Determination of Low Level Perchlorate in Environmental Media.

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Traditional Approach Problems

Analysis of perchlorate by Ion Chromatography with Suppressed Ionization Conductivity Detection is not sufficient for low level analysis is complex environmental matrices.

Leads to false positives and negatives (chromatography RT is the only distinguishing characteristic).

Deionized water MDL's are not applicable to complex environmental matrices.

Analytical Solutions

- Multiple avenues are pursued to improve and achieve realistic DL's
- We have focused primarily on preconcentration and interference removal treatments
- ICP-MS and ESI-MS are also under preliminary investigation

Current Analytical Systems

- IC Separation and Conductivity Detection
- Dionex-100 with up to 1 mL sample injection
  - DL of approximately 1 μg/L by EPA method.
- Dionex-500 with 10 µL sample injection
  - DL of approximately 200 μg/L by EPA method.
- Literature reports of DL as low as 0.6 µg/L for 1 mL injections.

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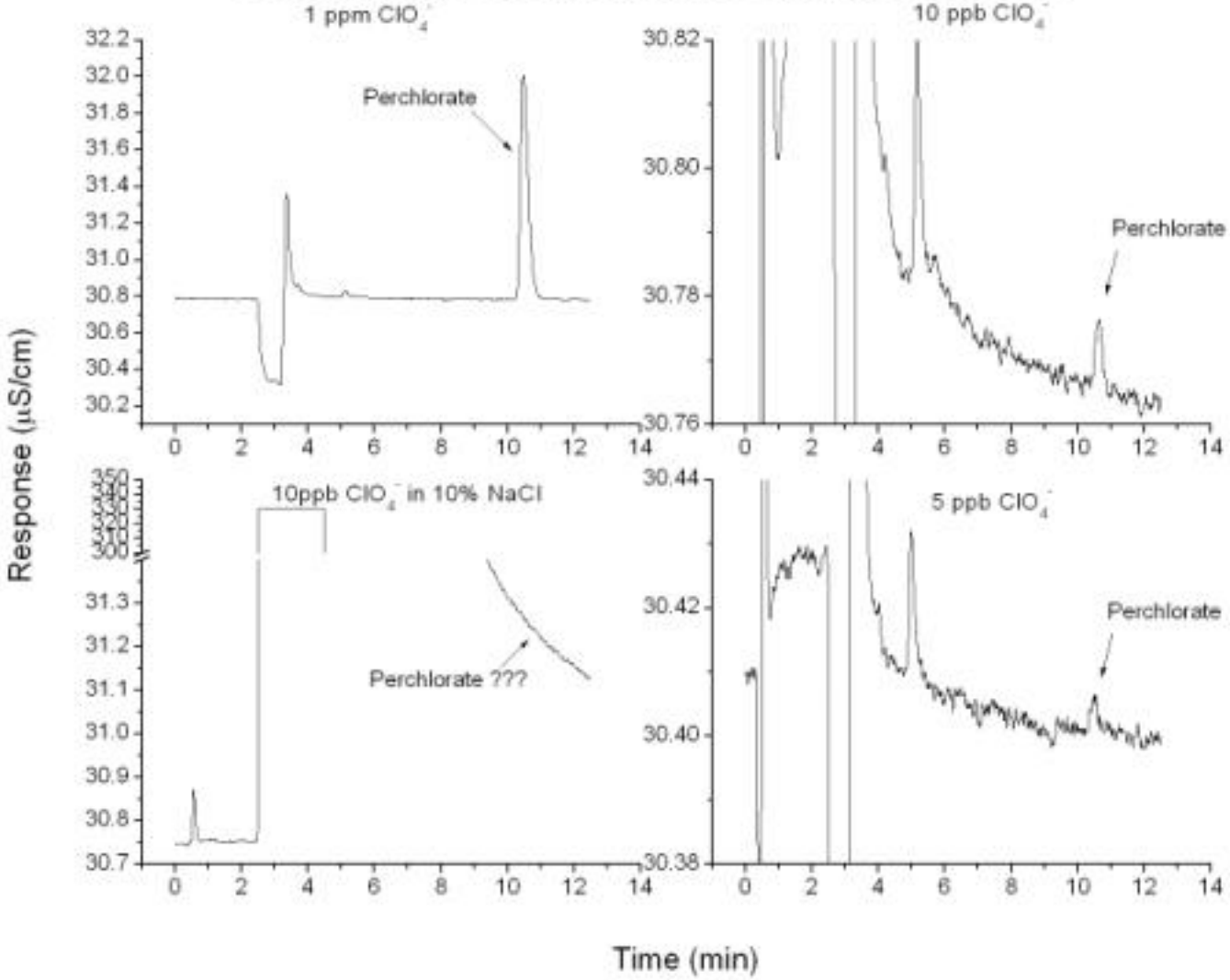
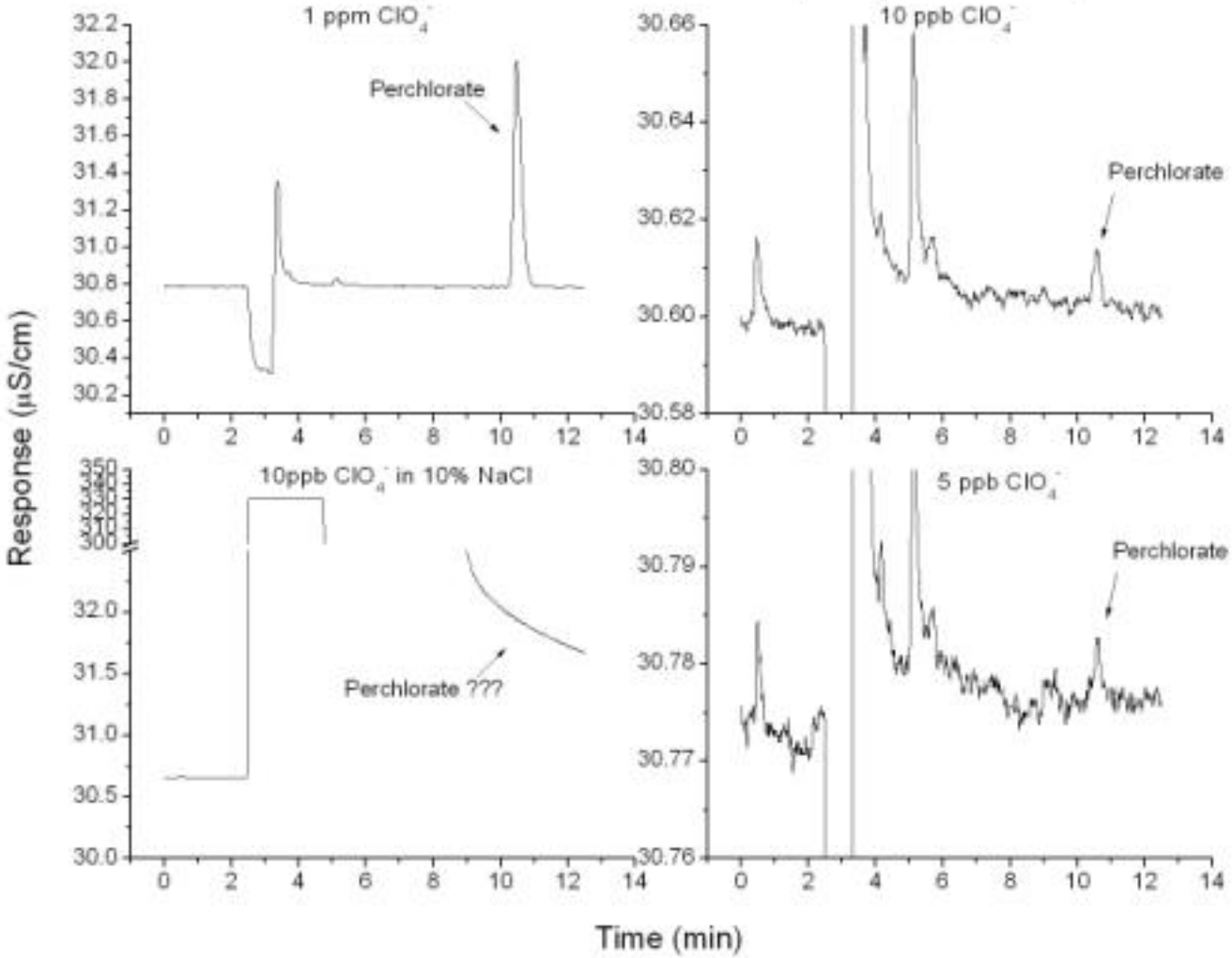
DX-500

DX-100

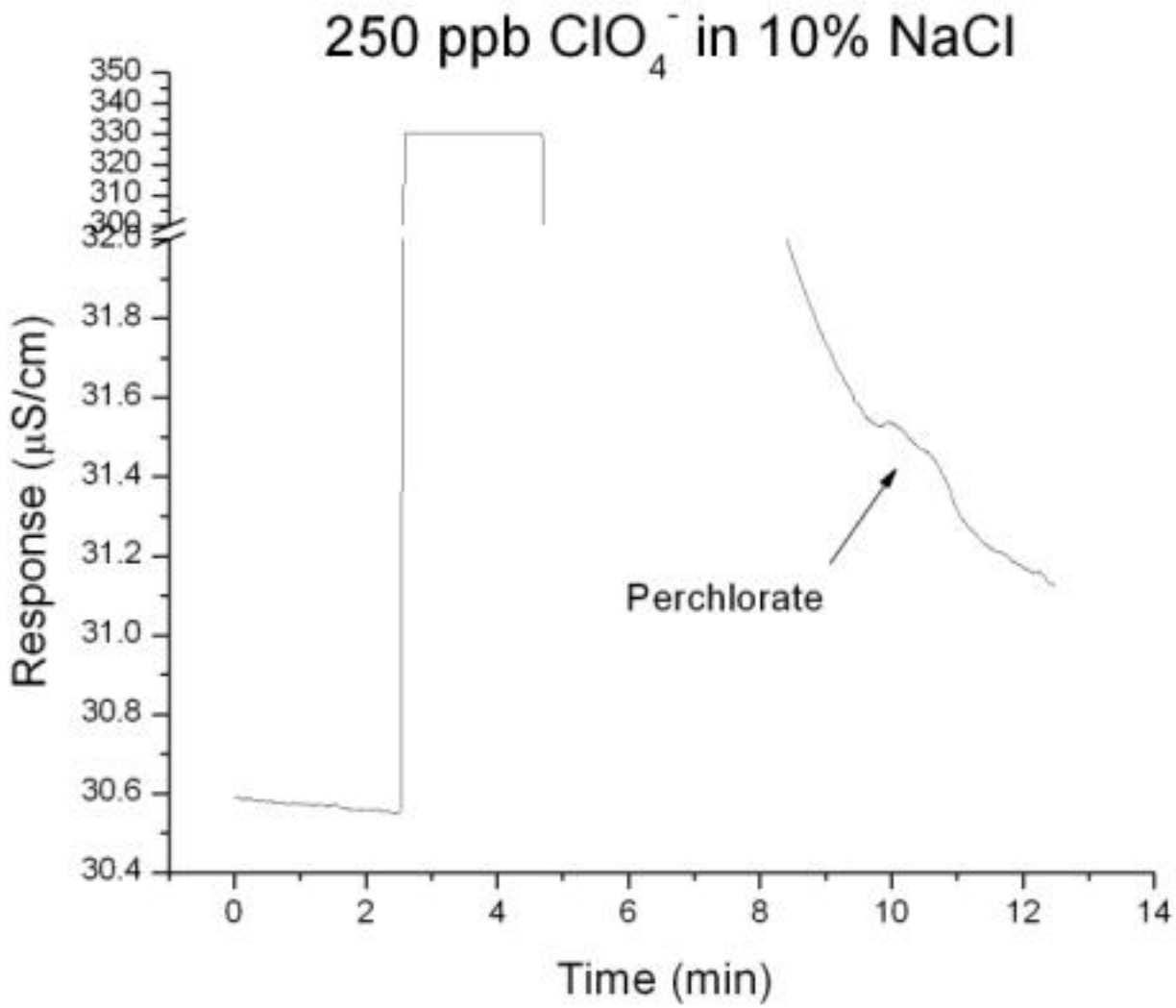
Conductivity Detection with 500 μL Injection Loop



Conductivity Detection with 1000 μL Injection Loop



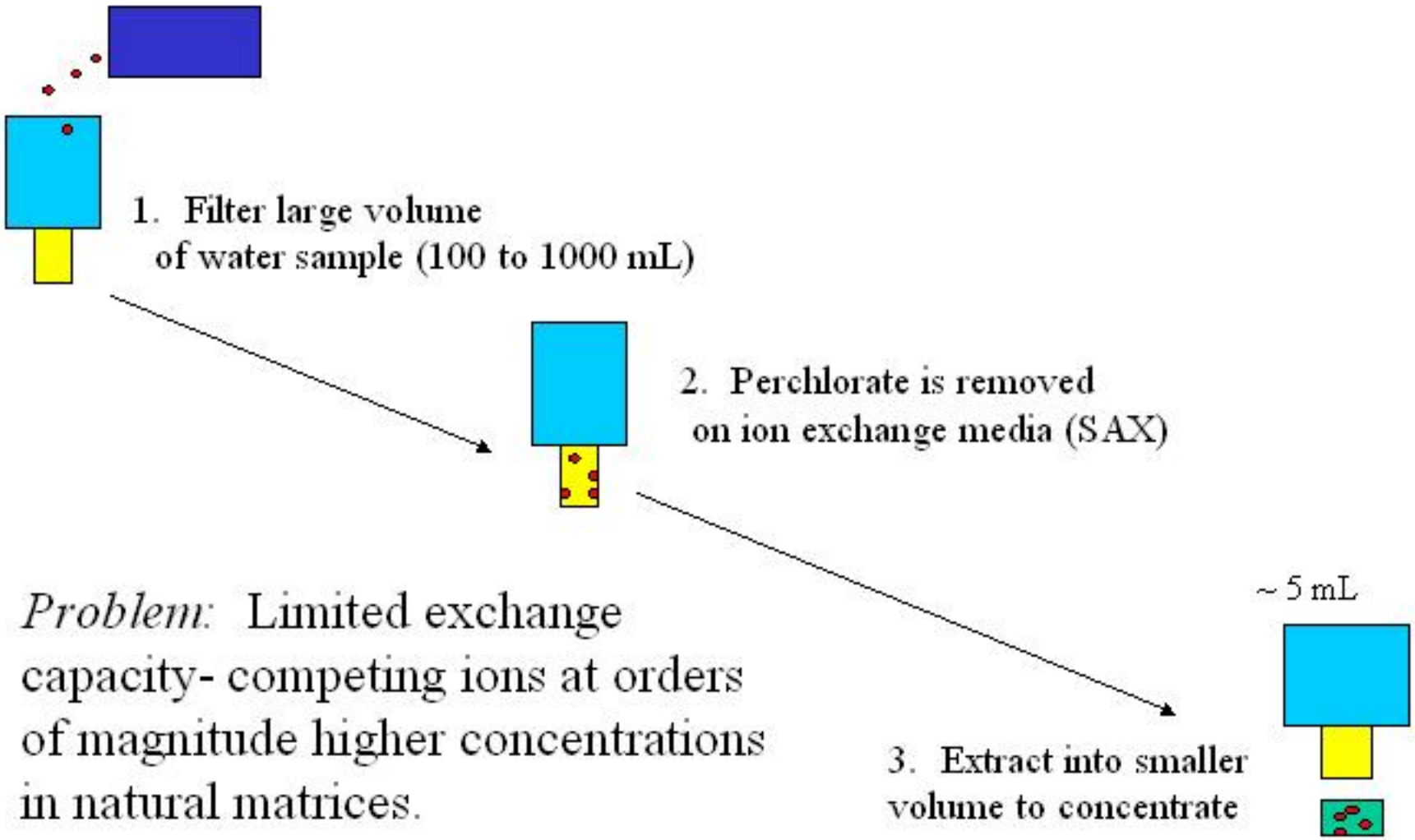
1 mL Sample Injection



Natural Matrix Interferences in Chromatography

- 10 % NaCl is not completely realistic for most natural matrices (Great Salt Lake), but shows worst case senario.
- However, our sample preconcentration methods use from 1 to 10 % 'salt' extractants (e.g. NaCl, NaOH, Na_3PO_4)
- Therefore, the need for sample cleanup treatment

Preconcentration Scheme



Problem: Limited exchange capacity- competing ions at orders of magnitude higher concentrations in natural matrices.

Detection Limits for Deionized Water using Preconcentration

SAX extraction fluid 1% NaOH

Analysis by 10 μL injection loop

SAX filter											
			Replicates (ppb)								
Initial Concentration	1	2	3	4	5	6	7	Average	stdev	MDL (ppb)	Recovery
2 ppb	2.38	2.13	1.77	2.21	1.64	1.83	1.94	1.99	0.26	0.82	99.27%
1ppb	0.57	0.84	0.68	0.75	1.01	0.80	0.80	0.78	0.14	0.43	77.76%
1 liter filtrations											
10 uL injection loop											

1% NaOH perturbs the chromatography system on the 1 mL injection loop system. Future work is focusing on Na_3PO_4 extraction fluid to allow analysis on the 1 mL injection loop system.

Sodium Phosphate Extractant

Extractant	Concentration in Extractant (µg/L)	Extractant Volume (mL)	Filtration Volume	Calculated Filtrate Solution Concentration (µg/L)	Measured Solution Concentration (µg/L)	Recovery (%)
5% Sodium Phosphate	1111	5	250	22.22	19.33	114.93%
10% Sodium Phosphate	1162	5	250	23.24	19.33	120.21%

Initial results showing good recovery on 1 mL injection loop

This is the focus of our future work combining preconcentration and larger sample injection loops.

Sample Cleanup Treatment

0.45 μm filtration to remove sediment

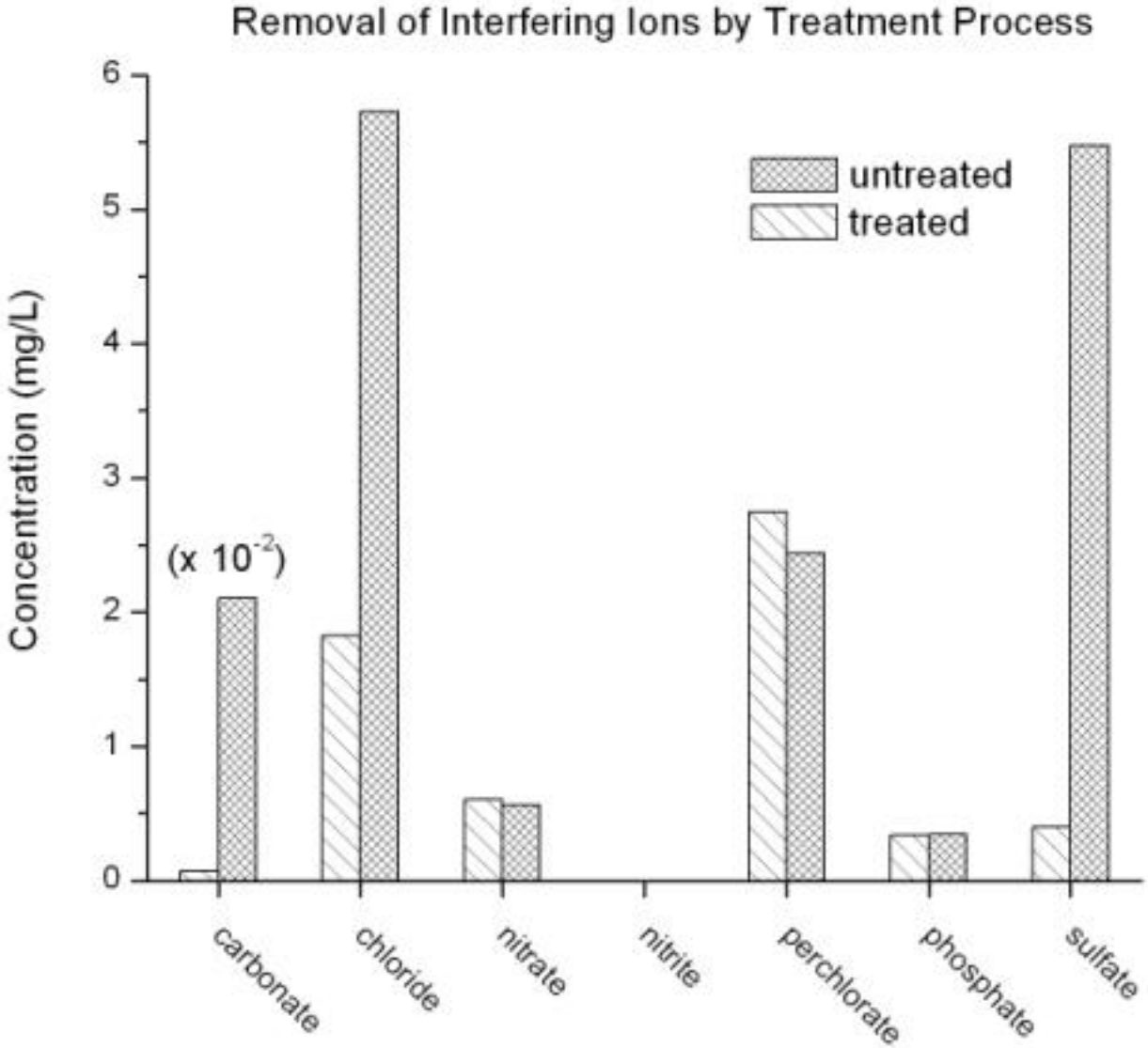
Add $BaCl_2$ to precipitate sulfate

Acidify with HCl (pH < 4) and sparge with N_2 to remove carbonate

0.45 μm filtration to remove precipitate

Filter through Dionex Silver Cartridge to remove chloride

Analyze by IC-CD


Removal of Interfering Ions by Treatment Process
Concentration (mg/L)
(x 10^{-2})
0
1
2
3
4
5
6
untreated
treated
carbonate
chloride
nitrate
nitrite
perchlorate
phosphate
sulfate

Detection Limits in Natural Waters

	Groundwater			Surface Water	
Replicate	Extractant Concentration (mg/L)	Calculated Solution Concentration (μg/L)		Extractant Concentration (mg/L)	Calculated Solution Concentration (μg/L)
1	3.50	70.06		0.85	16.99
2	3.69	73.81		0.81	16.12
3	3.39	67.75		0.83	16.59
4	3.52	70.33		0.87	17.40
5	3.52	70.38		0.87	17.49
6	3.54	70.83		0.80	16.04
7	3.68	73.63		0.77	15.46
Average (μg/L)		70.97			16.58
Solution Concentration (μg/L)		70			15
% Recovery		101%			111%
Standard Deviation (μg/L)		2.13			0.75
MDL (μg/L)		6.7			2.4

MDL Study and Results for Spiked Groundwater (70 μg/L solution, 200 mL filtration volume, 4 mL extraction volume) and Surface Water (15 μg/L solution, 200 mL filtration volume, 4 mL extraction volume). Analysis with 10 μL injection loop.

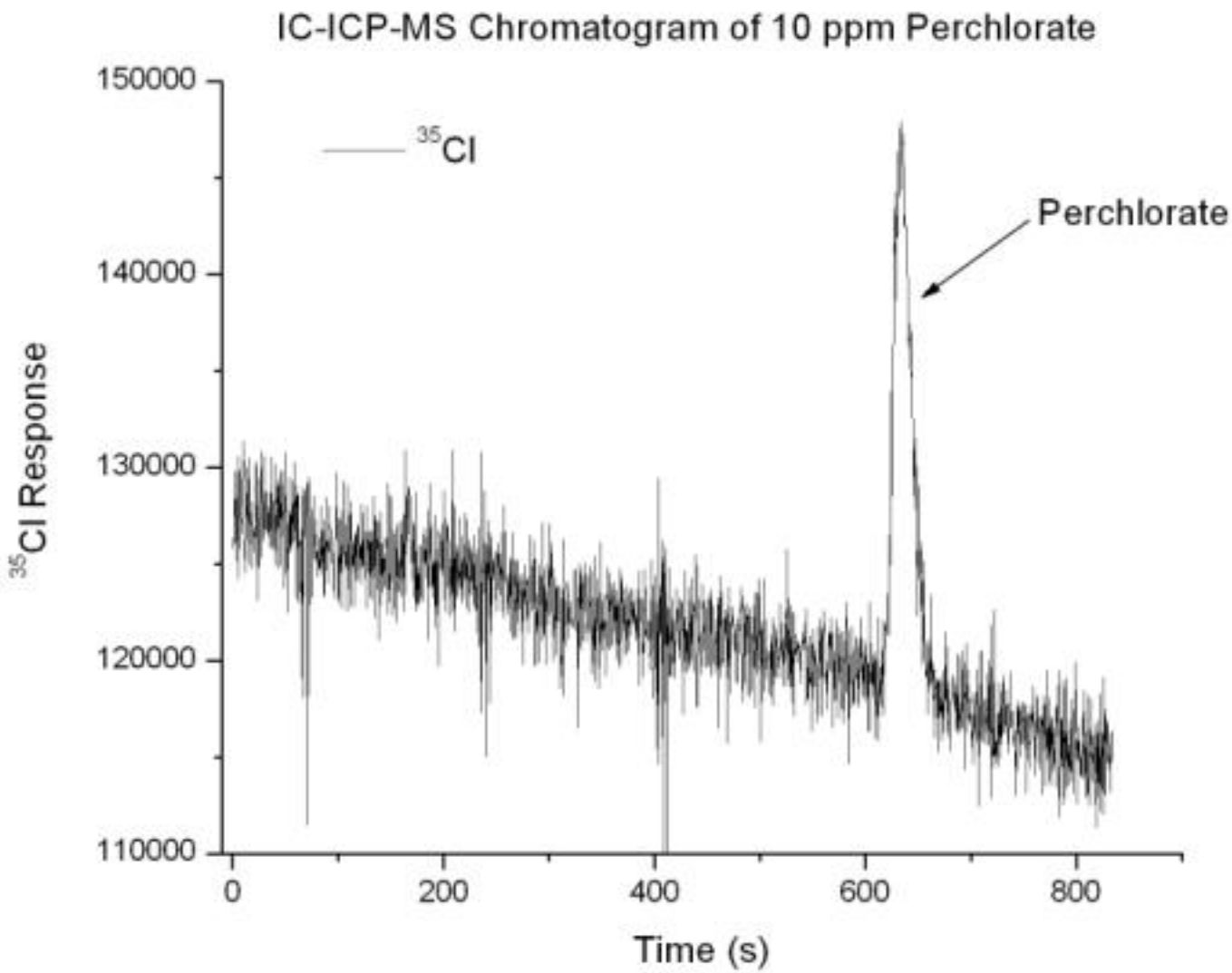
Ongoing Analytical Work

- Combination of preconcentration (with treatment process) using sodium phosphate extractant
  - Possibly develop a treatment for phosphate (Cobalt precipitation?)
- Extension to Mass Spectrometric techniques
  - IC- ESI- and ICP-MS

Development of Complimentary MS Techniques

- IC-ESI-MS
  - Detection limits reported ~ 0.05 μg/L
  - Monitor loss of single oxygen (m/z 99 → 83)
- IC-ICP-MS
  - Expected detection limits higher than ESI-MS
  - ICP-MS differs from ESI by 'complete' decomposition/ionization in the plasma (m/z 35)
  - m/z 83, 67, 51 are not observed
  - 'Plasma loading' is significant – 100 mM NaOH
- Combination of all techniques (preconcentration, large injection loop, MS detection) offers possibilities.

HPLC-ICP-MS


IC-ICP-MS Chromatogram of 10 ppm Perchlorate
^{35}Cl
Perchlorate
^{35}Cl Response
150000
140000
130000
120000
110000
0
200
400
600
800
Time (s)