An IC/MS Production Method for the Analysis of Perchlorate

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Need for Trace Level Perchlorate Analysis

• Trace level Perchlorate analysis has driven conventional methods (EPA 314.0) to the edge

• In high matrix interferences (TDS = 3000ppm), it is difficult to accurately measure Perchlorate by conductivity detection below 1 ppb

• A collaborative study between these three organizations has developed a method which will show…..
Goals And Solutions For IC/MS Analysis Of Perchlorate

• Simple and rugged
  • External standard method (within EPA 314)
  • Single stage MS (quadrupole)
  • 4mm column

• Accurate and precise to 1 ppb
  • MDL < 100 parts per trillion (ppt)
  • Must be able to meet QC for prolonged unattended operation
The Bottom Line

• Precision, Sensitivity and Accuracy
  • RSD <4% at 1 ppb for both m/z 99 and 101
  • MDL~70 parts per trillion (ppt)
  • >90% Recovery for Spikes at 0.5 and 1 ppb in heavy matrix and real samples

• Reliability for High Through-Put Laboratories
  • Meets standard QC procedures over 24 hour period
Instrument Set - Up

• Metrohm Advanced IC
  • 100 uL loop injection
  • Column: MetroSep ASUPP-5 (4mm x 100mm)
  • Eluant: 30mM NaOH + 30% Methanol
  • Flow rate: 0.8 ml/min with **NO SPLITTING**.

• Agilent 1100LC/MSD ESI
  • Negative mode “auto-tune”
  • $V_{cap} = 1400V$, Drying Gas = **9L/min @ 320 C**.
  • Nebulizer Pressure=20 psig.
  • Fragmentor = 140 V.
Agilent 1100 LC/MSD SL AP Electrospray

- HPLC inlet
- Nebulizer gas inlet
- Nebulizer
- Skimmer
- Vacuum Wall
- Lenses
- Quadrupole
- HED detector

Neutral Molecules
Analyte Ions
Clusters
Salts

Fragmentation zone (CID)

heated N₂

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Picture of Instrument Set-up
Calibration Data (m/z 99)

perchlorate 101, MSD1 99
Area = 143840.996*Amnt -2810.7345

Range for Calibration Standards
0.1ppb to 10ppb (ClO$_4$$^-_1$)

Correlation: 0.99942

Amount[ng/ml] vs Area graph
Calibration Data (m/z 101)

Range for Calibration Standards 0.1ppb to 10ppb (ClO$_4^{-}$)
Total Ion Chromatograms (TIC) Calib. Standards and Blank

Calibration Range from 0.1 ppb to 10.0 ppb

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0.79 ppb Standard

M/z = 99

M/z = 101
Extracted Ion Chromatograms for 0.5 ppb standard

MSD1 99, EIC=98.7:99.7 (ICDATA~1\ICBLK1D\IC000017.D) API-ES, Neg, SIM, Frag: 140, "neg sim"
MSD1 101, EIC=100.7:101.7 (ICDATA~1\ICBLK1D\IC000017.D) API-ES, Neg, SIM, Frag: 140, "neg sim"
# Results of UHP Water Fortified with Perchlorate

<table>
<thead>
<tr>
<th>SAMPLE ID</th>
<th>TRUE CONCENTRATION</th>
<th>PPB (M/Z = 99)</th>
<th>% Recovery (m/z99)</th>
<th>PPB (M/Z = 101)</th>
<th>% Recovery (m/z101)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 PPB</td>
<td>0.480</td>
<td>0.487</td>
<td>99.14%</td>
<td>0.519</td>
<td>108.33%</td>
</tr>
<tr>
<td>0.5 PPB</td>
<td>0.480</td>
<td>0.477</td>
<td>99.38%</td>
<td>0.471</td>
<td>98.13%</td>
</tr>
<tr>
<td>0.5 PPB</td>
<td>0.480</td>
<td>0.460</td>
<td>95.83%</td>
<td>0.490</td>
<td>102.08%</td>
</tr>
<tr>
<td>0.5 PPB</td>
<td>0.480</td>
<td>0.477</td>
<td>99.38%</td>
<td>0.492</td>
<td>102.50%</td>
</tr>
<tr>
<td>0.5 PPB</td>
<td>0.480</td>
<td>0.520</td>
<td>108.33%</td>
<td>0.505</td>
<td>105.21%</td>
</tr>
<tr>
<td>0.5 PPB</td>
<td>0.480</td>
<td>0.494</td>
<td>102.92%</td>
<td>0.509</td>
<td>106.04%</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td><strong>0.480</strong></td>
<td><strong>0.486</strong></td>
<td><strong>101.22%</strong></td>
<td><strong>0.498</strong></td>
<td><strong>103.68%</strong></td>
</tr>
<tr>
<td><strong>Std. Dev</strong></td>
<td><strong>0.020</strong></td>
<td><strong>0.042</strong></td>
<td><strong>0.017</strong></td>
<td><strong>0.035</strong></td>
<td></td>
</tr>
<tr>
<td><strong>RSD</strong></td>
<td><strong>4.18%</strong></td>
<td><strong>4.18%</strong></td>
<td><strong>3.41%</strong></td>
<td><strong>3.41%</strong></td>
<td></td>
</tr>
<tr>
<td>1.0 PPB</td>
<td>0.780</td>
<td>0.756</td>
<td>96.92%</td>
<td>0.768</td>
<td>98.46%</td>
</tr>
<tr>
<td>1.0 PPB</td>
<td>0.780</td>
<td>0.810</td>
<td>103.85%</td>
<td>0.830</td>
<td>106.41%</td>
</tr>
<tr>
<td>1.0 PPB</td>
<td>0.780</td>
<td>0.776</td>
<td>99.49%</td>
<td>0.772</td>
<td>98.97%</td>
</tr>
<tr>
<td>1.0 PPB</td>
<td>0.780</td>
<td>0.799</td>
<td>102.44%</td>
<td>0.754</td>
<td>96.67%</td>
</tr>
<tr>
<td>1.0 PPB</td>
<td>0.780</td>
<td>0.788</td>
<td>101.03%</td>
<td>0.768</td>
<td>98.46%</td>
</tr>
<tr>
<td>1.0 PPB</td>
<td>0.780</td>
<td>0.792</td>
<td>101.54%</td>
<td>0.807</td>
<td>103.46%</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td><strong>0.780</strong></td>
<td><strong>0.787</strong></td>
<td><strong>100.88%</strong></td>
<td><strong>0.783</strong></td>
<td><strong>100.41%</strong></td>
</tr>
<tr>
<td><strong>Std. Dev</strong></td>
<td><strong>0.019</strong></td>
<td><strong>0.024</strong></td>
<td><strong>0.029</strong></td>
<td><strong>0.037</strong></td>
<td></td>
</tr>
<tr>
<td><strong>RSD</strong></td>
<td><strong>2.40%</strong></td>
<td><strong>2.40%</strong></td>
<td><strong>3.70%</strong></td>
<td><strong>3.70%</strong></td>
<td></td>
</tr>
</tbody>
</table>
Synthetic Matrix Spikes Overlaid with 1ppb Standard

No Matrix
200ppm Cl, CO₃, SO₄
500ppm Cl, CO₃, SO₄
1000ppm Cl, CO₃, SO₄
Single Ion Chromatograms of High Matrix Spike

MSD1 99, EIC=98.7:99.7 (ICDATA~1\ICBLK1D\IC000048.D)  API-ES, Neg, SIM, Frag: 140, "neg sim"
MSD1 101, EIC=100.7:101.7 (ICDATA~1\ICBLK1D\IC000048.D)  API-ES, Neg, SIM, Frag: 140, "neg sim"

m/z = 99

m/z = 101
## Results of Matrix Fortified with Perchlorate

<table>
<thead>
<tr>
<th>SAMPLE ID</th>
<th>TRUE CONCENTRATION</th>
<th>PPB (M/Z = 99)</th>
<th>% Recovery (m/z99)</th>
<th>PPB (M/Z = 101)</th>
<th>% Recovery (m/z101)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200 PPM EACH OF CL,CO3 &amp; SO4</td>
<td>0.780</td>
<td>0.799</td>
<td>102.44%</td>
<td>0.784</td>
<td>100.51%</td>
</tr>
<tr>
<td>500 PPM EACH OF CL,CO3 &amp; SO4</td>
<td>1.000</td>
<td>0.804</td>
<td>80.40%</td>
<td>0.808</td>
<td>80.80%</td>
</tr>
<tr>
<td>1000 PPM EACH OF CL,CO3 &amp; SO4</td>
<td>1.000</td>
<td>0.930</td>
<td>93.00%</td>
<td>0.940</td>
<td>94.00%</td>
</tr>
<tr>
<td>200 PPM EACH OF CL,CO3 &amp; SO4</td>
<td>0.780</td>
<td>0.700</td>
<td>89.74%</td>
<td>0.770</td>
<td>98.72%</td>
</tr>
<tr>
<td>500 PPM EACH OF CL,CO3 &amp; SO4</td>
<td>1.000</td>
<td>0.870</td>
<td>87.00%</td>
<td>0.860</td>
<td>86.00%</td>
</tr>
<tr>
<td>1000 PPM EACH OF CL,CO3 &amp; SO4</td>
<td>1.000</td>
<td>0.973</td>
<td>97.30%</td>
<td>0.986</td>
<td>98.60%</td>
</tr>
<tr>
<td>200 PPM EACH OF CL,CO3 &amp; SO4</td>
<td>0.780</td>
<td>0.810</td>
<td>103.85%</td>
<td>0.796</td>
<td>102.05%</td>
</tr>
<tr>
<td>500 PPM EACH OF CL,CO3 &amp; SO4</td>
<td>1.000</td>
<td>0.851</td>
<td>85.10%</td>
<td>0.846</td>
<td>84.60%</td>
</tr>
<tr>
<td>1000 PPM EACH OF CL,CO3 &amp; SO4</td>
<td>1.000</td>
<td>0.990</td>
<td>99.00%</td>
<td>0.977</td>
<td>97.70%</td>
</tr>
<tr>
<td>BLANK</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>CC 10 PPB</td>
<td>0.780</td>
<td>0.747</td>
<td>95.77%</td>
<td>0.742</td>
<td>95.13%</td>
</tr>
<tr>
<td>200 PPM EACH OF CL,CO3 &amp; SO4</td>
<td>0.780</td>
<td>0.799</td>
<td>102.44%</td>
<td>0.777</td>
<td>99.62%</td>
</tr>
<tr>
<td>500 PPM EACH OF CL,CO3 &amp; SO4</td>
<td>1.000</td>
<td>0.920</td>
<td>92.00%</td>
<td>0.921</td>
<td>92.10%</td>
</tr>
<tr>
<td>1000 PPM EACH OF CL,CO3 &amp; SO4</td>
<td>1.000</td>
<td>1.000</td>
<td>100.00%</td>
<td>1.040</td>
<td>104.00%</td>
</tr>
<tr>
<td>200 PPM EACH OF CL,CO3 &amp; SO4</td>
<td>0.780</td>
<td>0.860</td>
<td>102.26%</td>
<td>0.830</td>
<td>106.4%</td>
</tr>
<tr>
<td>500 PPM EACH OF CL,CO3 &amp; SO4</td>
<td>1.000</td>
<td>0.930</td>
<td>93.00%</td>
<td>0.913</td>
<td>91.30%</td>
</tr>
<tr>
<td>1000 PPM EACH OF CL,CO3 &amp; SO4</td>
<td>1.000</td>
<td>1.090</td>
<td>109.00%</td>
<td>1.050</td>
<td>105.00%</td>
</tr>
<tr>
<td>200 PPM EACH OF CL,CO3 &amp; SO4</td>
<td>0.780</td>
<td>0.800</td>
<td>102.56%</td>
<td>0.850</td>
<td>108.97%</td>
</tr>
<tr>
<td>500 PPM EACH OF CL,CO3 &amp; SO4</td>
<td>1.000</td>
<td>0.890</td>
<td>89.00%</td>
<td>0.904</td>
<td>90.40%</td>
</tr>
<tr>
<td>1000 PPM EACH OF CL,CO3 &amp; SO4</td>
<td>1.000</td>
<td>1.040</td>
<td>104.00%</td>
<td>1.070</td>
<td>107.00%</td>
</tr>
</tbody>
</table>

**Average**: 96.67% 97.10%

**Std.Dev**: 0.082 0.080

**RSD %**: 8.48% 8.22%

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Sample and Sample Spike (with Sulfonate Detergents)

Sample 0.35ppb

Sample 0.35ppb + 1ppb Spiked ClO₄⁻

Sample 0.35ppb ClO₄⁻
Lettuce and Spike

MSD1 TIC, MS File (ICDATA~1!ICBLK1E!IC000037.D) API-ES, Neg, SIM, Frag: 140, "neg sim"

MSD1 TIC, MS File (ICDATA~1!ICBLK1E!IC000039.D) API-ES, Neg, SIM, Frag: 140, "neg sim"

Lettuce extract + 8ppb Perchlorate Spike

Lettuce extract

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500 ppb and sequential blank

500 ppb Perchlorate std in 3000ppm Matrix

Blank DI water after std.
1 ppb Perchlorate in 3000ppm Total Dissolved Salt (TDS) after 125 injections
95% Recovery

Matrix containing 1000ppm each of Cl\(^{-}\), CO\(_3\)\(^{2-}\), SO\(_4\)\(^{2-}\)
1 ppb Perchlorate Standard w/IS

MSD1 99, EIC=98.7:99.7 (EPA_PA006-0601.D)  API-ES, Neg, SIM, Frag: 150
MSD1 101, EIC=100.7:101.7 (EPA_PA006-0601.D)  API-ES, Neg, SIM, Frag: 150
MSD1 105, EIC=104.7:105.7 (EPA_PA006-0601.D)  API-ES, Neg, SIM, Frag: 150
MSD1 107, EIC=106.7:107.7 (EPA_PA006-0601.D)  API-ES, Neg, SIM, Frag: 150
Houston 1ppb spike
College Station 0.5 ppb spike

MSD 99, EIC=98.7:99.7 (EPA_PA\057-7301.D) API-ES, Neg, SIM, Frag: 150
MSD 101, EIC=100.7:101.7 (EPA_PA\057-7301.D) API-ES, Neg, SIM, Frag: 150
MSD 105, EIC=104.7:105.7 (EPA_PA\057-7301.D) API-ES, Neg, SIM, Frag: 150
MSD 107, EIC=106.7:107.7 (EPA_PA\057-7301.D) API-ES, Neg, SIM, Frag: 150
SF Bay Water with 1ppb IS
SF Bay Water with 1ppb IS
San Francisco Bay Water with 1ppb IS

IS Recovery is 107%

Quants as 20ppt
Current Work

• Current MeOH/NaOH mobile phase column combo is “bulletproof”
  • Little to no variation in retention/signal due to mobile phase composition, column lot #, MS (has worked on 1946D, 1956A, 1956B) or MS conditions
  
  but.....

• Get TAT under 15 minutes
  • Different mobile phases, different lengths of columns

• Explore unsuppressed mobile phases
Acknowledgements

• Rick McMillin, Deputy Branch Chief - USEPA Region 6
• Melvin Ritter, Team Leader - USEPA Region 6
• Diane Gregg, Team Leader - USEPA Region 6
• Dr. Carl Zhang, University of Houston, Clear Lake Campus
Alternate mobile phases

• NaOH/MeOH works but…
  • Peak shape
  • Sulfate tail
  • Turn around time
Analysis Parameters

- Agilent 1100 binary LC/1100 MSD
  - ESI
  - Drying Gas, 11L/min
  - Nebulizer pressure, 20 psi
  - SIM
  - Capillary voltage, 2500 V
- 80mM Ammonium Formate adjusted to pH 9 with ammonia
- 0.7ml/min
- 5cm x 3mm Alltech NovaSep A2
80mM Ammonium Formate pH9 20% ACN
5uL injection, 1 ppm Perchlorate
80mM Ammonium Formate pH9

MSD2 TIC, MS File (10_15\AF000009.D)  API-ES, Neg, SIM, Frag: 200
MSD2 TIC, MS File (10_15\AF000011.D)  API-ES, Neg, SIM, Frag: 200
MSD2 TIC, MS File (10_15\AF000012.D)  API-ES, Neg, SIM, Frag: 200

40% ACN
30% ACN
20% ACN
10 ppm perchlorate using ACN gradient (10-50% in 10 minutes) and 8 uL injection
Synthetic matrix with 0.5ppb Perchlorate spike
8 ul injection

Matrix containing 1000ppm each of Cl\(^{-}\), CO\(_3\)\(^{2-}\), SO\(_4\)\(^{2-}\)
Well Water from College Station
Can the injection size be scaled up?

- Peak width effects
- Matrix effects on retention time
- Sulfate behavior
Stability during a run without internal standard for 8uL injection

• Over 50 samples of “high matrix”, Houston and College Station tap

• CCV recovery (0.5 ppb) for 5 checks ranged from 92 to 107%

• All CCB’s (5) were neg.

• No Perchlorate was found in CS “blanks” 5 samples

• Recovery of 1 ppb in “high matrix” for 30 samples averaged 90% with RSD or 6%

• Recovery of 0.5 ppb in college station water (5 samples) ranged from 90 to 106%
8uL vs 50uL injections of 0.95 ppb Perchlorate on a 3 mm id column
Armand Bayou surface water

30 ppt Perchlorate
Short term observations of using an ammonium formate/ acetonitrile buffer

• Retention behavior and peak shape for perchlorate is excellent
• Retention time for perchlorate appears to be independent of matrix
• Interference from organic material appears to be minimal
• Daughter ions at 83/85 can be used for confirmation
• Different injection sizes can be used to fit the needed detection limit
1 ppb Perchlorate extracted ion chromatogram