration for EPA Method 326.0



Low Level DBP Anion Standard Using EPA Method 326.0

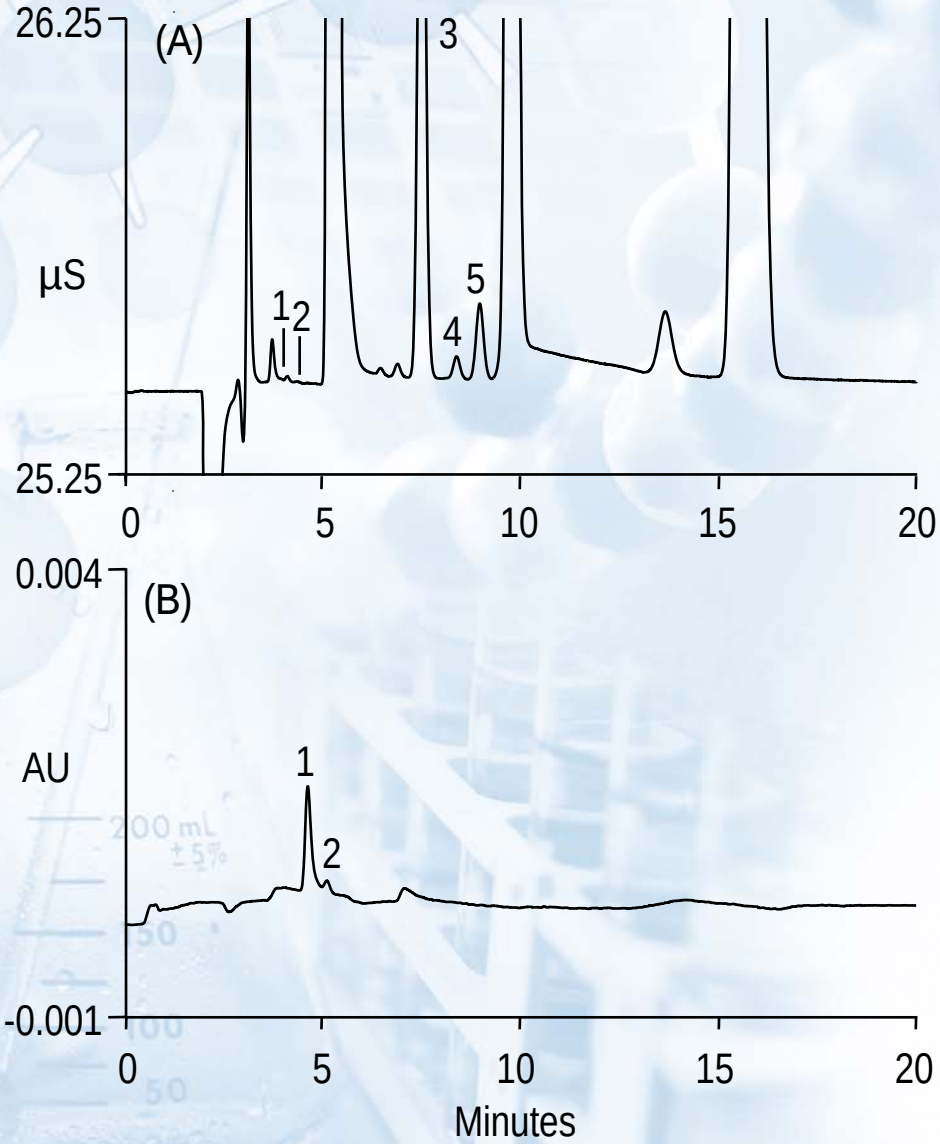


Column:	IonPac AG9-HC, AS9-HC
Eluant:	9 mmol/L Na_2CO_3
Temperature:	30°C
Flow rate:	1.3 mL/min
Inj. volume:	225 µL
Detection:	A) Suppressed conductivity, External water mode
	B) UV (352 nm)
Post-column reagent:	Acidified KI
PCR flow rate:	0.4 mL/min
Post-column heater:	80°C

Peaks:		
	1. Chlorite	5 µg/L
	2. Bromate	5
	3. DCA*	
	4. Bromide	5
	5. Chlorate	5

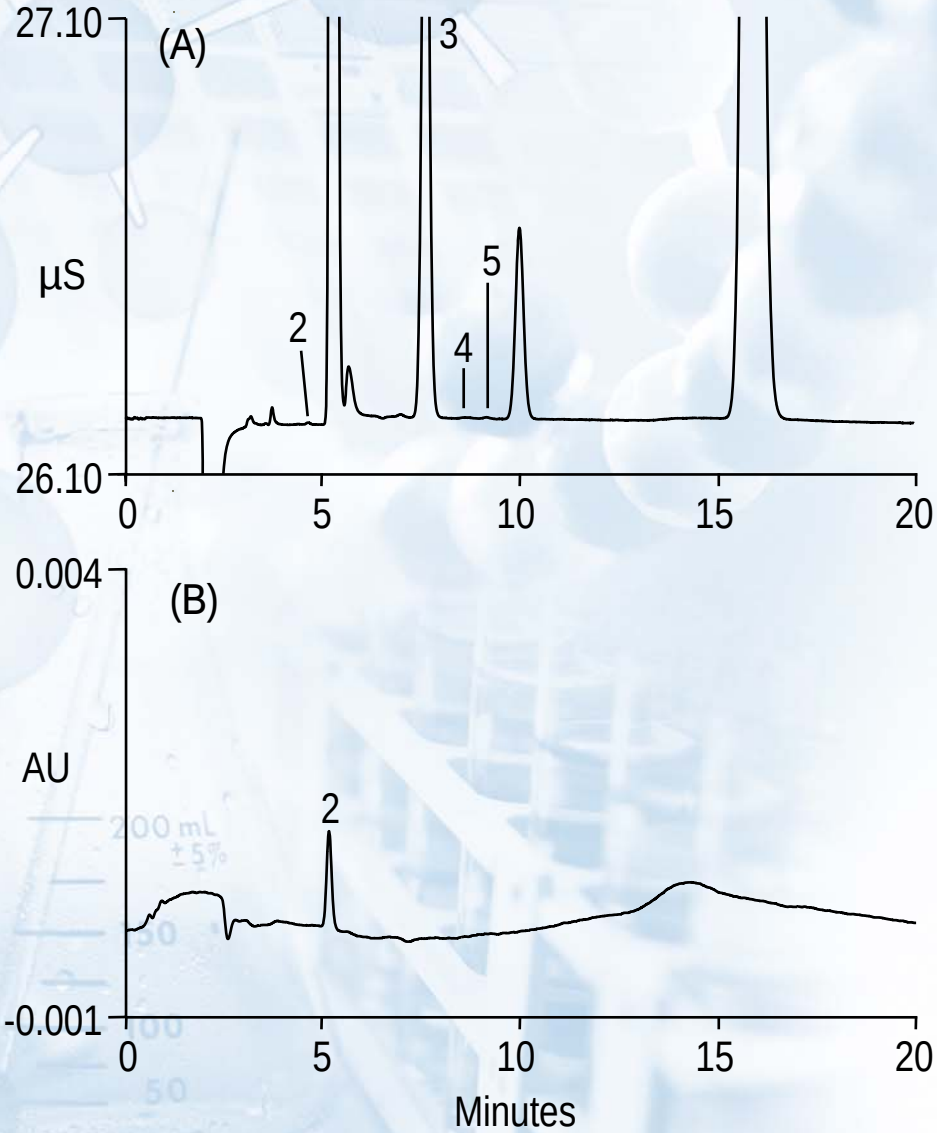
* DCA = Dichloroacetate
Quality control surrogate

Analysis of Drinking Water Using EPA Method 326.0



Column:	IonPac AG9-HC, AS9-HC
Eluant:	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
PCR flow rate:	0.4 mL/min
Post-column Heater:	80°C
Peaks:	(A)
	1. Chlorite 1.85 µg/L
	2. Bromate 0.33
	3. DCA*
	4. Bromide 20.3
	5. Chlorate 82.9
	(B)
	2. Bromate 0.21 µg/L

Analysis of Ozonated Bottled Water Using EPA Method 326.0



Column:	IonPac AG9-HC, AS9-HC
Eluant:	9 mmol/L Na_2CO_3
Temperature:	30 °C
Flow rate:	1.3 mL/min
Inj. volume:	225 µL
Detection: conductivity,	A) Suppressed External Water Mode
	B) UV(352 nm)
Post-column reagent:	Acidified KI
PCR flow rate:	0.4 mL/min
Post-column heater:	80°C

Peaks:

(A)	1. Chlorite	n.d.	µg/L
	2. Bromate	1.52	
	3. DCA*		
	4. Bromide	1.12	
	5. Chlorate	1.08	
(B)	2. Bromate	1.84	µg/L

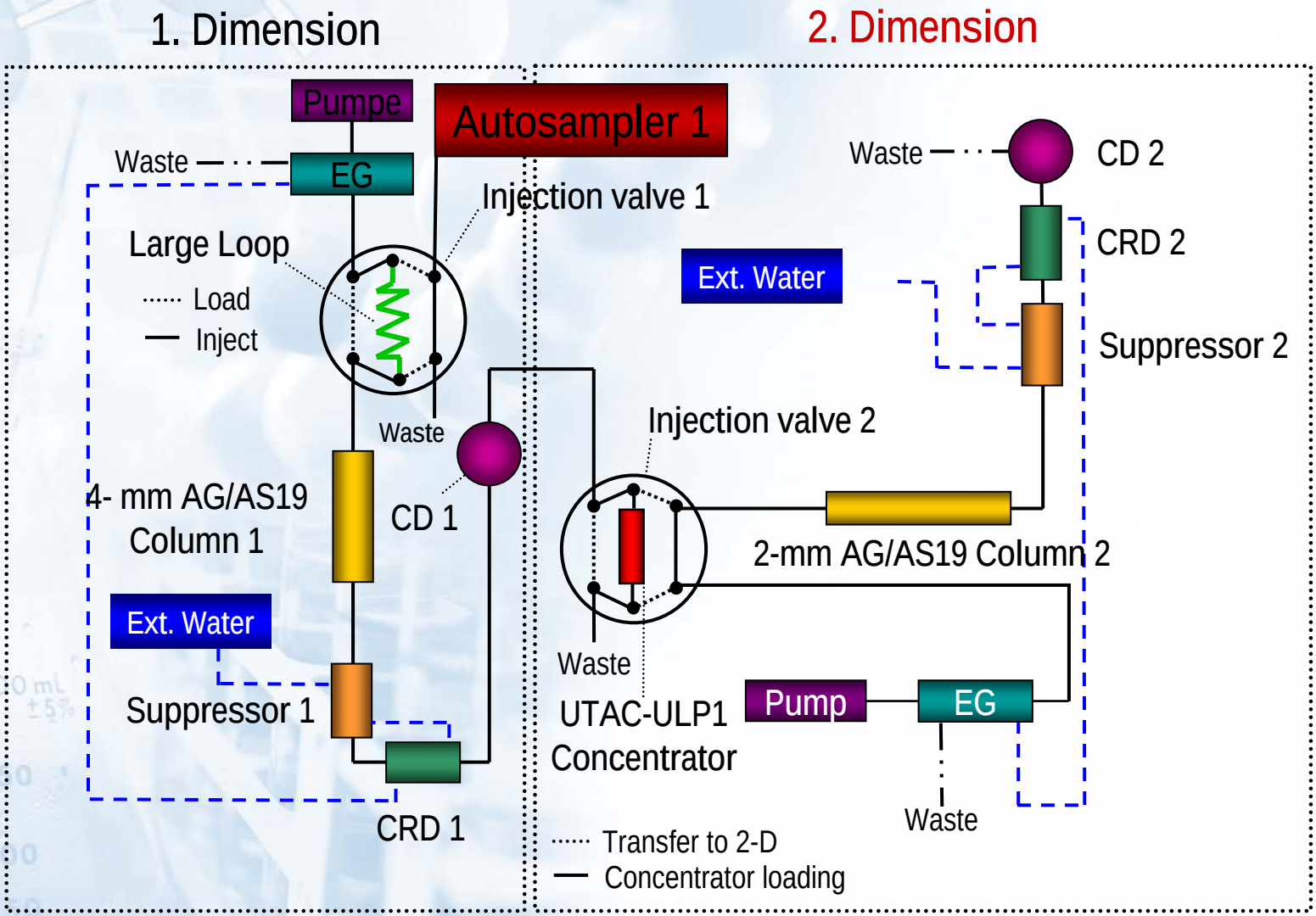
* DCA = Dichloroacetate
Quality control surrogate

Two-dimensional Analysis of Bromate with Suppressed Conductivity Detection

Requirements for Trace Analysis of Bromate in Drinking 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
- Solution
  - Matrix divertion with a 2-D technique with hydroxide eluants
    - » High selectivity
    - » High sensitivity with suppressed conductivity detection

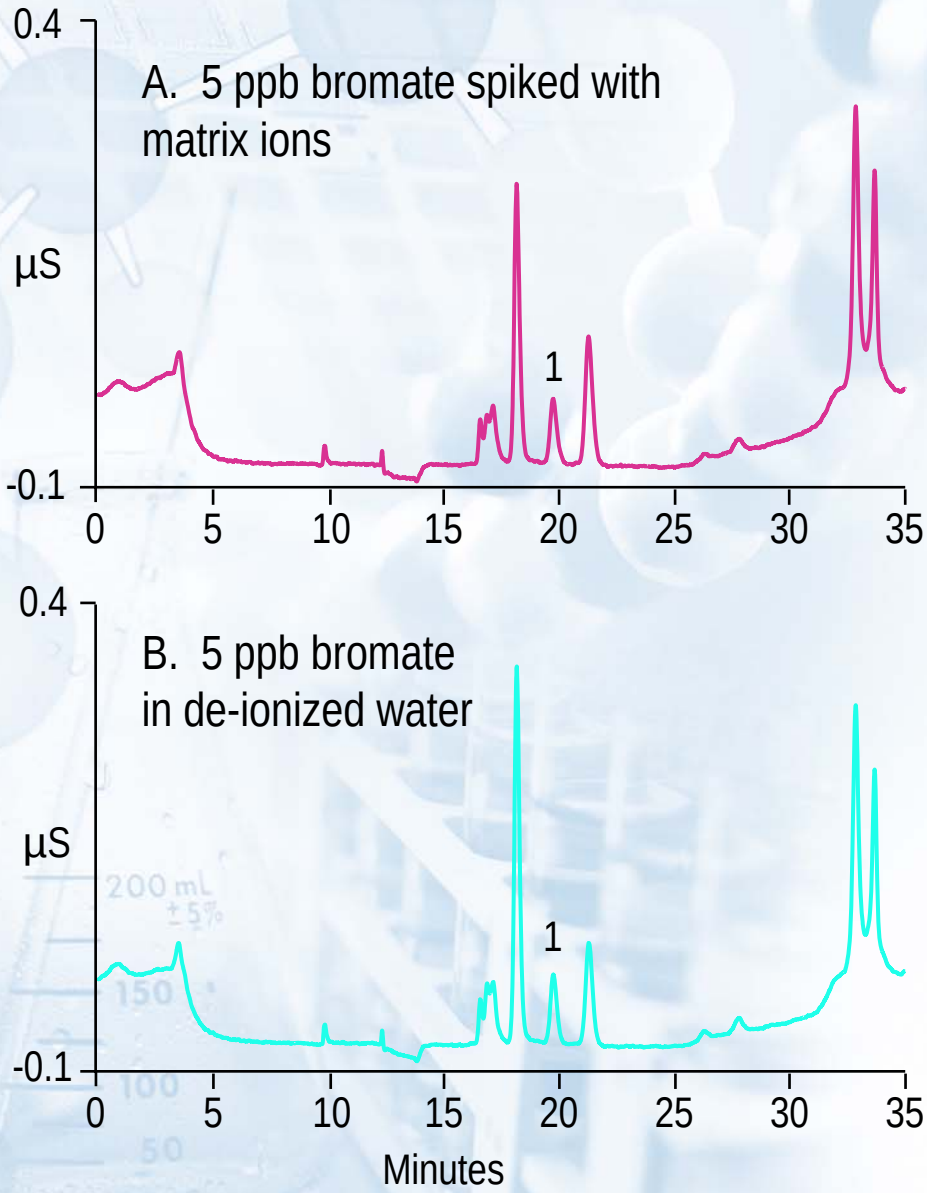
Instrumental Setup for Bromate Analysis



Features of the New 2-D Method

- Allows large-volume injection in the 1. dimension (4-mm column)
  - Possibility of large-volume injection in comparison to the standard method, because capacity and selectivity of the analytical column in the 1. dimension determines recovery; analyte analysis is carried out in the 2. dimension.
- Fokuses the analytes in the concentrator column after suppression in the 1. dimension
  - Hydroxide eluant is converted to water, ideal for focussing or pre-concentrating analytes
- Sensitivity increase by using a 2-mm column with the lower flow rate in the 2. dimension
- Possibility of using separator columns with different selectivity in the 2. dimension
  - Higher selectivity
- Easy implementation with the ICS-3000

2-D Gradient Elution of Bromate on IonPac AS19



Column:	A. IonPac AG19, AS19, 4 mm
	B. IonPac AG19, AS19, 2 mm
Eluant:	KOH (EG)
Flow rate:	A. 1.0 mL/min
	B. 0.25 mL/min
Suppressor:	A. ASRS ULTRA II, 4 mm
	B. ASRS ULTRA II, 2 mm
Inj. volume:	500 µL
Concentrator:	TAC-ULP1
Temperature:	30°C

Time	Gradient (mM)	Gradient (mM)
0	10	10
10	10	19,5
10	25	45
30	45	30,1
10	34,5	45
35	10	45

Peaks:	A	B
Bromate	0.005 mg/L	0.005 mg/L
Chloride	250	0.030
Sulfate	250	0.150

Bromate Recovery

Matrix Concentration [mg/L]	Bromate Peak Area	Recovery [%]
0	0.0248	100.0
50	0.0245	98.8
100	0.0250	100.8
150	0.0244	98.4
200	0.0249	100.4
250	0.0249	100.4

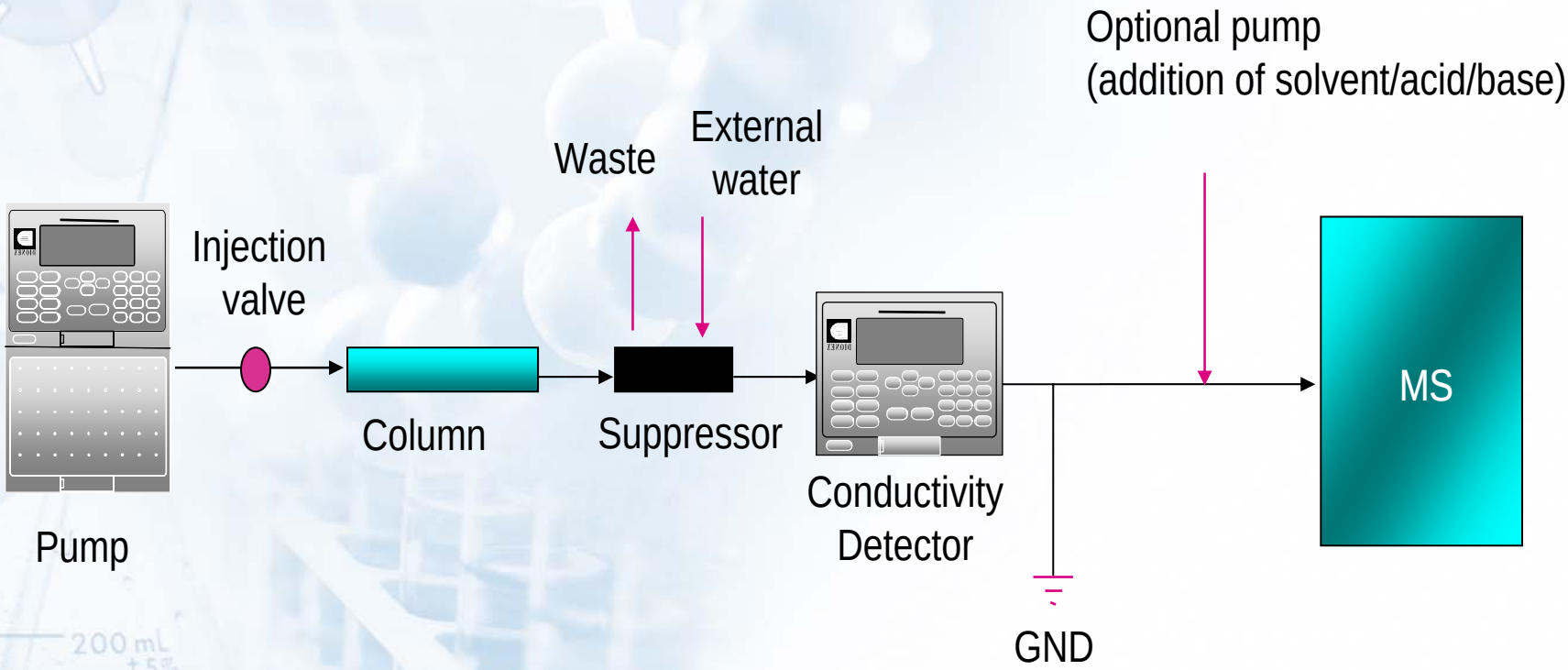
Sensitivity

Dimension	Peak Area	Flow Rate [mL/min]	Sensitivity
First (4 mm)	0.0063	1	1
Second (2 mm)	0.0248	0.25	3.936

Detection limit (MDL) for bromate, based on *n* = 7 runs (Student t Test), was calculated to be 0.2 ppb for a 500-µL injection with 200 ppm chloride and sulfate using suppressed conductivity detection.

Bromate and Haloacetic Acid Analysis with IC-MS

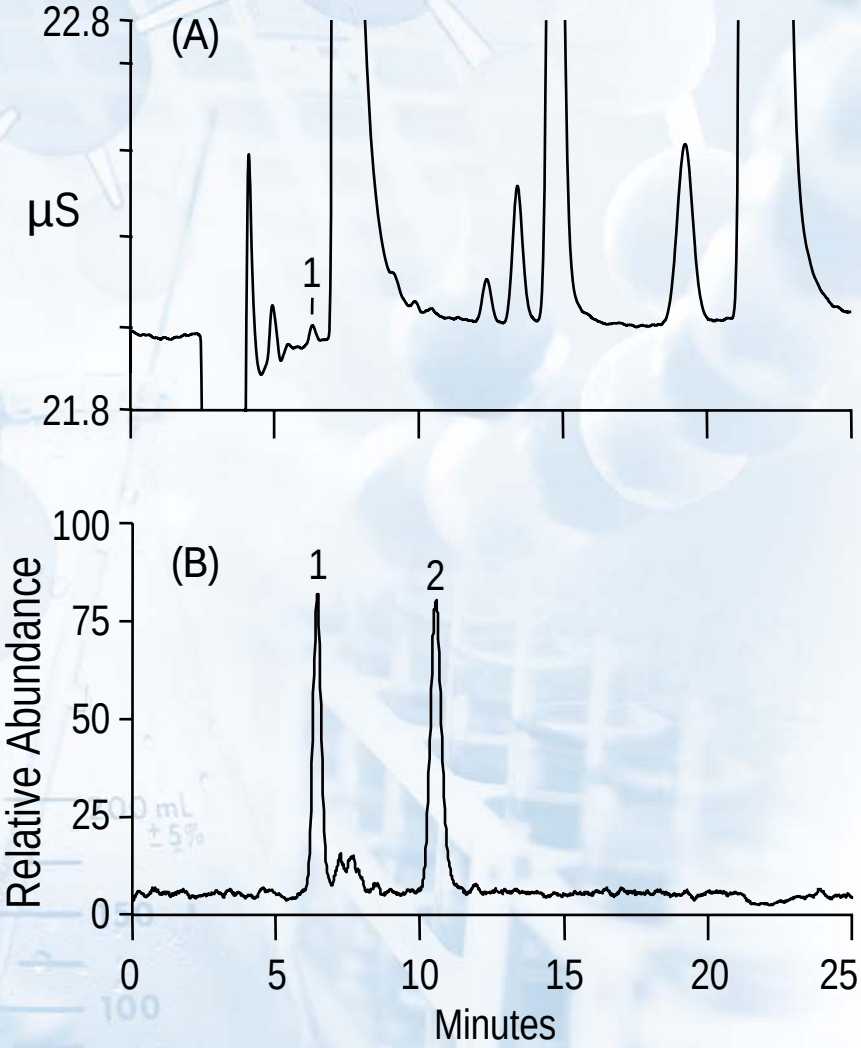
IC-MS Flow Diagram



ELMO = Enhanced Low Mass Option

MSQ is a trademark of ThermoFinnigan Corp.

Determination of Bromate in Drinking Water by IC-MS



Column:	IonPac AG9-HC, AS9-HC (2-mm ID)	
Eluant:	9 mmol/L Na_2CO_3	
Flow rate:	0.25 mL/min	
Inj. volume:	50 µL	
Detection:	A)	Suppressed conductivity, ASRS-ULTRA, AutoSuppression external water mode
	B)	Mass spec: -ESI mode, SIM, m/z = 127, Source: 10 V ESI probe: 275 °C, -2.5 kV Boxcar smoothing, 15 points
Peaks:	1.	Bromate 22 µg/L
	2.	DCAA NQ

DCAA = Dichloroacetic acid

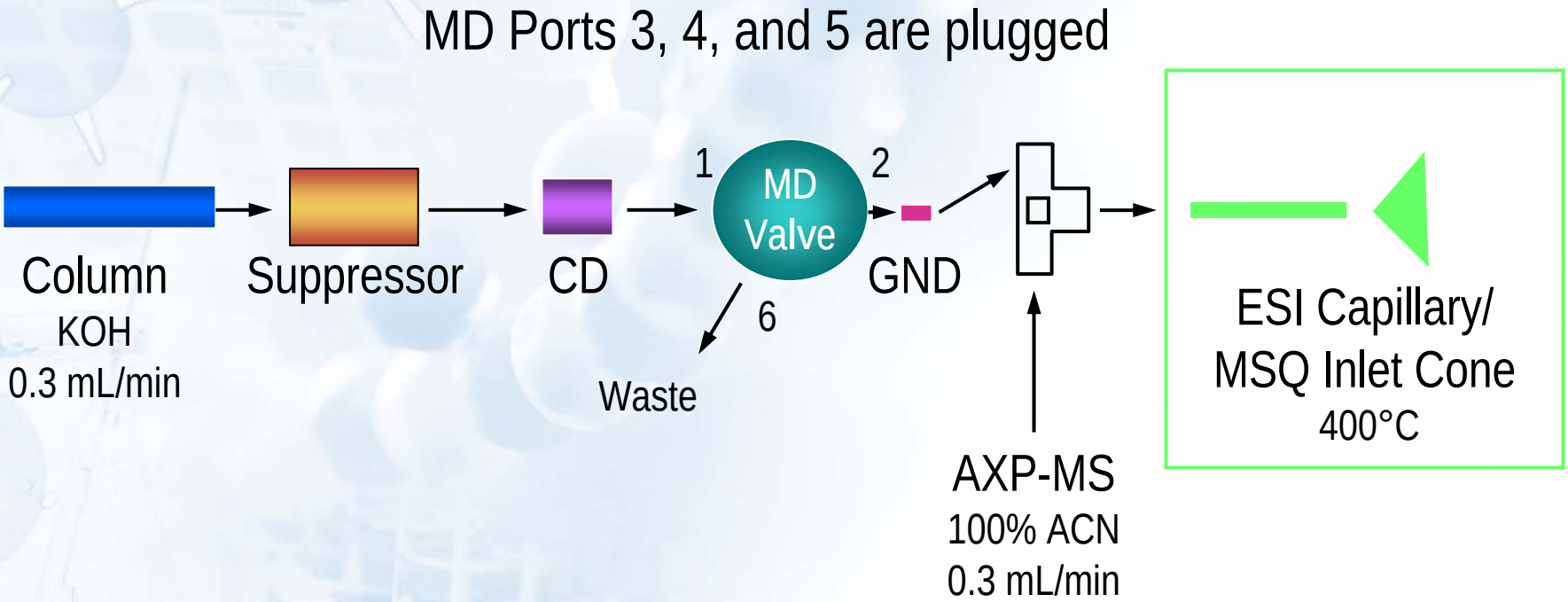
U.S. EPA Regulation for Haloacetic Acids

- 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

Development of a New IC-MS Method

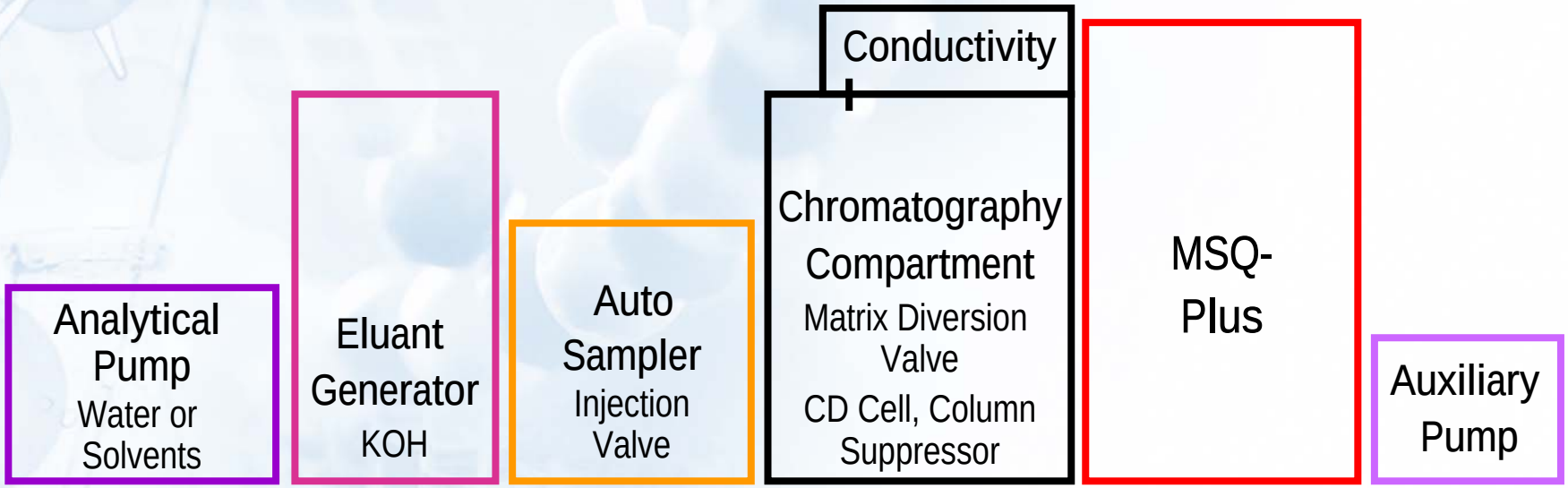
- New IC-MS method
  - Separation of 9 HAA's and bromate in drinking water matrix
  - No derivatization or sample pretreatment
  - Fully automated
  - Low MDL and high recoveries at high concentration of drinking water matrix
- Optimize ESI-MS conditions
  - Cone voltage: different for each analyte
  - Temperature
- Selection of an internal standard
  - Stable
  - No interference with analytes
- Selection of a suitable separator column
- Detection limits and recoveries

Flow Diagram with Matrix Diversion



In this configuration the AXP-MS delivers acetonitrile to the MSQ continuously. The matrix diversion valve is used to divert sample matrix to waste and then send the analytical stream to the MSQ. The analytical stream is mixed with solvent in a high-efficiency static-mixing tee before entering the MSQ.

Hardware Setup for IC/MS



Column Evaluation for Ion Chromatography

- Columns investigated: AS16, AS19, and AS20
  - AS16: inadequate separation
  - AS19:
    - » Poor recovery and high MDL in presence of matrix
    - » Co-elution of sulfate, DBCAA, and TCAA
    - » Very narrow window for matrix diversion
  - AS20:
    - » Similar performance to AS19
    - » Faster separation
    - » Low capacity: peak broadening in matrix; high MDL for MBAA
- Prototype column:
  - » Significantly higher capacity
  - » Large enough time window for chloride diversion: allows resolution at 250 ppm chloride
  - » Separation of SO_4^{2-}, TCAA, and DBCAA => able to separate nine HAAs

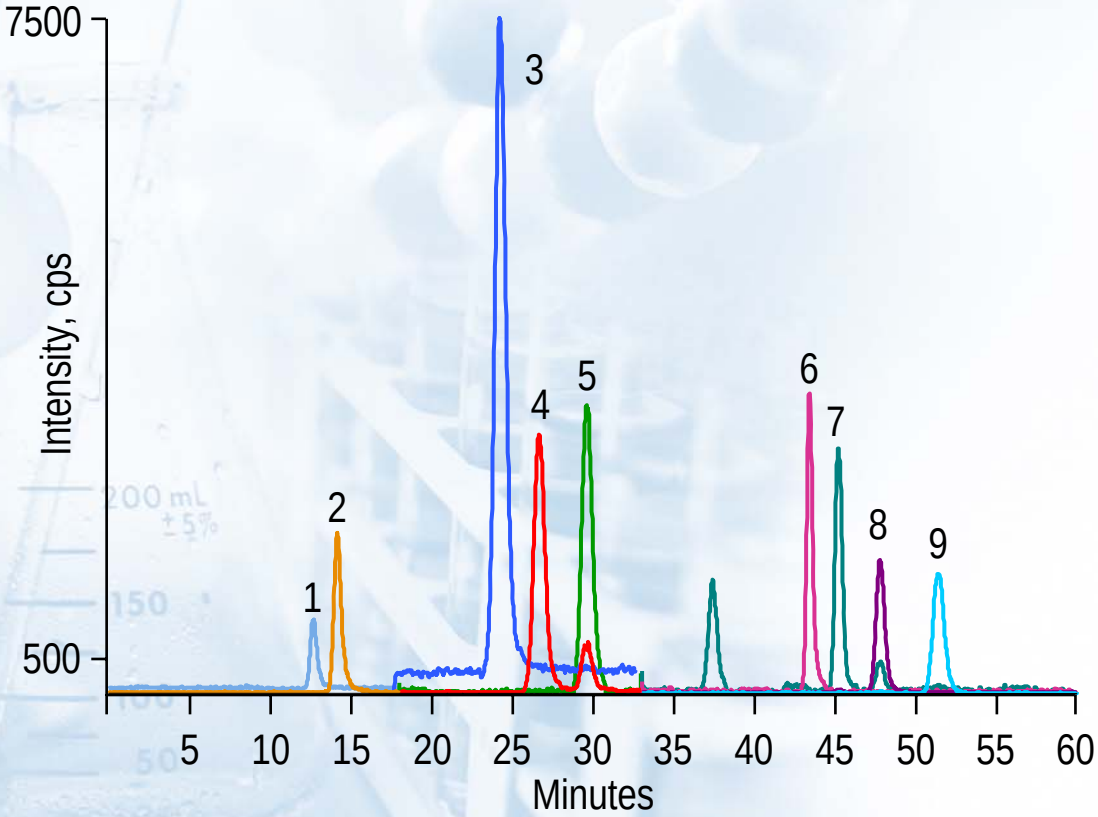
Separation of Haloacetic Acids on IonPac AS24

Column:	IonPac AG24, AS24 2 mm
Eluant:	EGC II KOH cartridge
Temperature:	15 °C
Flow rate:	0.3 mL/min
Inj. volume:	100 µL

Suppressor:	ASRS MS, 2 mm
Detector:	API 2000, MRM mode
Solvent:	MeCN, 0.20 mL/min

KOH Gradient:

Conc. (mM)	Time (min)
7.0	0.0
7.0	18.0
18.0	36.5
60.0	36.8
60.0	52.8
7.0	53.0
7.0	60.0



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

MDL Calculations for HAA and Bromate in DI Water and Simulated Matrix

Analyte (m/z)	D.I. 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 ppm; Chloride 250 ppm; Nitrate 20 ppm; NH_4Cl 100 ppm

Recovery

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	B.D.	B.D.	93.5	107.2
DBCAA	B.D.	B.D.	109.7	97.9
TBAA	B.D.	B.D.	88.4	93.5

B.D.—Below Detection

Recovery was determined in in a simulated sample containing 250 ppm chloride, 250 ppm sulfate, 20 ppm nitrate as compared to DI water.

Conclusions

- AS22 for conventional water analysis
- AS9-HC is ideal for high ionic strength samples
- AS17/19 for water analysis by RFIC
- High capacity cation exchangers for large Na/NH_4 concentration ratios
- Element-specific detection for chromium speciation
- Conventional IC and RFIC for DBPs
- IC-MS as an alternative to post-column derivatization and large volume injection for DBPs

Thank you

for your attention