

ANALYSIS OF PERCHLORATE

**Perchlorate Testing Roundtable
USEPA Region 6 QA Conference**

Dallas, TX

October 23, 2003



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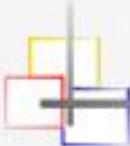
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Special thanks to:
Thomas Mckay
DataChem Laboratories, Inc.
Kham Lin
K' (Prime) Technologies

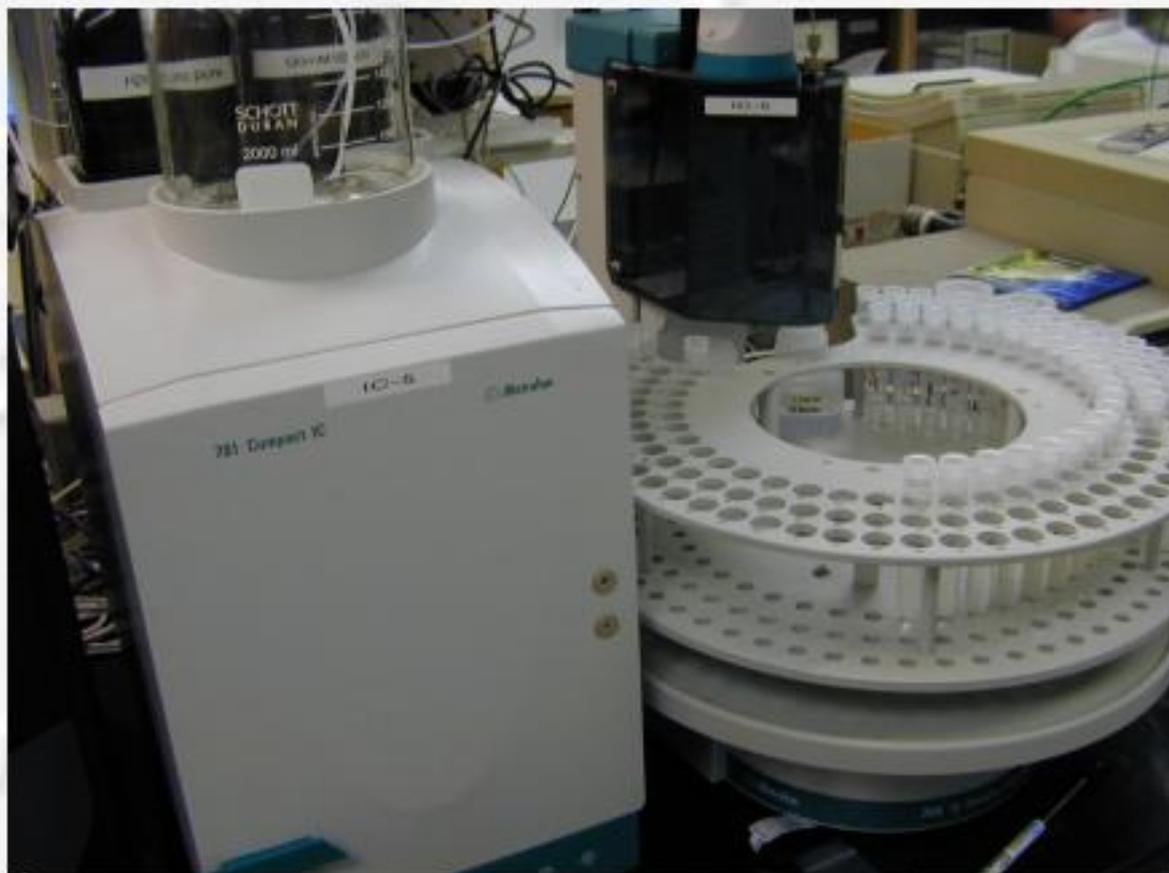


Agenda

- Equipment and Analytical System
- Method Chromatograms and common problems
- MDL Studies
- Conductivity and matrix interference
- Method and Laboratory Validation
- Method Development – Next Steps



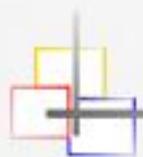
Equipment





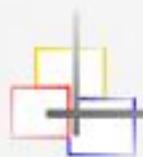
Equipment





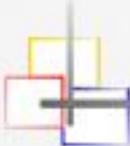
Equipment

- Metrohm 761 Compact IC with a 766 IC Autosampler, and 733 IC Separation Center
- The analytical column was a Dionex AS16 4mm with a AG16 guard column.



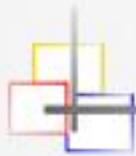
Equipment

- The pre-column was a Dionex TAC-LP1, a 20um styrene/divinylbenzene copolymer that is agglomerated with a anion exchange latex.



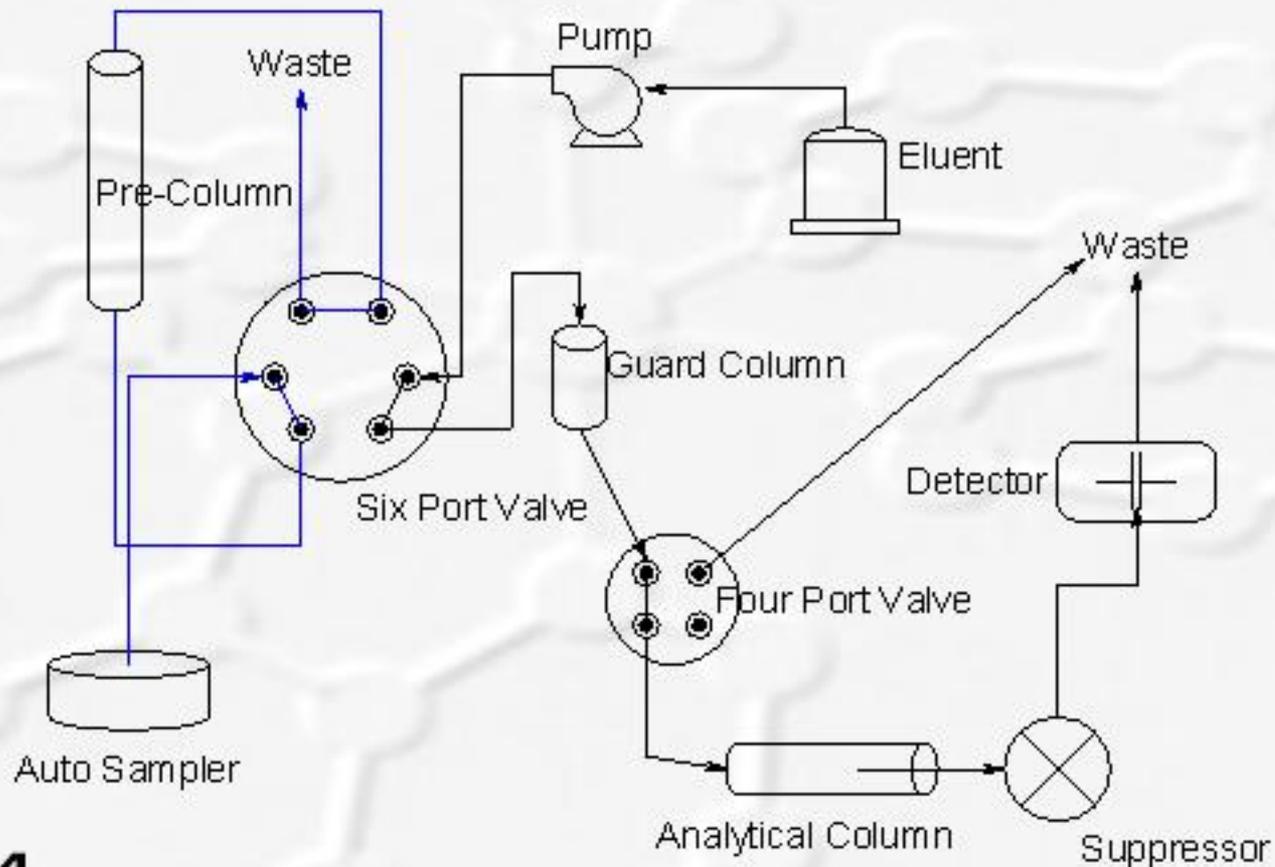
Analytical System

- Eluent: 40 mM NaOH and 4 mM p-cyanophenol
- Flow Rate: 1 mL/min
- Run Time: 15 minutes



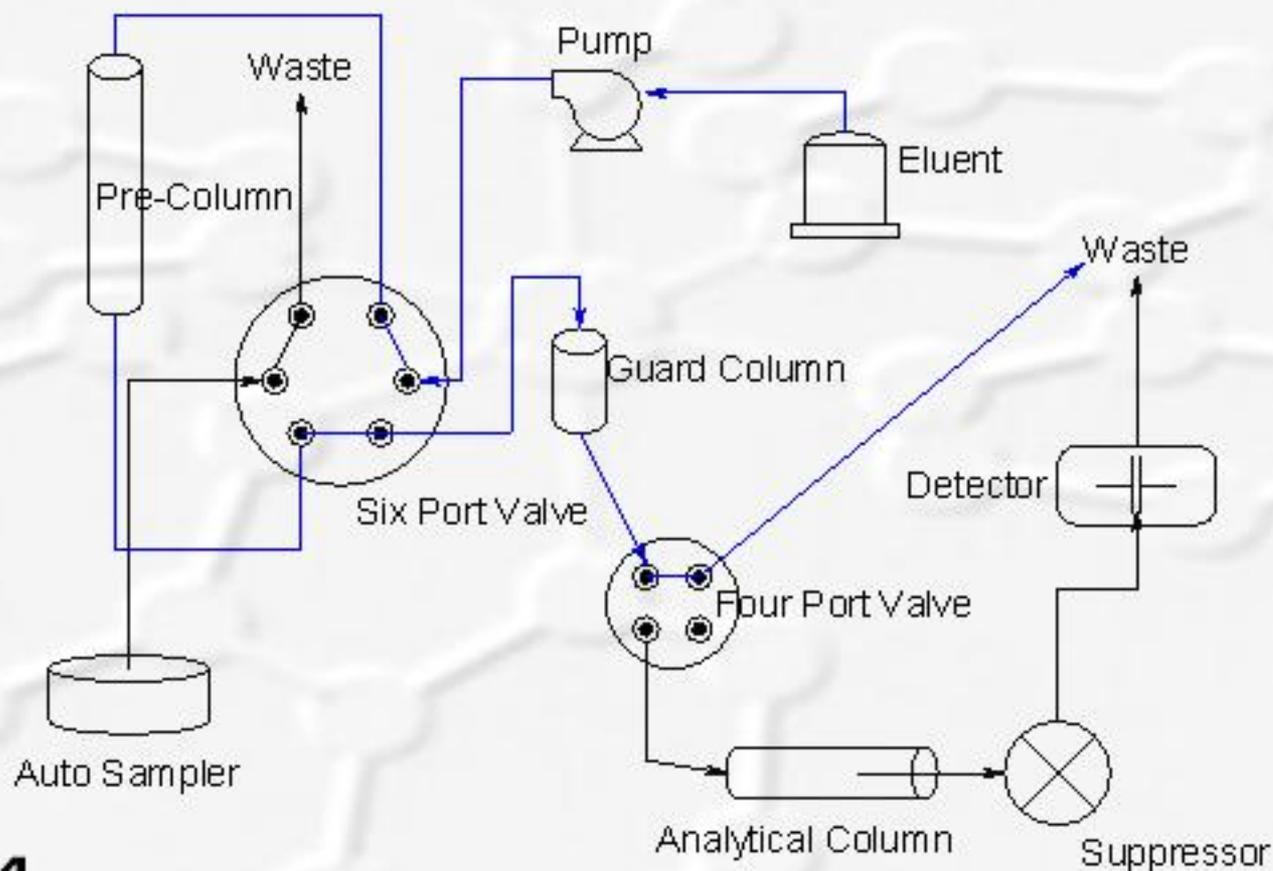
Analytical System

Load Pre-Column (1.5 min)



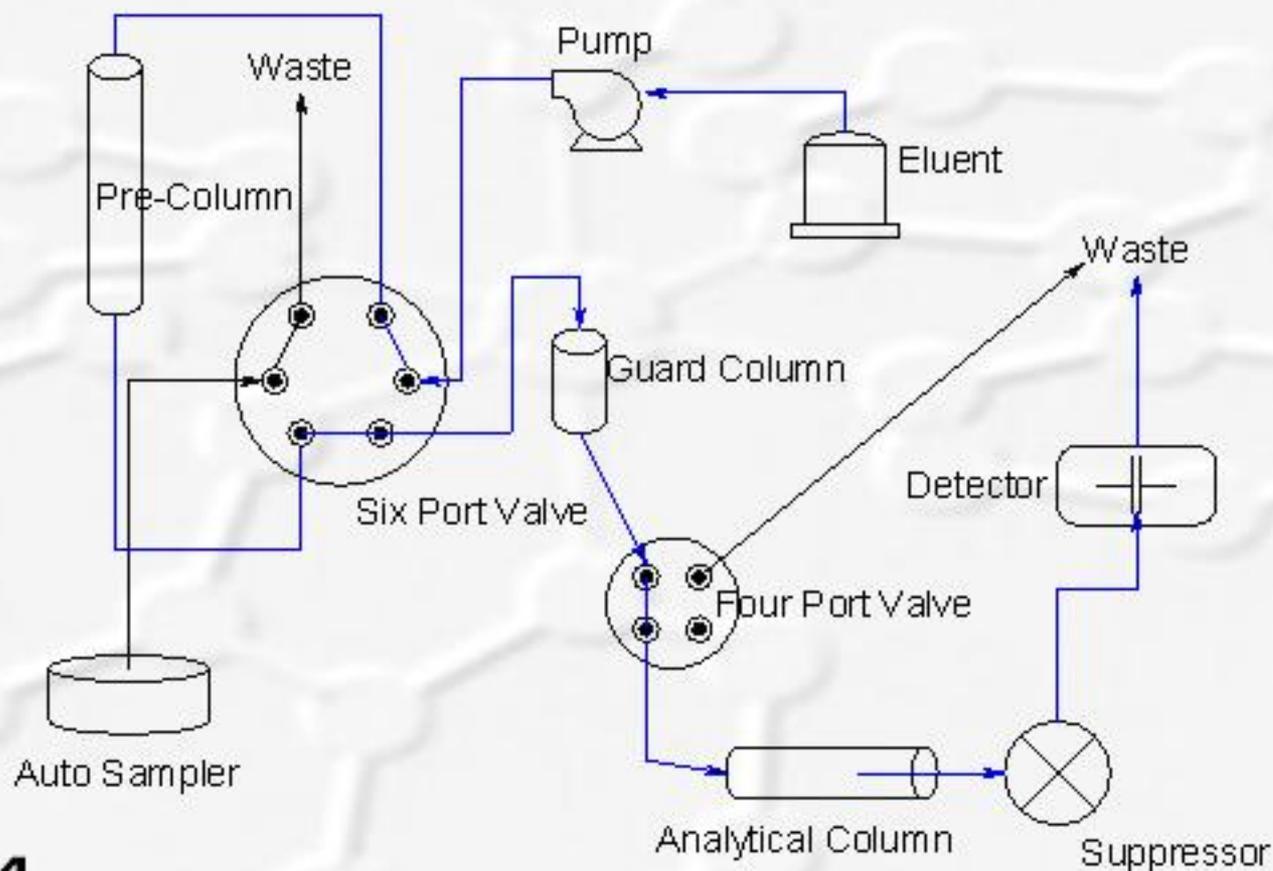
Analytical System

Interference Backflush Pre-Column (0.5 min)



Analytical System

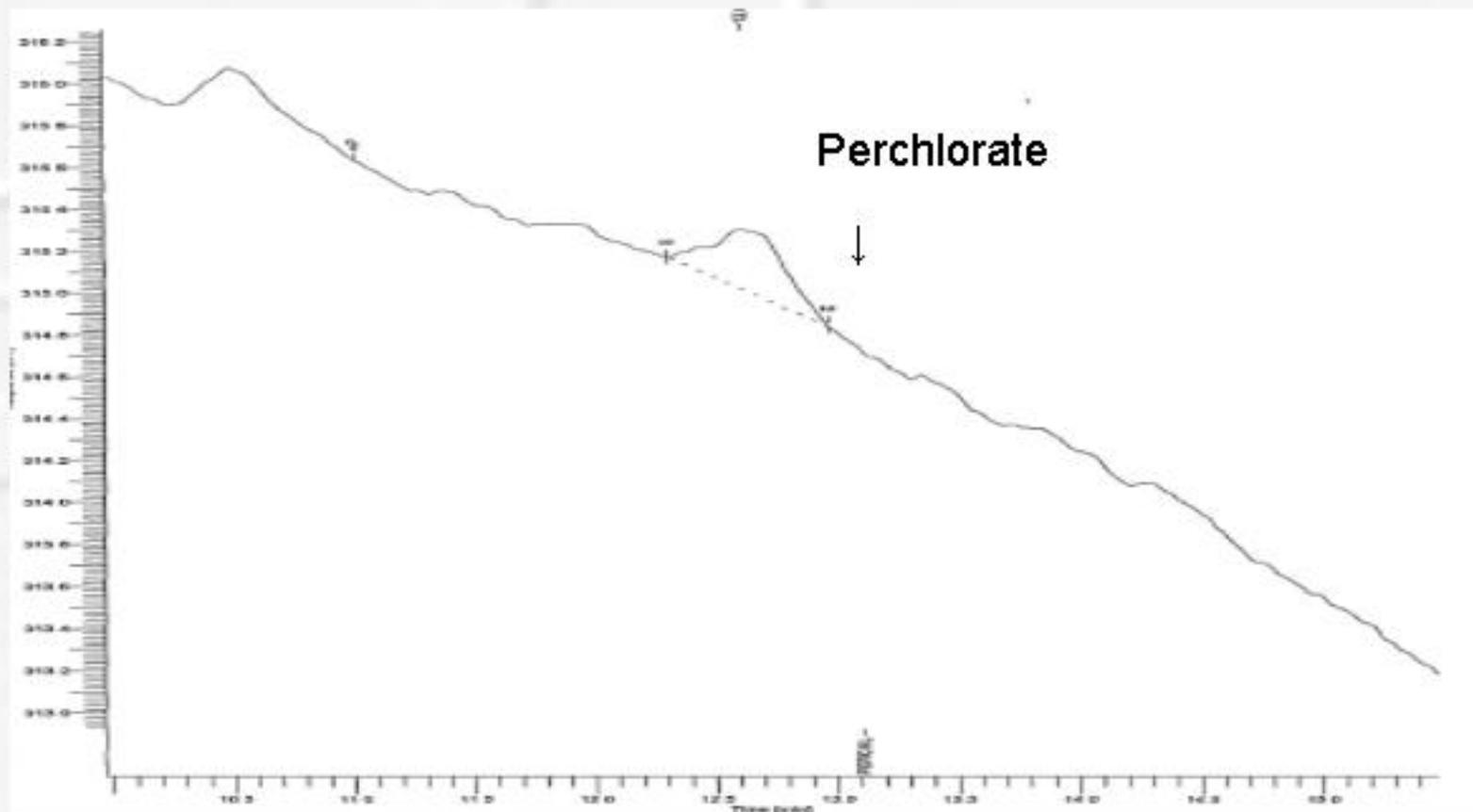
Analytical Backflush Pre-Column (0.5 min)





Chromatograms

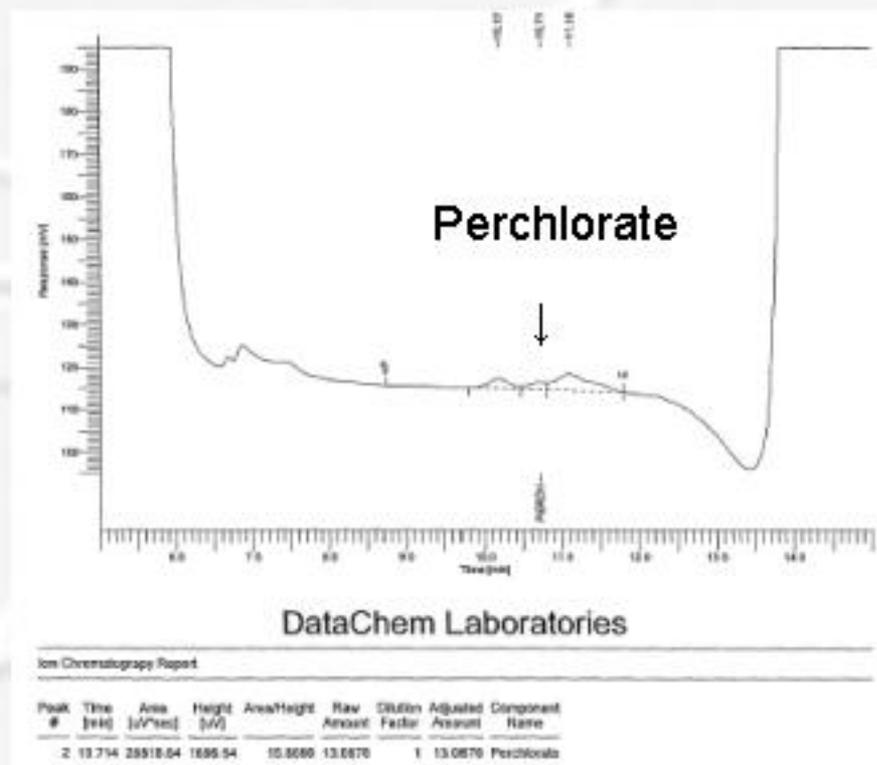
Water Sample #1 for Perchlorate (ND)

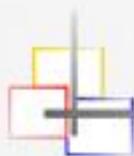




Chromatograms

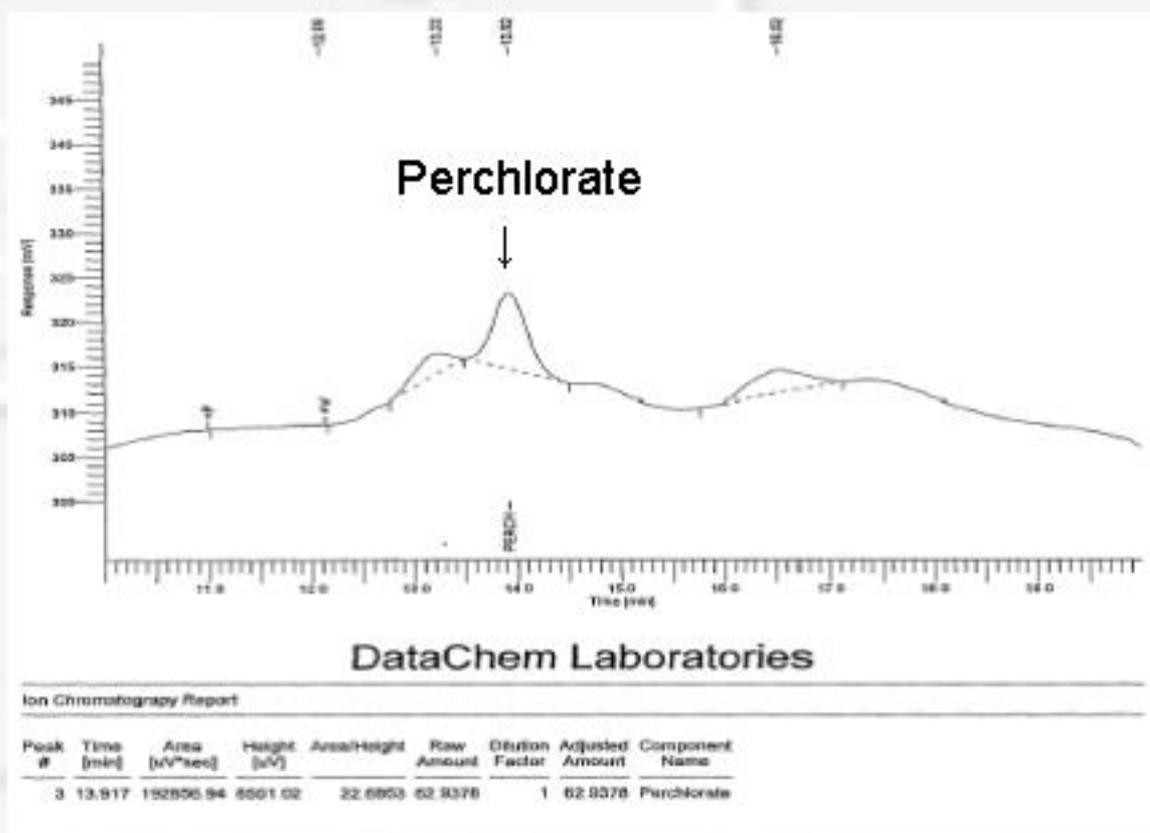
Water Sample #2 for Perchlorate (13 ppb)

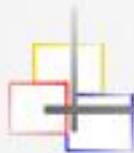




Chromatograms

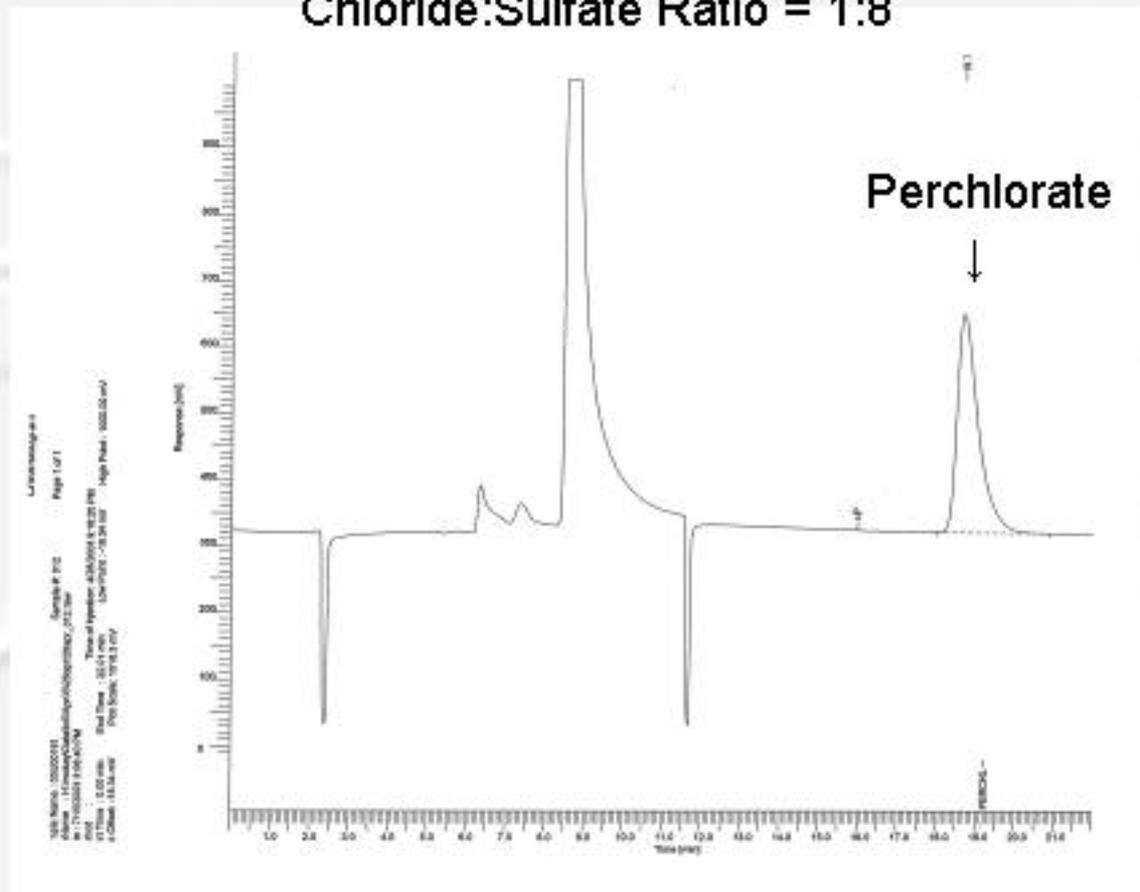
Grass Sample for Perchlorate (62 ppb)

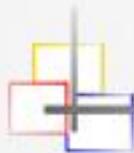




Chromatograms

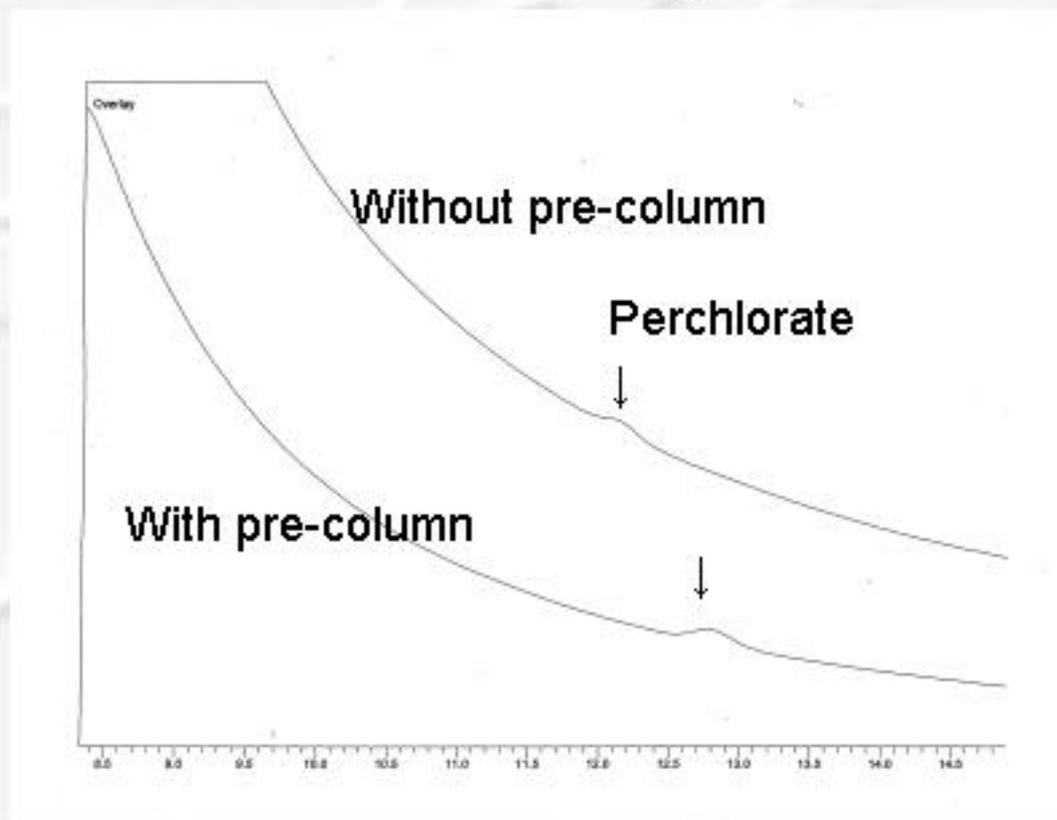
High Sulfate Interference with pre-column
Chloride:Sulfate Ratio = 1:8

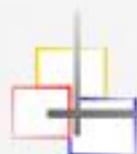




Chromatograms

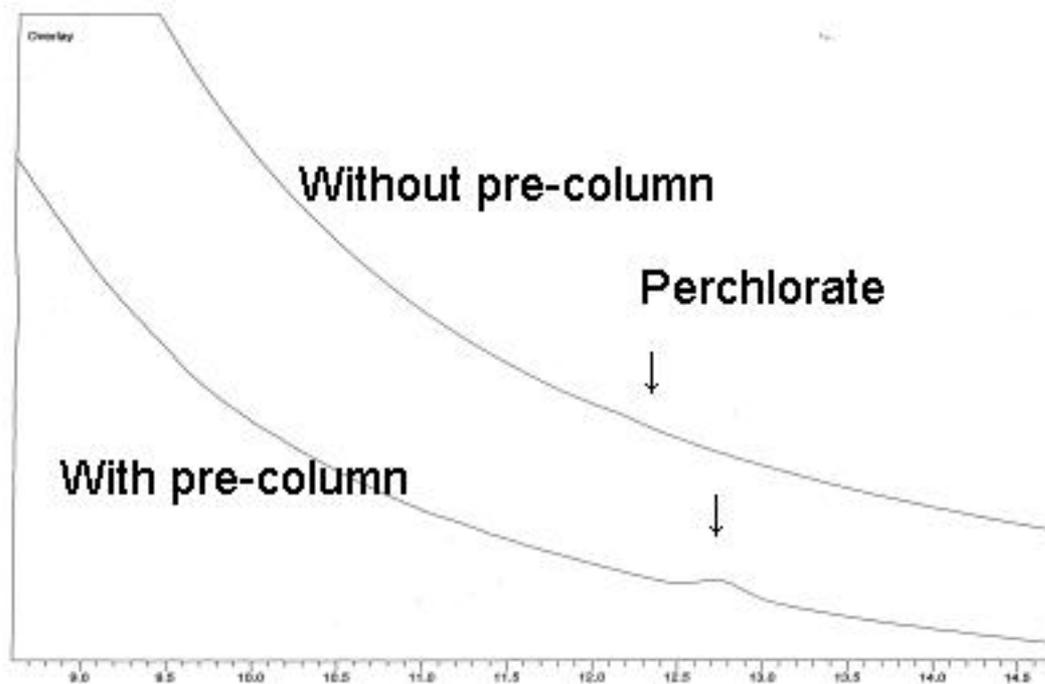
Overlay of 11,500 $\mu\text{S}/\text{cm}$ matrix with and without pre-column at 20 $\mu\text{g}/\text{L}$





Chromatograms

Overlay of 21,500 uS/cm matrix with and without pre-column at 20 ug/L





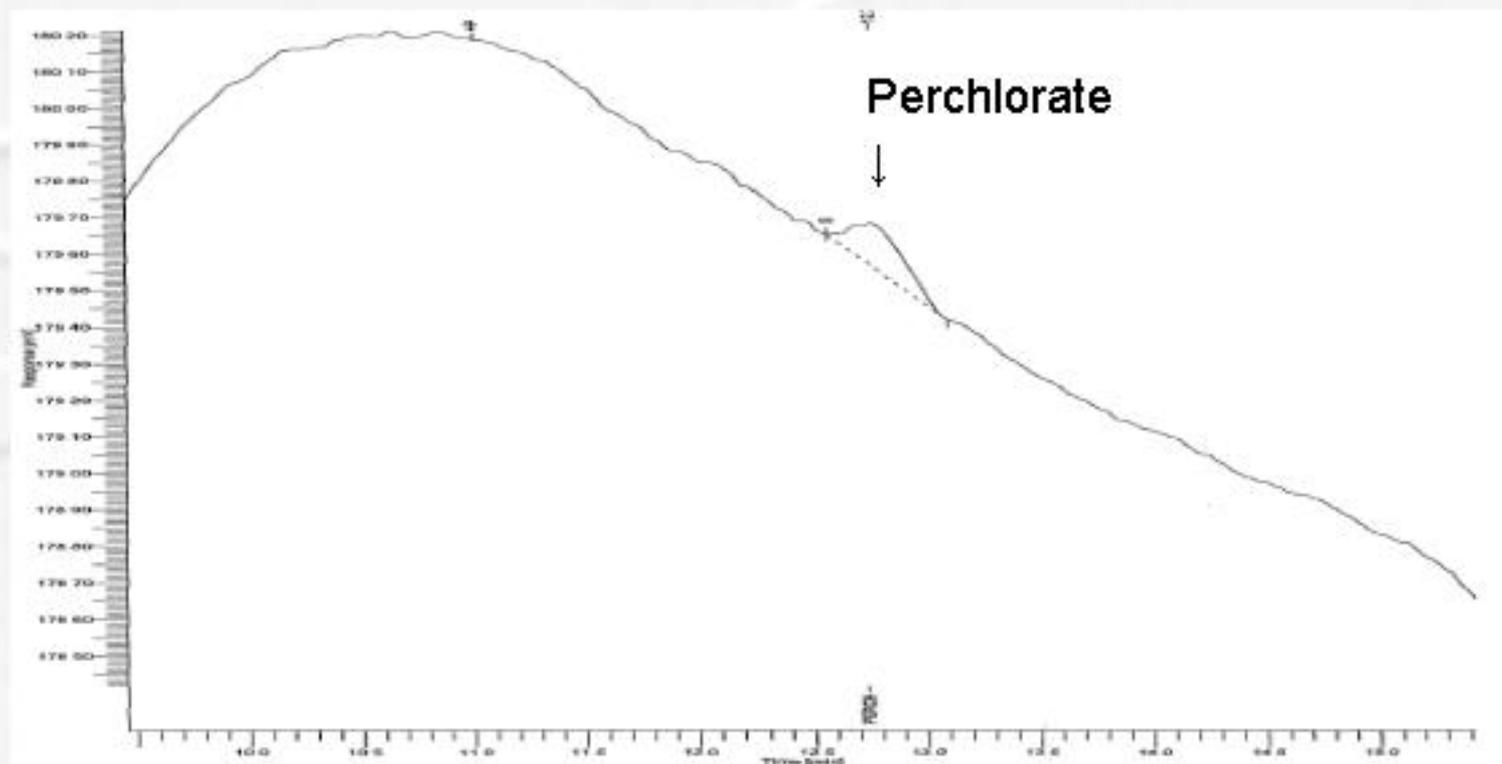
Detection Limits

Table 1. Limit of Detection (MDL Studies)

Conductivity (uS/cm)	< 1	7700 (MCT)	11500	14400	21500
Rep 1	0.6799	0.6863	0.8481	4.583	7.6979
Rep 2	0.5128	0.8826	3.4747	5.2326	8.1877
Rep 3	0.4979	1.0169	4.2362	7.3927	8.844
Rep 4	0.4408	0.8094	3.9216	4.0532	6.0182
Rep 5	0.4854	0.7299	4.1098	4.1955	7.42
Rep 6	0.554	0.9676	3.1164	4.1728	8.6709
Rep 7	0.4945	0.9277	3.8653	4.6885	8.7945
Target Value	0.5	0.8	3.5	4	8
Ratio of Target to MDL	2.07	2.07	2.91	1.09	2.51
Mean Result	0.524	0.86	3.8	4.9	7.95
Standard Deviation	0.0767	0.123	0.838	1.17	1.01
MDL	0.241	0.387	1.2	3.68	3.19
PQL	1	1	4	5	10

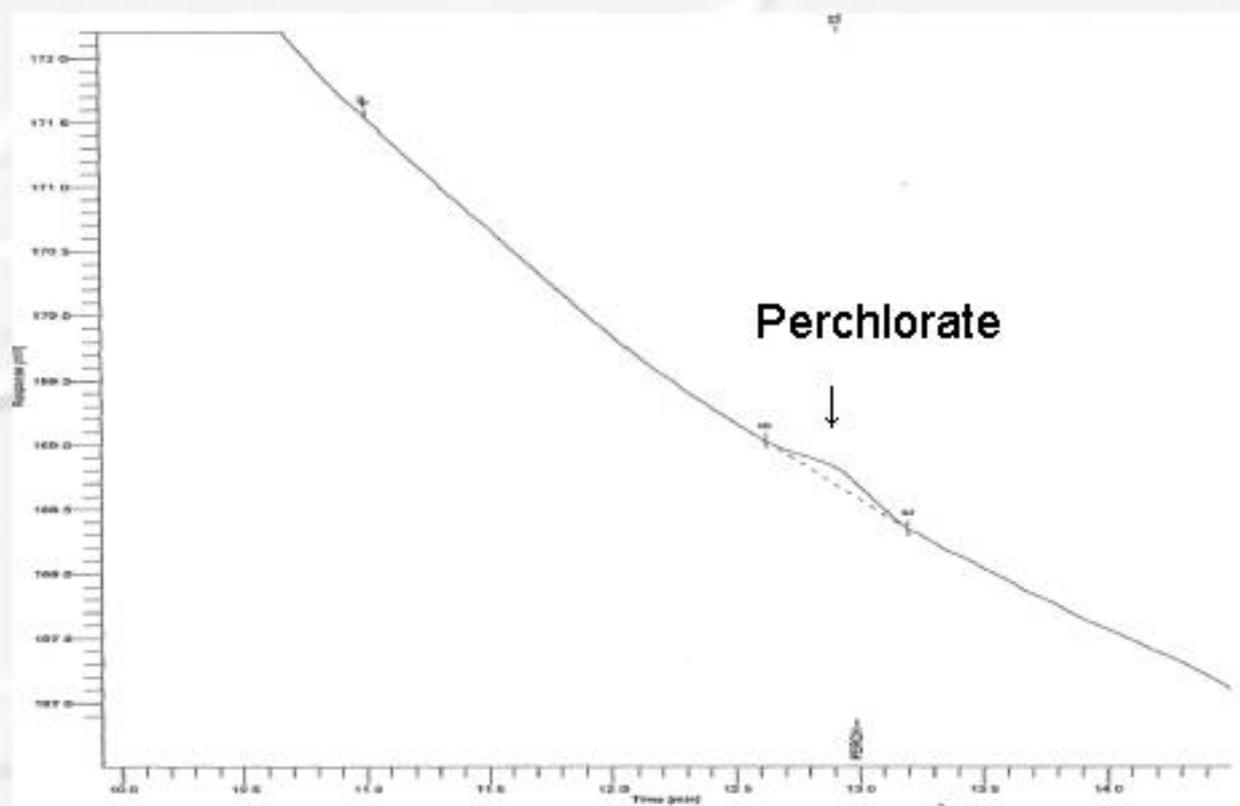
Chromatograms

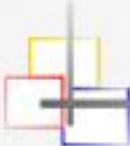
MDL Verification Chromatogram in Drinking Water



Chromatograms

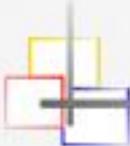
MDL Verification Chromatogram at MCT





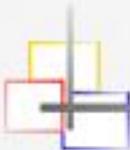
Experimental Design

- *Intent – Use of a pre-column to remove interferences from the matrix so the analysis can be completed with little or no dilution.*
- *Validation of this method based on the protocol adopted by NELAC in section C.3 “Initial Test Method Validation” of the 2003 Quality Systems chapter.*



Experimental Design

- Three matrices were evaluated.
- A naturally occurring water source, the Great Salt Lake (GSL), diluted to 11,500 $\mu\text{S}/\text{cm}$ and 21,500 $\mu\text{S}/\text{cm}$
- A synthetic saline water at 14400 $\mu\text{S}/\text{cm}$ was made by using chloride, sulfate and carbonate at 2000 mg/L



Summary of Method Validation Results for Bias

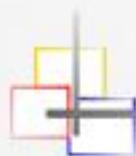
Average Recoveries All matrices and All Concentrations			
Matrix	11,500	21,500	14,400
Chloride:Sulfate Ratio	8.6:1	8.6:1	1:1
n =	27	27	27
Average Recovery	102.8	100.5	106.6
Standard Deviation	4.6	5.8	5.1
Relative Standard Deviation	4.5	5.8	4.8



Summary of Method Validation Results for Bias (Paired t -Test)

- Evaluation of all matrix method combinations for significance. “The means are not significantly different”.
- $P = 0.99$
- Critical Value of $|t| = 2.479$

$$t = \frac{\overline{\chi}_{\text{Difference}} \sqrt{n}}{S_{\text{Difference}}}$$



Summary of Method Validation Results for Bias (Paired t -Test)

	11,500 vs. 21,500 uS/cm	11,500 vs. 14,400 uS/cm	14,400 vs. 21,500 uS/cm
Paired t	1.9	2.7	-4.5



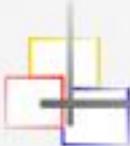
Conductivity and Matrix Interference

- The stronger the conductivity of the matrix the more impact was seen on the detection limit. The detection limits also varied depending on the ratio of chloride to sulfate.



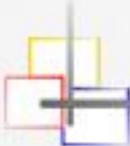
Conductivity and Matrix Interference

- The bias (accuracy) of the test method was evaluated and supports the conclusion that the ratio of chloride to sulfate has a significant impact on the analysis.



Method Validation

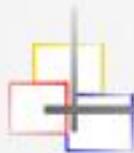
- Calculation of MDL values in drinking water (low conductivity) and at the MCT.
- For 314.0 the calculation of MCT at the reporting limit.
- Some sort of confirmation at low levels using matrix spikes or LC/MS confirmation of perchlorate.



Method Validation

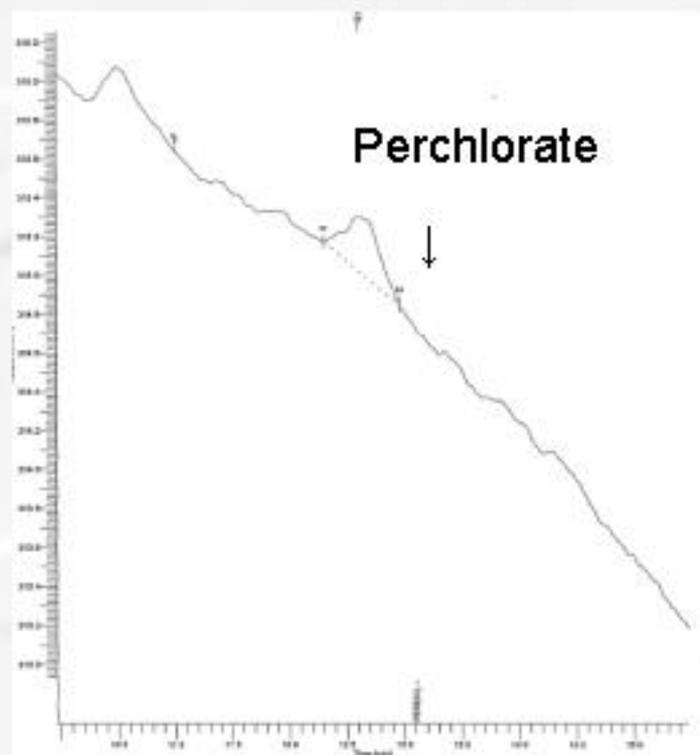
Maximum Conductivity Threshold (MCT) Study

Anion Concentration	Conductivity uS/cm	Area/Height Ratio	Percent Difference	Analytical Result	True Value	Recovery
0	1.27	16.48	"---	0.9807	1	98.07
500	4170	17.15	4.065533981	0.9971	1	99.71
600	4950	18.86	14.44174757	0.8742	1	87.42
700	5540	16.86	2.305825243	0.8548	1	85.48
800	6240	17.48	6.067961165	0.9513	1	95.13
1000	7680	15.68	-4.854368932	0.7815	1	78.15

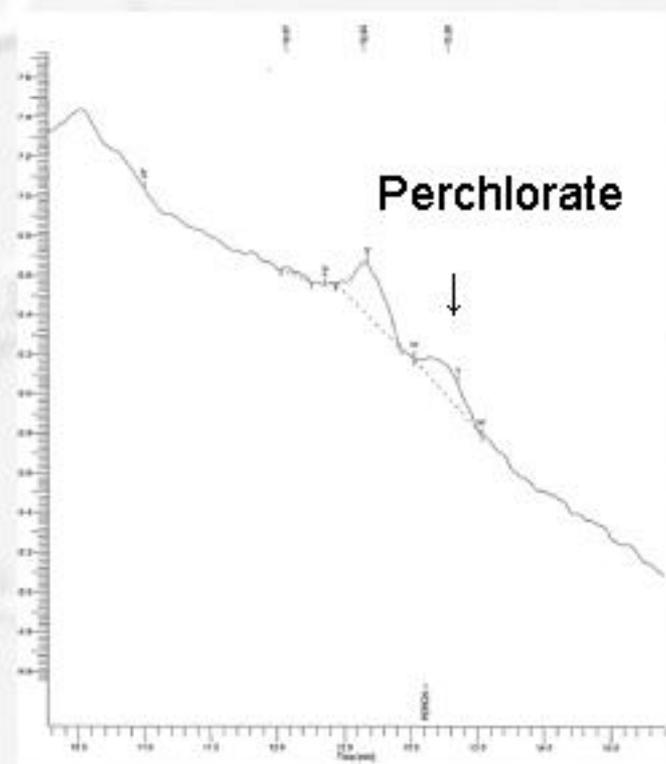


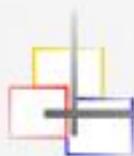
Method Validation

Water Sample #1 ND



Water Sample #1 Spiked at 1ppb

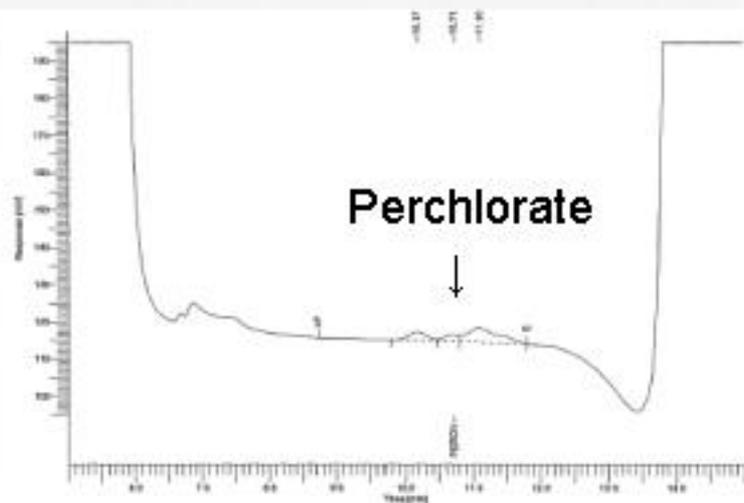




Method Validation

Water Sample #2 for Perchlorate

No Dilution 13 ppb

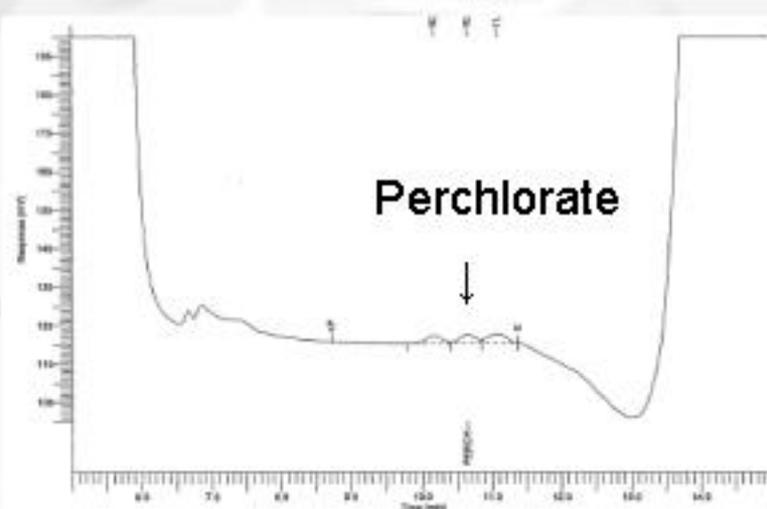


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Ion Chromatography Report

Peak #	Time (min)	Area (AU)	Height (AU)	ResHeight	Raw Amount	Dilution Factor	Adjusted Amount	Component Name
2	10.714	28510.04	1080.04	10.000	13.0075	1	13.0075	Perchlorate

Spiked at 10 ppb



DataChem Laboratories

Ion Chromatography Report

Peak #	Time (min)	Area (AU)	Height (AU)	ResHeight	Raw Amount	Dilution Factor	Adjusted Amount	Component Name
2	10.542	36190.25	2290.04	10.000	13.0248	1	13.0248	Perchlorate

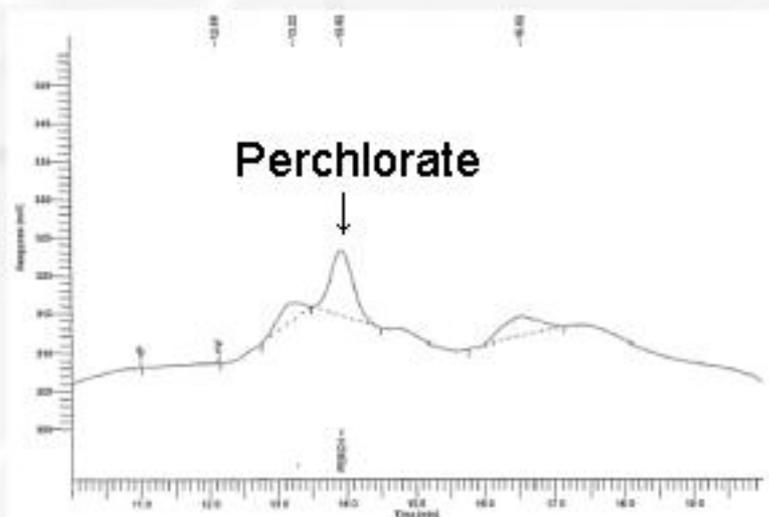


Chromatograms

Grass Sample for Perchlorate

Grass Sample at 62 ppb

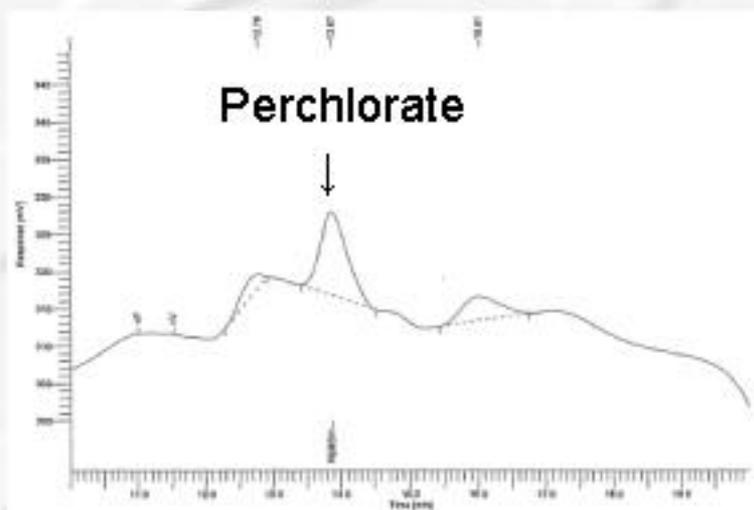
Grass Sample spiked with 25 ppb



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Ion Chromatography Report

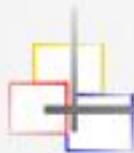
Peak #	Time (min)	Area (uV*sec)	Height (uV)	AreaHeight	Raw Amount	Dilution Factor	Adjusted Amount	Component Name
2	13.917	19295.94	6261.02	32.0952	62.9376	1	62.9376	Perchlorate



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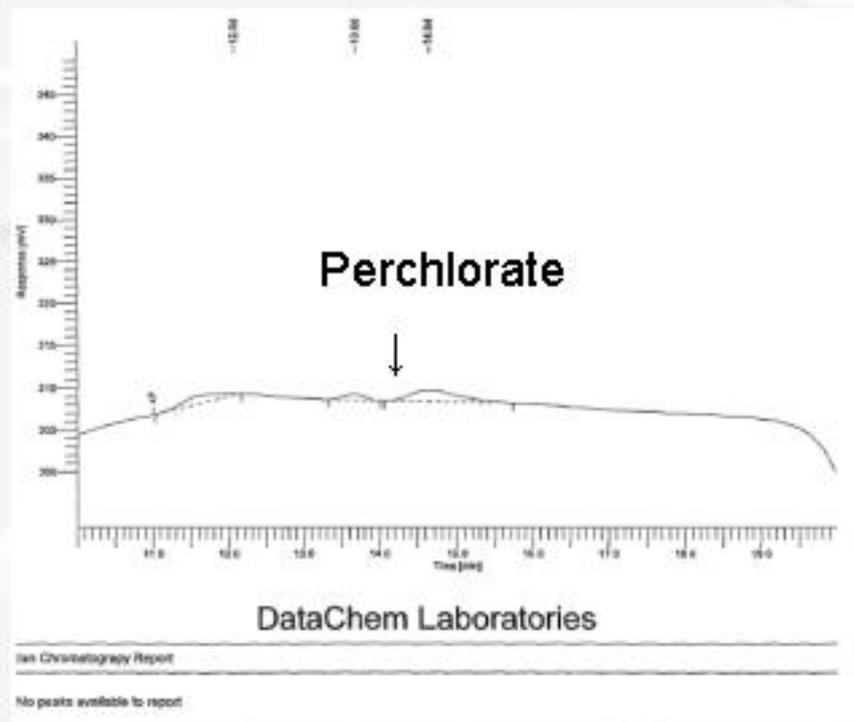
Ion Chromatography Report

Peak #	Time (min)	Area (uV*sec)	Height (uV)	AreaHeight	Raw Amount	Dilution Factor	Adjusted Amount	Component Name
2	13.967	32982.47	11055.43	27.4438	67.9798	1	67.9798	Perchlorate

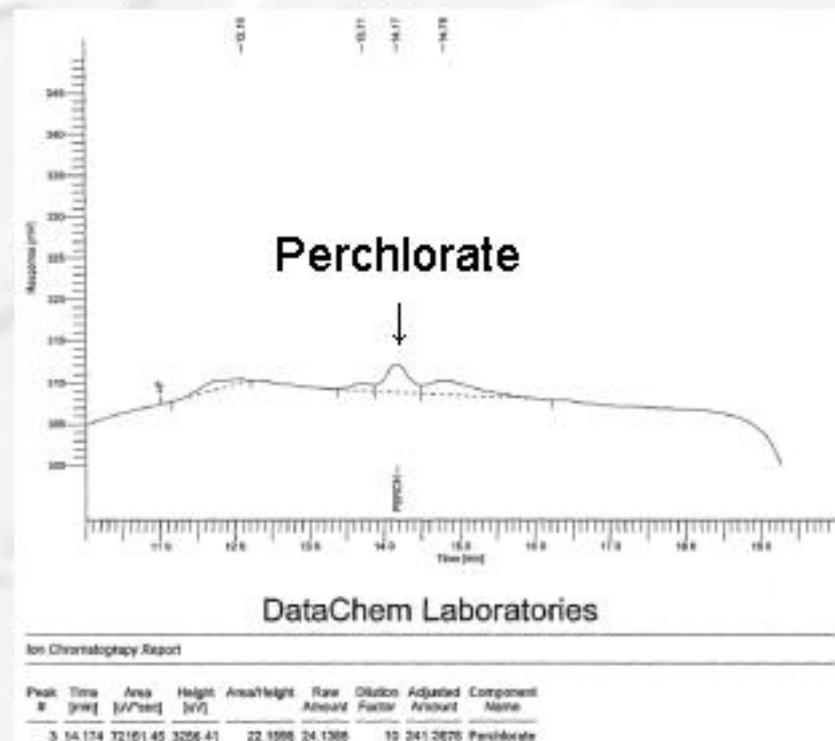


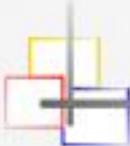
Method Validation

Grass Sample 10X Dilution ND



Grass Sample 10X Dilution spiked at 25ppb





Method Development

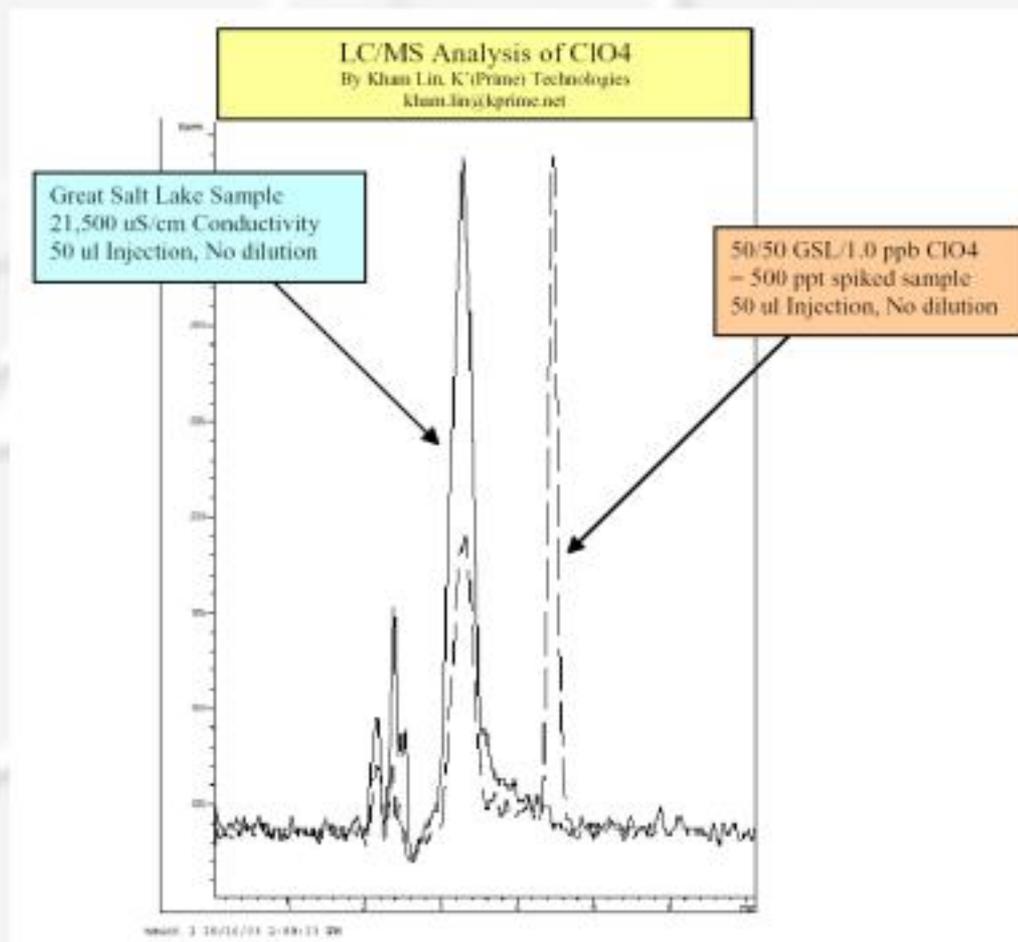
- The use of a pre-column to remove interference or pre-concentration using diluted samples.
- New Techniques for confirmation and/or analysis
- LC/MS Method Validation



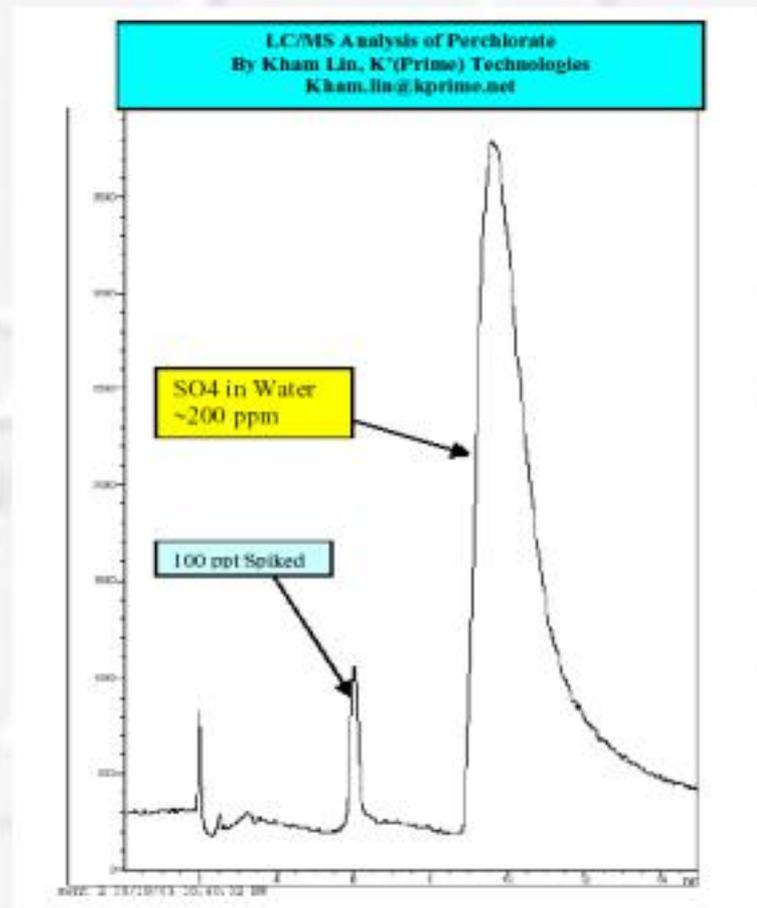
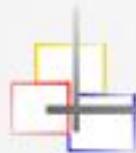
LC/MS Method Development

- Liquid Chromatography is preferable to Ion Chromatography for direct injection methods without using a precolumn to remove matrix interferences.
- LC/MS method will selectively retain Perchlorate for analysis.

LC/MS Method Development



LC/MS Method Development





Thank You

Questions?