Types of Surface Contamination

- Organic Impurities
- Adsorbed Molecules
- Ions
- Metals
- Particles

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

**Capillary (0.4 mm column) IC with 0.4 µL Injection Volume**

- Lithium
- Sodium
- Ammonia
- Potassium
- Magnesium
- Calcium

**Standard (4 mm column) IC with 40 µL Injection Volume**

- Lithium
- Sodium
- Ammonia
- Potassium
- Magnesium
- Calcium

Conductivity [µS]

Retention Time [min]
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

<table>
<thead>
<tr>
<th></th>
<th>Conventional RFIC</th>
<th>Capillary RFIC</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Column ID</strong></td>
<td>4 mm</td>
<td>0.4 mm</td>
</tr>
<tr>
<td><strong>Flow Rate</strong></td>
<td>1.0 mL/min</td>
<td>10 µL/min</td>
</tr>
<tr>
<td><strong>Injection Loop</strong></td>
<td>25 µL</td>
<td>0.4 µL</td>
</tr>
<tr>
<td><strong>Suppressor Dead Volume</strong></td>
<td>60 µL</td>
<td>0.6 µL</td>
</tr>
<tr>
<td><strong>EG Current (50 mM KOH)</strong></td>
<td>80.4 mA</td>
<td>0.804 mA</td>
</tr>
<tr>
<td><strong>EG Current (200 mM KOH)</strong></td>
<td>321.6 mA</td>
<td>3.216 mA</td>
</tr>
<tr>
<td><strong>K+ Consumption/Year</strong></td>
<td>26.3 Moles (50 mM KOH)</td>
<td>0.263 Moles (50 mM KOH)</td>
</tr>
<tr>
<td><strong>H₂O Consumption/Year</strong></td>
<td>525 L</td>
<td>5.25 L</td>
</tr>
</tbody>
</table>
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

Overlay of 30 consecutive runs

% retention time RSD:
0.09% for arsenate to 0.18% for fluoride

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-5 µm Column

Column: CS12A-5 µm 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

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

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

Reactor water sample, 75 ng/L Chloride

2 mm AS14 column
0.38 mL/ min

Retention time, minutes

2 mL Sample, Direct Injection
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 KOH (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

<table>
<thead>
<tr>
<th>Peak</th>
<th>Concentration (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Fluoride</td>
<td>0.2</td>
</tr>
<tr>
<td>2. Chloride</td>
<td>0.3</td>
</tr>
<tr>
<td>3. Nitrite</td>
<td>1.0</td>
</tr>
<tr>
<td>4. Bromide</td>
<td>1.0</td>
</tr>
<tr>
<td>5. Nitrate</td>
<td>1.0</td>
</tr>
<tr>
<td>6. Carbonate</td>
<td>–</td>
</tr>
<tr>
<td>7. Sulfate</td>
<td>1.0</td>
</tr>
</tbody>
</table>
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)

---

- Brand A bottled water (263 ng/L perchlorate)
- Brand B Bottled water (38.5 ng/L perchlorate)
- 30 ng/L perchlorate in DI water
- DI water
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)

- **AB 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

<table>
<thead>
<tr>
<th>Column:</th>
<th>Prototype AS20 (0.4 mm x 250 mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eluent Source:</td>
<td>Capillary EGC-KOH cartridge</td>
</tr>
<tr>
<td>Eluent:</td>
<td>4-55 mM KOH</td>
</tr>
<tr>
<td>Flow Rate:</td>
<td>15 µL/min</td>
</tr>
<tr>
<td>Temperature:</td>
<td>30 °C</td>
</tr>
<tr>
<td>Suppressor:</td>
<td>Electrolytic capillary anion suppressor</td>
</tr>
<tr>
<td>Detection:</td>
<td>API2000 MS/MS with post suppressor addition of acetonitrile at 15 µL/min; Negative ESI</td>
</tr>
<tr>
<td>Injection vol.:</td>
<td>10 µL</td>
</tr>
<tr>
<td>Peaks:</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Acetate</td>
<td>10 µg/L</td>
</tr>
<tr>
<td>2. Formate</td>
<td>10</td>
</tr>
<tr>
<td>3. Chlorite</td>
<td>10</td>
</tr>
<tr>
<td>4. Bromate</td>
<td>10</td>
</tr>
<tr>
<td>5. Bromoacetate</td>
<td>10</td>
</tr>
<tr>
<td>6. Dichloroacetate</td>
<td>10</td>
</tr>
<tr>
<td>7. Dibromoacetate</td>
<td>10</td>
</tr>
<tr>
<td>8. Chlorate</td>
<td>10</td>
</tr>
<tr>
<td>9. Bromide</td>
<td>10</td>
</tr>
<tr>
<td>10. Nitrate</td>
<td>10</td>
</tr>
<tr>
<td>11. Trichloroacetate</td>
<td>10</td>
</tr>
<tr>
<td>12. Tribromoacetate</td>
<td>10</td>
</tr>
<tr>
<td>13. Perchlorate</td>
<td>1.0</td>
</tr>
</tbody>
</table>

---

**Graph:**
- Intensity, cps (Y-axis)
- Minutes (X-axis)
- Peaks labeled from 1 to 13
- MRM values provided for selected peaks

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**Diagram:**
- Chromatogram showing separation of anions
- Peaks are labeled with corresponding values

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**Footer:**
- Dionex
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

Guard and Separation Column

CRD 200

Suppressor

Injection Valve

EG Degas

Side view of ACES Suppressor

DIONEX
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

**The Next Big Thing in IC is Small**
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

<table>
<thead>
<tr>
<th>Peak Name</th>
<th>Amount (ppt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>24.033</td>
</tr>
<tr>
<td>Cl</td>
<td>22.307</td>
</tr>
<tr>
<td>NO₂</td>
<td>42.532</td>
</tr>
</tbody>
</table>
Anion Sample

Overlay of 20 Runs

µS

FClNO2BrNO3PO4

Minutes

4.1 10 15 20 23.7
### Cation Sample

<table>
<thead>
<tr>
<th>Peak Name</th>
<th>Amount (ppt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>11.511</td>
</tr>
<tr>
<td>Na</td>
<td>28.403</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>13.499</td>
</tr>
<tr>
<td>K</td>
<td>15.197</td>
</tr>
<tr>
<td>Mg</td>
<td>7.729</td>
</tr>
<tr>
<td>Ca</td>
<td>11.238</td>
</tr>
</tbody>
</table>

The graph illustrates the concentration of different cations over time, with peaks for Li, Na, NH₄⁺, K, Mg, and Ca. The y-axis represents microsiemens (µS), and the x-axis represents minutes from 0 to 26.
Overlay—Cation Sample

Overlay of 20 Runs

 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

µS

Minutes