ICS-5000
Capillary Ion Chromatograph

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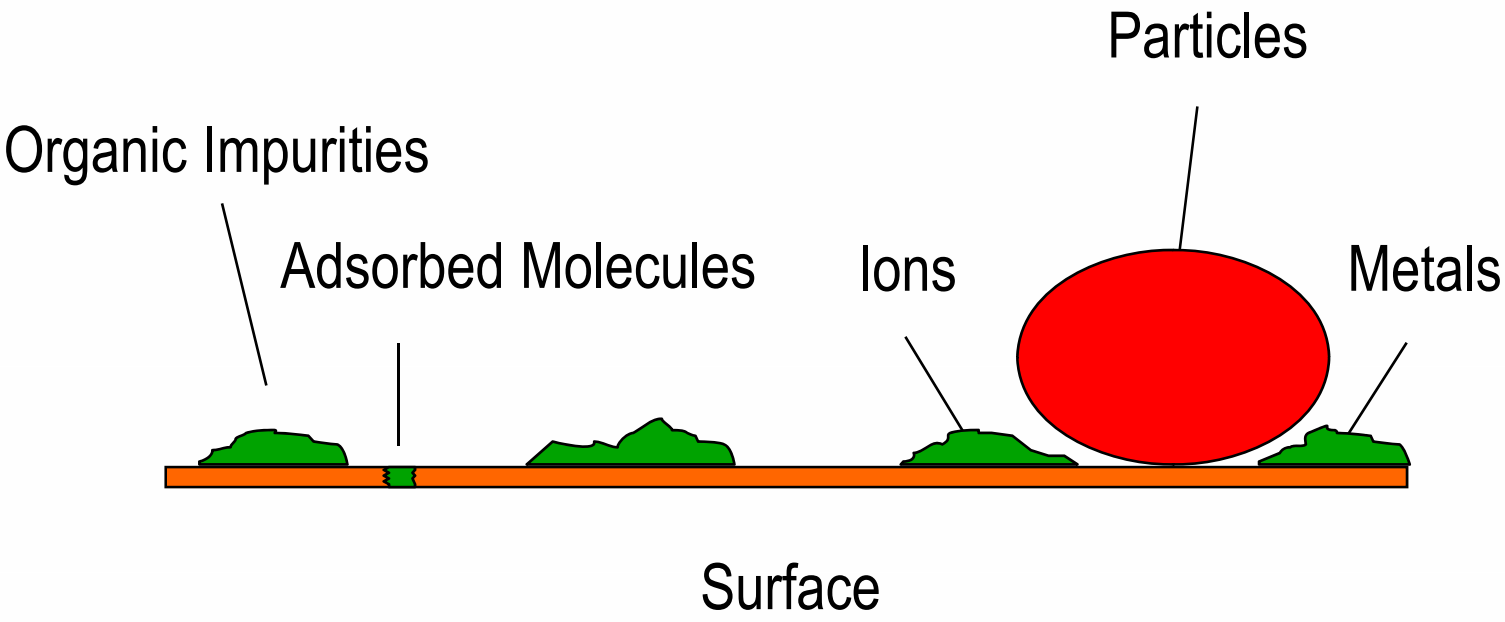
Types of Surface Contamination



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Standard Electronics Industry Methods Specifying Ion Chromatography (Part I)

- SEMI—Recommended Guidelines for Pure Water for Semiconductor Processing
- ASTM—Guidelines for Electronics Grade Water
- SEMI—Standard Test Method for Measurement of Ionic Contamination on Semiconductor Lead Frames
- SEMI—Standard Test Method for Trace Contaminants in Molding Compounds

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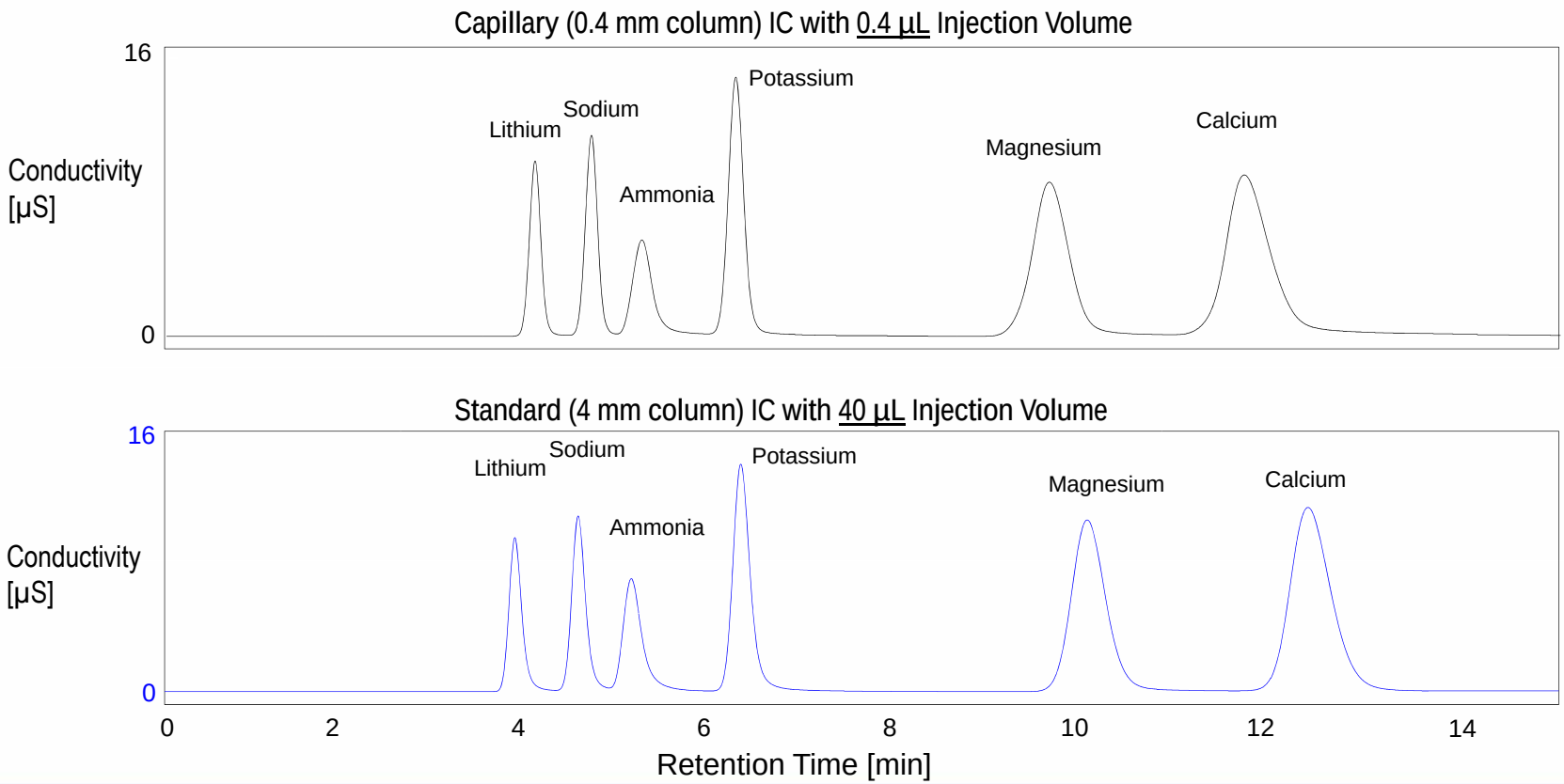
Standard Electronics Industry Methods Specifying Ion Chromatography (Part II)

- SEMI—Alternative to Wet Chemistry for the Analysis of Mixed Acid Etchants
- U.S. Military—Adhesives, Polymeric, Specifications for Use in Microcircuits
- IPC—Standard for Measurement of Residues on Circuit Boards
- IDEMA—Measurement of Extractable/Leachable Anion Contamination Levels on Drive Components by Ion Chromatography
- IDEMA—Special Cations Analysis

ICS-5000 - Dimension of Scale

Overlay of chromatograms from 2 mm and 0.4 mm with appropriate injection volumes



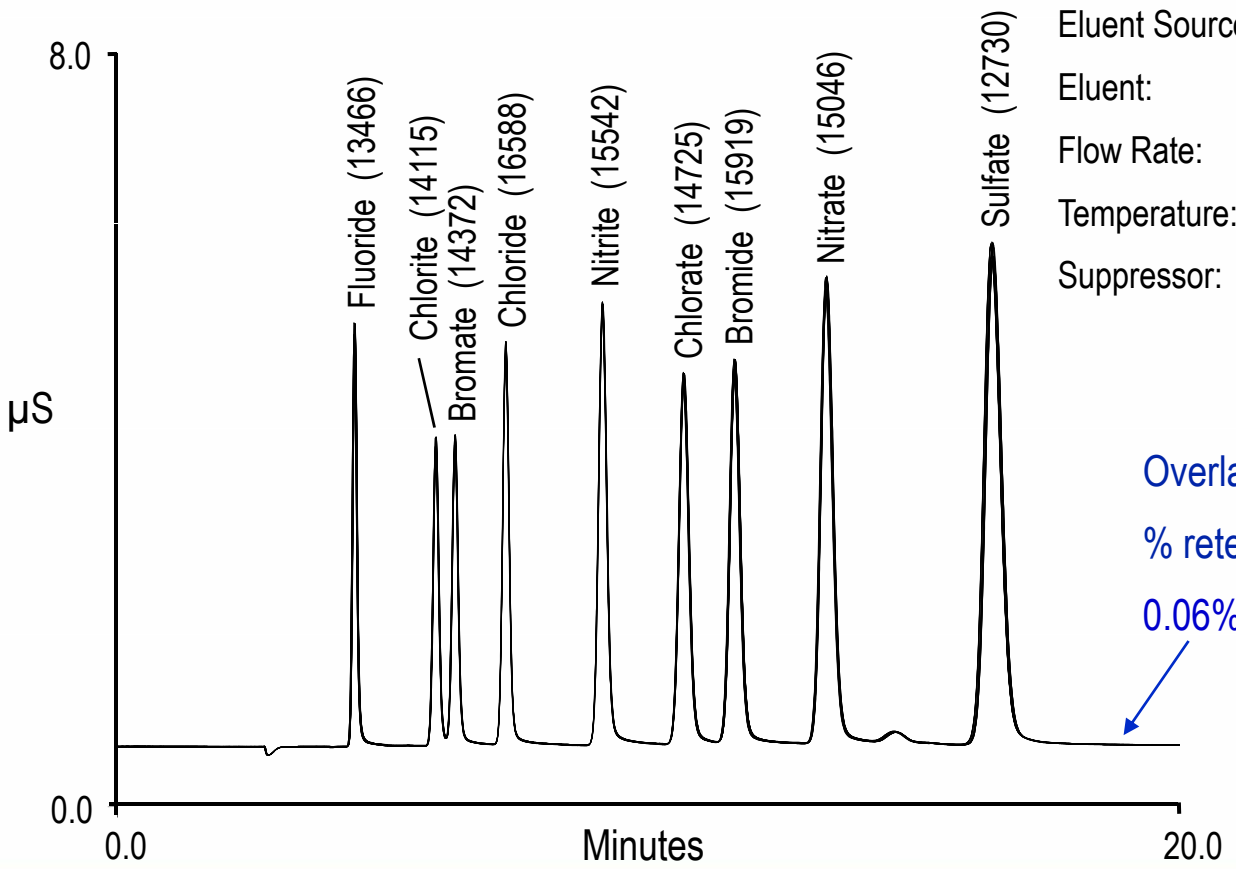
Advantages of Capillary Ion Chromatography

- Capable of continuous operation with minimal intervention
- Ease of use, higher sample throughput, and improved calibration
- Improved separation efficiency or speed
- Improved trace analysis (10 µL injection = large-loop injection)
- Improved compatibility with MS and “small sample size” applications
- Possibilities of offering new selectivity for difficult applications using new columns packed with more costly and difficult-to-make stationary phases

Typical Operating Parameters for Conventional and Capillary RFIC™ Systems

	Conventional RFIC	Capillary RFIC
Column ID	4 mm	0.4 mm
Flow Rate	1.0 mL/min	10 µL/min
Injection Loop	25 µL	0.4 µL
Suppressor Dead Volume	60 µL	0.6 µL
EG Current (50 mM KOH)	80.4 mA	0.804 mA
EG Current (200 mM KOH)	321.6 mA	3.216 mA
K+ Consumption/Year	26.3 Moles (50 mM KOH)	0.263 Moles (50 mM KOH)
H_2O Consumption/Year	525 L	5.25 L

Separation of 9 Anions on a Capillary AS19 Column



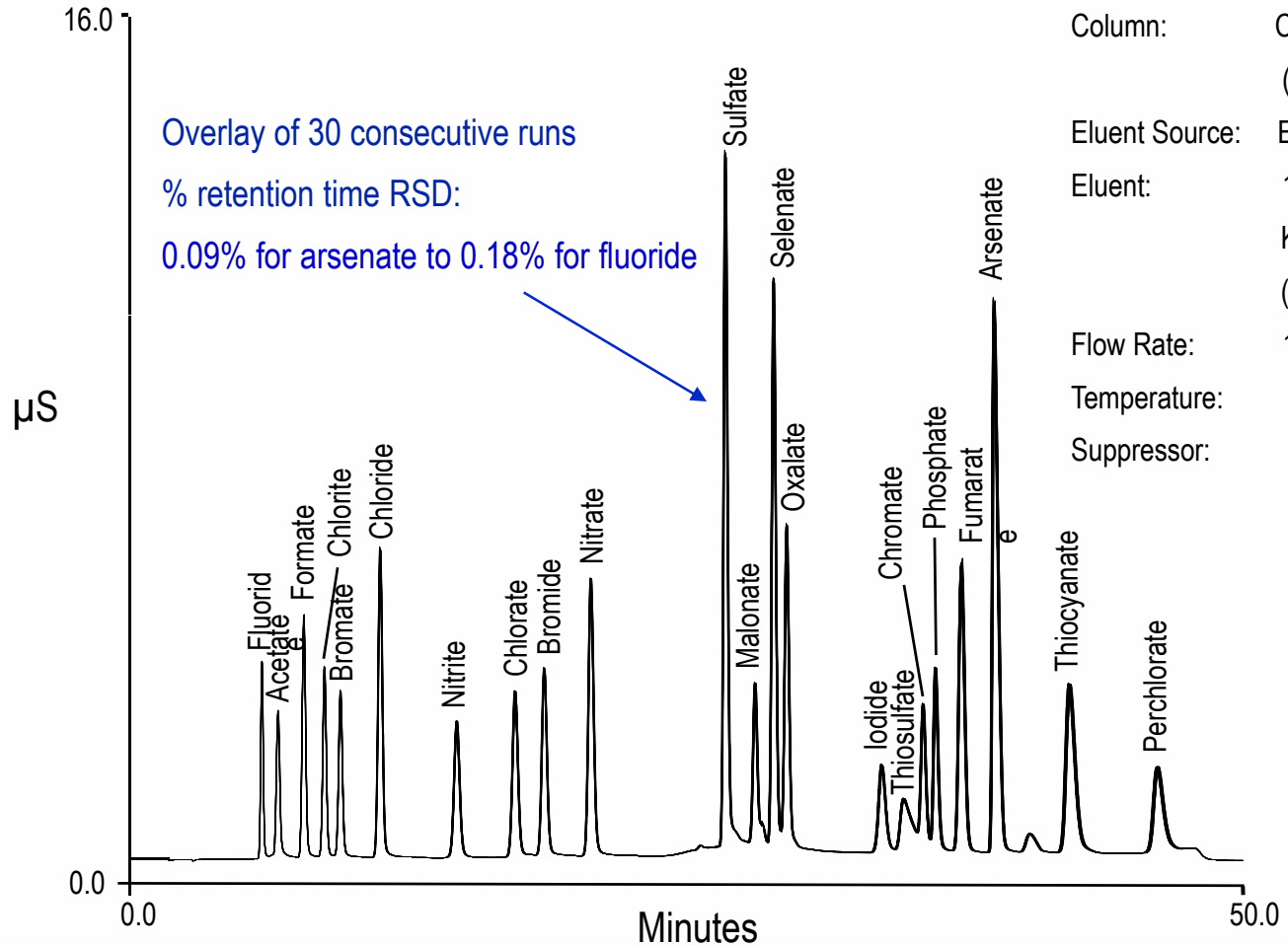
Column:	AS19 column (0.4 mm x 30 cm)
Eluent Source:	Capillary EGC-KOH cartridge
Eluent:	20 mM KOH
Flow Rate:	10 µL/min
Temperature:	30 °C
Suppressor:	Electrolytic capillary anion suppressor

Overlay of 30 consecutive runs

% retention time RSD:

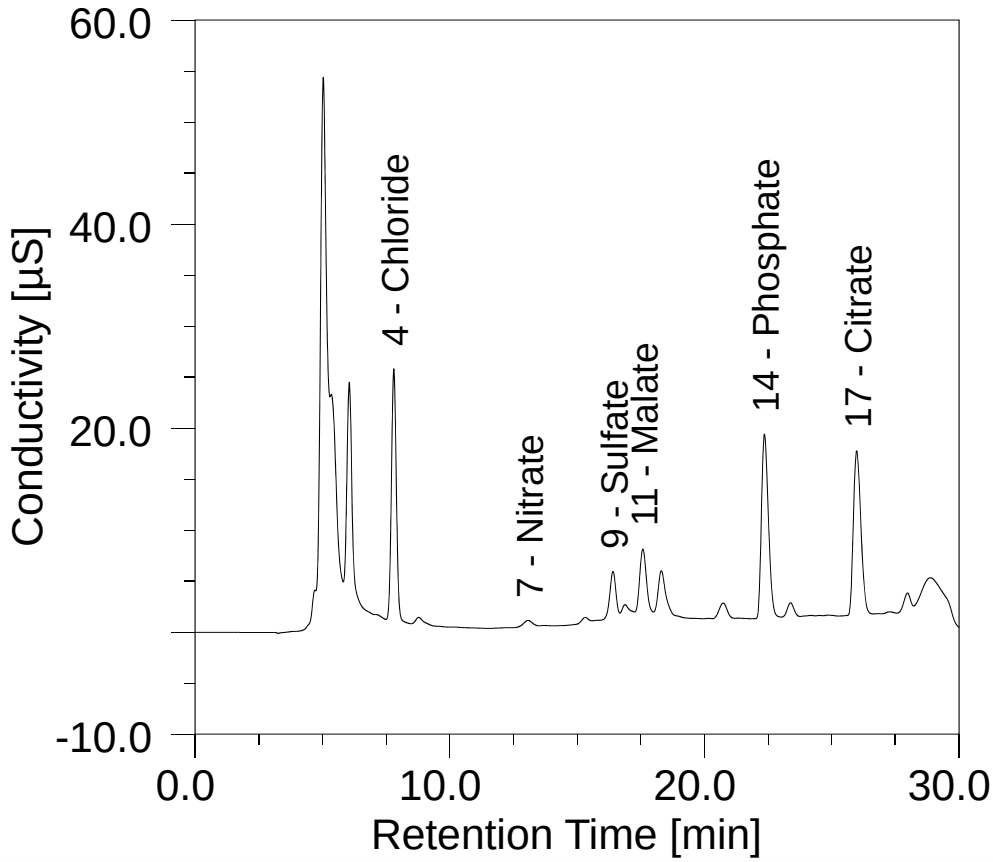
0.06% for chloride to 0.22% fluoride

Separation of 22 Anions on a Capillary AS19 Column



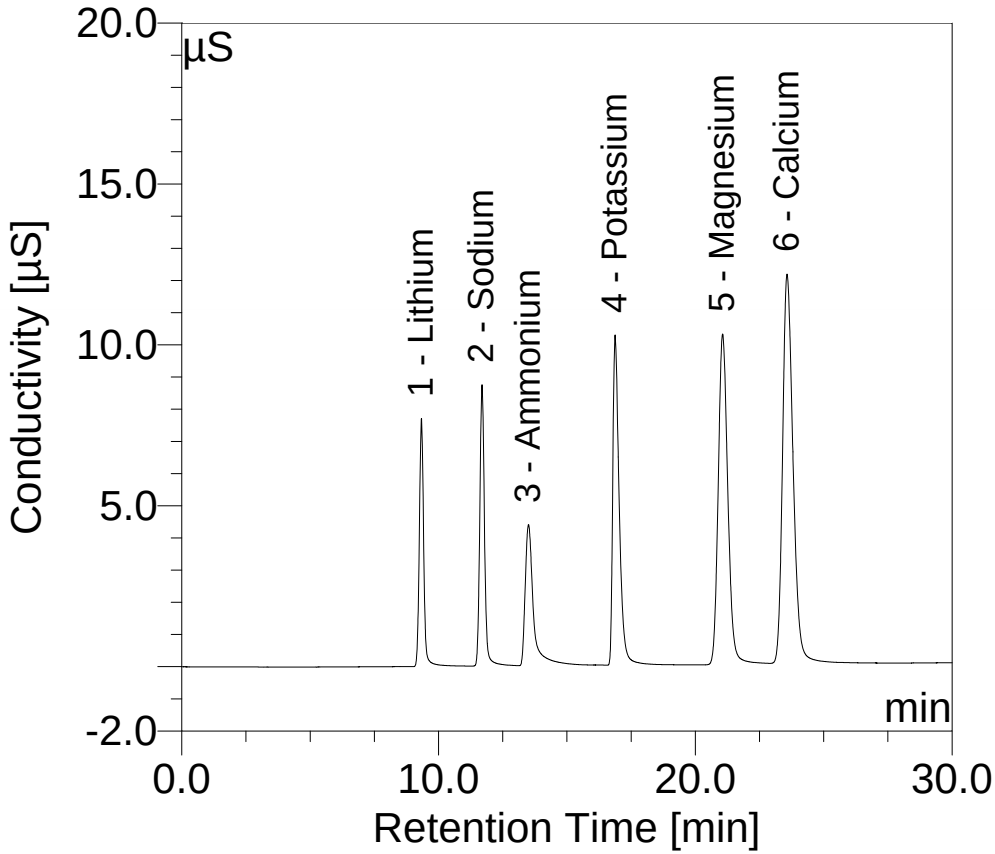
Column:	Capillary AS19 column (0.4 mm x 250 mm)
Eluent Source:	EGC-KOH cartridge
Eluent:	10 mM KOH (0 to 10 min), 10 to 52 mM KOH (10 to 42 min), 52 to 70 mM (42 to 45 min), 10 mM (45 to 50 min)
Flow Rate:	10 µL/min
Temperature:	30 °C
Suppressor:	Electrolytic capillary anion suppressor

Anions in Coke on a Capillary AS19 Column



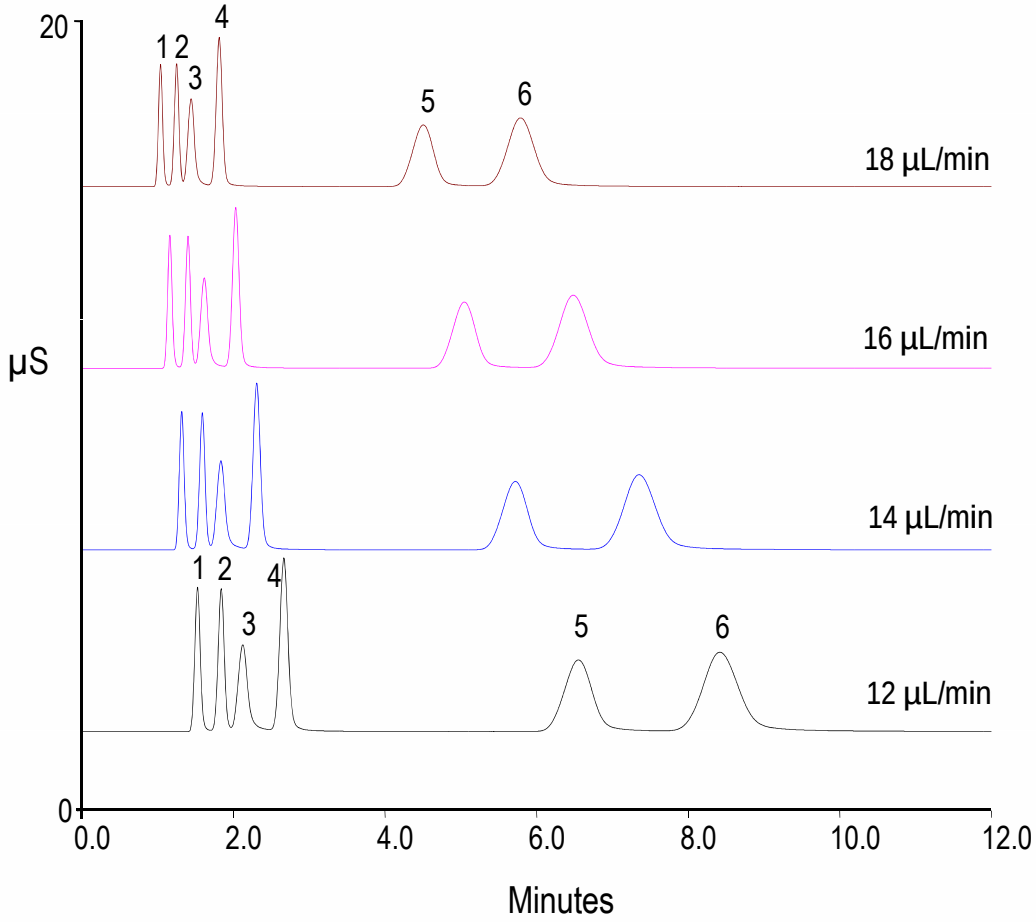
Column:	0.4 x 250 mm AS19 and 0.4 x 50 mm AG19
Eluent:	KOH (RFIC-EG)
Gradient:	7 min 15 mM isocratic, in 18 min to 60 mM gradient
Col. Temp.:	30 °C
Flow Rate:	10 µL/min
Inj. Volume:	0.4 µL
Detection:	Suppressed Conductivity
Sample:	Coke 1:10

Cation Standard on a Prototype Capillary CS16 Column



Column:	0.4 x 250 mm CS16 and 0.4 x 50 mm CG16
Eluent:	MSA (RFIC-EG)
Gradient:	6 mM in 30 min to 66 mM
Col. Temp.:	40 °C
Flow Rate:	0.010 mL/min
Inj. Volume:	0.4 µL
Detection:	Suppressed Conductivity
Sample:	6 Cation Standard 1:50

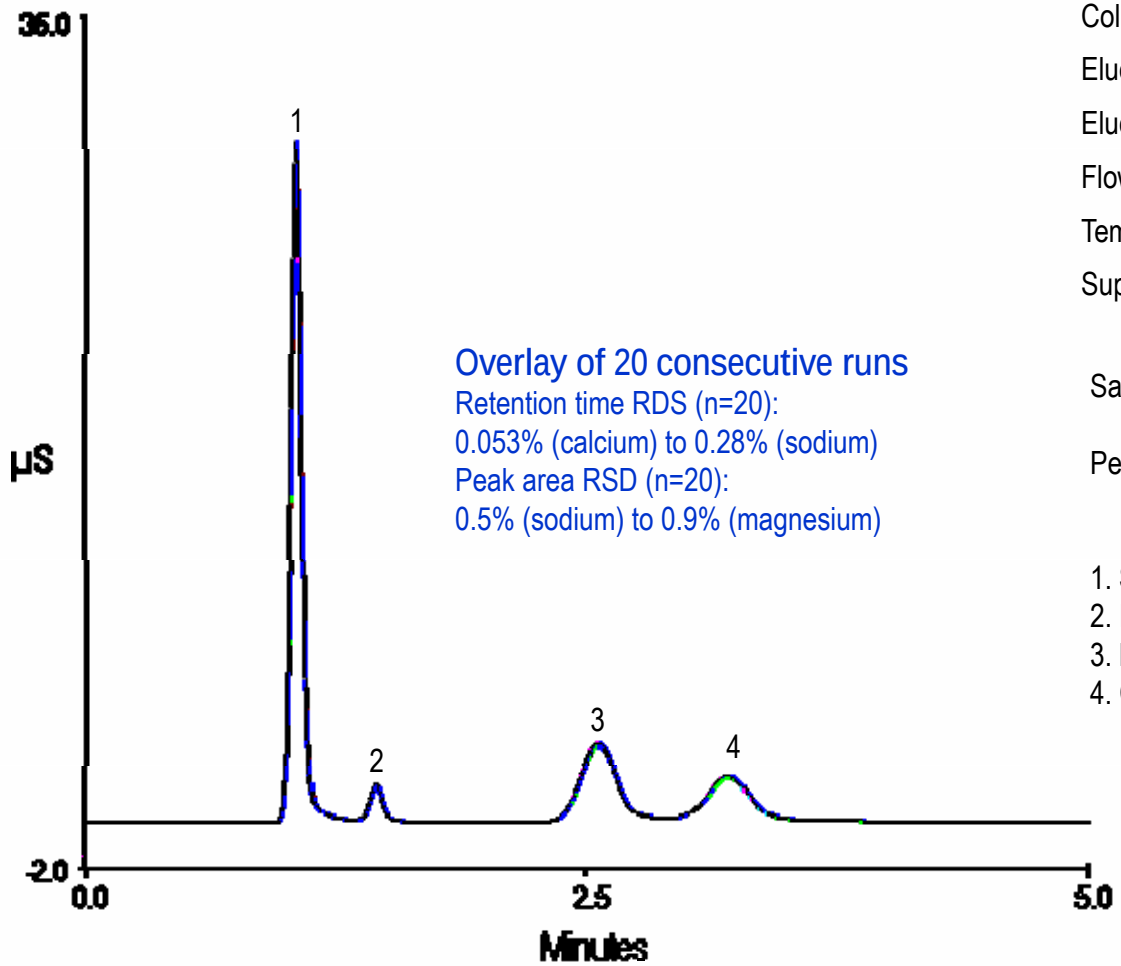
Fast Separation of Six Cations on a Capillary CS12A-5µ Column



Column:	CS12A-5µ column (0.4 mm x 15 cm)
Eluent Source:	Capillary EGC-MSA cartridge
Eluent:	20 mM MSA
Flow Rate:	12 to 18 µL/min
Temperature:	30 °C
Suppressor:	Electrolytic capillary cation suppressor

Peak	Retention Time at 18 µL/min (minutes)	Concentration (mg/L)
1. Lithium	1.037	0.5
2. Sodium	1.250	2.0
3. Ammonium	1.443	2.5
4. Potassium	1.813	5.0
5. Magnesium	4.507	2.5
6. Calcium	5.790	5.0

Rapid Determination of Cations - Treated Waste Water



Column:	CS12A-5µ column (0.4 mm x 15 cm)
Eluent Source:	Capillary EGC-MSA cartridge
Eluent:	28 mM MSA
Flow Rate:	18 µL/min
Temperature:	30 °C
Suppressor:	Electrolytic capillary cation suppressor

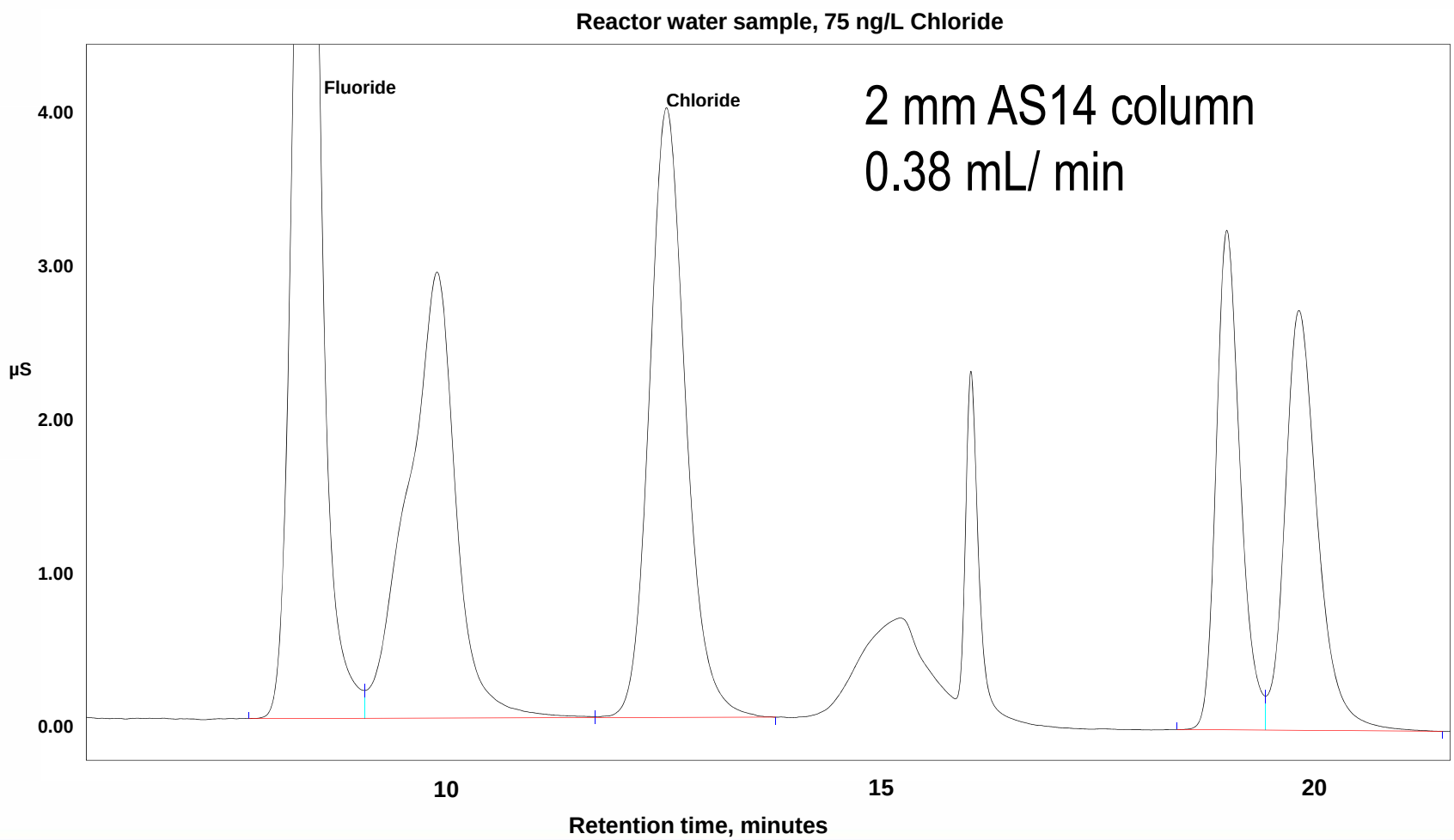
Sample: Treated Waste Water (1:10 dilution)

Peak	Concentration (mg/L)
1. Sodium	19.6
2. Potassium	0.8
3. Magnesium	3.5
4. Calcium	3.1

Trace Analysis Using Capillary Ion Chromatography

- Large-volume direct injection or pre-concentration
  - A 10 µL injection onto a 0.4 mm ID column is equivalent to a 1000 µL injection onto a 4 mm I.D. column.
  - Loading a 250 µL sample onto a capillary concentrator can be accomplished with an AS autosampler in shorter time than loading a 25 mL sample onto a conventional concentrator with an AS-HV.
  - Suitable for samples with low levels of matrix ions

Trace Analysis, Microbore IC



2 mL Sample, Direct Injection

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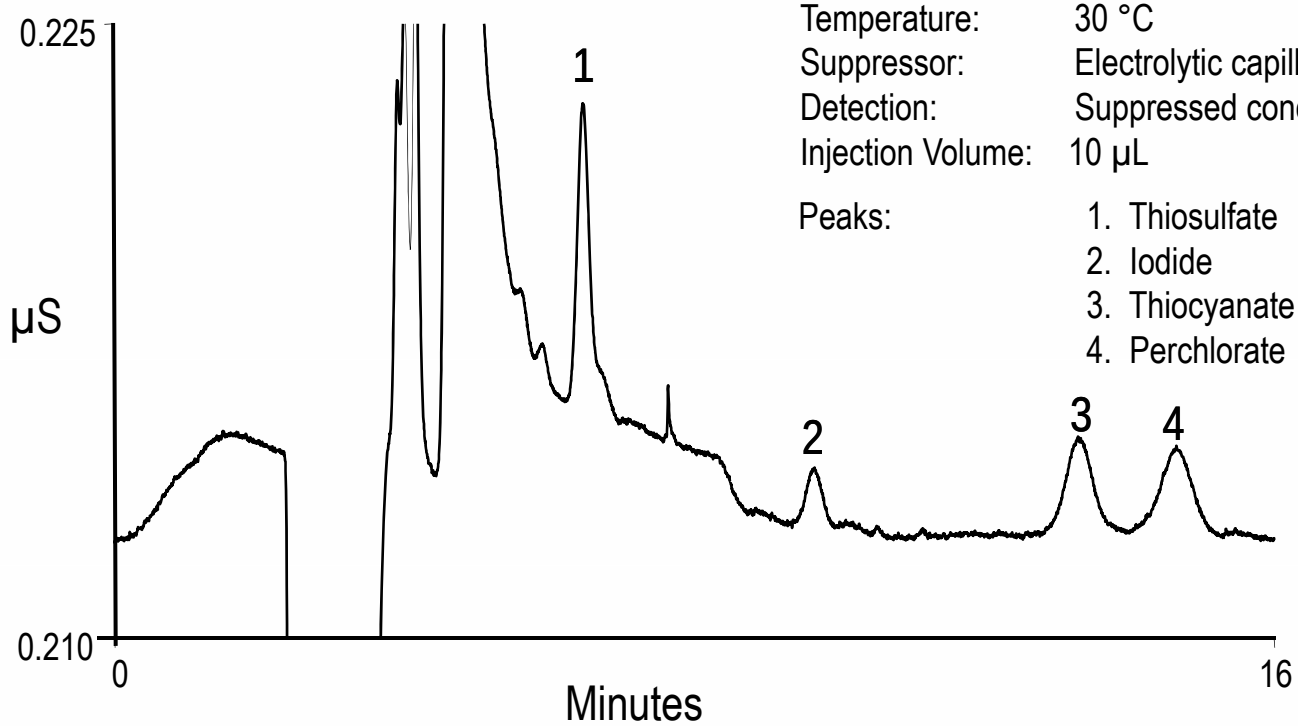
Inorganic Anions at Trace Concentrations with 10 µL Injection

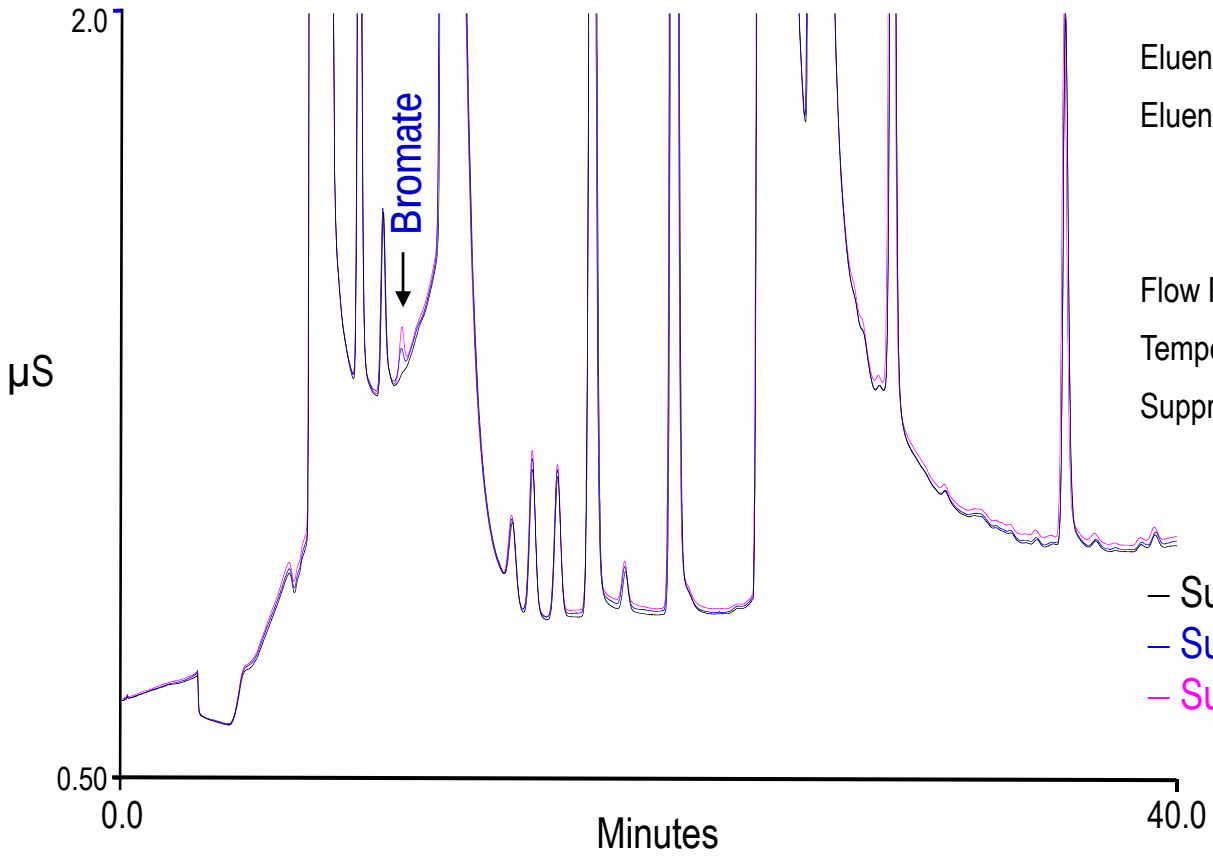


Column:	Prototype AS20 column (0.4 x 250 mm)
Eluent Source:	Capillary EGC-KOH cartridge
Eluent:	35 mM KOH
Flow Rate:	10 µL/min
Temperature:	30 °C
Suppressor:	Electrolytic capillary suppressor
Detection:	Suppressed conductivity
Injection Volume:	10 µL

Peaks:

1.	Thiosulfate	0.33 µg/L
2.	Iodide	0.67
3.	Thiocyanate	0.67
4.	Perchlorate	1.0

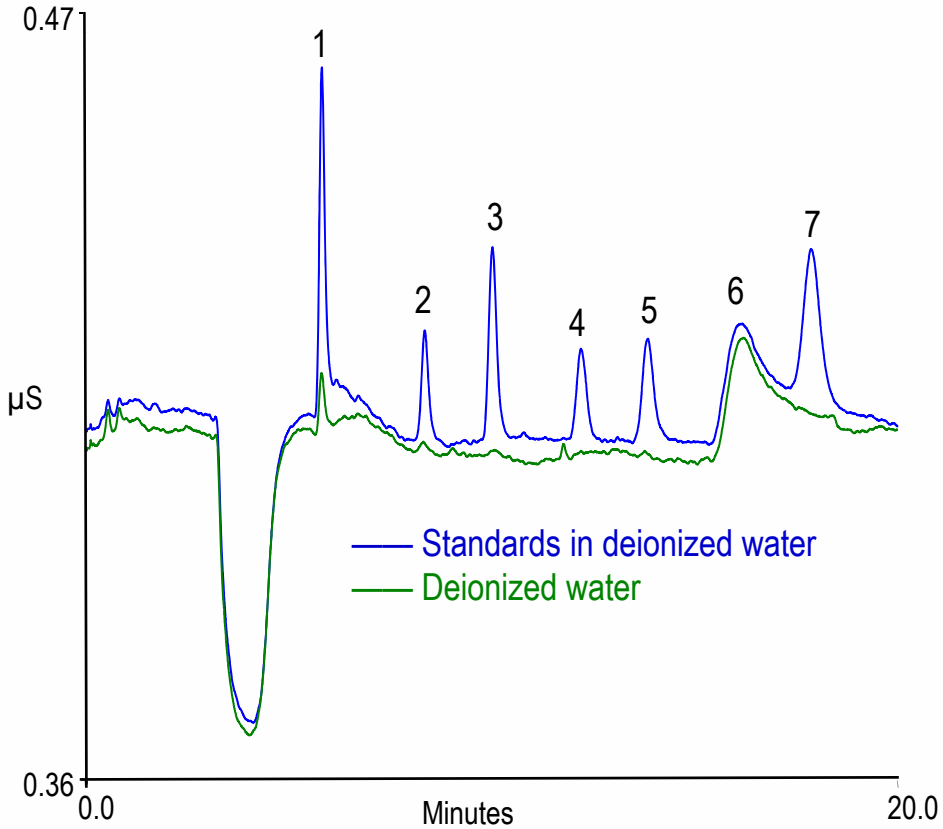
Trace Bromate in Drinking Water Large Loop (10 µL) Injections



Column:	Capillary AS19 column (0.4 x 250 mm)
Eluent Source:	Capillary EGC-KOH cartridge
Eluent:	10 mM KOH (0 to 10 min), 10 to 52 mM KOH (10 to 42 min), 52 to 70 mM (42 to 45 min), 10 mM (45 to 50 min)
Flow Rate:	10 µL/min
Temperature:	30 °C
Suppressor:	Electrolytic capillary anion suppressor

– Sunnyvale drinking water
– Sunnyvale drinking water + 2 ppb bromate
– Sunnyvale drinking water + 4 ppb bromate

Separation of Inorganic Anions at Trace Concentrations 10 µL Injection



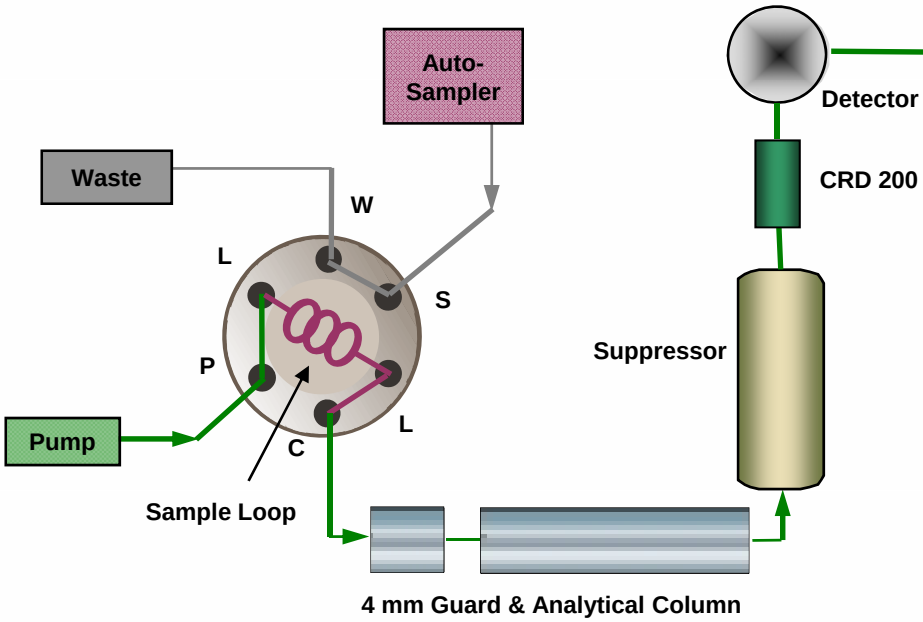
Column:	AS19 column (0.4 mm x 25 cm)
Eluent Source:	Capillary EGC-KOH cartridge
Eluent:	20 mM KOH
Flow Rate:	10 µL/min
Temperature:	30 °C
Suppressor:	Capillary anion suppressor
Detection:	Suppressed conductivity
Injection Volume:	10 µL

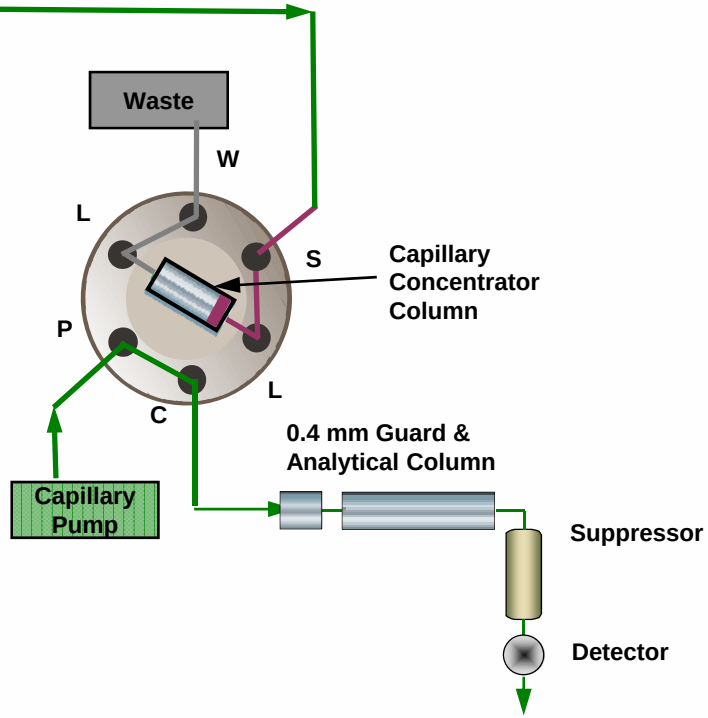
Peak	Concentration (µg/L)
1. Fluoride	0.2
2. Chloride	0.3
3. Nitrite	1.0
4. Bromide	1.0
5. Nitrate	1.0
6. Carbonate	–
7. Sulfate	1.0

Trace Analysis Using Capillary Ion Chromatography

- Two-dimensional ion chromatography using a capillary column in the second dimension
  - Perform large-loop injection and separation of matrix ions using a 4 mm ID column in the 1st dimension
  - Focuses the ions of interest in a concentrator column after suppression in the 1st dimension
  - Perform separation using a 0.4 mm ID column of different selectivity in the 2nd dimension
  - Provide sensitivity enhancement that is proportional to the flow rate ratio (e.g. a factor of 100)
  - Suitable for samples with high levels of matrix ions

ICS-5000 2D RFIC™ System Using a Capillary Column in the Second Dimension

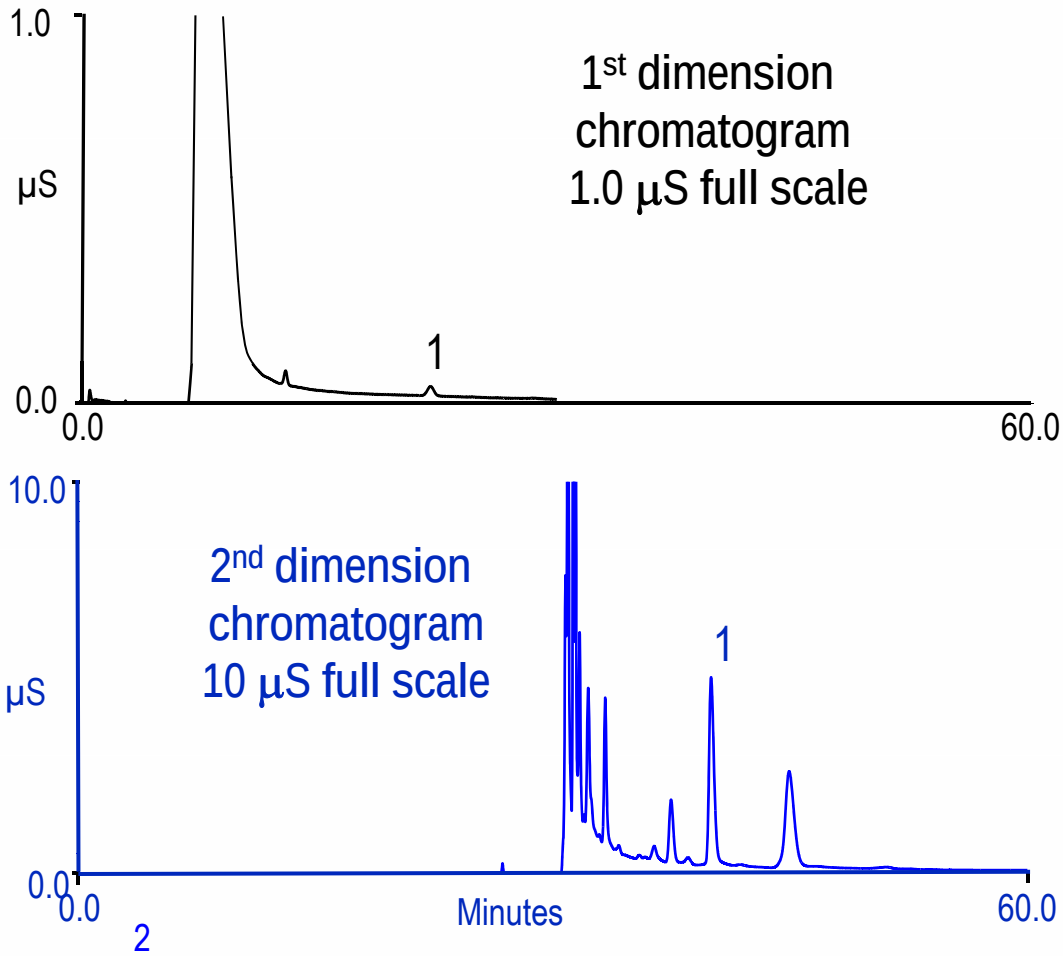




Standard Bore: 4 mm, 1 mL/min

Capillary: 0.4 mm, 10 µL/min

Determination of Trace Perchlorate Using a 2D RFIC™ System with a Second-Dimension Capillary Column



A. First-Dimension Conditions

Column:	IonPac® AG16, AS16, 4 mm
Flow Rate:	1.0 mL/min
Eluent:	65 mM KOH (EG)
Suppressor:	4 mm SRS 300
Inj. Volume:	4000 µL
Temperature:	30 °C

B. Second-Dimension Conditions

Column:	Prototype AS20 (0.4 mm x 25 cm)
Flow Rate:	10 µL/min
Eluent:	35 mM KOH
Suppressor:	Capillary Anion Suppressor
Temperature:	30 °C
Concentrator:	Capillary concentrator, 5000 µL of 1st dimension suppressed effluent (19 to 24 minutes)

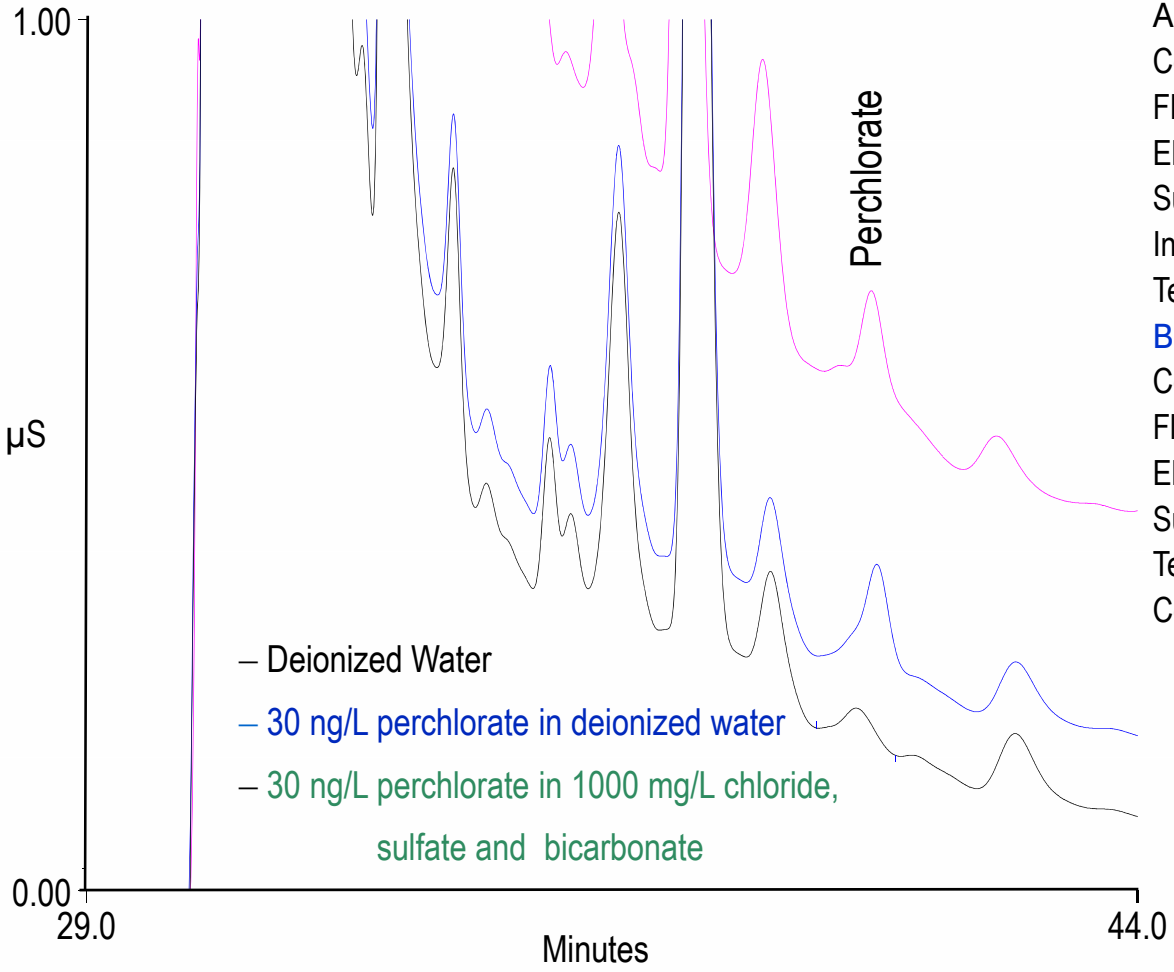
Peak: 1. Perchlorate 1.0 µg/L

Perchlorate Peak Area

1st Dimension: 0.0115 µS*min

2nd Dimension: 1.75 µS*min

Determination of Trace Perchlorate Using a 2D RFIC™ System with a Second-Dimension Capillary Column



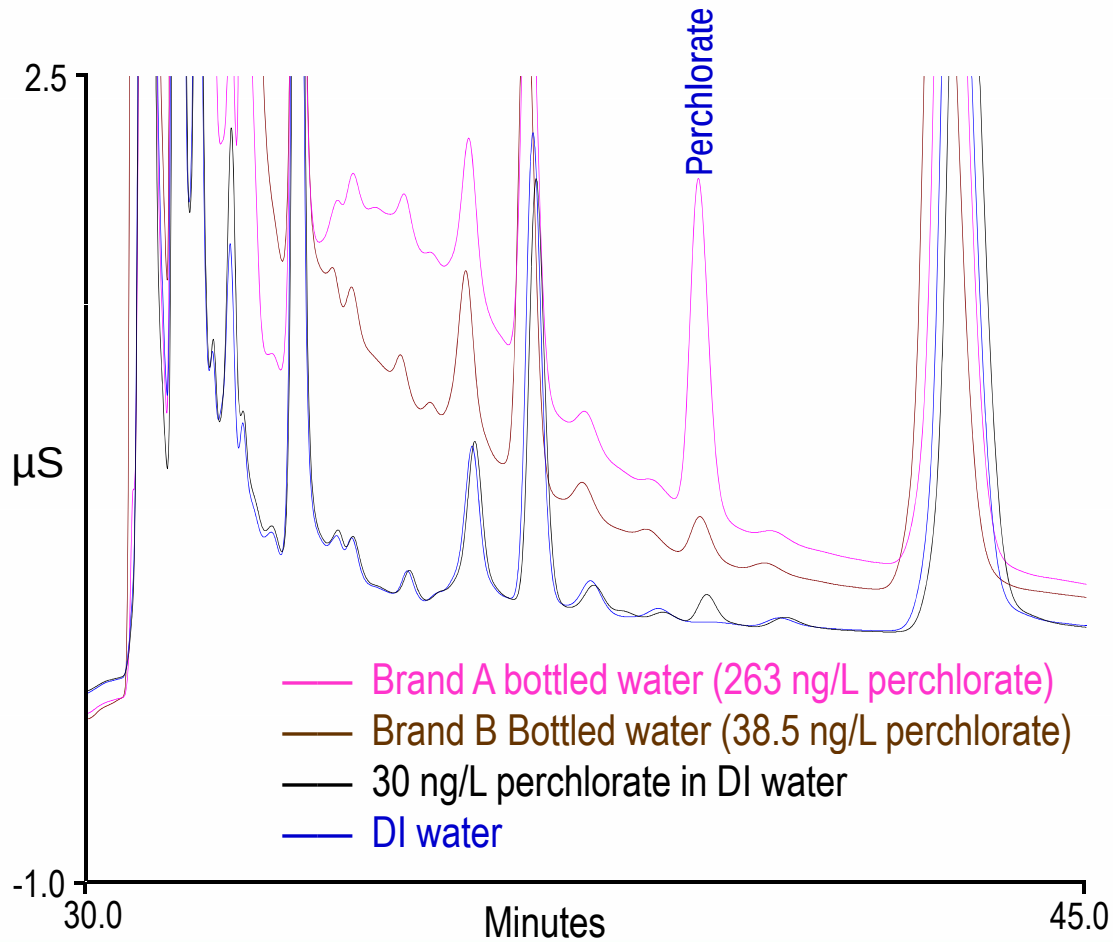
A. First-Dimension Conditions

Column:	IonPac® AG16, AS16, 4 mm
Flow Rate:	1.0 mL/min
Eluent:	65 mM KOH (EG)
Suppressor:	4 mm SRS 300
Inj. Volume:	4000 µL
Temperature:	30 °C

B. Second-Dimension Conditions

Column:	Prototype AS20 (0.4 mm x 25 cm)
Flow Rate:	10 µL/min
Eluent:	35 mM KOH (EG)
Suppressor:	Capillary Anion Suppressor
Temperature:	30 °C
Concentrator:	Capillary concentrator, 5000 µL of 1st dimension suppressed effluent (19 to 24 minutes)

Determination of Perchlorate in Bottled Water Samples Using an ICS-5000 2D RFIC™ System



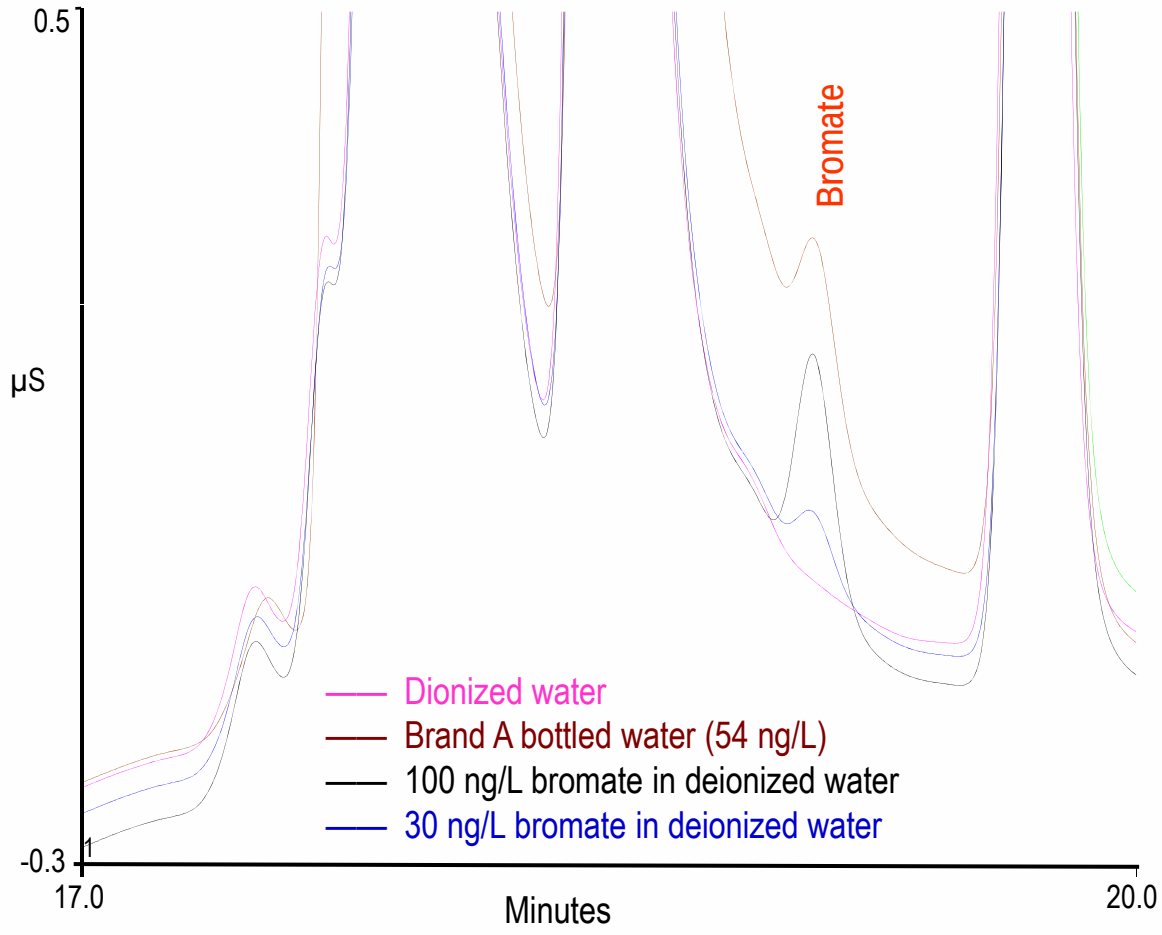
A. First-Dimension Conditions

Column:	IonPac® AG16, AS16, 4 mm
Flow Rate:	1.0 mL/min
Eluent:	65 mM KOH (EG)
Suppressor:	4 mm SRS 300
Inj. Volume:	4000 µL
Temperature:	30 °C

B. Second-Dimension Conditions

Column:	Prototype AS20 (0.4 mm x 25 cm)
Flow Rate:	10 µL/min
Eluent:	35 mM KOH (EG)
Suppressor:	Capillary Anion Suppressor
Temperature:	30 °C
Concentrator:	Capillary concentrator, 5000 µL of 1st dimension suppressed effluent (19 to 24 minutes)13

Determination of Trace Bromate in a Bottled Water Sample Using an ICS-5000 2D Capillary RFIC System



A. First-Dimension Conditions

Column:	IonPac® AG19, AS19, 4 mm
Flow Rate:	1.0 mL/min
Eluent:	10 to 60 mM KOH (EGC-KOH)
Suppressor:	4 mm SRS 300
Inj. Volume:	1000 µL
Temperature:	30 °C

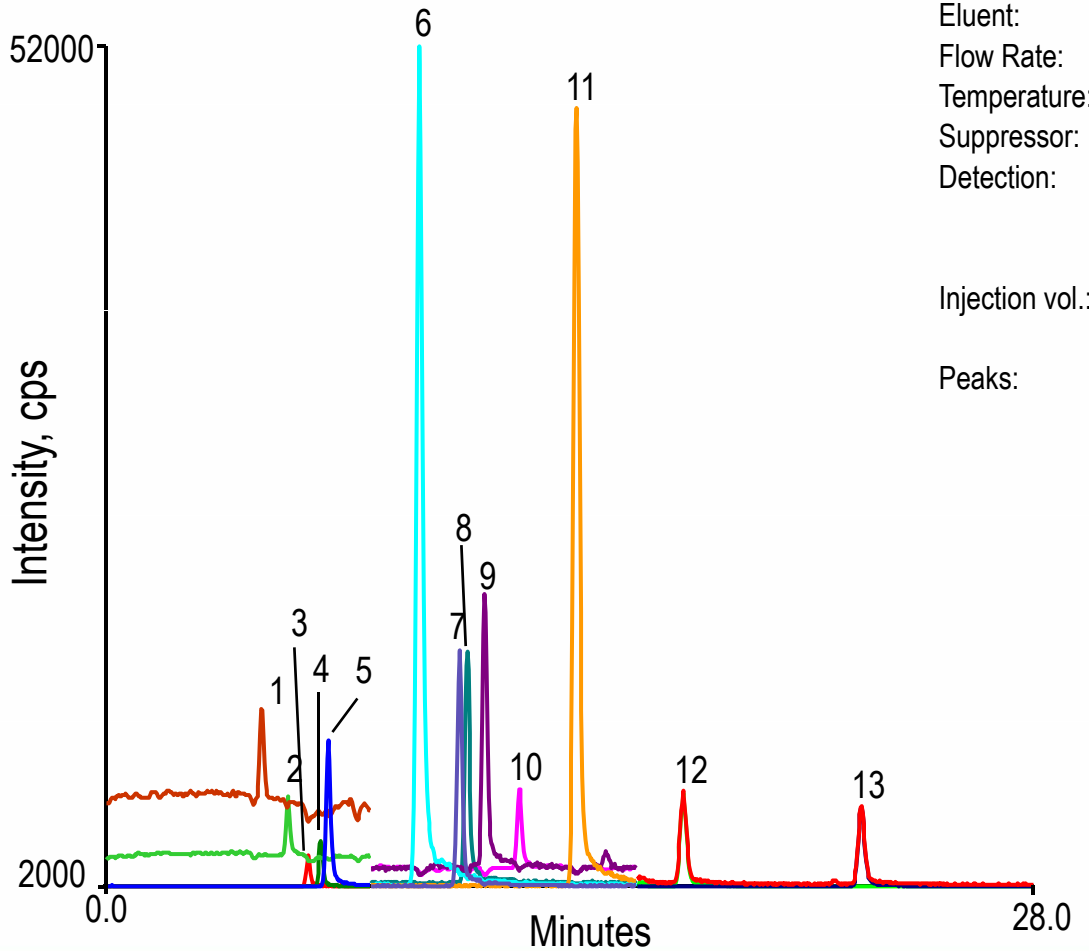
B. Second-Dimension Conditions

Column:	Prototype AS20 (0.4 mm x 25 cm)
Flow Rate:	10 µL/min
Eluent:	35 mM KOH (EGC-KOH)
Suppressor:	Capillary Anion Suppressor
Temperature:	30 °C
Concentrator:	Capillary concentrator, 2500 µL of 1st dimension suppressed effluent (7.5 to 10 minutes)

Operating Conditions of a Capillary IC System with MS/MS Detection

- Capillary IC System:
  - Column: Prototype AS20 (0.4 mm x 250 mm)
  - Eluent Source: Capillary EGC-KOH cartridge
  - Flow Rate: 10 to 20 µL/min
  - Temperature: 30 °C
  - Suppressor: Electrolytic capillary anion suppressor operated in the external water mode (20 µL/min)
- ABI SCIEX API 2000™ MS/MS System:
  - Post-suppressor addition of acetonitrile at 15 µL/min via a grounded 0.15 mm bore mixing Tee
  - Negative ESI with optimized probe position
  - Optimized multiple reaction monitoring (MRM) channels for target analytes.

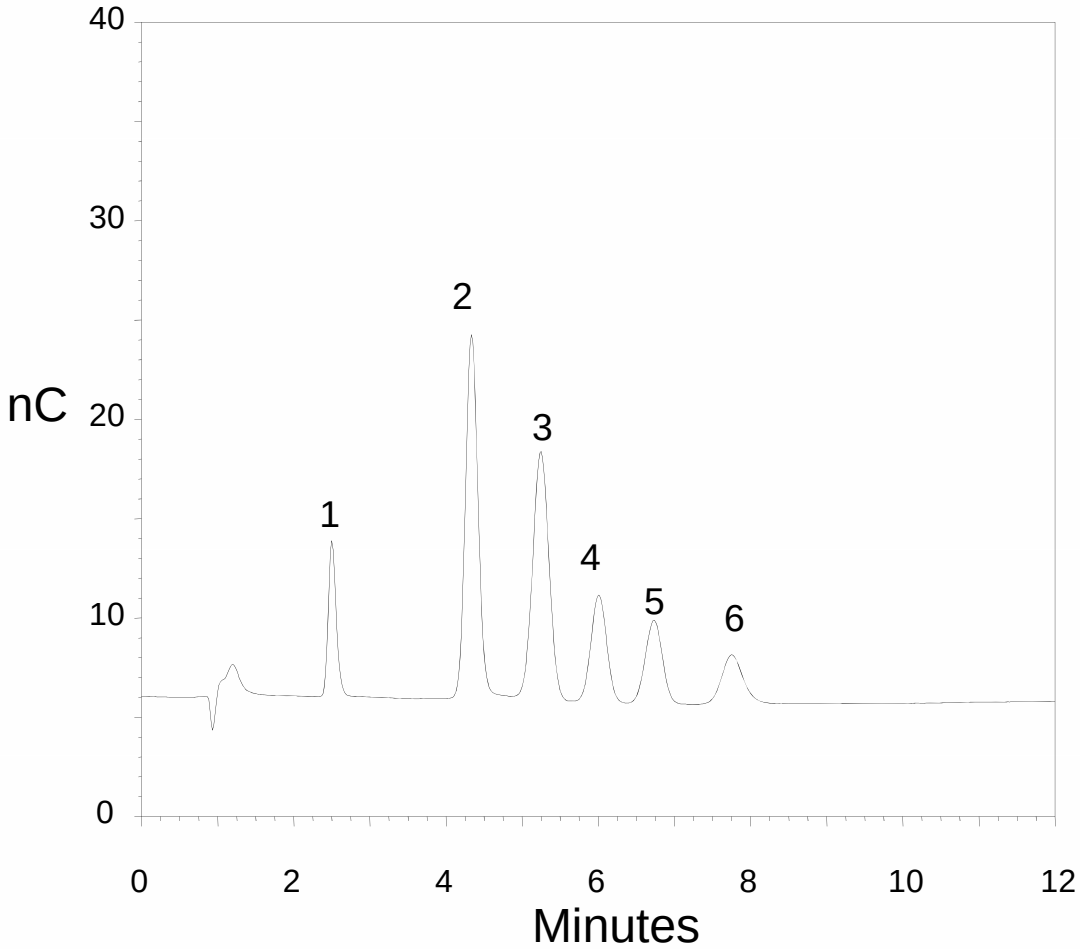
Determination of Inorganic and Organic Anions Using a Capillary IC and API 2000™ MS/MS System



Column:	Prototype AS20 (0.4 mm x 250 mm)
Eluent Source:	Capillary EGC-KOH cartridge
Eluent:	4-55 mM KOH
Flow Rate:	15 µL/min
Temperature:	30 °C
Suppressor:	Electrolytic capillary anion suppressor
Detection:	API2000 MS/MS with post suppressor addition of acetonitrile at 15 µL/min; Negative ESI
Injection vol.:	10 µL

Peaks:			MRM (*m/z*)
1. Acetate	10	µg/L	59/59
2. Formate	10		45/45
3. Chlorite	10		67/51
4. Bromate	10		126.7/110.8
5. Bromoacetate	10		137/78.8
6. Dichloroacetate	10		127/82.9
7. Dibromoacetate	10		214.7/170.7
8. Chlorate	10		83/66.9
9. Bromide	10		79/79
10. Nitrate	10		62/46
11.Trichloroacetate	10		161/116.8
12.Tribromoacetate	10		250.8/78.8
13.Perchlorate	1.0		99/83

Separation of Six Monosaccharides



Column:	CarboPac PA 20 (0.4 mm x 150 mm)
Temp.:	30 ° C
Eluent:	10 mM KOH
Flow Rate:	10 µl/min
Inj. Vol. :	0.4 µL
Detection:	PAD (Carbohydrate Quadruple Waveform)
Electrode:	ED Au
Sample:	Standards (10 µM)

Peaks:

1. Fucose (Fuc)
2. Galactoseamine (GalN)
3. Glucoseamine (GalN)
4. Galactose (Gal)
5. Glucose (Glc)
6. Mannose (Man)

ICS-5000 Technology – Ease of Use

CRD 200

Guard and Separation Column

Suppressor

Injection Valve

EG Degas

Side view of ACES Suppressor

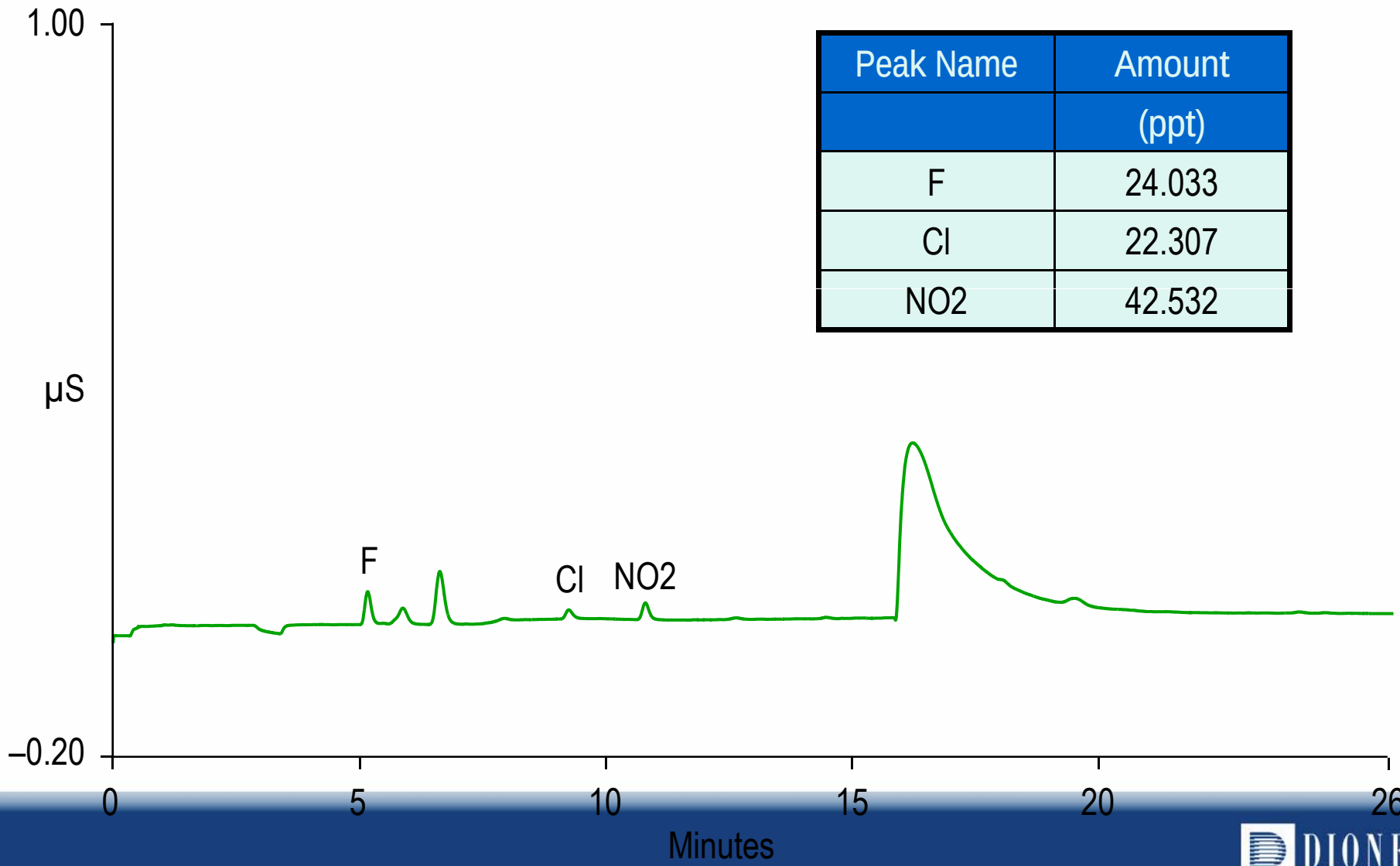
ICS-5000 System Top Values

- Just Add Water once a Quarter –
  Add Samples any Time
- Just Increase Sensitivity –
  Ultimate Sensitivity (IC x IC)
- Just Save Money –
  Low Cost of Ownership

Summary

- Capillary RFIC™ systems with suppressed conductivity detection offer highly reproducible isocratic and gradient separations of target analytes
- Capillary RFIC™ systems provide improved capability for trace analysis
- Capillary RFIC™ systems can be used to achieve fast separation (Fast IC) and determination of common anions and cations
- Capillary RFIC systems with MS/MS and electrochemical detection are highly sensitive analytical tools
- Capillary RFIC systems leads to improved ion chromatographic methods for determination of ionic analytes in CMP consumables, chemicals, DI water and on post-CMP surfaces

Anion Sample



Peak Name	Amount
	(ppt)
F	24.033
Cl	22.307
NO2	42.532

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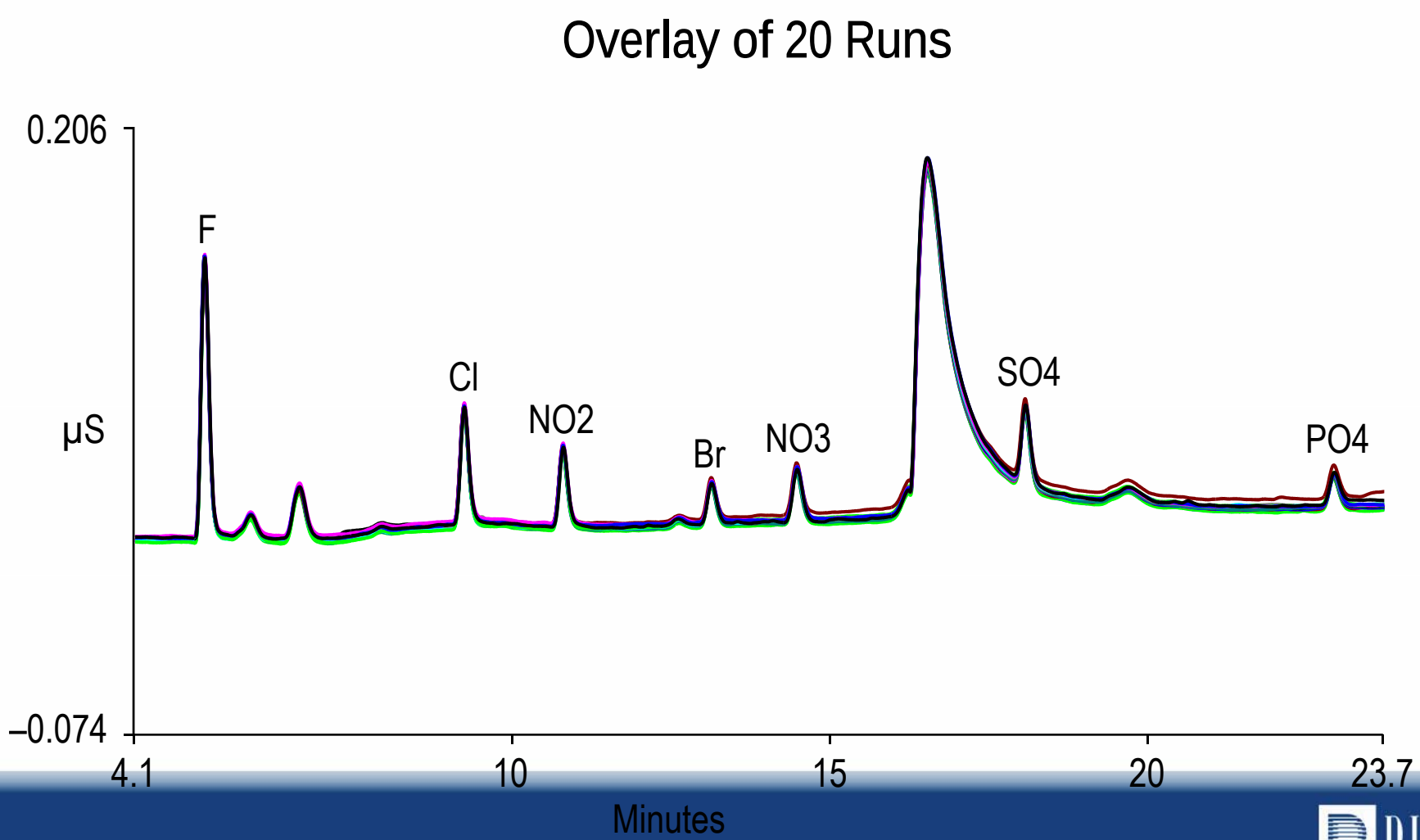
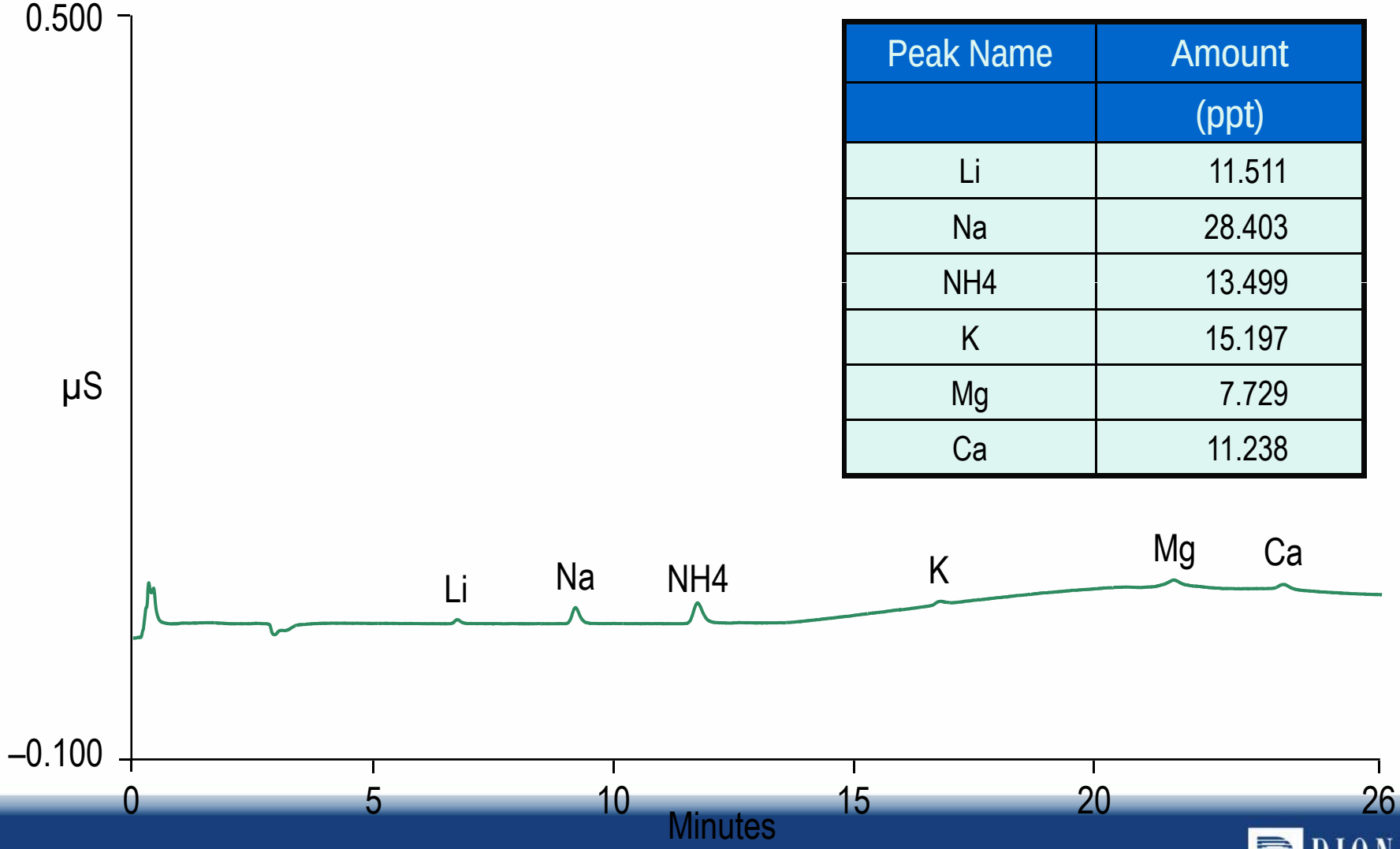
Anion Sample



Cation Sample



Peak Name	Amount
	(ppt)
Li	11.511
Na	28.403
NH4	13.499
K	15.197
Mg	7.729
Ca	11.238

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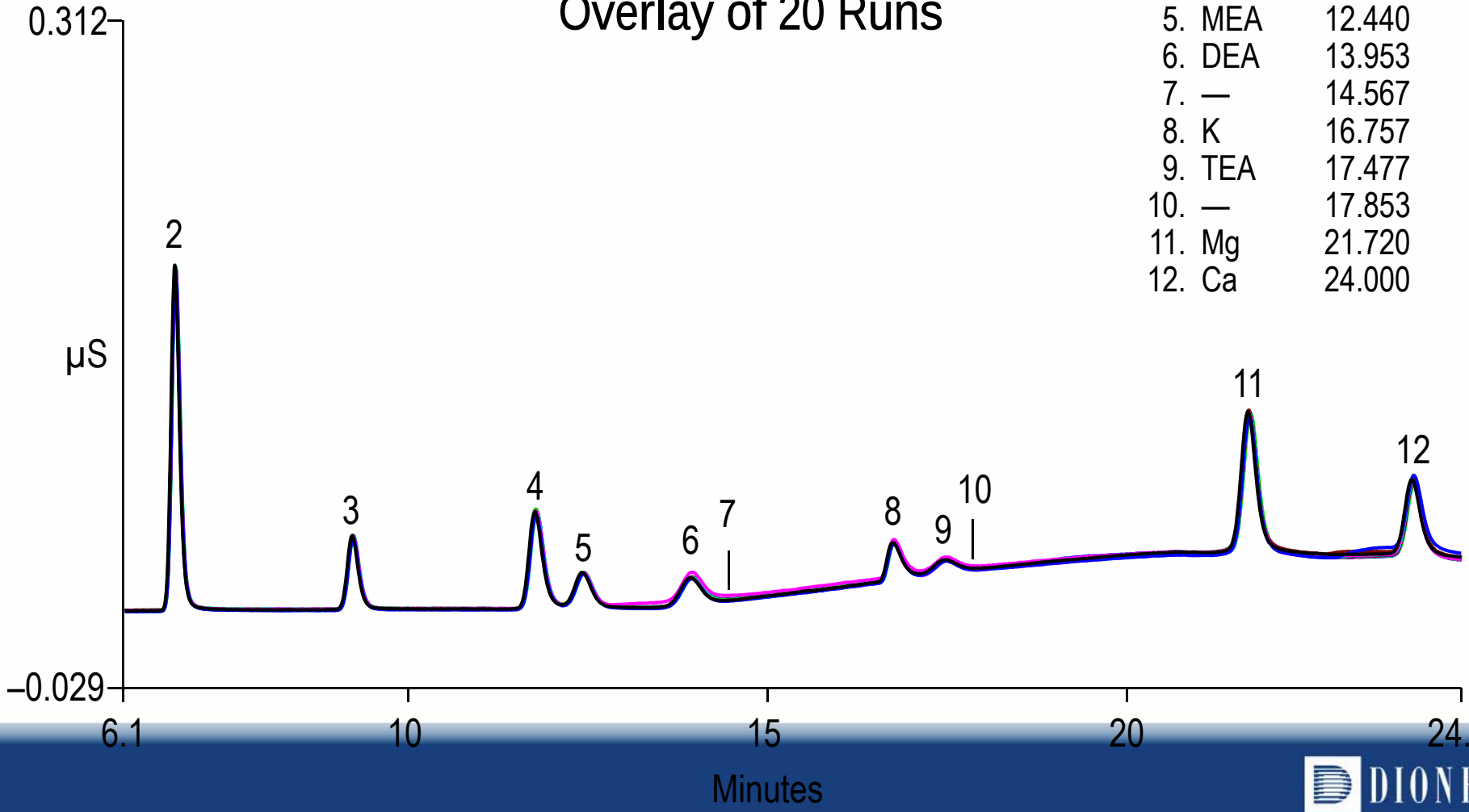
Overlay—Cation Sample



Peaks:			
	2.	Li	6.767
	3.	Na	9.233
	4.	NH4	11.780
	5.	MEA	12.440
	6.	DEA	13.953
	7.	—	14.567
	8.	K	16.757
	9.	TEA	17.477
	10.	—	17.853
	11.	Mg	21.720
	12.	Ca	24.000

Cation Blank