Measurement of Perchlorate in Water Using an Oxygen-18 Enriched Isotope Standard and Ion Chromatography Mass Spectrometric Detection

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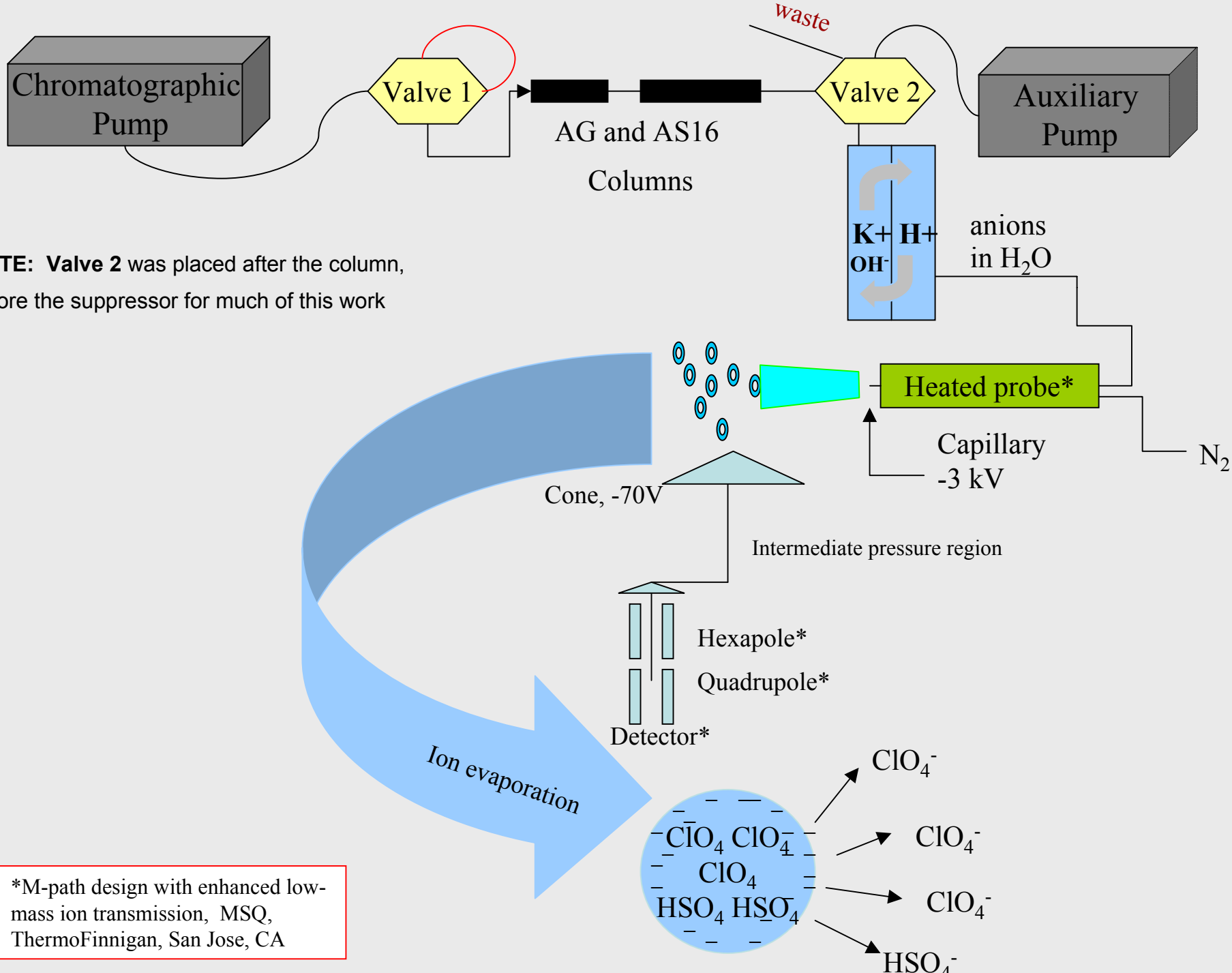
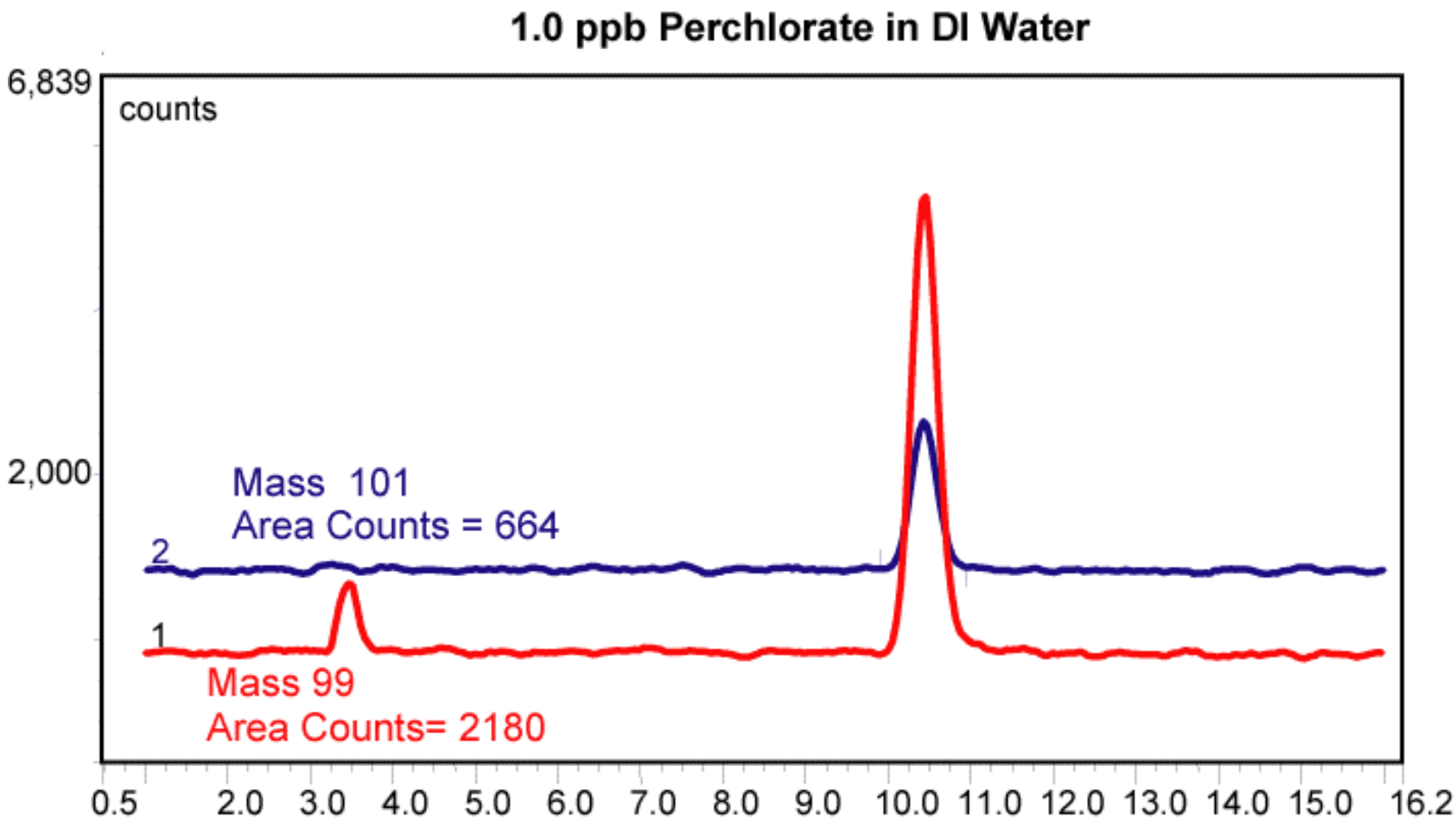
IC-MS Conditions

Ion Chromatograph	Dionex, Sunnyvale, CA
Mobile Phase	45 mM KOH
Separator Column	Dionex AS16, 2mm
Flow Rate	0.3 mL/min
Conductivity Suppressor and Current	ASRS Ultra II, 45 mA
Column Temperature	30 ^{o}C
Auxiliary Pump Flow rate	0.3 mL/min
Injection Loop Size	200 microliters
Mass Spectrometer	MSQ with Enhanced Low Mass Option, ThermoFinnigan, San Jose, CA
Capillary Voltage	-3 kV
Sampling Cone Voltage	-70 V
Probe Temperature	400 ^{o}C
Nitrogen pressure	80 psi
Masses 99,101	Select Ion Monitoring
Mass Scan Range	0.3 amu
Dwell Time	0.75 sec

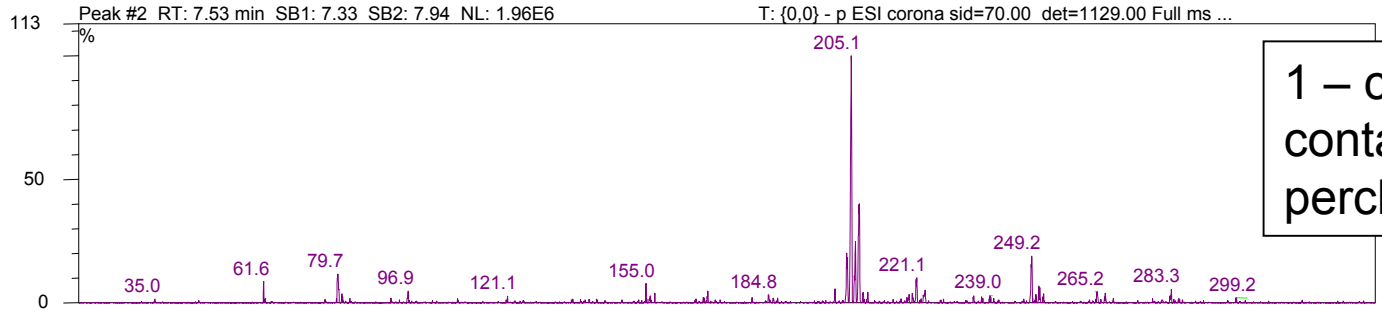


NOTE: Valve 2 was placed after the column, before the suppressor for much of this work

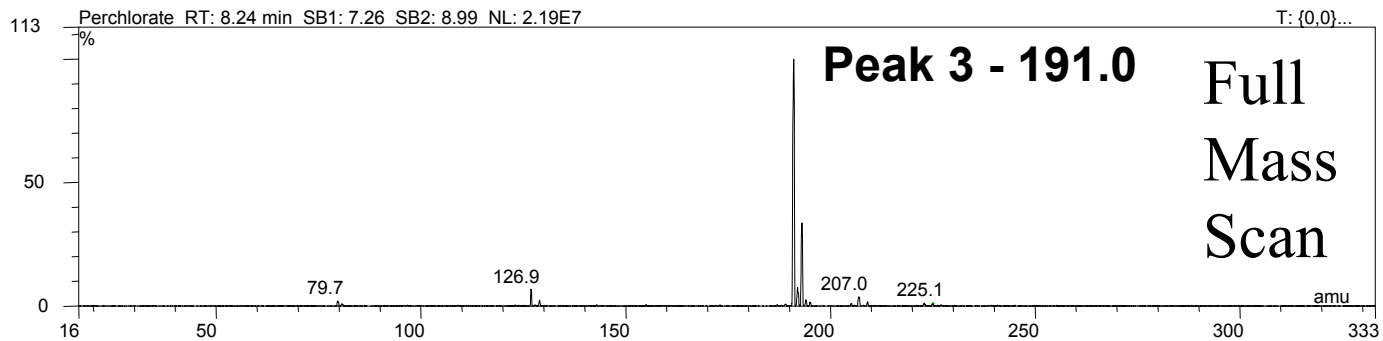
*M-path design with enhanced low-mass ion transmission, MSQ, ThermoFinnigan, San Jose, CA

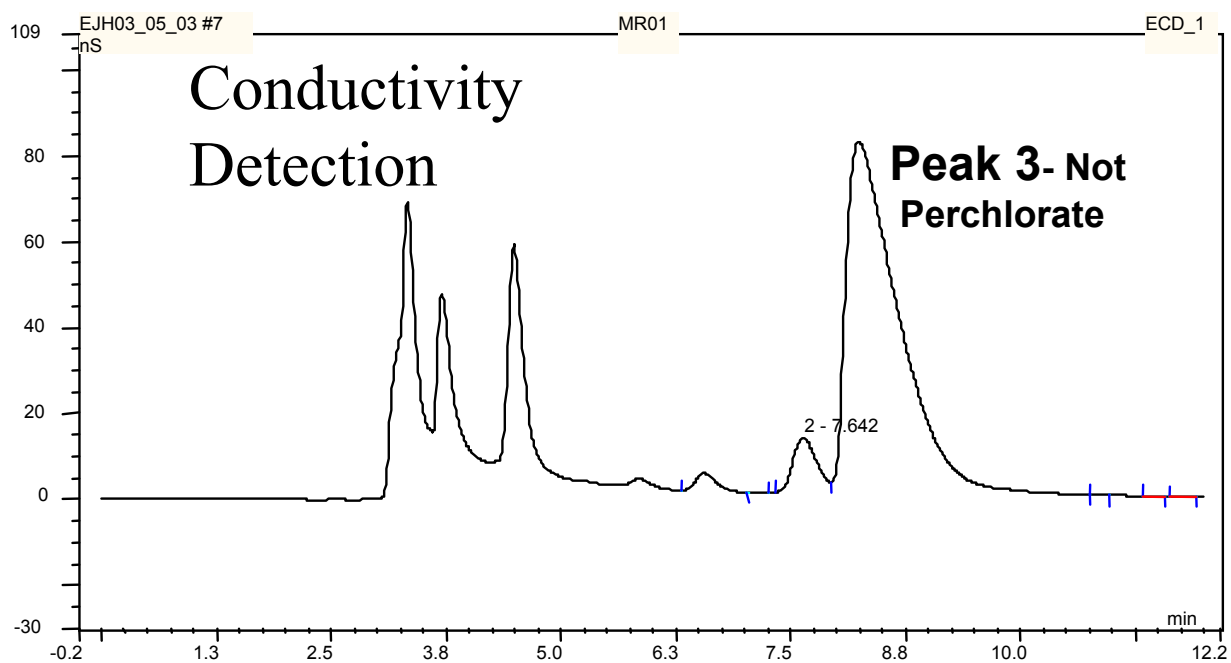

1.0 ppb Perchlorate in DI Water
6,839
counts
2,000
Mass 101
Area Counts = 664
2
1
Mass 99
Area Counts= 2180
0.5
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
16.2

A Good Thing!



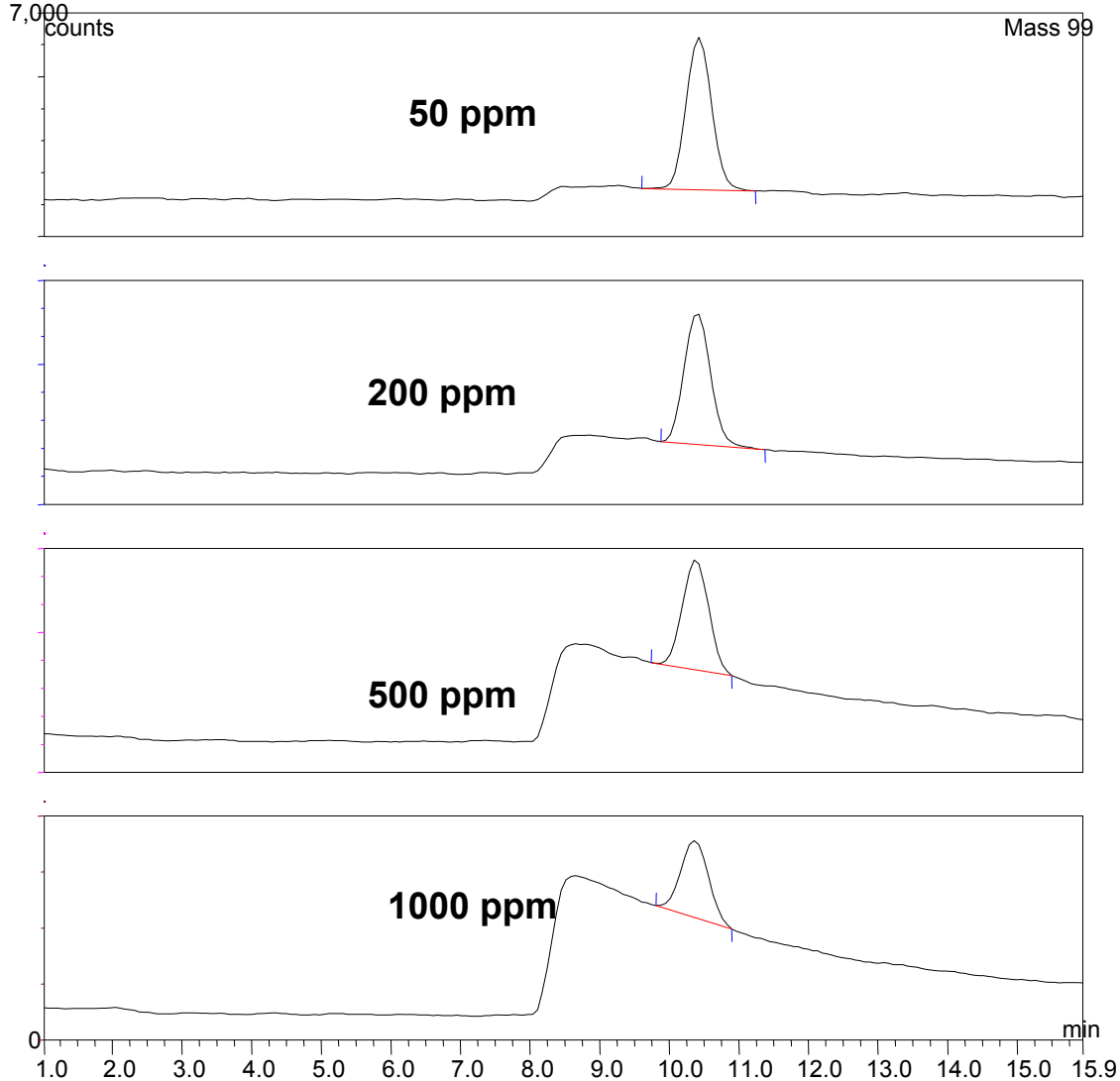
1 – co-elution of a contaminant with perchlorate





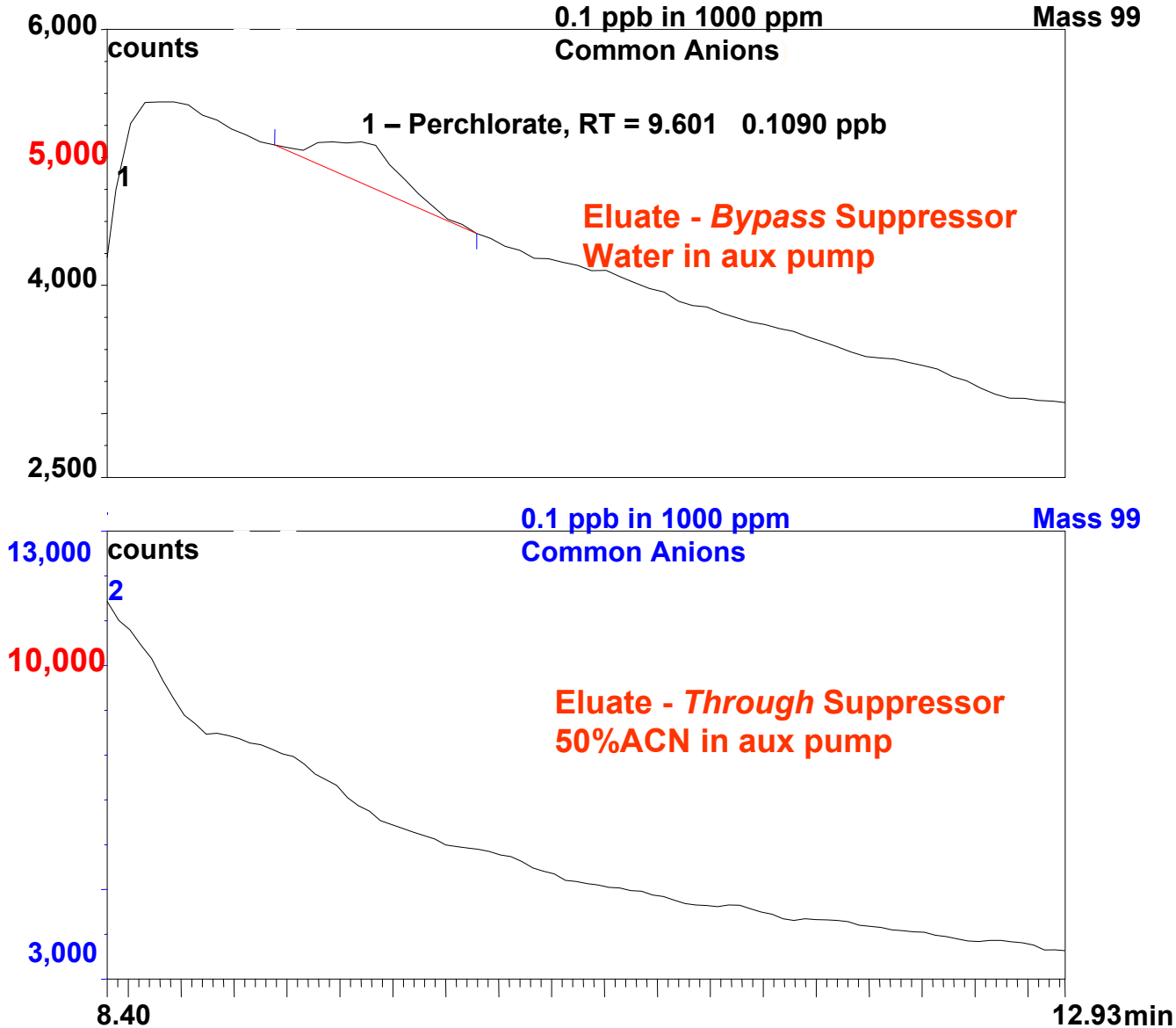
Region 9 Groundwater Sample

1.0 ppb Perchlorate in Varying Concentrations of Cl^-, SO_4^{2-} and CO_3^{2-}



2 – noise increases

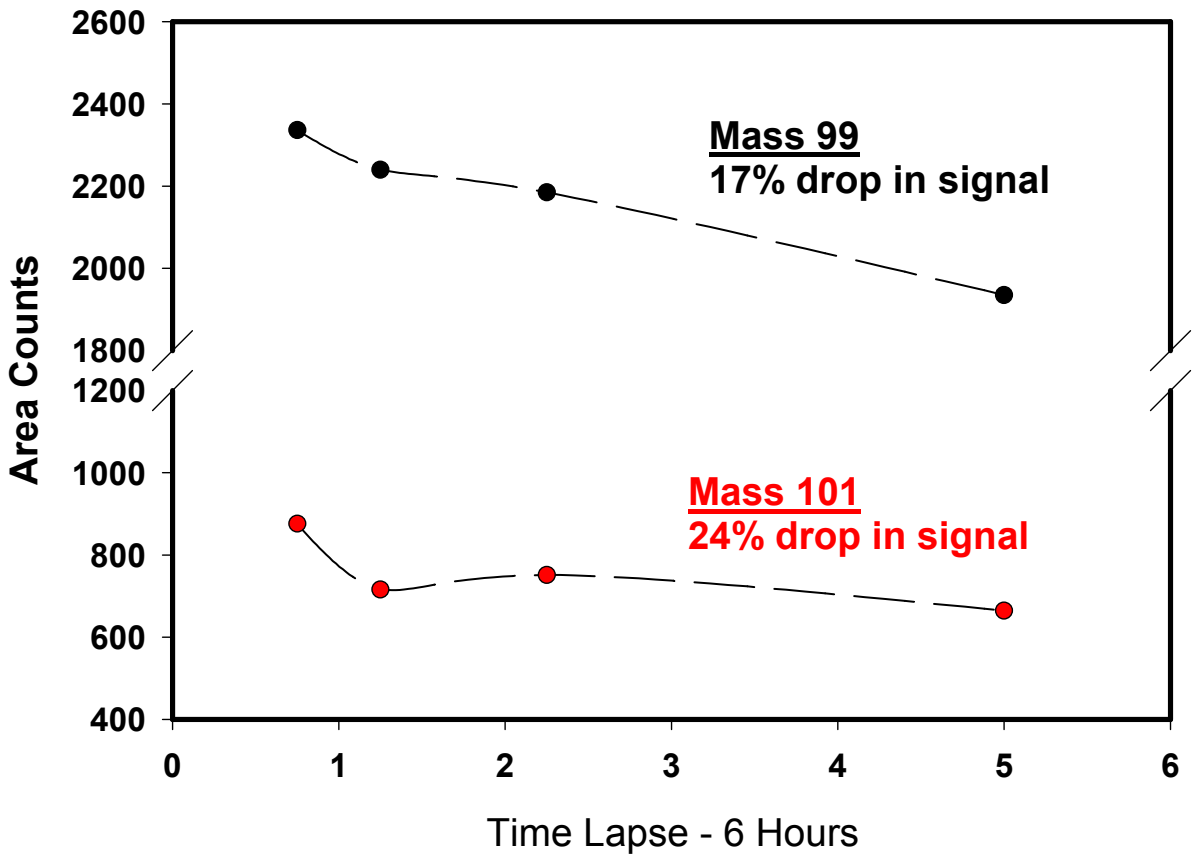
NOTE: Matrix cut to bypass MS until 2 minutes before ClO_4- elutes



*In both cases, the eluate is diverted from the mass spec until two minutes prior to the elution of perchlorate

Response of 1 ppb Check Standard Over Time

(after analyses high ionic matrices)

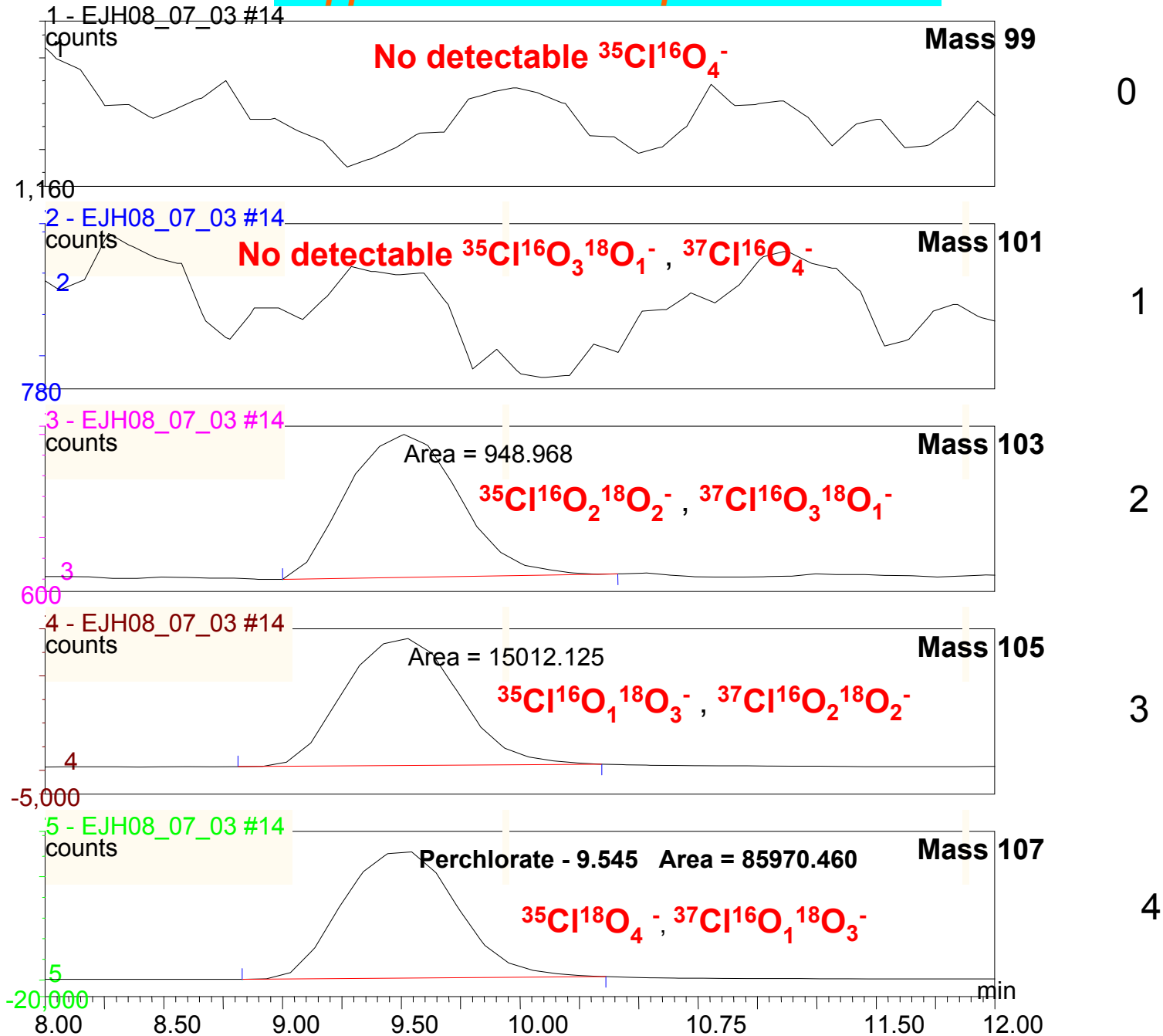


3 – loss of signal due to cone fouling

Enriched Isotope Standard

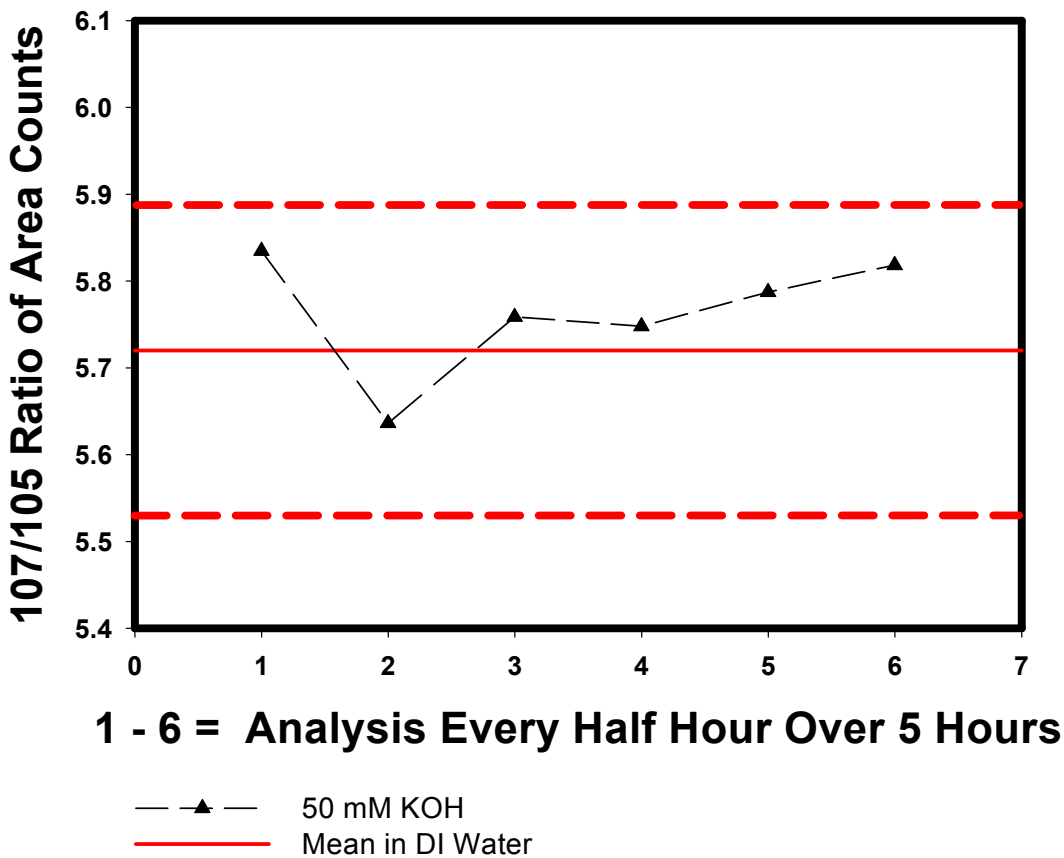
- *Source* – Isotec, Inc., Miamisburg, Ohio. (www.isotec.com) 1-800-448-9760)
- *Preparation* - synthesis of $NaClO_4$ using a starting material that was 90% O-18 .
- The $NaClO_4$ ***will contain*** some O-16.
- Measured O-16-containing ClO_4^- was less than expected . ☺
- We are monitoring enriched isotope for oxygen exchange in water over time.

40 ppb Enriched Isotope in DI Water

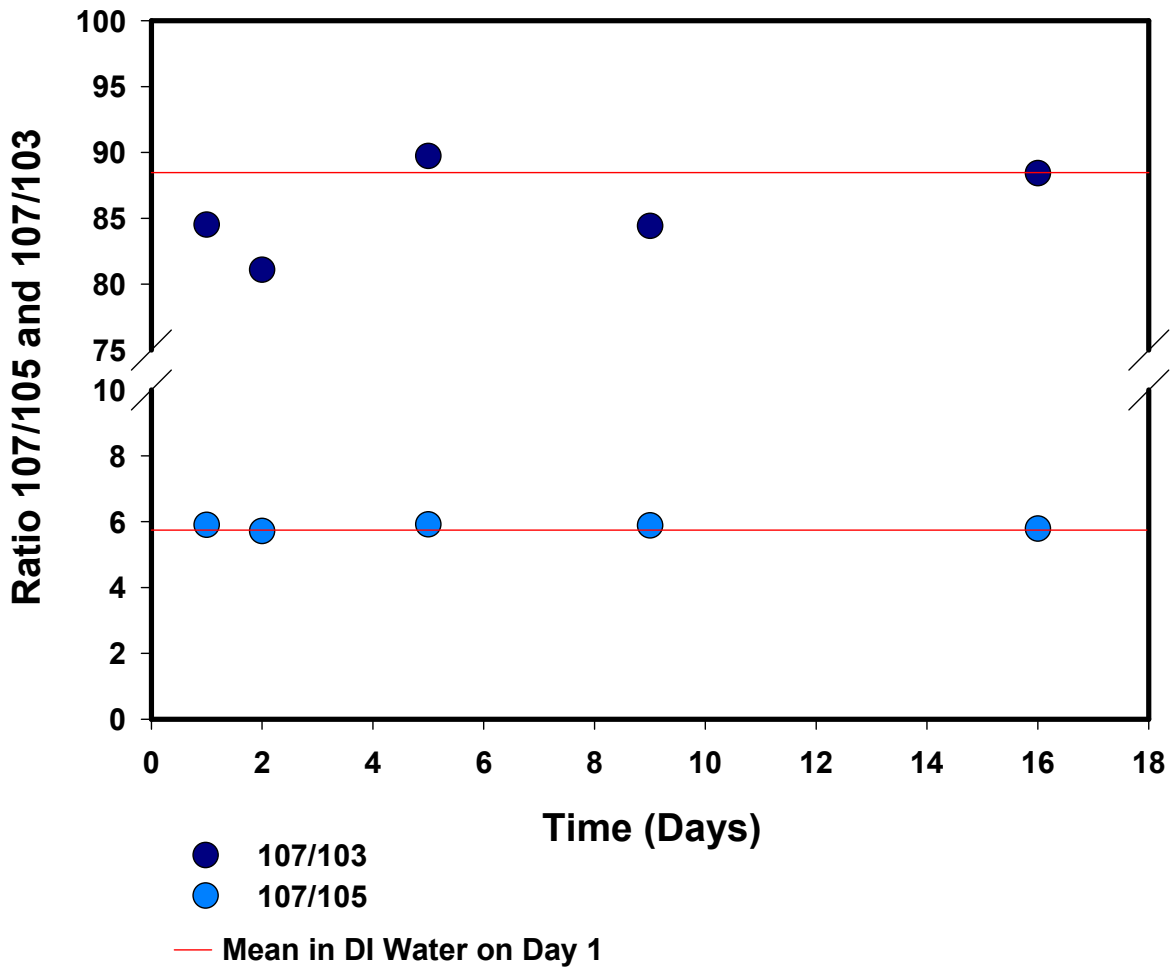


Stability of 50 ppb Enriched Isotope in Hydroxide

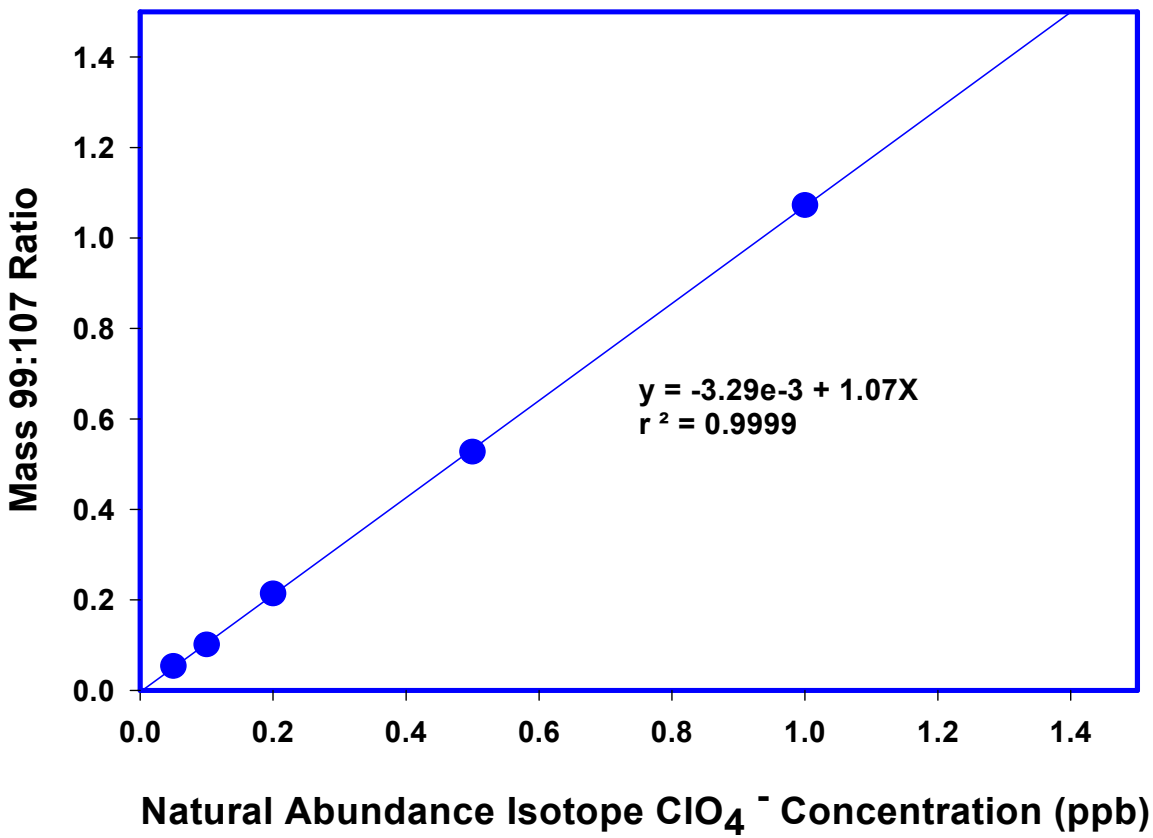
$^{35}Cl^{18}O_4^-$, $^{37}Cl^{18}O_3{}^{16}O^-$ / $^{35}Cl^{18}O_3{}^{16}O^-$, $^{37}Cl^{18}O_2{}^{16}O_2^-$

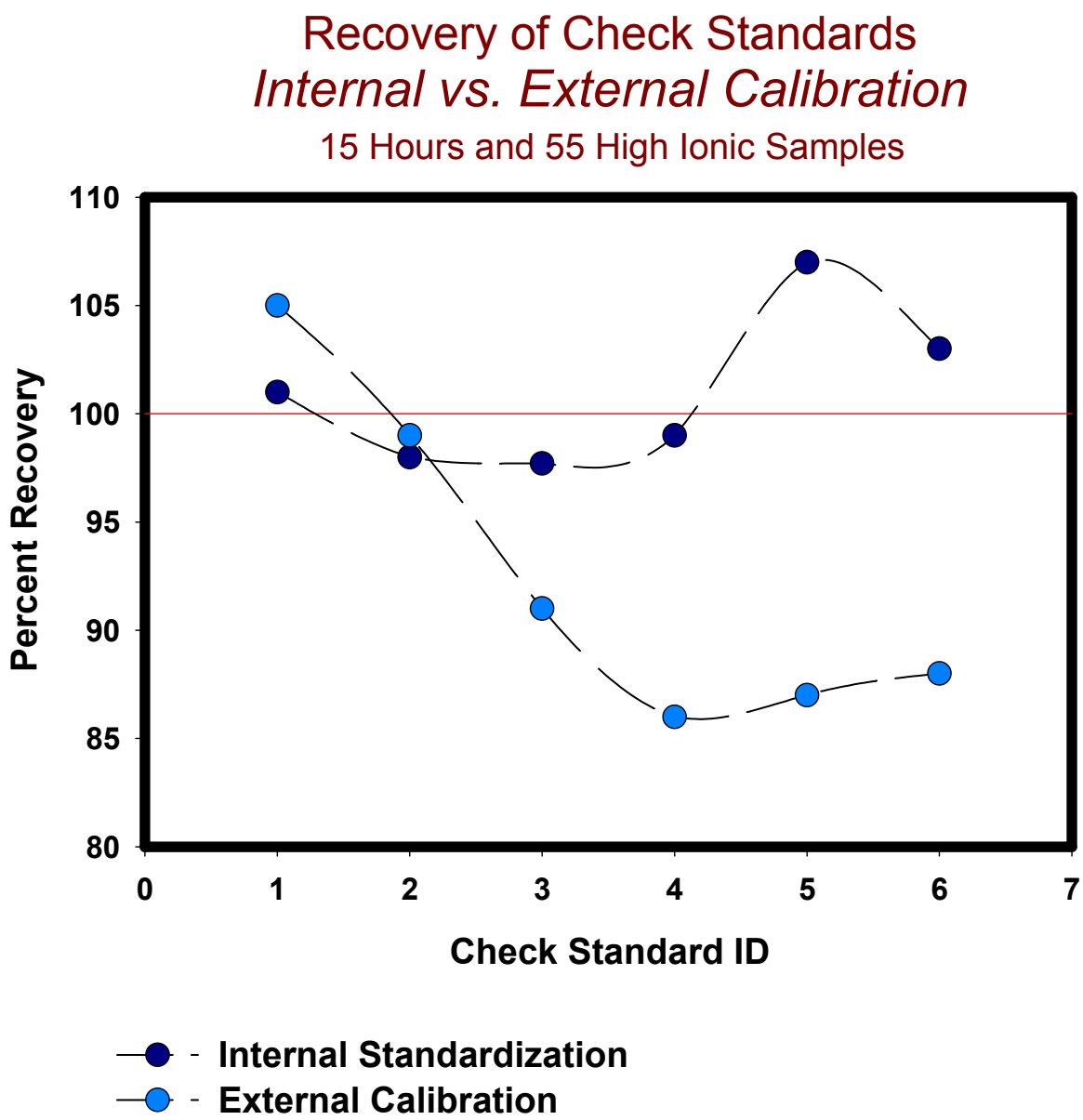


Stability of Enriched Isotope in Tap Water



Enriched ClO_4^- Isotope Internal Standard Calibration
Mass 99:107




Recovery of Check Standards
Internal vs. External Calibration
15 Hours and 55 High Ionic Samples
Percent Recovery
110
105
100
95
90
85
80
0
1
2
3
4
5
6
7
Check Standard ID
Internal Standardization
External Calibration

Method Detection Limits Using Enriched Isotope Internal Standardization

Matrix	SIM Mass	Spike Level (ppb)	Average %Recovery	% RSD	MDL (ppb)
DI Water	99	0.05	102	9.7	0.015
	101	0.05	94	22	0.034
200 ppm*	99	0.1	97	15.4	0.047
	101	0.1	92	10.1	0.029
500 ppm*	99	0.1	90	17.5	0.050
	101	0.1	97	18.6	0.057
1000 ppm**	99	0.1	0	**	**
	101	0.1	108	15.5	0.053

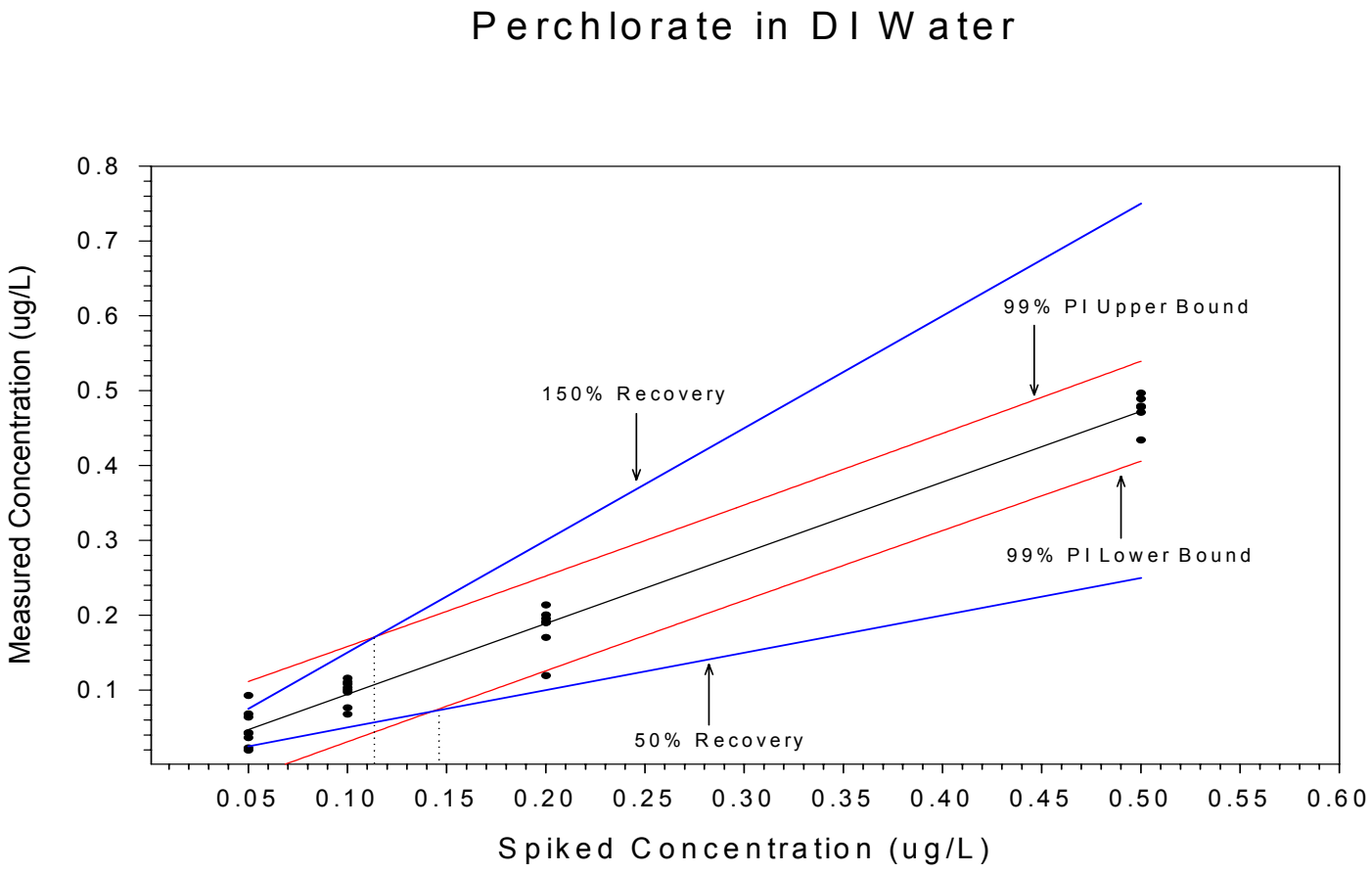
*ppm each of chloride, sulfate and carbonate

** high background caused by HSO_4^- resulted in no peak detected at mass 99. This can be avoided by bypassing suppressor and MS until two minutes prior to elution of perchlorate

Determination of the LCMRL

- Analysis of replicate samples at several concentrations
  - Typically seven replicates, four concentrations
  - Concentrations range from the Method Detection Limit (MDL) to the Practical Quantitation Limit (PQL)
- Plot measured vs. known concentration
- Linear regression of measured vs. known concentration
  - Include 99% prediction interval of regression line
  - Include 50% and 150% recovery lines
- LCMRL is the lowest concentration where both the upper and lower bound of the 99% prediction interval are contained within the 50% and 150% recovery lines

Example LCMRL Determination



LCMRL = 0.15 ug/L

Analysis of Raw Ground Waters

Using Internal Standardization

Ground Water ID	Perchlorate Conc (ppb)	%Recovery of 1ppb Spike
FF3-1 (548uS)	0.11	101
FF3-2 (664uS) (diluted 1:20)	20.45	93
FF3-4 (889uS)	0.50	107

Perchlorate in Water Before and After Disinfection

Water Type	Concentration ClO_4^- (ppb)	Disinfection/Treatment
Raw River Water	**2.4**	None *(1 ppb spike Recovery = 84%)*
Stage 1	**1.2**	Settling,coagulation,sand filtration
Stage 2	**0.6**	Granular activated carbon, chlorination

Summary IC-Suppressed Conductivity ESI-MS Method

- ***Low-level linear calibration*** **from 0.01 - 1.0 ppb, $R^2 \geq 0.999$.**
- ***Method detection limits (MDLs)*** **in DI *and* HIW (up to 1000 ppm common anions sulfate, chloride and carbonate) from 0.02 - 0.06 ppb whether using internal or external calibration.**
- ***Precision*** **replicate injections at 1 ppb, <10% RSD.**
- ***Accuracy*** **$\pm$5% of certified reference standard in deionized water.**
- ***Ruggedness*** **percent recovery of 0.5 or 1.0 ppb check standards analyzed periodically over a day of continuous analysis of high ionic matrices**
  - **external calibration (~15% drop in recovery of check standards over time after analyses of HIW samples)**
  - **internal standardization (no such drop)**
  - **Matrix diversion essential.**
  - **Bypassing the conductivity suppressor, as well as the MS, is preferred.**

Future Directions
(methods with MRLs < 0.3 ppb)

- IC-Conductivity Method

- Confirmational column
- Trapping column
- Post-column derivatization

- Mass Spectrometric Methods

- IC-suppressed conductivity ESI-MS
- IC-ESI-MS/MS using volatile mobile phases

Acknowledgements

- Herb Wagner, Shaw, Inc.
- Steve Wendelken, Shaw, Inc.
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The End

Recoveries in Tap and Ground Waters

Sample ID*	Background Concentration (ppb)**	Percent Recovery			Average % Recovery
		Mass 99	Mass 101	Mass 83***	
Ohio Tap	0.29	94	99	99	97
Kentucky Tap	0.35	97	77	111	95
Indiana Tap	0.52	100	84	102	95
Site 25	0.38	110	113	103	109
Site 4	ND - problem matrix	52	65	75	64

*Tap spiked at 1 ppb, ground water spiked at 4 ppb

**Based on primary mass 99

***In-source collisionally activated dissociation (CAD) at -100V cone voltage