

# ANALYSIS OF PERCHLORATE IN DRINKING WATER, GROUND WATER, SALINE WATER, SOIL, AND BIOTA BY LC/MSD

## Author

Kham Lin  
K'(Prime) Technologies  
Unit 105, 90 Freeport Blvd. NE  
Calgary, AB T3J 5J9  
Canada  
E-mail: sales@kprime.net

## Abstract

**A new method has been developed and validated for the determination of perchlorate in drinking water, soil, biota, ground water, and saline water using liquid chromatography / mass spectrometry (LC/MS) without sample pretreatment by K'(Prime) Technologies, Inc. Mass spectrometry is used to monitor perchlorate at mass 83. The 83/85 isotopic ratio is used for additional identification of perchlorate along with an internal standard containing Oxygen-18. The method can achieve a method detection limit in aqueous samples of 0.05 ug/L and can easily quantify Perchlorate at 0.2 ug/L in any aqueous environmental sample matrix. This method uses simple determinative techniques available to normal LC/MS technologies and does not require any instrumentation additions or systematic pretreatment of samples. Inadequacies of current USEPA Method 314.0 caused by matrix interference, high dissolved solids and high conductivity are eliminated and confirmation of perchlorate is accomplished with this new method.**

## Introduction

Perchlorate can occur naturally or as a manmade by-product. It is of analytical interest, as perchlorate is known to disrupt iodine absorbance by the thyroid gland. Iodine is an essential component in thyroid hormones, and additionally perchlorate is thought to cause thyroid tumors.

Perchlorate has been produced in 39 states and has been found in drinking water in 18 states. Prior to 1997 perchlorate could not be detected at less than 400 ppb. A new method developed by the California Department of Health Services <sup>(1)</sup> in 1997 could detect perchlorate to 4ppb in drinking water. Perchlorate was listed by the USEPA on the "Contaminant Candidate List" for consideration for possible regulation in 1998.

Recent studies have detected perchlorate in drinking water in major metropolitan areas and ground water associated with the production of solid rocket propellant. Even more recent is the discovery of perchlorate in lettuce samples that were irrigated with Colorado River water. These and other recent events have increased the need for the low detection of Perchlorate in matrices such as ground water, saline water, soil and plant material. This level of concern about perchlorate detection in matrices other than drinking water has motivated instrument manufacturer, academia and commercial laboratories to develop methods for analyzing perchlorate in difficult matrices.

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(Continued..) In 1999 the USEPA<sup>(2)</sup> published method 314.0 designed for drinking water at or below 4 ppb and required drinking water monitoring for perchlorate under the Unregulated Contaminant Monitoring Rule (UCMR). The current published method, USEPA 314.0, was developed for drinking water and is sufficient to detect perchlorate at 1 to 4 ppb. The current method is based on Ion Chromatography with conductivity detection. Method interferences include contaminants in the reagent water, reagents, glassware, and other sample processing apparatus leading to discrete artifacts or elevated baseline in ion chromatograms. These interferences can lead to false positive results for the target analyte as well as increasing detection limits as a consequence of elevated baseline noise. Sample matrices with high concentrations of common anions such as chloride, sulfate, and carbonate can make the analysis problematic by destabilizing the baseline. Furthermore highly ionic samples or dissolved solids can cause column degradation.

A new method for the detection and confirmation of perchlorate has been developed. This new method utilizes reverse phase liquid chromatography to separate perchlorate from interferences and mass spectrometry to confirm and quantify. This new method is of significant importance because it will enable the detection of perchlorate in drinking water, ground water, saline water, soil and biota samples at low part per trillion levels (ppt) with better scientific confirmation than current method USEPA 314.0.

## Method and Experimental Design

### *Instrumentation*

An Agilent 1100 LC/MSD system was utilized for this method. This method uses simple determinative techniques available to normal LC/MS technologies and does not require any instrumentation additions or systematic pretreatment of samples. The analysis is accomplished in under thirteen minutes and can process up to 20 samples in an eight hour sequence with all appropriate quality control and additional perchlorate identification by mass spectrometry.

Agilent 1100 LC/MSD system consisting of:

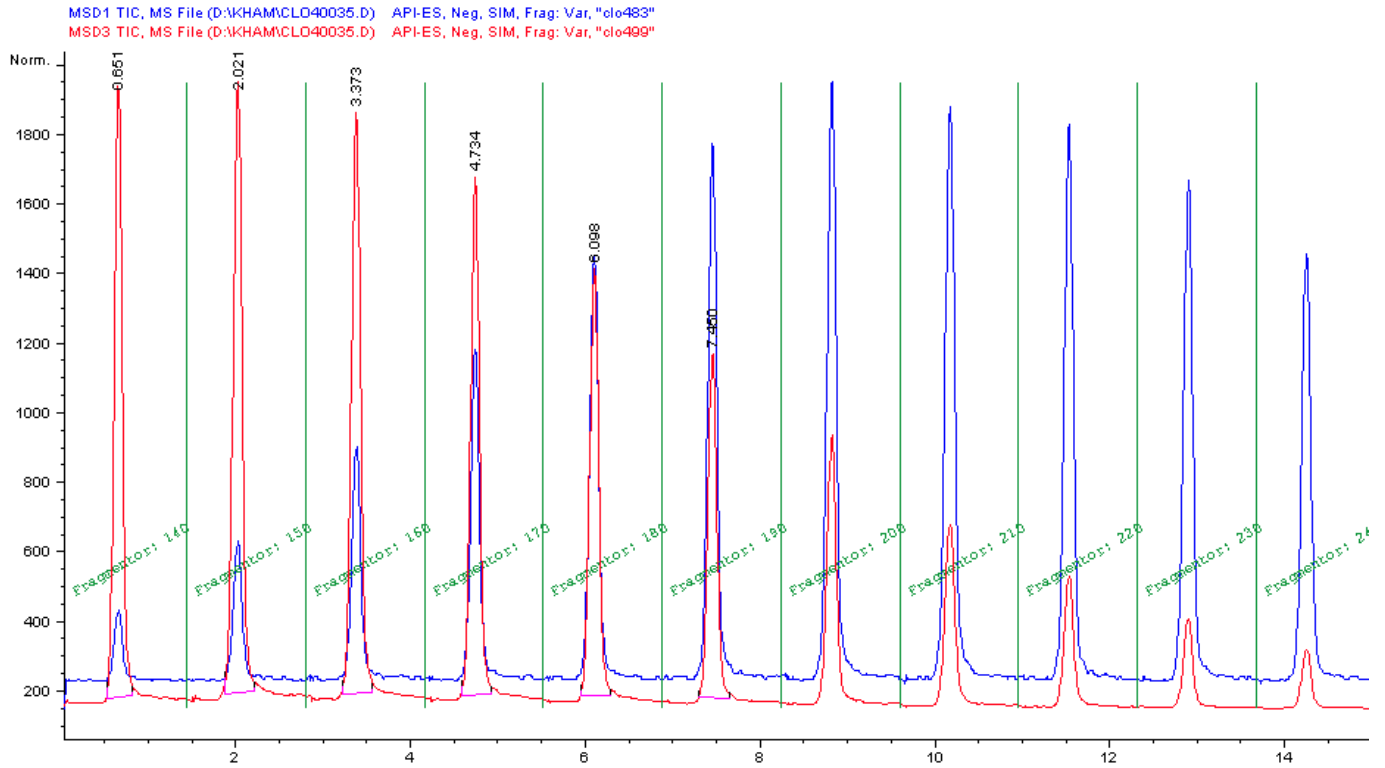
- Binary Pump G1312A
- Micro-degasse, G1379A
- Autosampler G1313A
- Column Compartment G1316A
- 1100 LC/MSD G2708DA
- Agilent LC/MSD Chemstation G2710AA

### Conditions

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Column:	K'(Prime) Technologies KP-RPPX series columns 4.0 x 250 mm
Pump Flow:	0.5 to 0.6 ml/min
Mobile Phase:	50% Eluent A, 50% Eluent B
Sample Volume:	5-100 ul
Column Temp:	35°C
LC/MSD setting:	SIM Mode (masses 83, 85, and 89 ), Fragmentor Voltage 200, Dry Gas 12L/min, and Cap Voltage 3000.

# Figure 1: Fragmentor setting optimization for Mass 83 by Flow Injection Analysis



03

## Reagents and Standards

Eluent was prepared with ASTM Type II water and acetonitrile (CAN).

**Eluent A:** 95% ACN and 5% water, with a small aliquot of acetic acid (approximately 0.1%).

**Eluent B:** 95% water, and 5% ACN, with a small aliquot of acetic acid (approximately 0.1%).

The solutions from the two bottles will be mixed at the instrument pump at 53% eluent A and 47% eluent B.

Standard concentrations used to calibrate were 0.2, 0.5, 1.0, 2.0, 5.0, and 10.0  $\mu\text{g/L}$ . The standards were prepared in a 50% ACN, and 0.1% acetic acid solution. The Internal Standard of Oxygen-18 labeled

perchlorate(O18LP) was at 5.0  $\mu\text{g/L}$ , and added to each standard and sample.

## Calibration and quality control

A minimum of six calibration standards was used for internal standard calibration. The standard curve for perchlorate was established by plotting the area for each standard/internal standard ratio against the concentration. The calibration was verified immediately after calibration by the analysis of an Initial Calibration Verification (ICV) Standard. The ICV was prepared from a separate source of perchlorate at 1.0  $\mu\text{g/L}$ .

Continuing Calibration Verification (CCV) standards were used for each analysis batch prior to conducting any analysis, every tenth sample, and at the end of the analysis sequence.

## Sample Preparation

04

**Water samples** were prepared by adding an aliquot of sample to a 15-mL disposable centrifuge tube. An appropriate aliquot of O18LP and glacial acetic acid was added to each sample. Each sample was filtered through a 0.45- $\mu$ m filter into an autosampler vial for analysis.

**Soil samples** were prepared by adding an aliquot of sample and 10 mL of ASTM Type II water to a 15-mL centrifuge tube. An appropriate aliquot of O18LP and glacial acetic acid was added to each sample. The mixture was vortexed, then sonicated for at least 10 minutes. If necessary, the sample was centrifuged. The extract was then filtered thru 0.45- $\mu$ m filter into an autosampler vial for analysis.

**Biota (Plant) samples** were prepared by using at least 10 grams of sample. The sample was ground through a hand-operated stainless steel grinder. 30 mL of ASTM Type II water is added to an aliquot of biota sample in a 50-mL centrifuge tube. An appropriate aliquot of O18LP and glacial acetic acid is added to each sample. The mixture was vortexed and left overnight, which allows for complete saturation of the sample. Prior to analysis, the sample is vortexed again, then centrifuged at 5000 rpm for 30 minutes. A portion of the supernatant was then drawn through an activated C18 column, which removes a large portion of organic contaminants. Supernatant is then filtered through a 0.45- $\mu$ m filter into an autosampler vial for analysis. The five matrices evaluated by this LC/MS method are presented in Table 1.

**Table 1: Matrix Description and Preparation**

<b>Drinking Water (DW)</b>	Laboratory Distilled Water Conductivity = 1 uS
<b>Soil</b>	Soil extracted with water
<b>Biota</b>	Grass Sample were homogenized, extracted with water and C-18 column cleanup
<b>Synthetic Ground Water (SGW)</b>	Laboratory Distilled Water with 1000 mg/l of chloride, sulfate, and carbonate. Conductivity = 7700 uS
<b>Great Salt Lake (GSL) Water</b>	Water taken from the Great Salt Lake and diluted 10x Conductivity = 21000 uS

05

## Experimental Design

### *Sensitivity*

Method Detection Limits (MDL) studies following the USEPA<sup>(3)</sup> procedure were analyzed to determine sensitivity of this LC/MS method. Practical Quantitation Limits (PQL) in aqueous, soil and biota samples were based of the DoD Quality System Manual<sup>(4)</sup> guidance.

### *Selectivity*

Mass spectrometry was used to monitor perchlorate at mass 83, which was achieved by the partial fragmentation of perchlorate to remove an oxygen atom. Using mass 83 eliminates known interference caused by sulfate at mass 99. Confirmation of perchlorate was obtained not only by retention time and mass but also by using the naturally occurring isotopic ratio of chlorine 35 to 37 of 3.065<sup>(8)</sup> to monitor the ratio of mass 83 and 85 from perchlorate. O18LB was used as an internal standard and added to each standard and sample. This internal standard was used for retention time confirmation, monitoring instrument performance, and internal standard calibration.

### *Precision and Bias*

Precision and Bias validation studies were performed using the guidance presented in the NELAC 2003 Standard<sup>(5)</sup> Chapter 5, appendix C3. Briefly, five matrices including drinking water, soil, biota, simulated ground water, and saline water were spiked with perchlorate and analyzed. Three different concentrations in each matrix were analyzed on three consecutive days. Additionally, all samples submitted for analysis having difficult matrices and/or positive detections by method USEPA 314.0 were confirmed by this new method. A proficiency-testing sample was also analyzed to assess bias of this method.

### *Robustness*

A known amount of O18LB was added to each sample and standard and monitored at mass 89 as internal standard. The use of internal standard calibration adds stability to the calibration and eliminates the need for monitoring transition of perchlorate from mass 99 to 83.

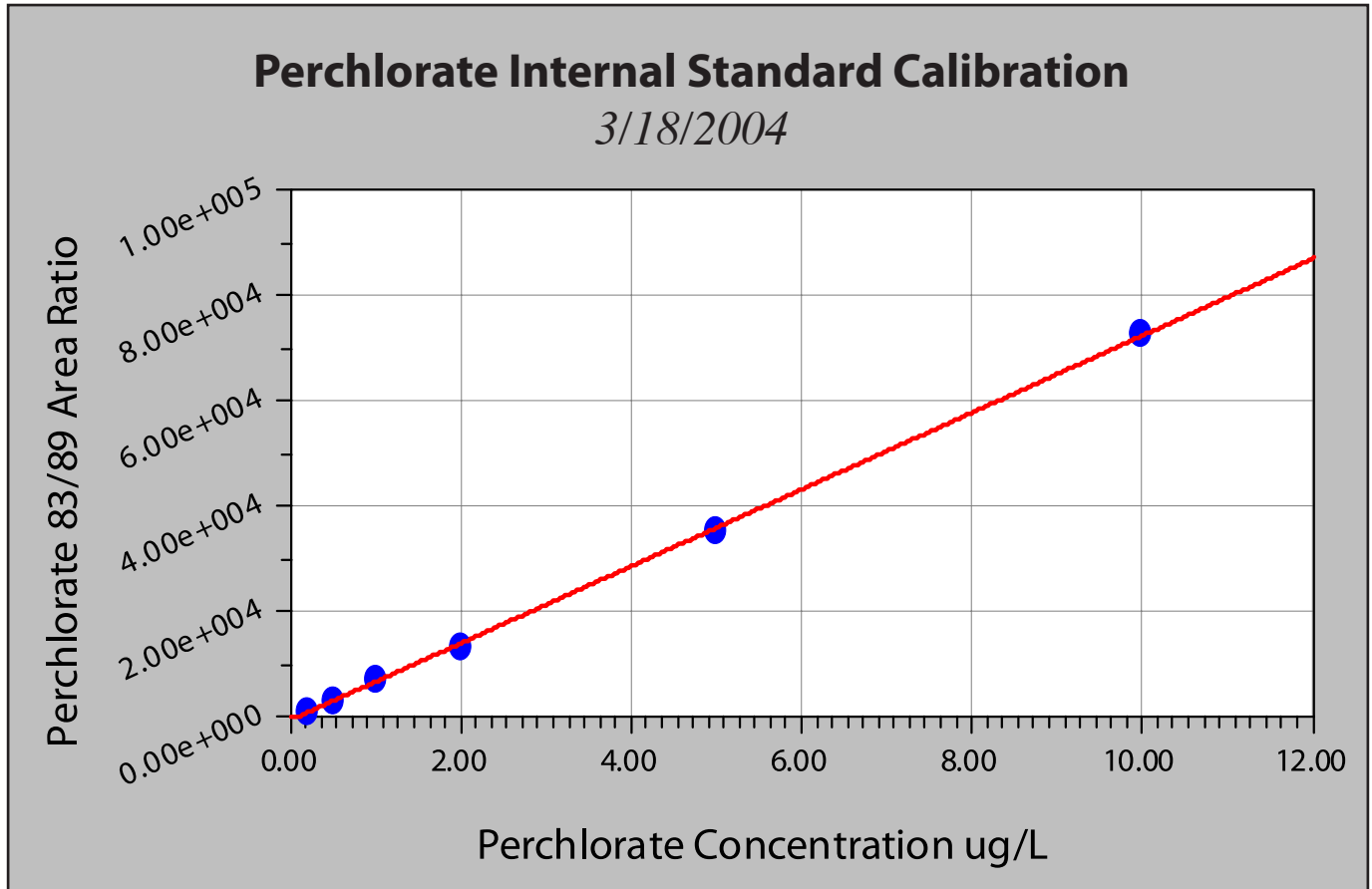
## Results and Discussion

### Calibration

The calibration curve used for this study is presented in Figure 2. Calibration acceptance criterion for the initial calibration curve is a

correlation coefficient of 0.995 or higher. ICV and CCV calibration verifications are presented in Table 10 and control limits were set at  $\pm 15\%$  from the true value.

06



Linear Fit:  $y=a+bx$

Standard Error: 563.0881871

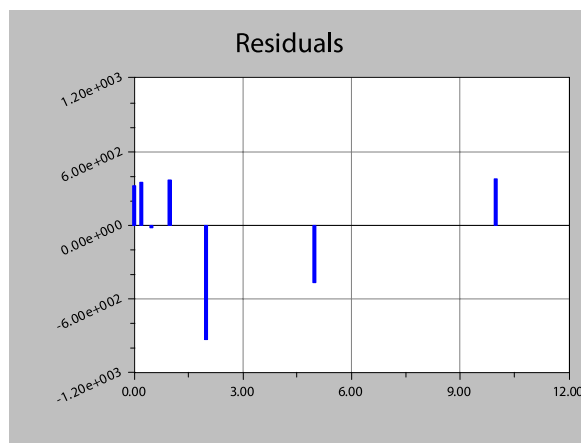
Correlation Coefficient: 0.9998145

Linear regression completed successfully. No weighting used.

## Residuals

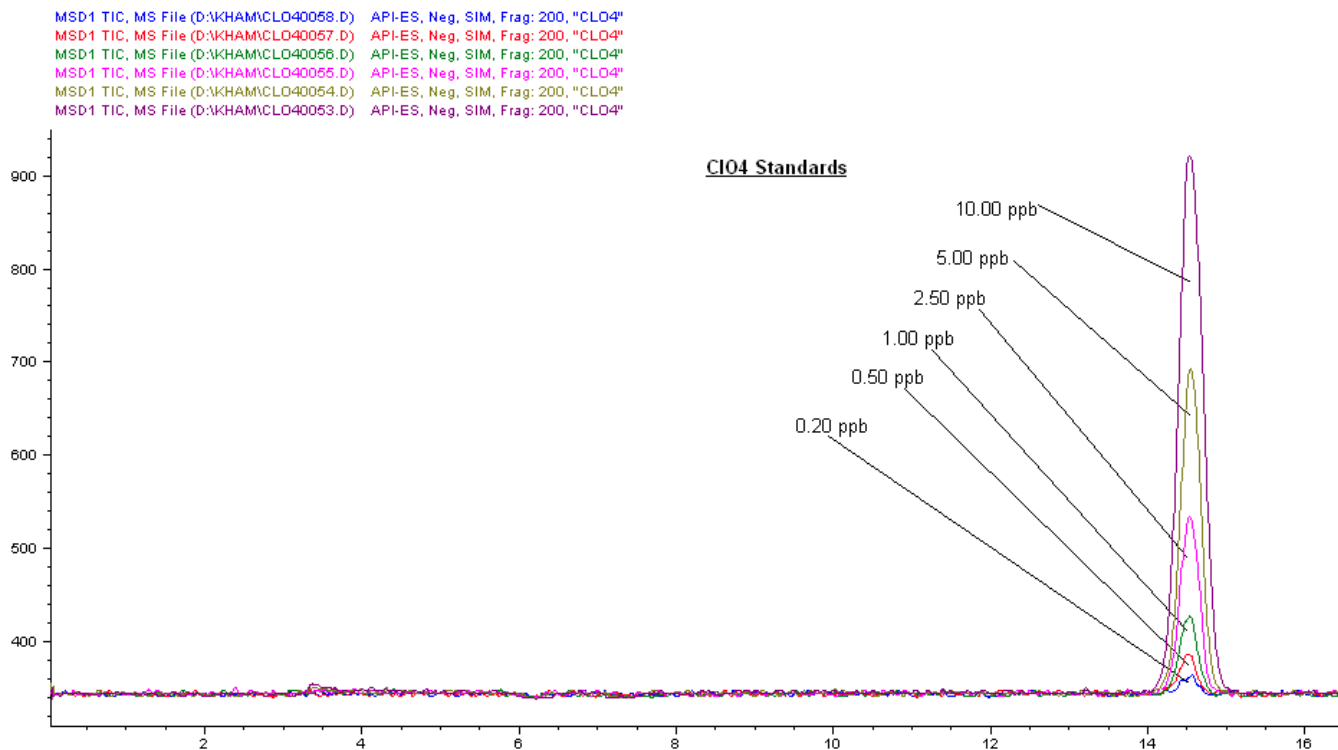
Concentration ug/L	Residual
0.20	347.4
0.50	-18.3
1.0	372.5
2.0	-928.1
5.0	-469.4
10.0	377.1

## Plot



07

Figure 3: Comparative chromatograms for 0.2 to 10.0ppb injections of standard



## Sensitivity

The MDLs for five matrices were calculated using the procedures specified by the USEPA<sup>(3)</sup>. Seven aliquots of a fortified spike or indigenous level were analyzed. The MDL is calculated by multiplying the standard deviation of results by 3.143 (t statistic). The drinking water (DW), simulated ground water (SGW) and soil samples were spiked with perchlorate while indigenous levels of perchlorate in biota and Greater Salt Lake water (GSL) were used to

calculate MDLs. The MDLs were additionally verified by analysis of a MDL verification sample for each matrix. This procedure is described in the DoD Quality System Manual<sup>(4)</sup>.

The PQL was set no less than the lowest calibration standard. Values below the PQL are reported with appropriate qualifiers. Additionally, the PQL was set at 3 to 5 times the MDL value. MDL and PQL data are presented in Table 2 and MDL Verification Results in Table 3.

**Table 2: MDL and PQL Determinations**

Matrix	n	Spiked Conc.	Mean Conc	Standard Deviation	%RSD	Ratio	MDL	PQL
Drinking Water	7	0.200 ug/L	0.200	0.0108	5.40%	5.89	0.0339	0.20
Soil	7	2.00 ug/Kg	2.26	0.258	11.4%	2.47	0.811	2.0
Biota*	7	4.49 ug/Kg	4.49	0.609	13.6%	2.34	1.92	6.0
SGW	7	0.200 ug/L	0.209	0.0257	12.3%	2.48	0.0807	0.20
GSL*	7	0.219 ug/L	0.219	0.0196	8.96%	3.55	0.0617	0.20

\* Indigenous levels in these matrices were used to calculate MDLs

SGW = Simulated Ground Water 1000mg/L of Chloride, Sulfate, Carbonate (Conductivity = 7700 uS)

GSL= Great Salt Lake Water diluted 10X (Conductivity = 21,000 uS)

**Table 3: MDL Verification Results**

Matrix	MDL Verification Concentration	MDL Verification Result
Drinking Water	0.10	0.11
Soil	1.0	1.0
Biota	2.5	1.6
SGW	0.10	0.11
GSL	0.11	0.12

SGW = Simulated Ground Water 1000mg/L of Chloride, Sulfate, Carbonate (Conductivity = 7700 uS)

GSL= Great Salt Lake Water diluted 10X (Conductivity = 21,000 uS)

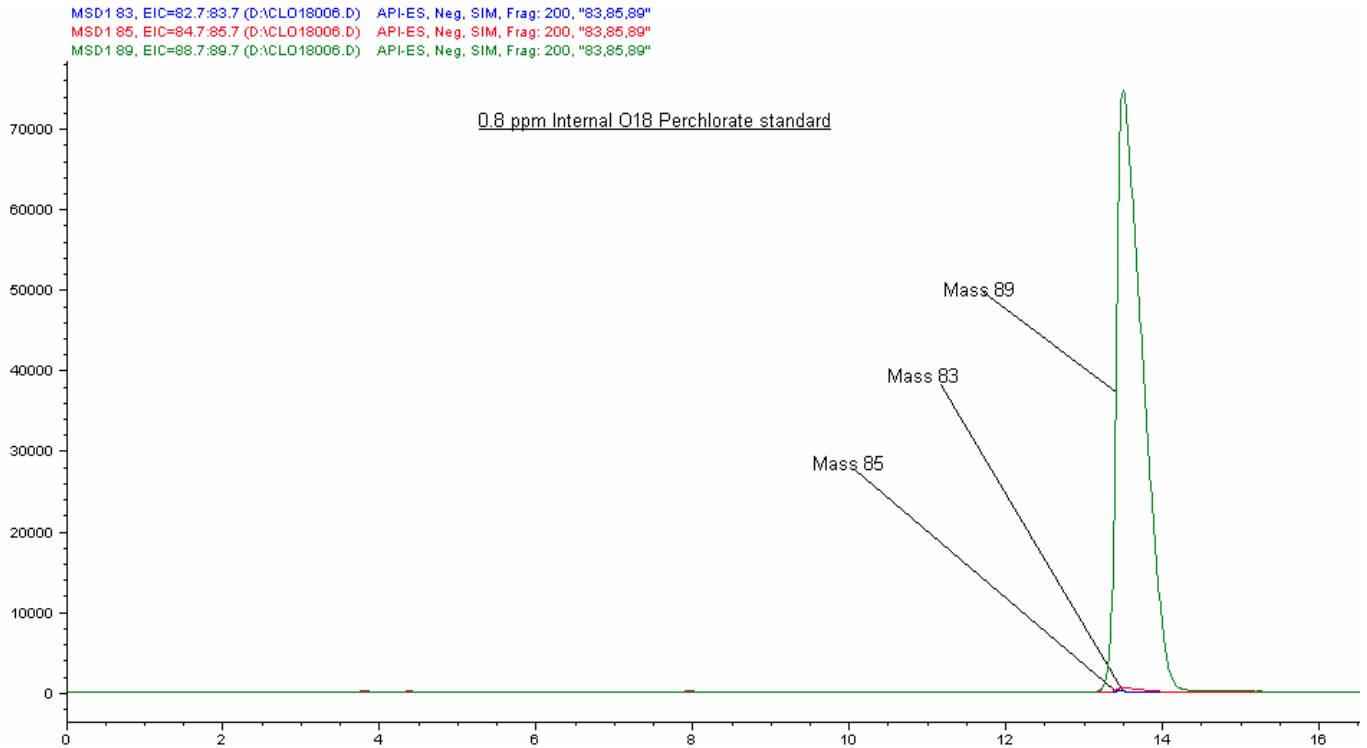
### *Selectivity*

Mass spectrometry was used to monitor perchlorate at masses 83 and 85. O18LP is

monitored at mass 89. Figures 4-8 show chromatograms of perchlorate at mass 83, 85 and 89 in each matrix.



Figure 4: O18 Internal Standard Chromatogram at 0.8 ppm



09

Figure 5: Drinking Water Sample Chromatogram at 0.5 ug/L

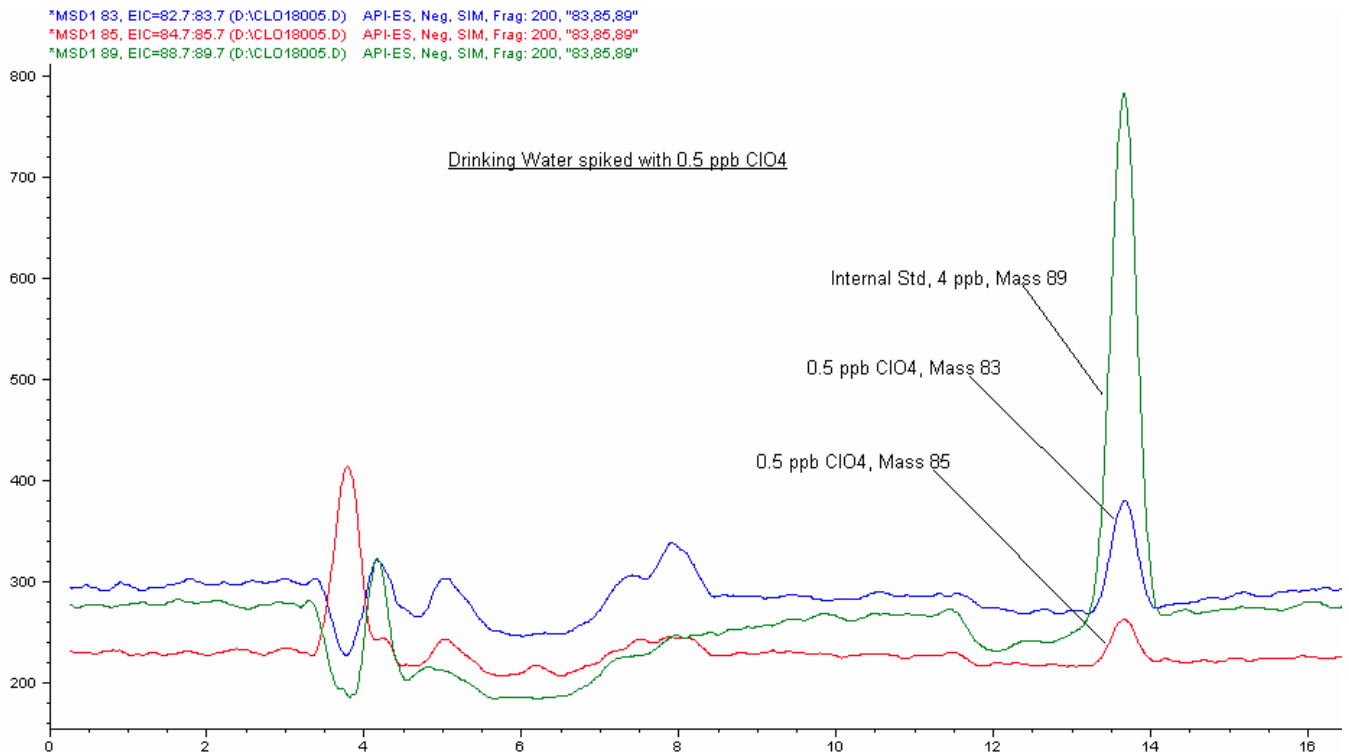


Figure 6: Soil Sample Chromatogram at 1 ug/Kg

10

\*MSD1 83, EIC=82.7:83.7 (D:\CLO18007.D) API-ES, Neg. SIM, Frag: 200, "83,85,89"  
\*MSD1 85, EIC=84.7:85.7 (D:\CLO18007.D) API-ES, Neg. SIM, Frag: 200, "83,85,89"  
\*MSD1 89, EIC=88.7:89.7 (D:\CLO18007.D) API-ES, Neg. SIM, Frag: 200, "83,85,89"

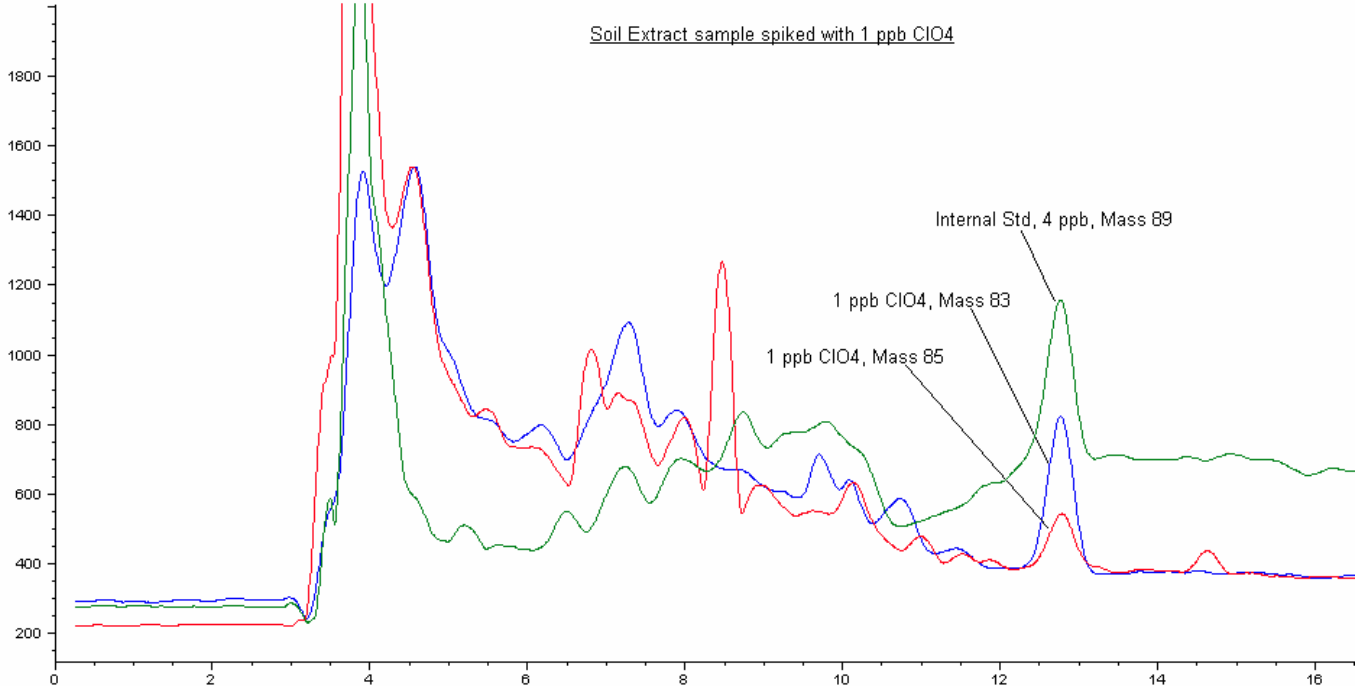


Figure 7: Biota (Spinach) Sample Chromatogram at 71.33 ppb

\*MSD1 83, EIC=82.7:83.7 (D:\NOV30008.D) API-ES, Neg. SIM, Frag: 200, "83,85,89"  
\*MSD1 85, EIC=84.7:85.7 (D:\NOV30008.D) API-ES, Neg. SIM, Frag: 200, "83,85,89"  
\*MSD1 89, EIC=88.7:89.7 (D:\NOV30008.D) API-ES, Neg. SIM, Frag: 200, "83,85,89"

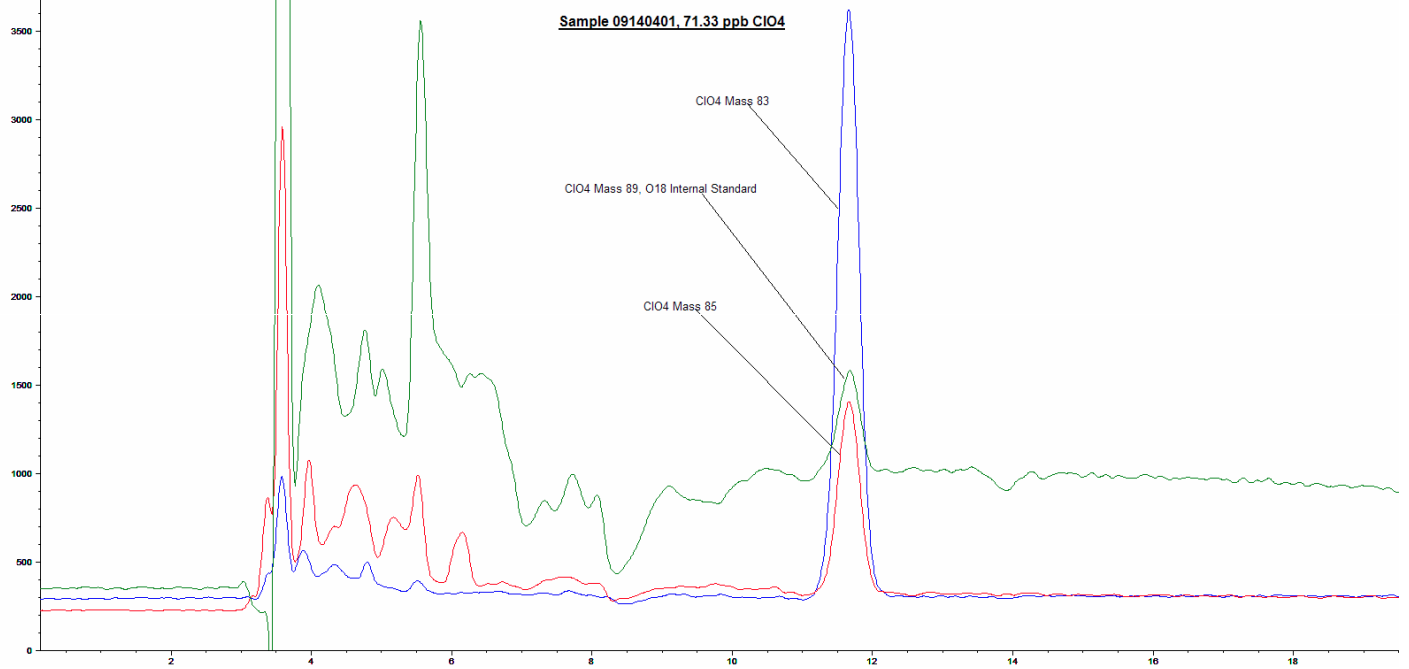
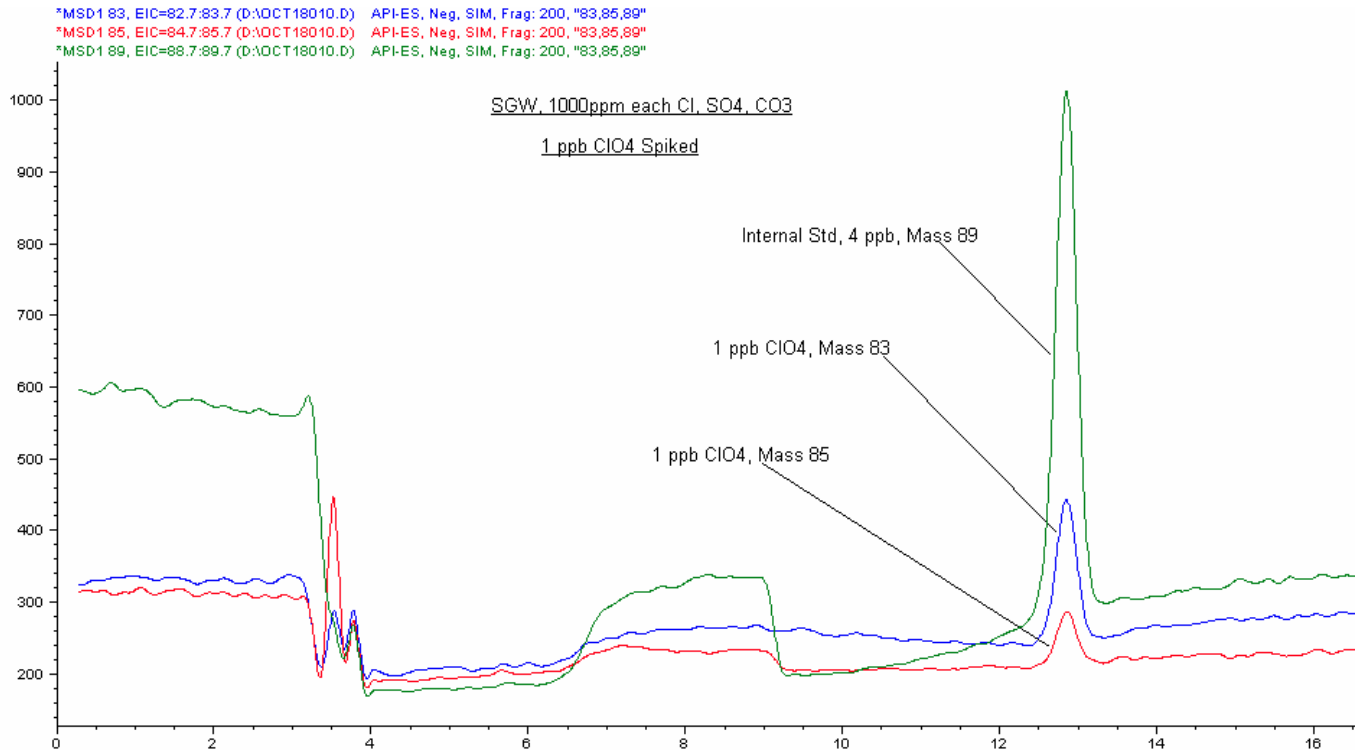
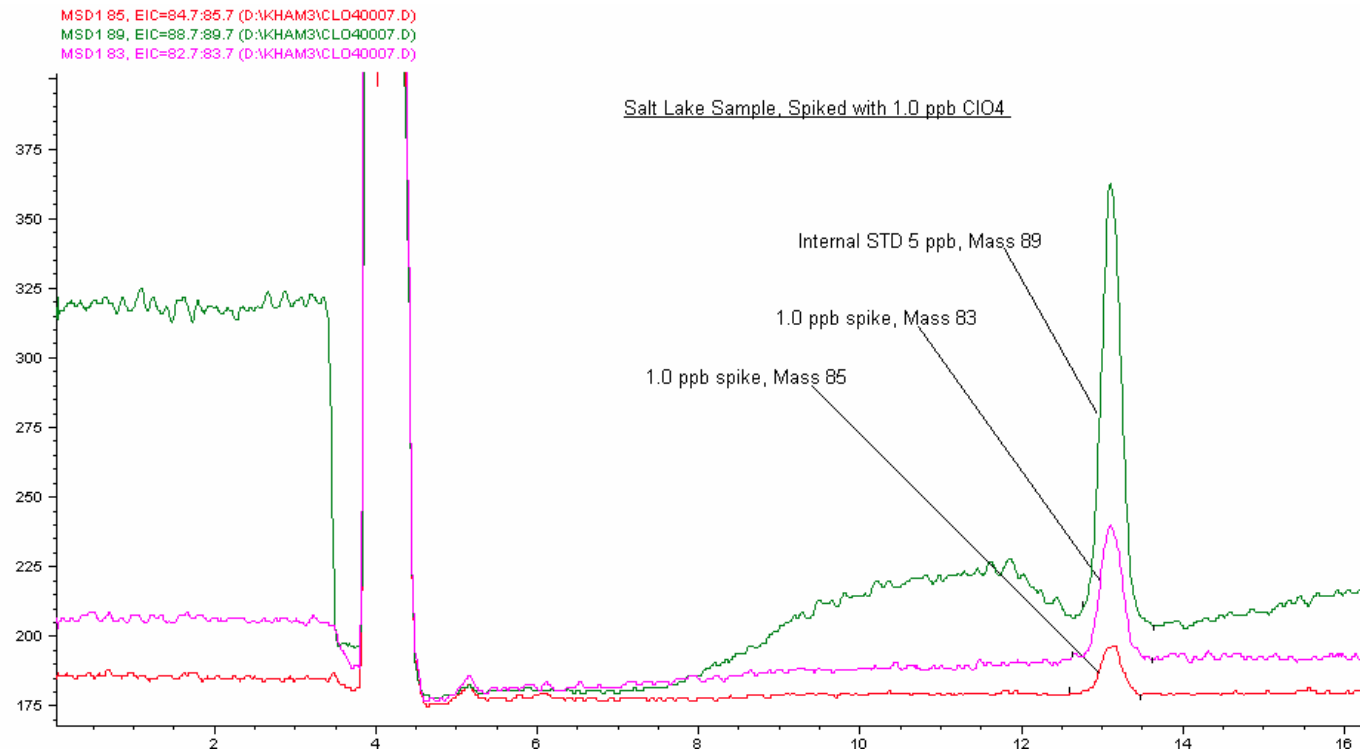


Figure 8: Simulated Ground Water (SGW) Sample Chromatogram at 1 ug/L



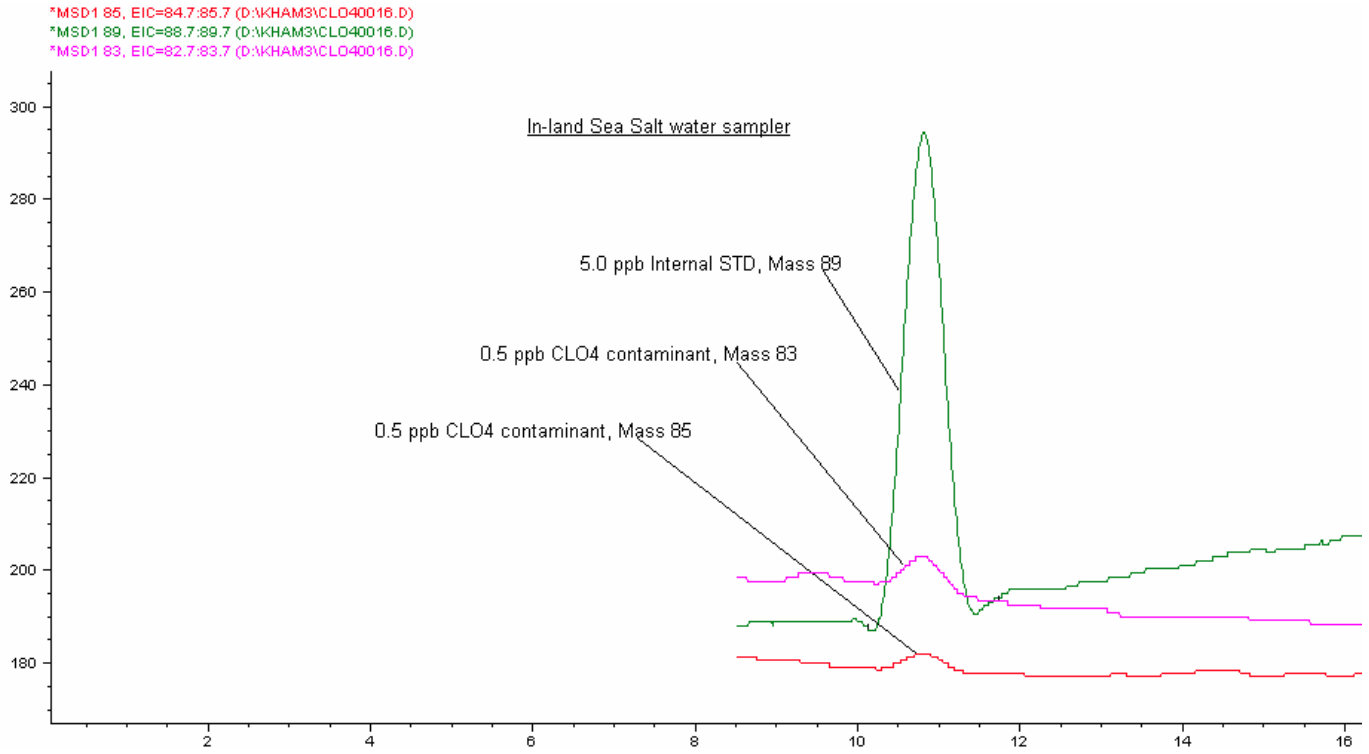
11

Figure 9: Great Salt Lake (GSL) Water Sample Chromatogram at 1 ug/L

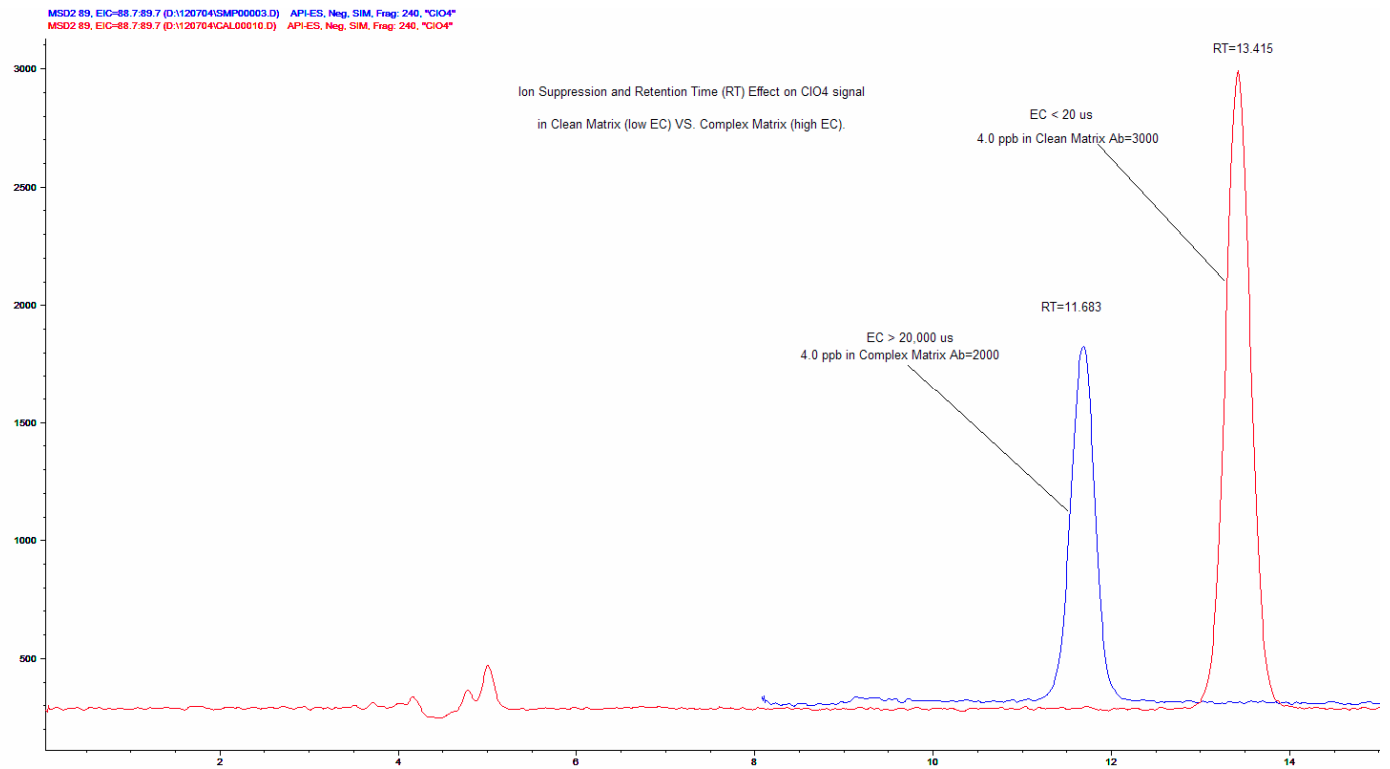


### Figure 10: In-Land Sea Salt Water Sample Chromatogram with ClO4

12



### Figure 11: Ion Suppression and Retention Time Effect on ClO4 Signal In Clean Matrix (Low EC) Vs. Complex Matrix (High EC)

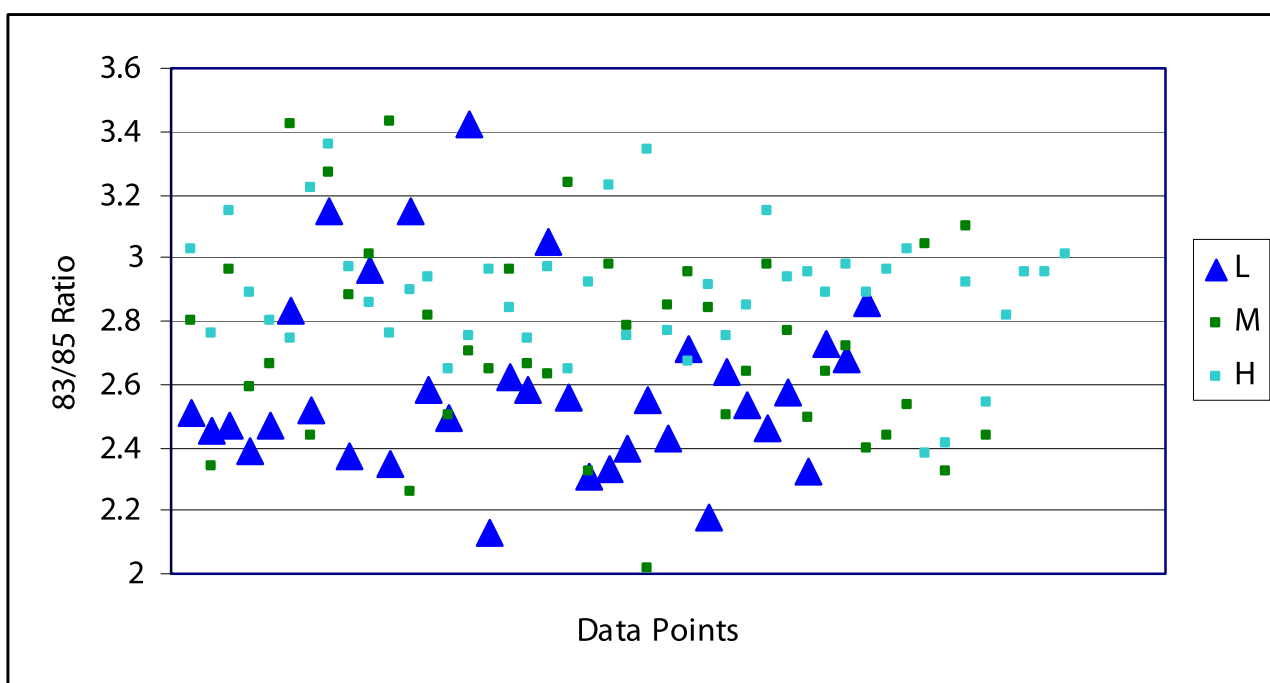


The ratio of 83/85 masses was monitored during this study for all matrices analyzed by this method. The data generated is shown in Figure 9 and was used to calculate statistical process control limits. Statistical limits are shown for all concentrations in Table 4. Differences in measurement error discussed in “Experimental Statistics”<sup>(6)</sup> may have an impact on the low and medium concentration

samples shown in Table 4. The results of this scatter plot and table shows a lower 83/85 mean ratio at low concentrations of perchlorate. Based on error of measurement associated with low levels and the importance of confirming perchlorate the 83/85 isotopic ratio statistical process control limits are set using  $\pm 2$  standard deviations at 2.2 to 3.3 which is calculated as follows.

$$MeanRatio_{83/85} \pm (2 \times Stdev_{83/85})$$

Figure 10: Plot of Mass 83/85 Ratio in all Samples



**Table 4: Perchlorate 83/85 Isotopic Ratio and Control Limits**

Mean 83/85 Ratio by Concentration				
Low Conc	Average	2.59	Std Dev	0.28
	LCL <sup>(1)</sup>	1.74	UCL <sup>(1)</sup>	3.44
Med Conc	Average	2.73	Std Dev	0.32
	LCL <sup>(1)</sup>	1.78	UCL <sup>(1)</sup>	3.68
High Conc	Average	2.89	Std Dev	0.20
	LCL <sup>(1)</sup>	2.27	UCL <sup>(1)</sup>	3.50
Total 83/85 Ratio				
	Average	Std Dev	n	LCL <sup>(2)</sup>
	2.75	0.29	121	2.16
				UCL <sup>(2)</sup>
				3.34

*(1) ± 3 SD, (2) ± 2 SD (2)*

14

### Precision and Bias

Validation studies based on NELAC Chapter 5<sup>(5)</sup> were generated for five matrices by analyzing samples over three consecutive days at varying concentration levels. The study designed analyzed nine replicates for each matrix on a daily basis. The three concentrations are at or near the limit of quantitation, at the upper-range of the calibration (upper 20%) and at a mid-range concentration.

#### Precision

To compare the variability of performance (precision) the F-Test was performed on each matrix. Matrices were evaluated based on concentration levels, and combined daily results. Data for this section is presented in Data Table I. The equations used in this section are discussed in “Experimental Statistics”<sup>(6)</sup> and “Statistics for Analytical Chemistry”<sup>(7)</sup>.

Table 5 summarizes precision for this method with respect to concentrations in same matrix.

The significance of  $\alpha = 0.01$  and Degrees of Freedom (DF = 8) were used to determine critical values used to assess variability of performance. When using this test to compare the precision at different concentration levels the user must be concerned with the fact that errors of measurement<sup>(6)</sup> may have more affect on one of the concentrations.

Critical Values of  $F_{1-\alpha}(8,8)$  and  $1/F_{1-\alpha}(8,8)$  are 6.03 and 0.17, respectively.

The null hypothesis is stated as follows. If  $F > 6.03$  and  $F < 0.17$  then the variability of performance for this method with respect to concentrations in the same matrix is not different.

$$F = \frac{(RSD_{ConcX})^2}{(RSD_{ConcY})^2}$$

**Table 5: Variability of Performance with Respect to Concentrations in the Same Matrix**

Matrix	Low Conc. vs. Med Conc.	Low Conc. vs. High Conc.	Med Conc. vs. High Conc.
Drinking Water	2.86	8.05	2.81
Soil	1.18	3.52	2.98
Biota	0.38	1.88	4.98
SGW	2.70	9.79	3.62
GSL	0.71	2.15	3.03

15

Table 6 summarizes precision for this method with respect to daily analysis for all concentrations same matrix. The significance of  $\alpha = 0.01$  and Degrees of Freedom (DF = 8) was used to determine critical values used to assess variability of performance. Critical Values are the same as used for Table 4.

performance for this method with respect to daily analysis for all concentrations in the same matrix is not different

$$F = \frac{(RSD_{Day\#})^2}{(RSD_{Day\#})^2}$$

The null hypothesis is stated as follows. If  $F > 0.17$  and  $F < 6.03$  then the variability of

**Table 6: Variability of Performance with Respect to Daily Analysis for all Concentrations in the Same Matrix**

Matrix	Day 1 vs. Day 2	Day 1 vs. Day 3	Day 2 vs. Day 3
Drinking Water	1.89	1.89	1.00
Soil	1.16	2.04	1.75
Biota	0.41	0.65	1.60
SGW	0.60	0.92	1.53
GSL	1.69	0.67	0.40

Table 7 summarizes precision for this method with respect to matrix for all concentrations on all days. The significance of  $\alpha = 0.01$  and Degrees of Freedom (DF = 26) were used to determine critical values used to assess variability of performance. Critical Values of  $F_{1-\alpha}(26,26)$  and  $1/F_{1-\alpha}(26,26)$  are 2.50 and 0.40, respectively.

The null hypothesis is stated as follows. If  $F > 0.40$  and  $F < 2.55$  then the variability of performance for this method with respect to matrix for all concentrations on all days is not different.

$$F = \frac{(RSD_{MatrixX})^2}{(RSD_{MatrixX})^2}$$

**Table 7: Variability of Performance with Respect to Matrix for all Concentrations on all Days**

Matrix	Soil	Biota	SGW	GSL
Drinking Water	1.46	0.95	0.51	0.69

16 *Bias*

Analysis of the data to determine if the method was bias with respect to aqueous matrices was accomplished by multiple techniques.

A proficiency-testing sample analyzed by LC/MS and compared to analysis by method UPEPA 314.0 is presented in Table 8.

**Table 8: Proficiency Testing Results**

PT Study	Result 314.0	Result LC/MS	True Value
WS04-1	47.3 ug/L	51.2 ug/L	52.7 ug/L

To compare the variability of the means of each aqueous matrix the Paired t-Test was used. The equations used in this section are discussed in “Experimental Statistics” (6) and “Statistics for Analytical Chemistry” (7). The differences between each pair of results on the aqueous matrices were calculated and the mean difference and mean standard deviation were computed. Data for this section is presented in Data Table II. For the

Paired t-test the level of significance was p = 0.99. The critical value of  $t_{0.99}$  is 2.479. Table 9 summarizes the results of the Paired t-Test.

The null hypothesis is stated as follows. If  $|t| < 2.479$  the variability of means of each aqueous matrix with respect to this method are not significantly different.

$$t = \text{MeanDifference}_{\text{MatrixX}-\text{MatrixY}} \times \frac{\sqrt{n}}{\text{StdevDifference}_{\text{MatrixX}-\text{MatrixY}}}$$

**Table 9: Results of Paired t-Statistic for Aqueous Matrices**

Matrix:	DW vs. SGW	DW vs. GSL	SGW vs. GSL
t	1.74	0.51	2.07



LC/MS confirmation of positive result for samples analyzed by method USEPA 314.0

was performed. Table 10 presents data on samples analyzed by both methods.

**Table 10: LC/MS Confirmation of Perchlorate**

Sample Matrix	Result by USEPA 314.0	Result by LC/MS	Confirmation Achieved
Water 04C00326	0.76 ug/L	0.87 ug/L	Yes
Water 04C00327	0.87 ug/L	1.1 ug/L	Yes
Water 04C00328	1.8 ug/L	1.8 ug/L	Yes
Water 04C00329	1.6 ug/L	1.8 ug/L	Yes
Water 04C00330	1.6 ug/L	1.4 ug/L	Yes
Water 04C00331	1.2 ug/L	1.5 ug/L	Yes
Water 04C00426	ND	ND	Yes
Water 04E02488	0.36	0.40	Yes
Water 04E01966	0.40	0.41	Yes

17

*Robustness*

A single calibration curve was used for this entire study. Results of CCV analysis during the validation study are presented in Table 11 and are used to assess the stability of the instrument calibration. Use of O18LP as an internal standard has reduced calibration runs and

eliminates worrisome variation in the mass spectrometer due to matrix interferences. The internal standard area counts are monitored and must be within  $\pm 30\%$  of the daily calibration verification response. By using O18LP the retention time of naturally occurring Perchlorate is the equivalent and fluctuations due to temperature and pressure are negated.

**Table 11: Calibration Verification Results (Initial Calibration 3/18/04)**

Date/Time	Result	Nominal Value	% Difference
4/2/04 4:29 PM	10.45	10.0	4.5%
4/2/04 7:16 PM	1.005	1.00	0.5%
4/2/04 9:48 PM	9.25	10.0	7.6%
4/3/04 5:24 AM	0.998	1.00	0.2%
4/3/04 11:52 AM	10.45	10.0	4.5%
4/3/04 2:40 PM	0.949	1.00	5.1%
4/3/04 5:12 PM	10.51	10.0	5.1%
4/3/04 7:44 PM	0.989	1.00	1.1%
4/3/04 10:16 PM	10.66	10.0	6.6%
4/4/04 9:52 AM	11.008	10.0	10.1%
4/4/04 12:39 PM	1.027	1.0	2.7%
4/4/04 3:11 PM	10.14	10.0	1.4%
4/4/04 5:43 PM	0.983	1.0	1.7%
4/4/04 8:15 PM	10.52	10.0	5.2%
4/4/04 10:47 PM	1.015	1.00	1.5%

## Conclusions

### *Quality Control Requirements*

At a minimum the following quality control practices should be employed when using this method.

- 18
- > MDL procedures to determine the sensitivity based on accepted reference.
  - > PQL determinations to establish the reporting level for accurate quantitation.
  - > Validation studies for specific matrices.
  - > Instrument calibration should using at least five levels of standards and having acceptability parameters defined.
  - > Internal standard using Oxygen-18 Labeled Perchlorate added to each standard and sample and monitored to ensure instrument performance.
  - > Internal standard calibration used for quantitation.
  - > The isotopic ratio of 83/85 for perchlorate identification is assessed and statistical process control limits are employed to ensure identification.
  - > Retention time of internal standard and perchlorate are monitored and a retention time window of no more than 0.3%.
  - > Calculated Control Limits for LCS.  
See Table 12
  - > Batch QC should include at a minimum method blanks and laboratory control samples and, if the project requires, both matrix spikes and matrix spike duplicates should be analyzed.

### *Statistical Analysis of Precision and Bias*

Statistical analysis of precision and bias were employed to validate this method. The technique employed by this study ensures that data of known and documented quality can be generated using this method. In fact the statistical approach validates exactly what has always been thought. As we push detection limits and reporting limits lower the precision at these low concentration levels are usually different then higher concentrations levels. Each specific level must be assessed for acceptability for the level of documented quality needed for a particular project. There are two factors which question if methods should be assessed with statistics only as prescribe by NELAC<sup>(5)</sup>. One factor is that the instrument error of measurement might affect the low concentration data more than the high concentration data. The second factor is the variability in data points at any level acceptable to meet specific project data quality objectives, even though specific concentrations levels produce precision that may be statistically different. Table 12 summarizes control limits for data presented in Data Table 1. The use of the control limits for all levels and all concentration would be an appropriate measure of performance on LCS samples for this method on the five matrices.

**Table 12**  
**Calculated Control Limits using all Concentrations**

Matrix	Mean Recovery	Standard Deviation	Lower Control Limit (LCL)	Upper Control Limit (UCL)
DW	103.9%	7.8%	80.5%	127.2%
Soil	102.9%	6.3%	83.8%	121.9%
Biota	105.9%	8.0%	81.8%	130.1%
SGW	98.9%	10.4%	67.6%	130.2%
GSL	104.8%	9.3%	76.9%	132.6%
All Matrices	103.3%	8.7%	77.2%	129.4%

19

In addition to statistics, other techniques should be employed to validate a method. These techniques include replicates, the analysis of samples with a different method, reproducibility, the analysis of duplicate and spikes samples, and proficiency testing samples.

*Method Applications*

This method has been validated to analyze samples in drinking water, soil, biota, ground water and saline water. The method can analyze samples with both low and high levels of common ions, organic interferences and even highly saline samples. Any analysis of perchlorate with positive results without historical support should be at least analyzed to confirm the identity of perchlorate using a mass spectrometry technique.

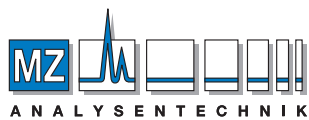
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MZ-Analysentechnik GmbH  
Barcelona-Allee 17 • D-55129 Mainz  
Tel +49 6131 880 96-0  
Fax +49 6131 880 96-20  
e-mail: info@mz-at.de  
www.mz-at.de

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