

Analysis of Perchlorate in the sub-ppb Range using Ion Chromatography

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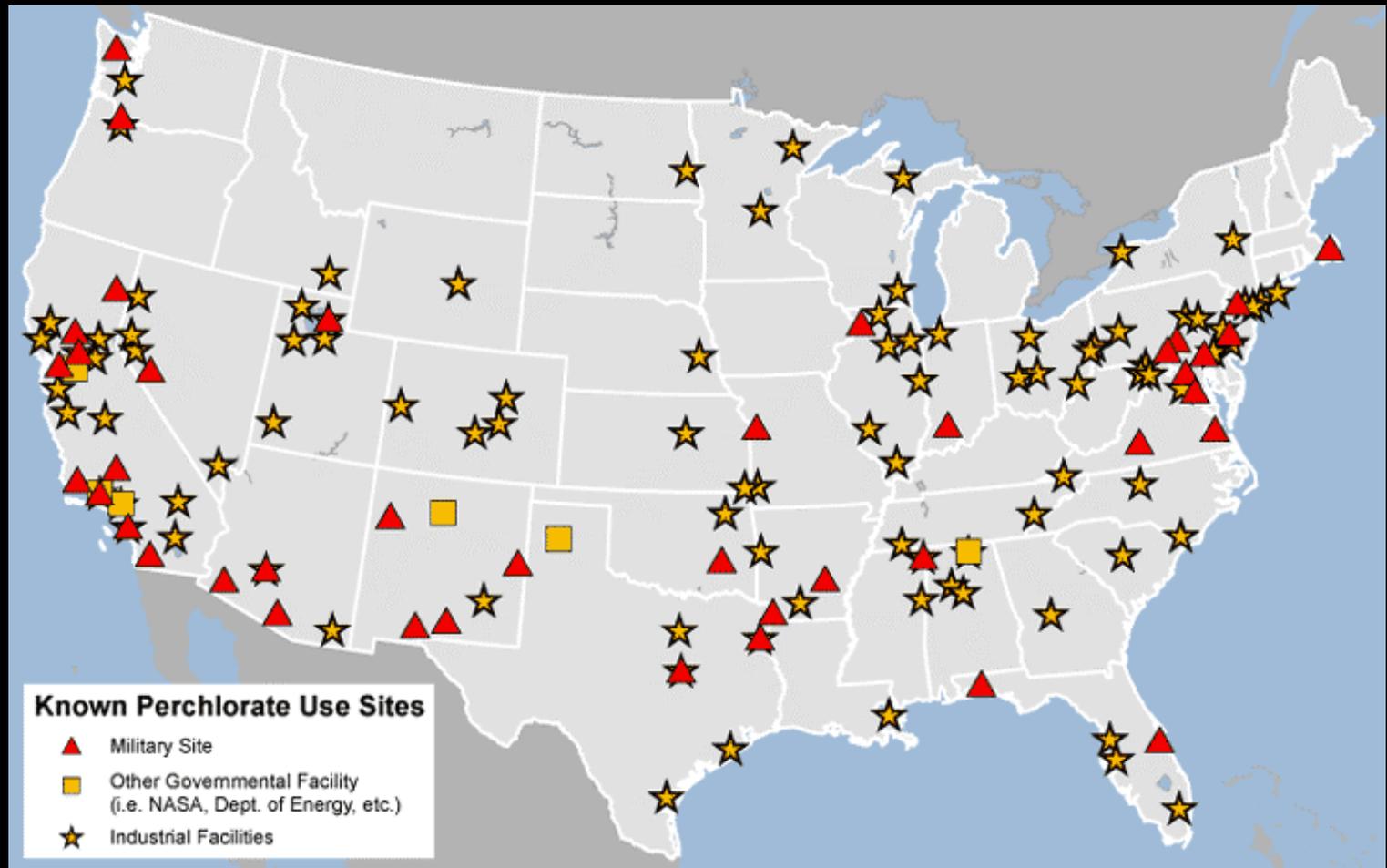
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Why Care About ClO_4 Analysis at this Level?

- ◆ No Current MCL
 - Several states have set ppb action levels
 - CA Public Health Goal (PHG) = 2 or 6 ppb
 - EPA Risk Assessment suggests 1 ppb limit
- ◆ Limited Data at low levels
 - DOD sites with reported ppb level contamination
 - ClO_4 one of the few compounds detected in UCMR, but....
 - UCMR MRL is 4 ppb and therefore....
 - No national data below 4 ppb
 - EPA looking at ClO_4 again for next UCMR.

The Potential to Detect ClO_4 is Widespread



Current Approved Techniques

- ◆ IC with conductivity detection - EPA 314
 - Already uses large sample size (1 ml)
 - Sensitive to TDS with larger sample
 - Tight QC criteria at the 4 ppb MRL
- ◆ No other APPROVED methods, but
 - LC-MS-MS methods
 - IC-MS-MS potential method
 - Options to increase sensitivity of 314

LC-MS-MS and IC-MS or MS-MS Methods

- ◆ Expensive Instrumentation
- ◆ Methods still in development
- ◆ Sensitivity of < 100 ppt (MDL < 50 ppt) for IC-MS or MS-MS; LC-MS-MS can be even lower (Snyder et al, 2003)
- ◆ High degree of specificity because of MS Detector and ability to monitor transitions

Why Not Go With One of These Alternate -MS Methods?

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- ◆ Instruments cost \$100-300K
- ◆ Too many potential samples to tie up an expensive instrument and may be too expensive for some labs
- ◆ On the flip side, IC-MS is much more specific than any traditional IC method, and with its sensitivity, the cost may not be out of line, especially for difficult matrices.

Options to Increase Sensitivity of 314

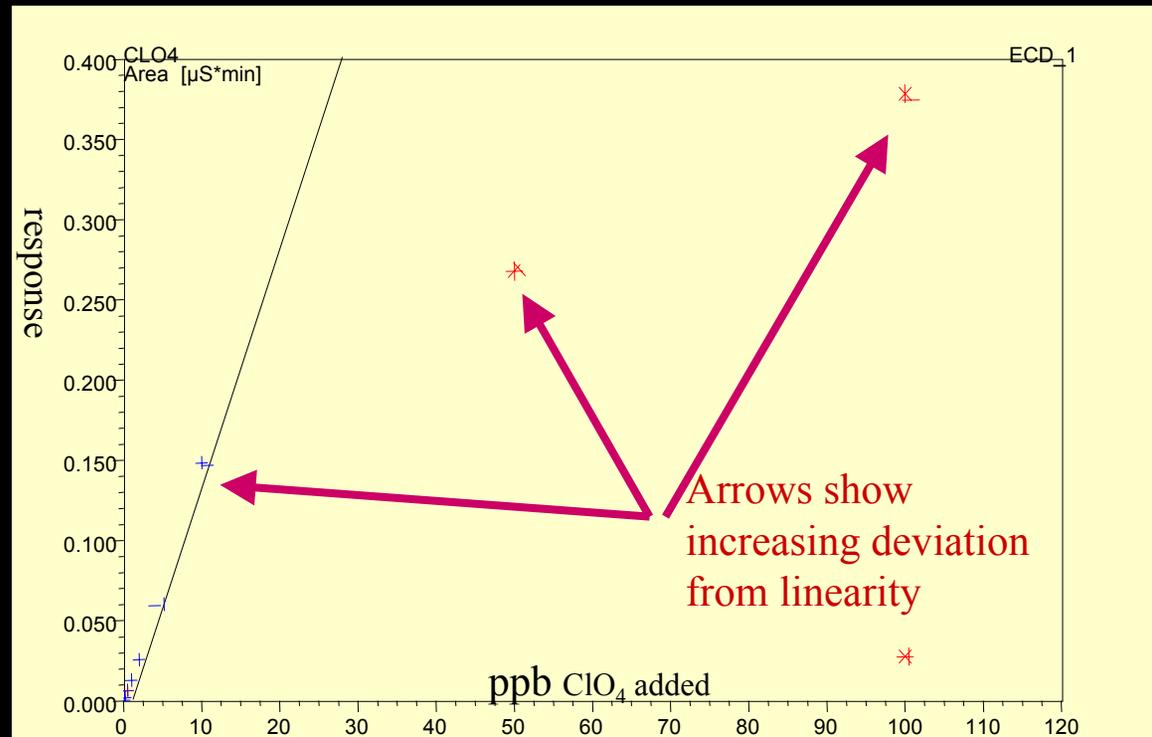
- ◆ Larger Sample Size
 - e.g. 5 ml; 10 ml?
- ◆ Pre-Concentration Techniques
 - ClO₄ specific resins
 - Heart Cutting/Column Switching
- ◆ Reduce noise through better suppression of background EC
 - e.g. Achieve 0.5 nS noise level

Options Investigated for 314

- ◆ Preconcentration with TAC-LP1 Column
- ◆ Impact of large sample size (5 ml) with heart cutting for matrix elimination
- ◆ Suppressor noise control under routine conditions using different suppressors
- ◆ Still to be tested (and may be most promising for a low cost method)
 - More ClO_4 Specific Resins as concentrator

Preconcentration - Based on DasGupta et al (2003)

- ◆ Used a TAC-LP1 Column to concentrate ClO_4^-
- ◆ Looked very promising at very low levels, but limited linearity (0.2 to 10 ppb)



But TAC-LP1 Inadequate in Presence of Solids

- ◆ 25 ppb spike in the presence of 1000 ppm TDS gives <1 ppb response
- ◆ Also non linearity above 10 ppb in DI suggested potential problems
- ◆ High ionic strength samples were causing the ClO_4 peaks to broaden. Conclusions - TAC-LP1 not an option because it's not specific enough for ClO_4 to be used as the primary.

Other Pre-Concentration Options or Direct Analysis

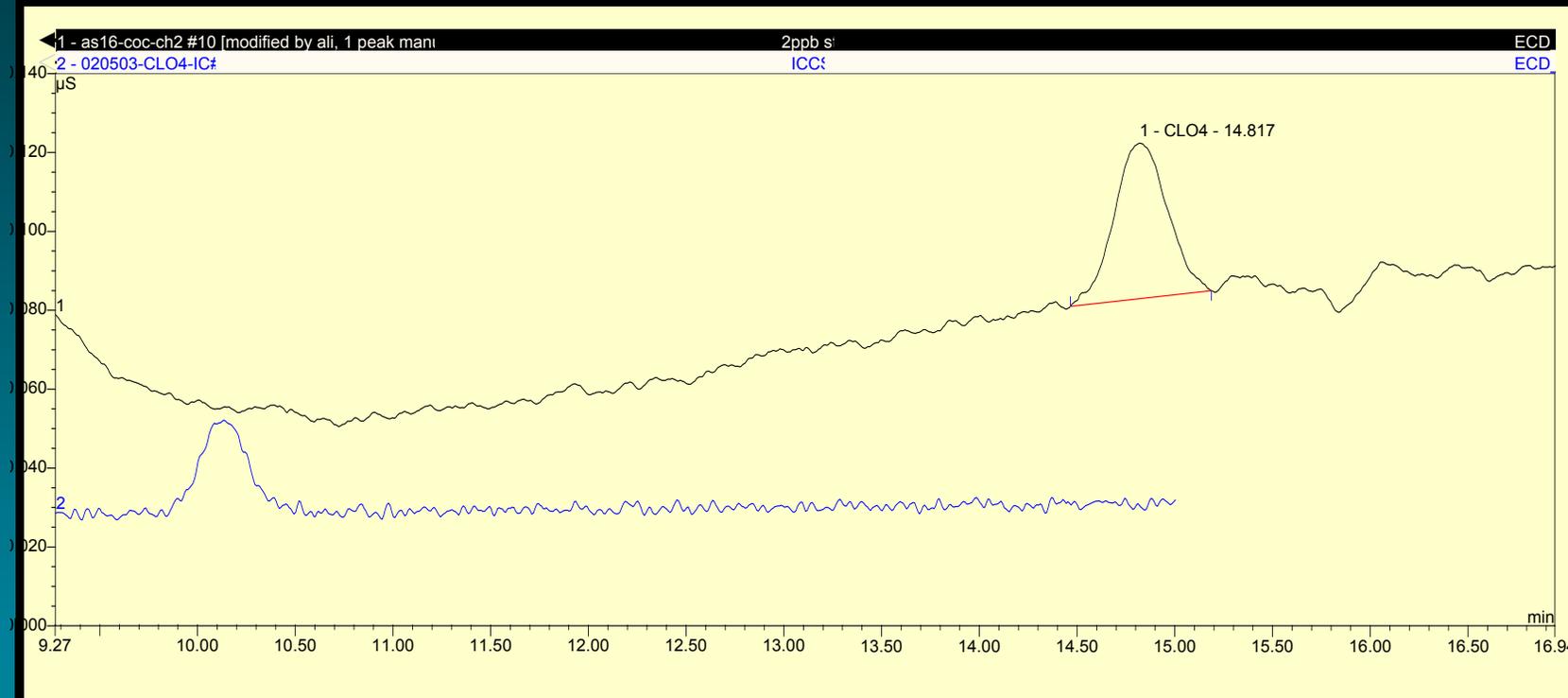
- ◆ Different functional group on Column to make it more ClO_4 specific
 - The more specific, the higher the concentration factor that can be achieved either by injection of larger sample or pre-concentration. Dionex developed new resins, now available for testing - Cryptand

Heart Cutting Based Techniques

- ◆ Inject Large Sample (e.g. 5 ml)
- ◆ Trap ClO_4 fraction on different column to eliminate the “pre-eluting” matrix
- ◆ Same approach was used by EPA in ICR for Bromate analysis at sub ppb levels
- ◆ Method is:
 - time consuming
 - as much an art as a science
 - you have to be sure you trap the ClO_4 (so having an IS/Surrogate is very helpful)

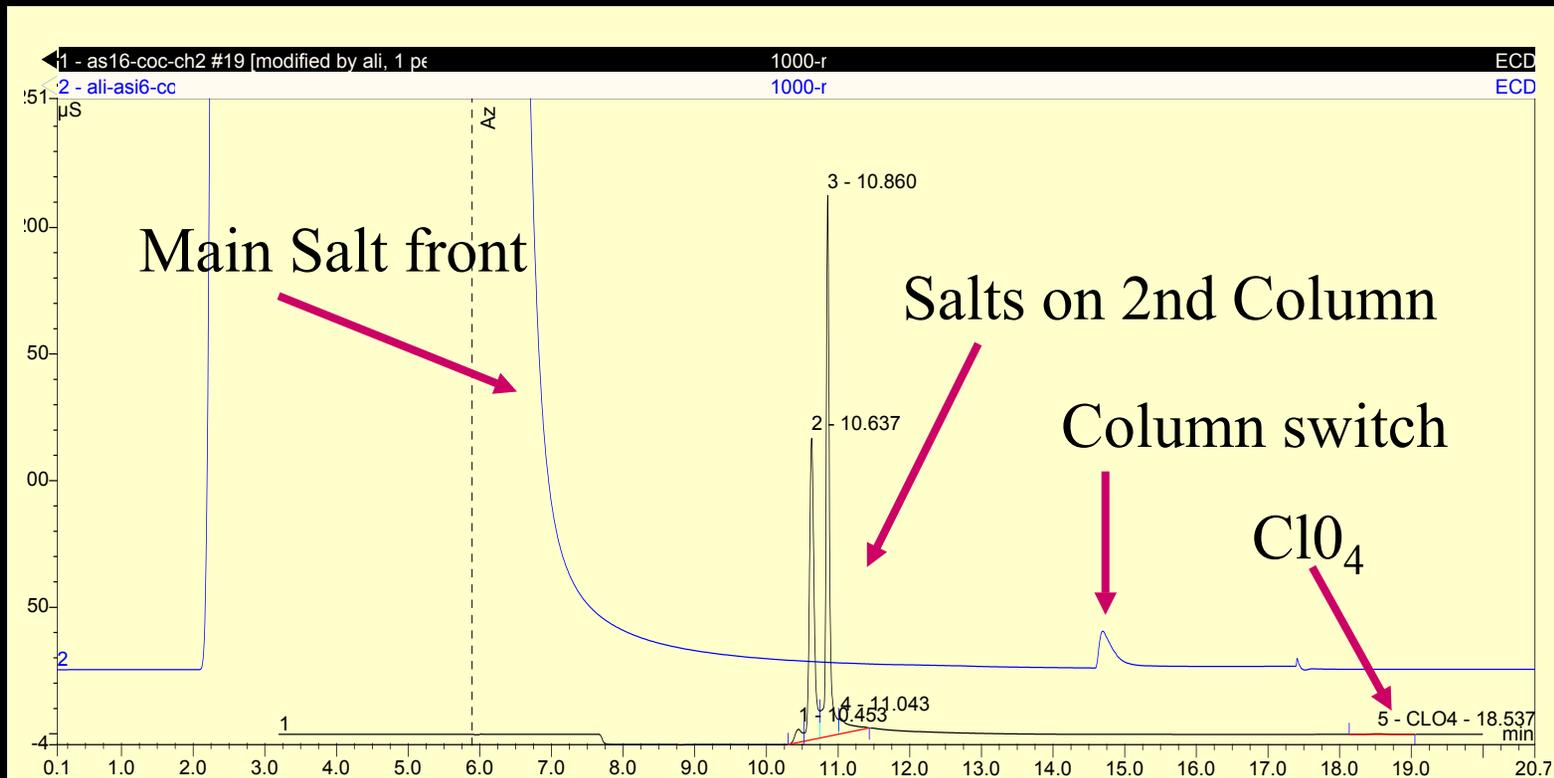
Large Volume Injection and Heart Cutting Looks Great in DI water

- ◆ Using a 5 ml loop, the 2ppb peak is retained at 15min vs a 4ppb peak with 1ml loop at 10 min. It's clear one can get signal enhancement, in DI water



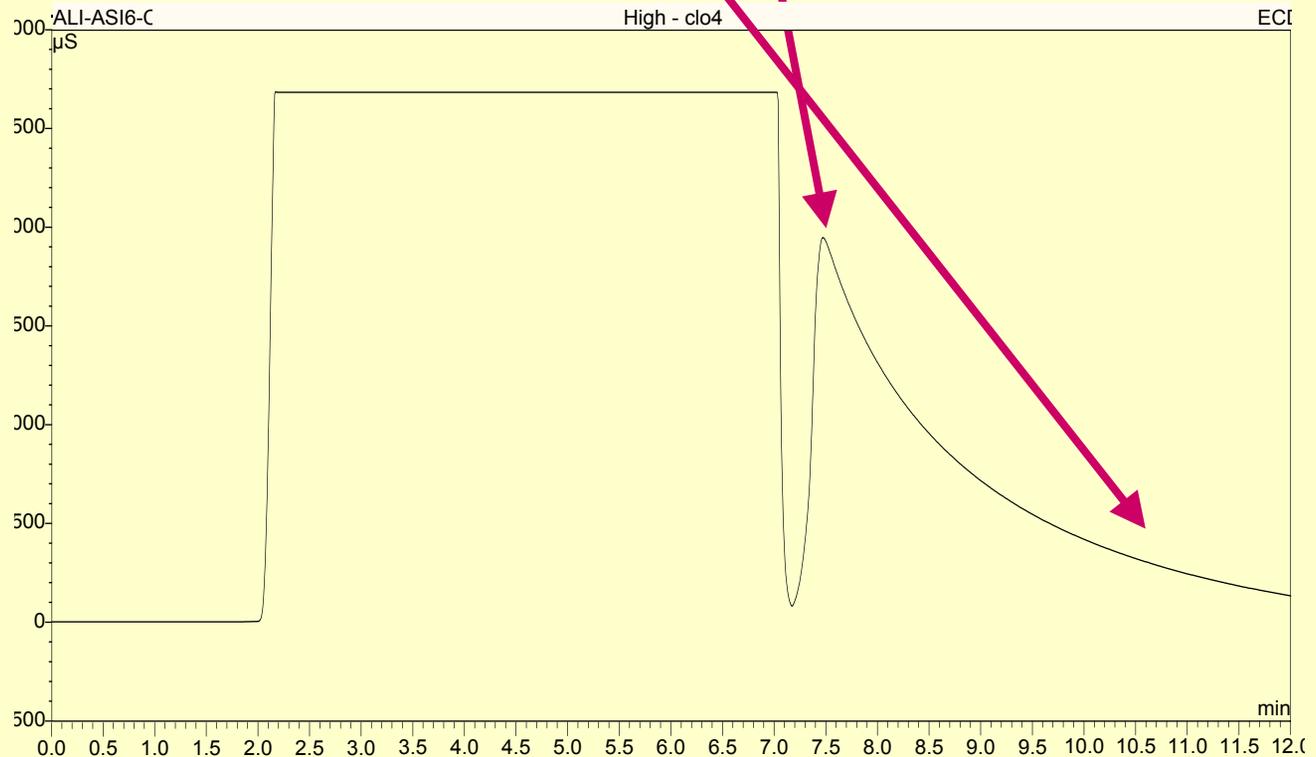
Example from Heart Cutting Approach (25 ppb in 1000 ppm TDS)

- Monitor both columns to be sure you know what's happening



Heart Cutting with Very High ClO4 and Very High Salts

- It's easy to miss the perchlorate, since normal heart cutting would start much later... thus an ART in some matrices.



Reducing Noise as an Alternative Is Clearly the Simplest Approach

- ◆ Changes in suppressor operation
- ◆ Changes in suppressor type
- ◆ For 1 ml loop, 1 ppb gives about 5 nS peak height, so CONSISTENT baseline noise of 0.5 ns would allow quantitation at 0.5 ppb (e.g. 5/1 S/N)
- ◆ Goal should be to get to < 0.5 nS baseline noise

Suppressor Options

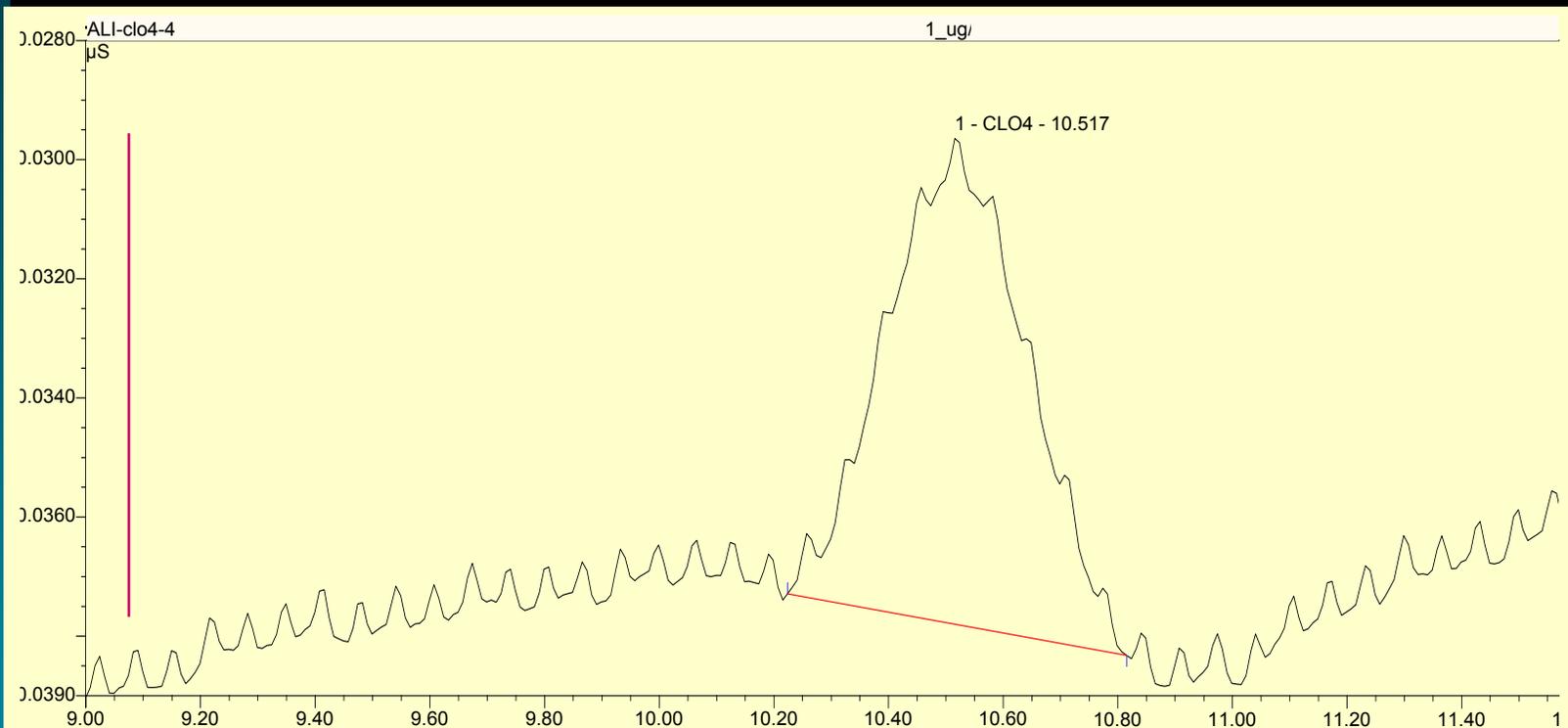
- ◆ Suppressor Types
 - Self Regenerating Suppressor (ASRS)
 - Chemical Suppression (AMMS-III) (H_2SO_4 at 100 mM)
 - Self Regenerating Suppressor (ASRS Ultra II)
- ◆ Two modes of operation
 - External Water Mode
 - Recycled Mode
- ◆ Any of these options works fine for ClO_4 at 4 ppb, but 1-2 ppb is a different story...

What's the Difference Between Suppressors?

- ◆ Normal ASRS generates noise
- ◆ ASRS Ultra II produced by using different materials, better sealing, and better cleaning, but not consistent.
- ◆ Fresh AMMS-III is generally low noise
- ◆ There are differences in noise on operation.

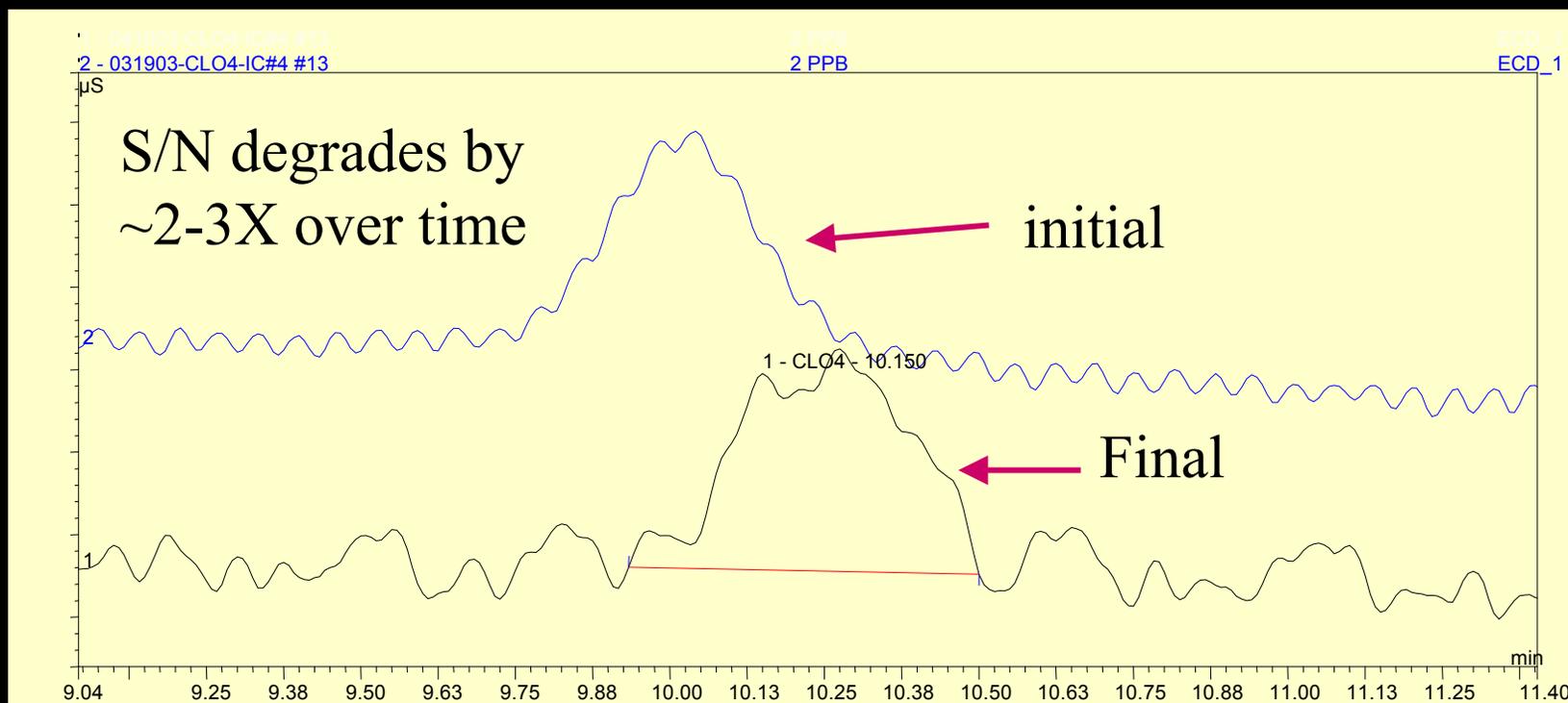
A Fresh AMMS-III Suppressor Has a Great Signal at 1 ppb

- ◆ 1 ppb in DI Water with a fresh AMMS-III Suppressor gives $>10/1$ S/N ratio

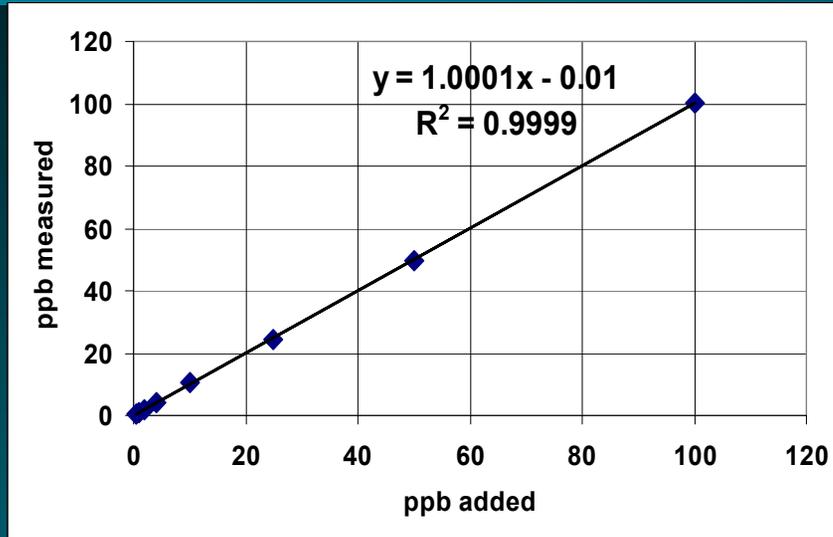


A Fresh ASRS Ultra-II Yields Slightly Better S/N than AMMS-III, but Signal Degrades After Extensive Use

- ◆ Comparison of 2 ppb ClO_4^- S/N after 1st injection vs after ~ 500 injections

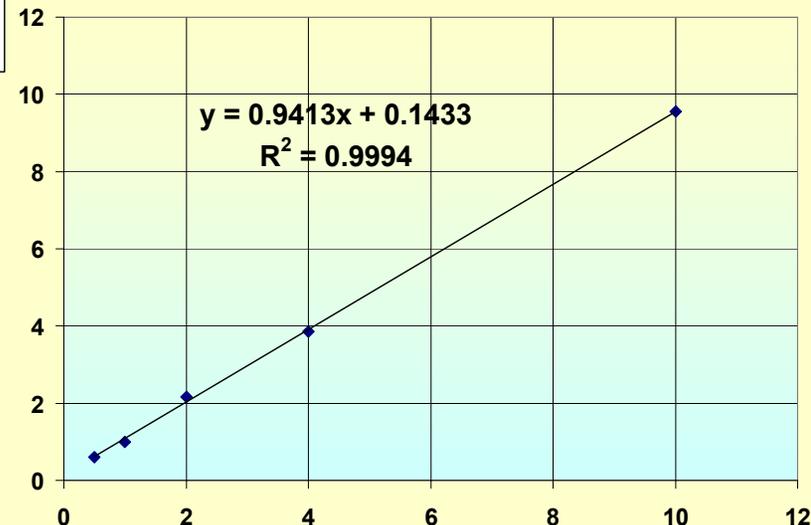


IC with AMMS-III Offers High Sensitivity and Linearity



Calibration Curve
0.5 to 100 ppb

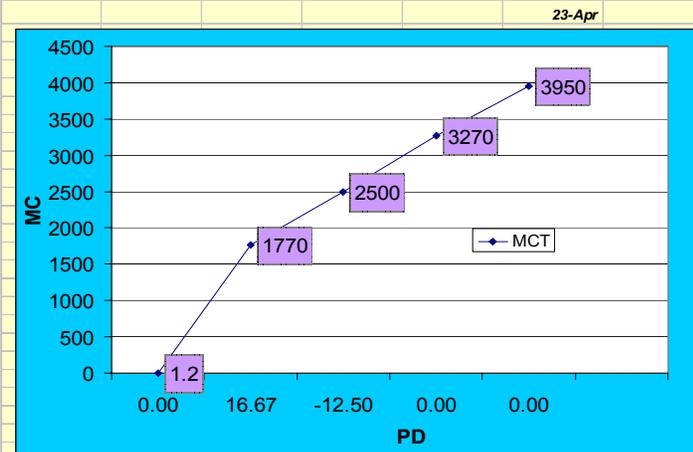
0.5 to 10 ppb
Calibration Curve



Recoveries are Consistently Good at 2 ppb, Even in High Salts

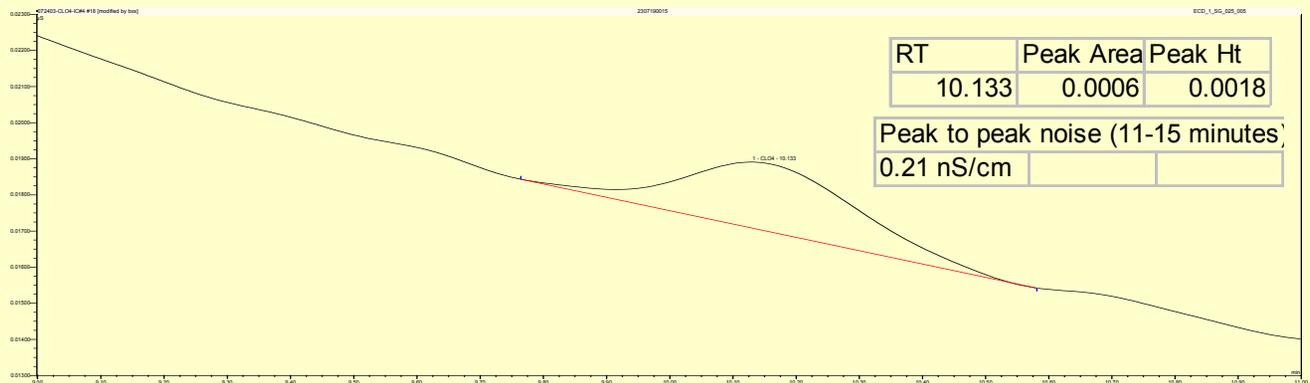
- ◆ Data are for ASRS ULTRA-II after 500 injections
- ◆ The MCT concept was not designed for use at 2 ppb, but rather for 25 ppb. YOU CAN'T USE 25 PPB DATA TO PROVE THAT YOU CAN MEASURE AT 2 OR 1 OR..
- ◆ Appropriate acceptance criteria need to be developed to verify low level recovery - e.g. 70-130%

RAW DATA FOR SALT MCT STUDY_ULTRAI



| SALT | AREA | HEIGHT | A/H | EC | CONC | PD% |
|-----------------|-------|--------|-------|------|----------|--------|
| | | | | | C1O4 ppb | |
| 0 | 0.002 | 0.007 | 28.57 | 1.2 | 1.88 | 0.00 |
| 200 | 0.002 | 0.006 | 33.33 | 1770 | 1.45 | 16.67 |
| 300 | 0.002 | 0.008 | 25.00 | 2500 | 2.01 | -12.50 |
| 400 | 0.002 | 0.007 | 28.57 | 3270 | 1.77 | 0.00 |
| 500 | 0.002 | 0.007 | 28.57 | 3950 | 2.19 | 0.00 |
| MEAN LFB | | | | | 1.86 | |

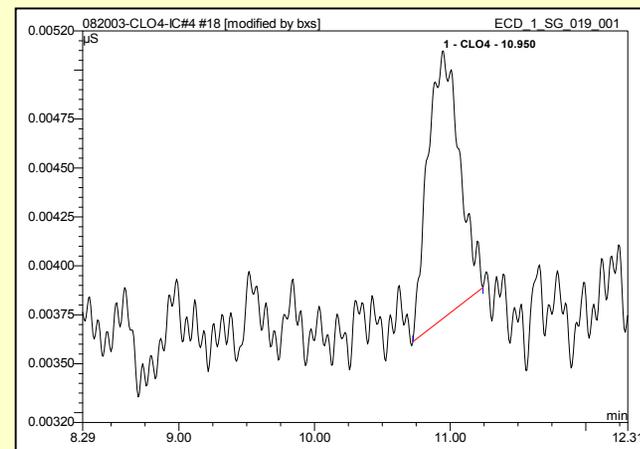
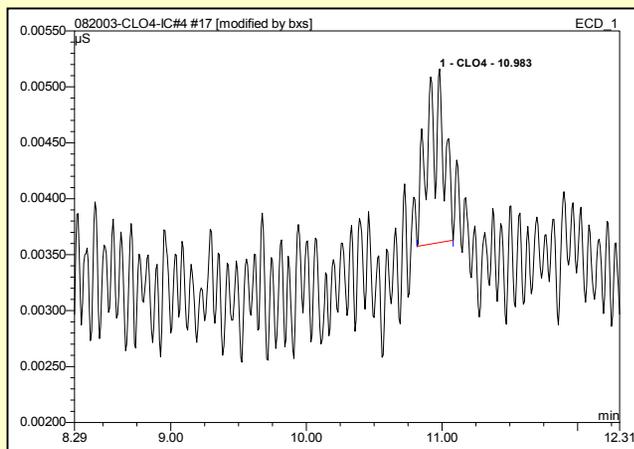
Ability to Smooth Chromatograms Using Algorithms Significantly Improves Ability to Measure at Sub PPB



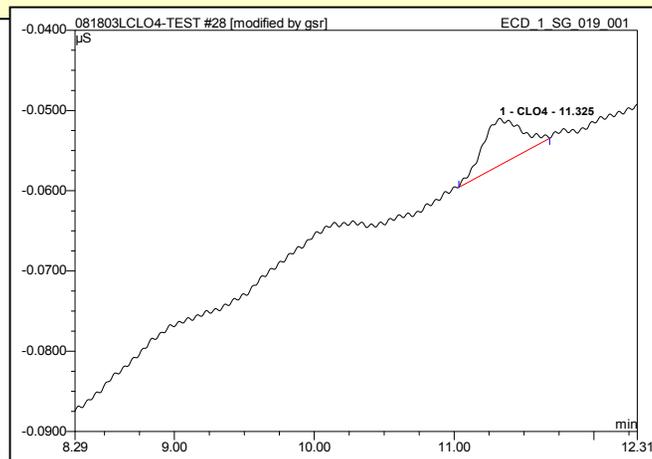
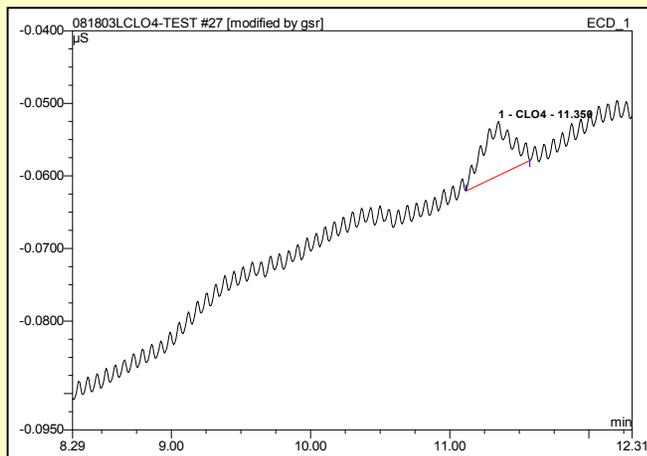
4x improvement in S/N at < 1 ppb Measured Value

Smoothing Has a Big Impact on the Ability to Quantitate at These Levels

ASRS
Ultra II
0.5 ppb
1ml
loop



ASRS
AMMS
-III
0.5 ppb
2 mL
loop



0.2 to 0.3 ppb MDLs are Determined Using a 2 ml Loop and AMMS-III

**Table 1: Replicate analysis of 0.5 ug/L and 1 ug/L ClO₄ in DI Water
Processed with and without mathematical smoothing**

| replicate | 0.5 ug/L in DI 1 ug/L in DI no smoothing | | 0.5 ug/L in DI 1 ug/L in DI Smoothed using K-S function | |
|-----------------|---------------------------------------------|--------------|------------------------------------------------------------|--------------|
| | 1 | 0.51 | 1.07 | 0.34 |
| 2 | 0.59 | 0.986 | 0.48 | 0.9 |
| 3 | 0.47 | 1.03 | 0.5 | 0.93 |
| 4 | 0.48 | 1.03 | 0.45 | 1.03 |
| 5 | 0.39 | 0.96 | 0.2 | 0.81 |
| 6 | 0.50 | 1 | 0.45 | 0.73 |
| 7 | 0.51 | 1.15 | 0.55 | 1.04 |
| ave | 0.491 | 1.032 | 0.424 | 0.907 |
| s.d. | 0.058 | 0.063 | 0.118 | 0.111 |
| calc MDL | 0.183 | 0.197 | 0.370 | 0.349 |

note: 2 ml sample loop and AMMS-III suppressor in external water mode

Similar MDLs are Determined using the ASRS-ULTRA-II and a 1 ml Loop

Table 2: Replicate analysis of 0.5 ug/L and 1 ug/L ClO₄ in DI Water Processed with and without mathematical smoothing

| replicate | 0.5 ug/L in DI | 1 ug/L in DI | | 0.5 ug/L in DI | 1 ug/L in DI |
|-----------------|----------------|--------------|--|-----------------------------|--------------|
| | no smoothing | | | Smoothed using K-S function | |
| 1 | 0.36 | 0.93 | | 0.48 | 0.85 |
| 2 | 0.45 | 0.79 | | 0.44 | 0.93 |
| 3 | 0.45 | 0.71 | | 0.43 | 0.94 |
| 4 | 0.54 | 0.77 | | 0.51 | 0.92 |
| 5 | 0.36 | 0.91 | | 0.54 | 0.96 |
| 6 | 0.36 | 0.8 | | 0.55 | 0.99 |
| 7 | 0.44 | 0.93 | | 0.620 | 1.11 |
| ave | 0.423 | 0.834 | | 0.510 | 0.957 |
| s.d. | 0.068 | 0.088 | | 0.050 | 0.080 |
| calc MDL | 0.212 | 0.277 | | 0.158 | 0.251 |

note: 1 ml sample loop and ASRS Ultra II Suppressor

Does the Suppressor Based Approach Still Work on Real Sample Types?

- ◆ DI water and samples with salts are not necessarily the same for ClO_4 analysis, as we saw on the other approaches.
- ◆ So we tested the method using a variety of real groundwater samples, containing varying levels of TDS and varying “potential” low levels of ClO_4 .
- ◆ Samples were analyzed, and then many were spiked with 1 ppb perchlorate.

Low Level Performance with AMMS-III is Acceptable, Even After >500 injections

| Sample | Initial | +1 ppb | % Rec |
|--------|-----------|--------|-------|
| A | 1.5 | 2.77 | 127% |
| B | 2.0 | 3.07 | 107% |
| C | ND (<0.5) | 1.33 | 133% |
| D | 1.58 | 2.57 | 99% |
| E | ND (<0.5) | 1.44 | 144% |
| F | 3.39 | 4.48 | 109% |
| G | ND (<0.5) | 1.41 | 141% |
| H | 0.76 | 1.92 | 116% |
| I | ND (<0.5) | 1.33 | 133% |

The Best Way to Know if You're Accurate (vs Precise) is to Analyze by an Independent Method

| Sample | AMMS-III | Prototype ASRS* | IC-MS (99/101) |
|--------|-----------|-----------------|----------------|
| A | 1.5 | 1.66 | 1.8/1.75 |
| B | 2.0 | 1.44 | 2.2/2.1 |
| C | ND (<0.5) | NA | 0.6/0.6 |
| D | 1.58 | 1.84 | 1.7/1.75 |
| E | ND (<0.5) | NA | <0.05/<0.1 |
| F | 3.39 | NA | 2.9/3.1 |
| G | ND (<0.5) | NA | 0.1/<0.1 |
| H | 0.76 | NA | 1.2/1.35 |
| I | ND (<0.5) | NA | 0.4/0.5 |

* ASRS ULTRA-II performance degraded at low level before analysis could be completed.

An Inter-laboratory Comparison of Blind Unknown Low Level Samples by Method 314 with No Modifications Shows Good Agreement

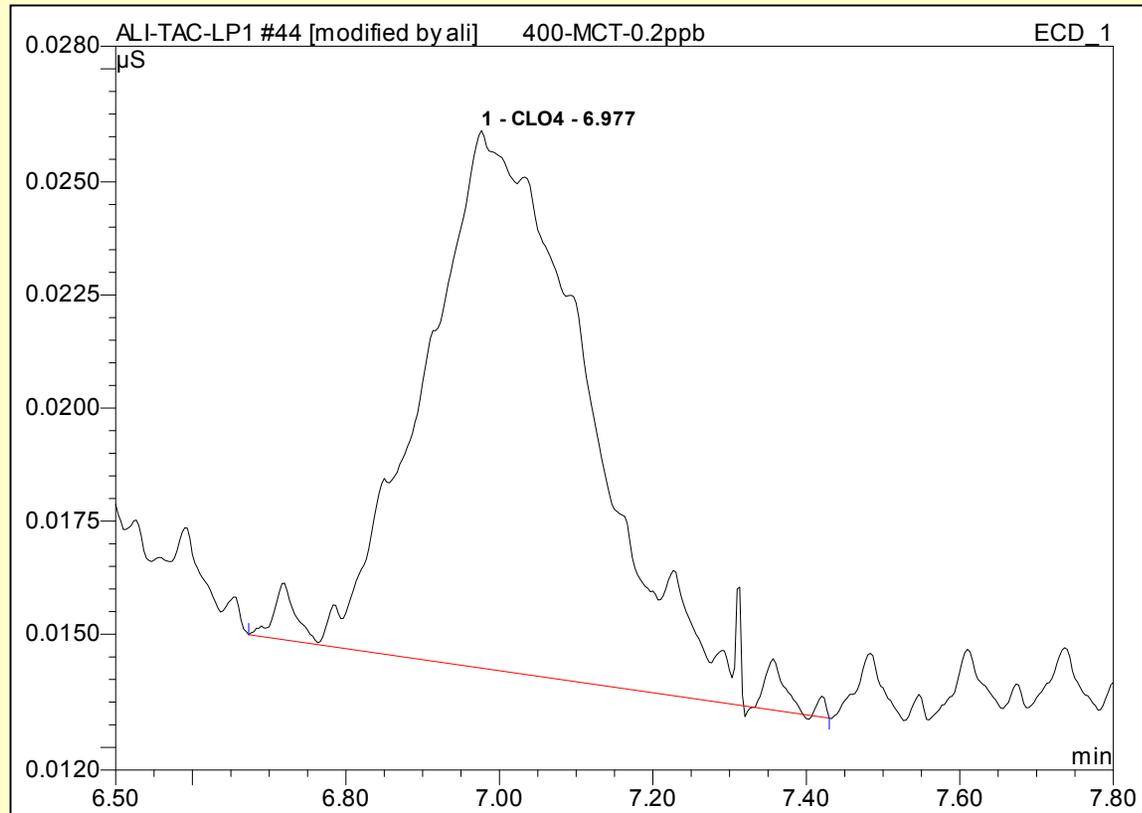
| | Lab 1- AMMS III | Lab 2- ASRS Ultra |
|----|--------------------|----------------------|
| #1 | 0.89 | 0.80 |
| #2 | 1.06 | 1.02 |
| #3 | 0.89 | 0.83 |
| #4 | 1.13 | 0.83 |
| #5 | 0.84 | 0.88 |

So how can we use IC reliably at sub ppb.

The approach is still the same:

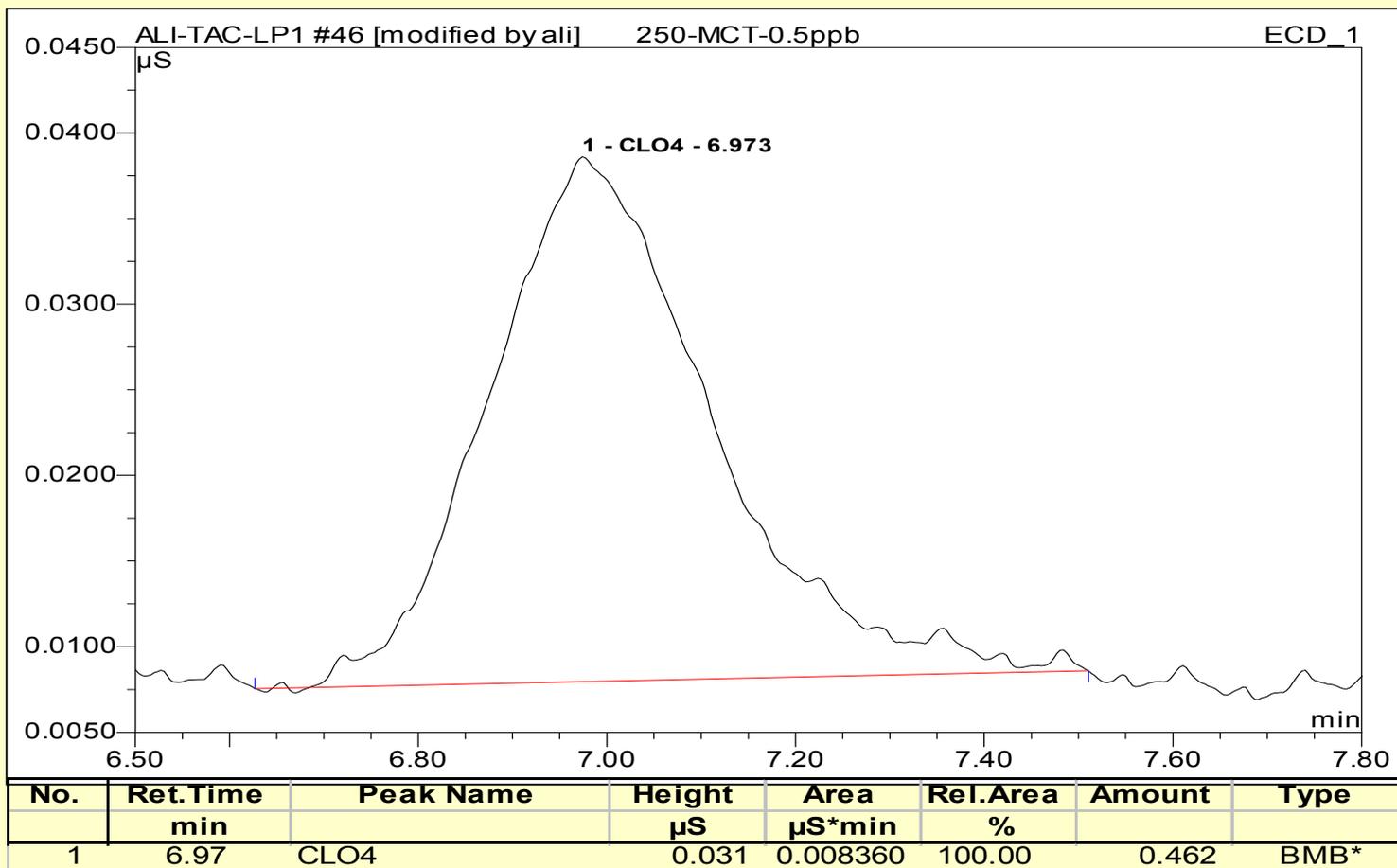
1. Injecting a larger sample or preconcentration.
2. Reducing the back ground on line or off line described by EPA 314.0.
3. Reducing the supressor noise.

By using two channels, IC can achieve 0.2-0.5 ppb reliably on high ionic strength samples.



| No. | Ret.Time min | Peak Name | Height μS | Area μS*min | Rel.Area % | Amount | Type |
|-----|-----------------|-----------|--------------|----------------|---------------|--------|------|
| 1 | 6.98 | CLO4 | 0.012 | 0.003021 | 28.52 | 0.157 | BMB* |

Chromatogram for a 0.5ppb perchlorate in 250 ppm Cl, SO₄, NO₃ and carbonate.



Semi MDL study in synthetic samples. Please note no fluctuation in RT.

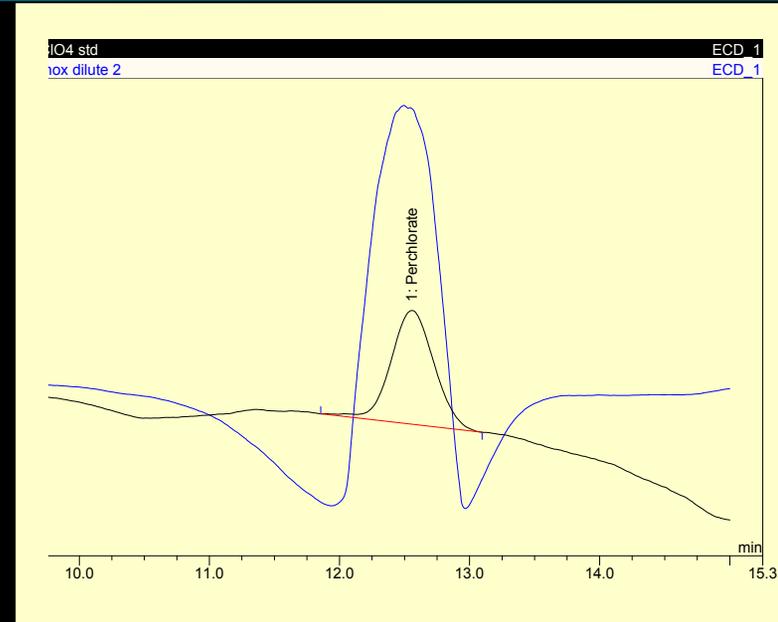
Replicate of analysis of 0.5ppb in 50-250ppm synthetic ionic strength.

| | Replicate | RT | Conc. | | | |
|--------|-----------|----------|----------|--|--|--|
| 50ppm | 1 | 7.06 | 0.44 | | | |
| 100ppm | 2 | 6.97 | 0.4661 | | | |
| 150ppm | 3 | 7.03 | 0.3502 | | | |
| 250ppm | 4 | 7.09 | 0.4538 | | | |
| 250ppm | 5 | 7 | 0.3239 | | | |
| 250ppm | 6 | 6.973 | 0.4623 | | | |
| 250ppm | 7 | 6.977 | 0.3325 | | | |
| | | | | | | |
| Avg. | | 7.014286 | 0.404114 | | | |
| SD | | 0.047134 | 0.065133 | | | |
| %RSD | | 0.671965 | 16.1175 | | | |
| MDL | | | 0.204518 | | | |

There are Interfering Substances

-e.g. Alconox..

Like any analytical method, be aware of the potential for interference, but this one will be unlikely in drinking water.



Most reported chromatographic interferences are from waste sites

So How Close Are We to Routine Sub-ppb Measurements by 314?

- ◆ Using two channels and two concentrators - The primary concentrator being a Cryptand and the second one being a TAC-LP1
- ◆ Using AMMS II Suppressor between the two concentrators
- ◆ Injecting large sample 5-10ml.

Conclusion

- ◆ Sub ppb measurements of ClO_4 using method 314 with very limited modifications are realistic.
- ◆ Using two channels can provide a confirmation tool at sub ppb. And it can also be used to reduce the back-ground TDS effect on the perchlorate analysis up to a point.

Right- Channel one

Left Channel two

