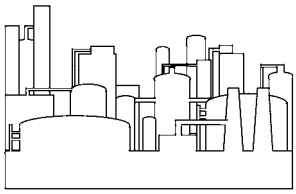


Analysis of Perchlorate in Difficult Matrices by LC/MS

Robert P. Di Rienzo, Kham Lin, Thomas T. McKay, and Richard W. Wade

A method has been developed and validated for the determination of perchlorate in drinking water, soil, biota, groundwater, and saline water using high-performance liquid chromatography/mass spectrometry (LC/MS) without sample pretreatment. 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 isotopic labeled perchlorate. The method can achieve a method detection limit in aqueous samples of 0.05 µg/L and can easily quantify perchlorate at 0.2 µg/L in any aqueous environmental sample matrix. This method uses simple determinative techniques available to LC/MS technologies and does not require any instrumentation additions or systematic pretreatment of samples. Inadequacies of current EPA Method 314.0 caused by matrix interference, high dissolved solids, and conductivity are eliminated and confirmation of perchlorate is accomplished with this new method. © 2005 Wiley Periodicals, Inc.

INTRODUCTION

A new method for the detection and confirmation of perchlorate has been developed. This new method utilizes liquid chromatography to separate perchlorate from interferences and mass spectrometry to confirm and quantify.

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[1] in 1997 could detect 4 ppb of perchlorate in drinking water. Perchlorate was listed by the EPA on the

Robert P. Di Rienzo *is a vice president of quality assurance and information technology for DataChem Laboratories, Inc. He is responsible for the quality systems in the Salt Lake City laboratory, corporate ethics and data integrity program, and DCL On-Line, an intranet used corporately for the distribution of information.* ***Kham Lin*** *is the president of K'(Prime) Technologies Inc.* ***Thomas T. McKay*** *is a Chemist 4 in the Organic Chemistry Section at DataChem Laboratories, Inc. He analyzes samples by ion chromatography, high-performance liquid chromatography, and liquid chromatography/mass spectrometry to detect anions, organic acids, and perchlorate.* ***Richard W. Wade*** *is the manager of the Organic Chemistry Section at DataChem Laboratories, Inc. He directs activities of the section, including qualitative and quantitative analysis for industrial hygiene and environmental samples.*

 DOI: 10.1002/ffej.20033

"Contaminant Candidate List" for consideration for possible regulation in 1998.

In 1999, the EPA[2] 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). This method was developed for drinking water and is sufficient to detect perchlorate at 1 to 4 ppb. Method 314.0 is based on ion chromatography with conductivity detection. Method interferences can be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatuses leading to discrete artifacts or elevated baseline noise in ion chromatograms. These interferences leading to elevated baseline can lead to false positive and increased detection limits for perchlorate. 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.

Method 314.0 is based on ion chromatography with conductivity detection.

Perchlorate has been detected in drinking water in major metropolitan areas and groundwater 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 groundwater, saline water, soil, and plant material. This level of concern about perchlorate detection in matrices other than drinking water has motivated instrument manufacturers, academia, and commercial laboratories to develop methods for analyzing perchlorate in difficult matrices.

DataChem Laboratories, Inc. in conjunction with K' (Prime) Technologies, Inc., has developed a new liquid chromatography/mass spectrometry (LC/MS) method for the detection and confirmation of perchlorate in drinking water, groundwater, saline water, soil, and biota samples.

METHOD

Instrumentation

An Agilent 1100 liquid chromatograph/mass selective detector 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 13 minutes and can process up to 20 samples in an eight-hour sequence, with all appropriate quality control and perchlorate identification by mass spectrometry. This new method uses a newly developed, commercially available liquid chromatography column (KP-RPPX series columns) developed by K' (Prime) Technologies, Inc.

Eluent was prepared with two one-liter bottles containing a mixture of ASTM Type II water and acetonitrile (ACN). One bottle will

contain 95 percent ACN and 5 percent water (v/v), and the other will contain 95 percent water and 5 percent ACN. A small aliquot of acetic acid will be added to each bottle. The solutions from the two bottles will be mixed at the instrument pump at 47 percent water and 53 percent ACN.

Calibration

A minimum of six calibration standards were used for internal standard calibration. Standard concentrations used to calibrate were 0.2, 0.5, 1.0, 2.0, 5.0, and 10.0 µg/L. The Internal Standard of Oxygen-18 Labeled Perchlorate (O18LP) was at 5.0 µg/L. The standard curve for perchlorate is 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 µg/L. Continuing Calibration Verification (CCV) standards were used for each analysis batch prior to conducting any analysis, for every tenth sample, and at the end of the analysis sequence. Calibration is verified if the relative percent difference is less than 15 percent.

A minimum of six calibration standards were used for internal standard calibration.

Sample Preparation

Water samples are prepared by adding an aliquot of sample to a 15-mL disposable centrifuge tube. An appropriate aliquot of internal standard and glacial acetic acid is added to each sample. Each sample is filtered through a 0.45-µm filter into an autosampler vial for analysis.

Soil samples are 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 internal standard and glacial acetic acid is added to each sample. The mixture is vortexed, sonicated for at least 10 minutes, and vortexed again. If necessary, the sample is centrifuged. The extract is then filtered through a 0.45-µm filter into an autosampler vial for analysis.

Biota (plant) samples are prepared by using a sufficient portion (at least 10 grams) of sample and ground through a hand-operated stainless steel grinder. ASTM Type II water is added to an aliquot of biota sample in a 50-mL centrifuge tube. An appropriate aliquot of internal standard and glacial acetic acid is added to each sample. The mixture is vortexed and left overnight, which allows for complete saturation of the sample. Prior to analysis, the sample is vortexed again, then centrifuged at 5,000 rpm for 30 minutes. A portion of the supernatant is then drawn through an activated C-18 column, which removes a large portion of organic contaminants. The final extract is then filtered through a 0.45-µm filter into an autosampler vial for analysis.

The five matrices evaluated by this LC/MS method are presented in **Exhibit 1**.

Exhibit 1. Matrix Description and Preparation

Matrix	Sample Preparation
Drinking Water (DW)	Laboratory Distilled Water Conductivity = 1 µS
Soil	Soil extracted with water
Biota	Grass samples were homogenized, extracted with water and C-18 column cleanup
Synthetic Groundwater (SGW)	Laboratory-distilled water with 1000 mg/L of chloride, sulfate, and carbonate. Conductivity = 7,700 µS
Great Salt Lake (GSL) Water	Water taken from the Great Salt Lake and diluted tenfold. Conductivity = 21,000 µS

EXPERIMENTAL DESIGN

Sensitivity

Method detection limit (MDL) studies following the US EPA[3] procedure were analyzed to determine sensitivity of this LC/MS method. Practical quantitation limits (PQLs) in aqueous, soil, and biota samples were based on the DOD Quality System Manual[4] guidance.

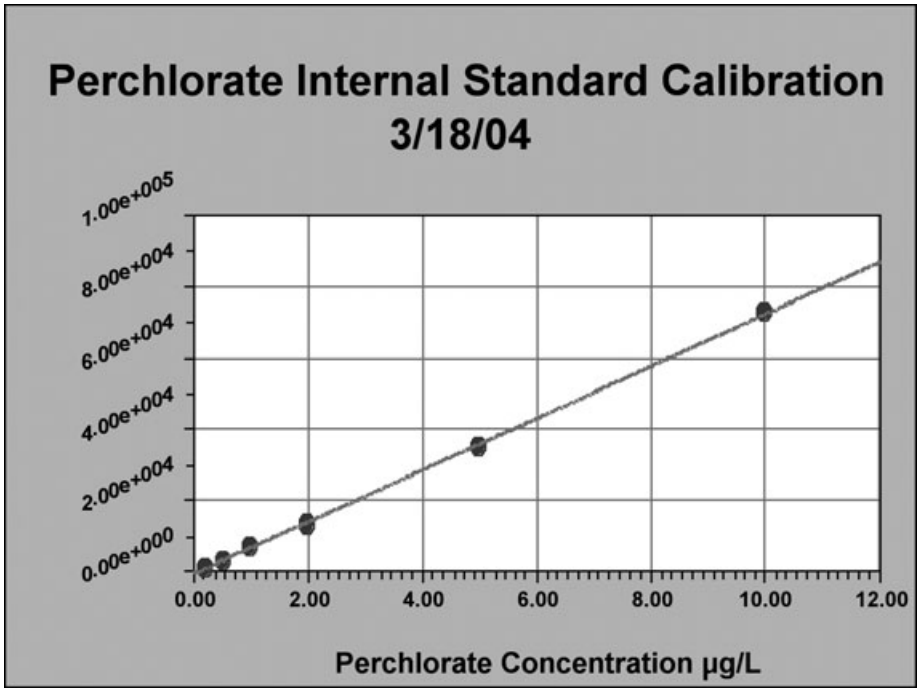
Selectivity

Mass spectrometry is used to monitor perchlorate at mass 83, which is 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 is obtained not only by retention time and mass, but also by using the naturally occurring isotopic ratio of ^{35}Cl to ^{37}Cl, which is 3.065,[5] to monitor the ratio of mass 83 and 85 from perchlorate. The isotopic ratio of ^{35}Cl to ^{37}Cl is used to improve the selectivity of the method and to provide confidence that the detected signal is due to perchlorate and not an interfering compound.[6] Isotopically labeled perchlorate O18LP is used as an internal standard and added to each standard and sample. This internal standard is used for relative 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 National Environmental Laboratory Accreditation Conference (NELAC) 2003 Standard,[7] Chapter 5, Appendix C3. Briefly, five matrices including drinking water, soil, biota, simulated groundwater, and saline water were spiked with perchlorate and analyzed. Three different concentrations in each matrix

Exhibit 2. Perchlorate Internal Standard Calibration, 3/18/04



Linear Fit: y = a + bx, no weighting used.

Standard Error: 563.0881871

Correlation Coefficient: 0.9998145

were analyzed on three consecutive days. Additionally, all samples submitted for analysis having difficult matrices and/or positive detections by Method 314.0 were confirmed by this new method. Proficiency-testing samples were also analyzed to assess the bias of this method.

Robustness

A known amount of internal standard O18LP was added to each sample and standard and monitored at mass 89. 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 **Exhibit 2**. Calibration acceptance criterion for the initial calibration curve is a correlation coefficient of 0.995 or higher. CCV calibration verifications are presented in **Exhibit 3**, and acceptance limits for ICV and CCV were set at ± 15 percent difference from the true value.

Exhibit 3. Calibration Verification Results (Initial Calibration 3/18/04)

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

Sensitivity

The MDLs for five matrices were calculated using the procedures specified by the US EPA.[8] 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), synthetic groundwater (SGW), and soil samples were spiked with perchlorate, while indigenous levels of perchlorate in biota and Great 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.[9]

The practical quantitation limit (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 three to five times the MDL value. MDL and PQL data are presented in **Exhibit 4** and MDL verification results in **Exhibit 5**.

Selectivity

Mass spectrometry is used to monitor perchlorate at masses 83 and 85. Internal standard O18LP is monitored at mass 89. **Exhibit 6** shows typical chromatograms of perchlorate at masses 83, 85, and 89.

The ratio of 83/85 masses was monitored during this study for all matrices analyzed by this method. The data generated are shown in

Exhibit 4. MDL and PQL Determinations

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

* Indigenous levels in these matrices were used to calculate MDLs

Exhibit 7 and were used to calculate statistical process control limits. Statistical limits are shown for all concentrations in **Exhibit 8**. Differences in measurement error discussed in Experimental Statistics[10] may have an impact on the low and medium concentration samples shown in Exhibit 8. 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 ± 2 standard deviations at 2.2 to 3.3, which is calculated as follows:

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

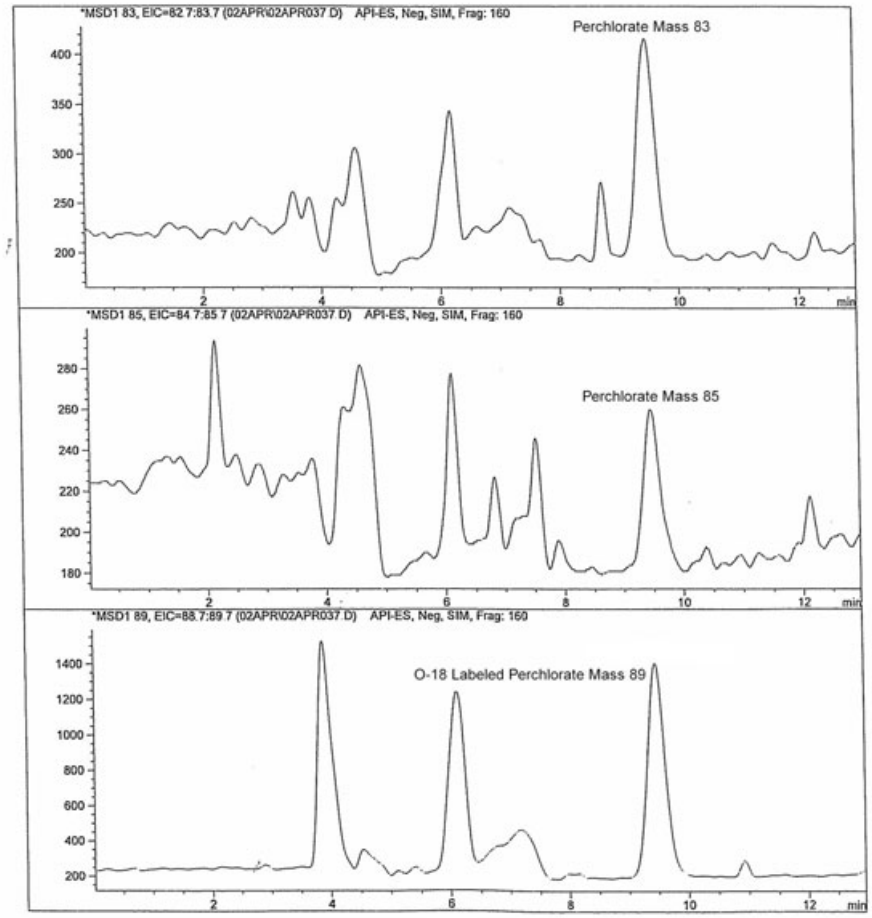
Validation Study

Validation studies based on NELAC Chapter 5[11] 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

Exhibit 5. MDL Verification Results

Matrix	MDL Verification Concentration	MDL Verification Result
Drinking Water	0.10 µg/L	0.11 µg/L
Soil	1.0 µg/kg	1.0 µg/kg
Biota	2.3 µg/kg	1.6 µg/kg
SGW	0.10 µg/L	0.11 µg/L
GSL	0.11 µg/L	0.12 µg/L

Exhibit 6. Simulated Groundwater Sample Chromatogram 1 µg/L



or near the limit of quantitation, at the upper range of the calibration (upper 20 percent), and at a mid-range concentration.

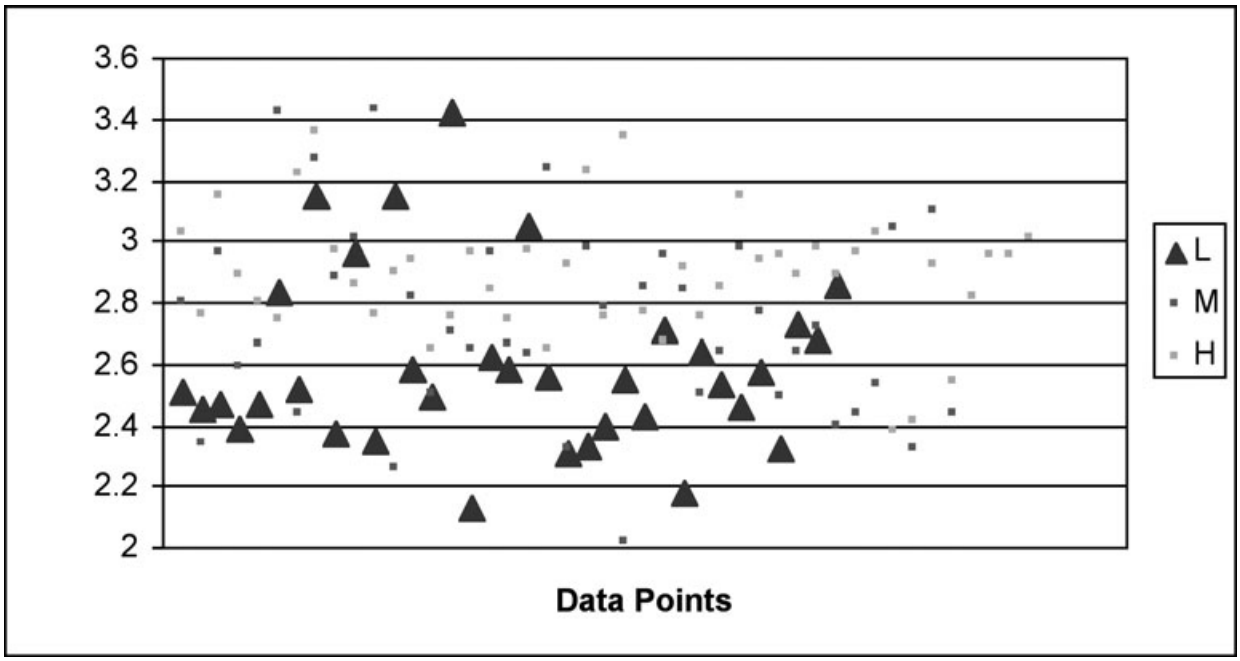
Precision

To compare the variability of performance (precision) the F-Test was performed on each matrix. Matrices were evaluated based on concentration levels, combined daily results, and used to compare the precision of this method on the five matrices. Data for this section are presented in Appendix A. The equations used in this section are discussed in *Experimental Statistics*[12] and *Statistics for Analytical Chemistry*.[13]

Exhibit 9 summarizes precision for this method with respect to concentrations in the 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 con-

Exhibit 7. Plot of Mass 83/85 Ratio in All Samples



L = Low Concentration

M = Medium Concentration

H = High Concentration

Actual concentrations are listed in Appendix A. This plot shows data points from results for all matrices listed in Appendix A.

Exhibit 8. Perchlorate 83/85 Isotopic Ratio and Control Limits

Mean 83/85 Ratio by Concentration

Low Conc	Average:	2.59	Std Dev:	0.28
	LCLa:	1.74	UCLa:	3.44
Med Conc	Average:	2.73	Std Dev:	0.32
	LCLa:	1.78	UCLa:	3.68
High Conc	Average:	2.89	Std Dev:	0.20
	LCLa:	2.27	UCLa:	3.50

Total 83/85 Ratio

Average	Std Dev	n	LCLb	UCLb
2.75	0.29	121	2.16	3.34

a ± 3 SD

b ± 2 SD

Exhibit 9. 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

centration levels, the user must be concerned with the fact that errors of measurement[14] may have more effect 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 > 0.17 and F < 6.03, then the variability of performance for this method with respect to concentrations in the same matrix is not different.

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

Exhibit 10 summarizes precision for this method with respect to daily analysis for all concentrations in the 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 Exhibit 6.

The null hypothesis is stated as follows:

If F > 0.17 and F < 6.03, then the variability of performance for this method with respect to daily analysis for all concentrations in the same matrix is not different.

Exhibit 10. 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

Exhibit 11. Variability of Performance with Respect to the Matrix for All Concentrations on All Days

Matrix/Matrix	Soil	Biota	SGW	GSL
Drinking Water	1.46	0.95	0.51	0.69

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

Exhibit 11 summarizes precision for this method with respect to the 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 the matrix for all concentrations on all days is not different.

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

Bias

Analysis of the data to determine if the method has bias with respect to aqueous matrices was accomplished by multiple techniques. Proficiency testing samples analyzed by LC/MS and compared to analysis by Method 314.0 are presented in **Exhibit 12**.

To compare the variability of means of each aqueous matrix, the Paired *t*-Test was used. The equations used in this section are discussed in *Experimental Statistics*[15] and *Statistics for Analytical Chemistry*.[16] The differences between each pair of results on the aqueous matrices were calculated and the mean difference and mean standard deviation were computed. For the Paired *t*-Test, the level of significance was $p = 0.99$. The critical value of $t_{0.99}$ is 2.479. **Exhibit 13** summarizes the results of the Paired *t*-Test.

Exhibit 12. Proficiency Testing Results

PT Study	Result 314.0	Result LC/MS	True Value
WS04-1	47.3 µg/L	51.2 µg/L	52.7 µg/L
Portable WatR™ Perchlorate 052004A	NA	5.64 µg/L	5.48 µg/L
WS04-3	89.7 µg/L	83.8 µg/L	90.0 µg/L

Exhibit 13. Results of Paired *t*-Test for Aqueous Matrices

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

The null hypothesis is stated as follows:

If $|t| < 2.479$, the variability of means of each aqueous matrix with respect to this method is not significantly different.

$$t = MeanDifference_{\ MatrixX–MatrixY} \times \frac{\sqrt{n}}{StdevDifference_{\ MatrixX–MatrixY}}$$

To compare the bias of LC/MS analysis with the established Method 314.0, the confirmation of positive results by Method 314.0 was performed on samples. **Exhibit 14** presents data on samples analyzed by both methods.

Robustness

A single calibration curve was used for this entire study. Results of CCV analysis during the validation study are presented in Exhibit 4

Exhibit 14. LC/MS Confirmation of Perchlorate

Sample Matrix	Result by 314.0	Result by LC/MS	Confirmation Achieved
Water 04C00326	0.76 µg/L(J)	0.87 µg/L	Yes
Water 04C00327	0.87 µg/L(J)	1.1 µg/L	Yes
Water 04C00328	1.8 µg/L	1.8 µg/L	Yes
Water 04C00329	1.6 µg/L	1.8 µg/L	Yes
Water 04C00330	1.6 µg/L	1.4 µg/L	Yes
Water 04C00331	1.2 µg/L	1.5 µg/L	Yes
Water 04E02488	0.36 µg/L(J)	0.40 µg/L	Yes
Water 04E01966	0.40 µg/L(J)	0.41 µg/L	Yes
Water 04C00732	1.1 µg/L	1.4 µg/L	Yes
Water 04C00736	1.4 µg/L	1.6 µg/L	Yes
Water 04C00737	1.1 µg/L	1.4 µg/L	Yes
Soil 04C00678	6.7 µg/kg	4.5 µg/kg	Yes
Soil 04C00680	8.9 µg/kg	< 2 µg/kg	No

(J) = Estimated value, below reporting limit and above MDL for Method 314.0

Exhibit 15. 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%

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 ±30 percent of the daily calibration verification response. By using O18LP, the retention time of naturally occurring perchlorate is equivalent, and fluctuations due to temperature and pressure are negated.

CONCLUSIONS

LC/ MS Method Quality Control Requirements

The minimum quality control practices employed by LC/MS to analyze perchlorate should include:

- 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 using at least five levels of standards and having acceptability parameters defined;
- Internal standard using Isotopic 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;
- Calculated control limits for LCS (see **Exhibit 15**); and
- 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 Analyses of Precision and Bias

Statistical analyses of precision and bias are employed to validate this method. These techniques ensure that data of known and documented quality can be generated using this method. In fact, the statistical approach validates the premise that as detection limits and reporting limits are pushed lower, the precision at these low-concentration levels is usually statistically different then higher-concentration levels. If the documented precision of the low concentration meets the desired data quality objectives and decision-making criteria, it matters little if the low-concentration data for precision is statistically different from the high-concentration data. Each specific level must be assessed for acceptability for the level of documented quality needed for a particular project.

There are two reasons that methods should not be assessed with statistics only as prescribed by NELAC.[17] First, the instrument error of measurement might affect the low-concentration data more than the high-concentration data. Second, the largest variability in performance at any level is acceptable to meet specific project data quality objectives even though specific concentration levels produce precision that may be statistically different.

Exhibit 15 summarizes control limits for data presented in Appendix A. The use of the control limits for all levels and all concentrations would be an appropriate measure of performance on LCS samples for this method on the five matrices.

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

Method Applications

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

NOTES

1. State of California, Department of Health Services. (1997, June 3). Determination of perchlorate by ion chromatography, Rev. No. 0.

2. United States Environmental Protection Agency (1999, November), Determination of perchlorate in drinking water using ion chromatography. US EPA Method 314.0, Rev. 1.

3. 40 CFR 36, Appendix B.

4. United States Department of Defense. (2002, June). Department of Defense quality systems manual for environmental laboratories. Final version 2.

5. Hawley, G. G. (1981). The condensed chemical dictionary (10th ed.). New York: Van Nostrand Reinhold.

6. Koester, C. J., Beller, H. R., & Halden, R. U. (2000). Analysis of perchlorate in groundwater by electrospray ionization mass spectrometry/mass spectrometry. Environmental Science and Technology, 34, 1862–1864.

7. National Environmental Laboratory Accreditation Conference: Constitution, Bylaws, and Standards. Chapter 5, Appendix C3. EPA 600/R-04/003.

8. See note 3.

9. See note 4.

10. Natrella, M. G. (1963). Experimental statistics. National Bureau of Standards Handbook 91. Washington, DC: United States Department of Commerce.

11. See note 7.

12. See note 10.

13. Miller, J. C., & Miller, J. N. (1984). Statistics for analytical chemistry. New York: Halsted.

14. See note 6.

15. See note 10.

16. See note 13.

17. See note 5.

Appendix A. LC/MS Validation Study Data for Perchlorate

Matrix	Perchlorate Concentration Found and Percent Recovery							
Day 1	True Value	Units	Amt Found	Recovery	Amt Found	Recovery	Amt Found	Recovery
DW	0.2	µg/L	0.17	85.0%	0.23	115.0%	0.21	105.0%
DW	1	µg/L	1	100.0%	0.99	99.0%	1.1	110.0%
DW	5	µg/L	4.7	94.0%	4.9	98.0%	4.9	98.0%
Soil	2	µg/kg	2.2	110.0%	2.2	110.0%	2.1	105.0%
Soil	10	µg/kg	9.2	92.0%	11	110.0%	11	110.0%
Soil	50	µg/kg	48	96.0%	48	96.0%	51	102.0%
Biota (Grass)	6	µg/kg	6.4	106.7%	6.3	105.0%	6.8	113.3%
Biota (Grass)	10	µg/kg	11	110.0%	9.3	93.0%	11	110.0%
Biota (Grass)	50	µg/kg	52	104.0%	54	108.0%	55	110.0%
SGW (7,700µS)	0.2	µg/L	0.23	115.0%	0.23	115.0%	0.19	95.0%
SGW (7,700µS)	1	µg/L	0.92	92.0%	0.98	98.0%	0.86	86.0%
SGW (7,700µS)	4	µg/L	4	100.0%	4.1	102.5%	4.2	105.0%
GSL (21,000µS)	0.2	µg/L	0.24	120.0%	0.22	110.0%	0.2	100.0%
GSL (21,000µS)	1	µg/L	1.2	120.0%	0.96	96.0%	1.2	120.0%
GSL (21,000µS)	5	µg/L	5.7	114.0%	5.5	110.0%	5.5	110.0%
Day 2	True Value	Units	Amt Found	Recovery	Amt Found	Recovery	Amt Found	Recovery
DW	0.2	µg/L	0.22	110.0%	0.19	95.0%	0.24	120.0%
DW	1	µg/L	1.1	110.0%	1.1	110.0%	1.1	110.0%
DW	5	µg/L	5.3	106.0%	5.1	102.0%	5.2	104.0%
Soil	2	µg/kg	2.3	115.0%	2.2	110.0%	1.9	95.0%
Soil	10	µg/kg	11	110.0%	9.8	98.0%	9.9	99.0%
Soil	50	µg/kg	50	100.0%	54	108.0%	52	104.0%
Biota (Grass)	6	µg/kg	6.7	111.7%	7.2	120.0%	7.2	120.0%
Biota (Grass)	10	µg/kg	12	120.0%	10	100.0%	9.3	93.0%
Biota (Grass)	50	µg/kg	54	108.0%	53	106.0%	54	108.0%
SGW (7,700µS)	0.2	µg/L	0.2	100.0%	0.24	120.0%	0.18	90.0%
SGW (7,700µS)	1	µg/L	0.83	83.0%	0.81	81.0%	0.9	90.0%
SGW (7,700µS)	4	µg/L	4.2	105.0%	4	100.0%	3.9	97.5%
GSL (21,000µS)	0.2	µg/L	0.19	95.0%	0.19	95.0%	0.2	100.0%
GSL (21,000µS)	1	µg/L	1.1	110.0%	0.95	95.0%	1.1	110.0%
GSL (21,000µS)	5	µg/L	5	100.0%	4.8	96.0%	5	100.0%
Day 3	True Value	Units	Amt Found	Recovery	Amt Found	Recovery	Amt Found	Recovery
DW	0.2	µg/L	0.2	100.0%	0.23	115.0%	0.22	110.0%
DW	1	µg/L	0.99	99.0%	1.1	110.0%	0.94	94.0%
DW	5	µg/L	5.1	102.0%	5	100.0%	5.2	104.0%
Soil	2	µg/kg	1.9	95.0%	1.9	95.0%	2	100.0%
Soil	10	µg/kg	10	100.0%	11	110.0%	9.7	97.0%
Soil	50	µg/kg	51	102.0%	51	102.0%	53	106.0%
Biota (Grass)	6	µg/kg	6.7	111.7%	6.7	111.7%	6	100.0%
Biota (Grass)	10	µg/kg	9	90.0%	10	100.0%	10	100.0%
Biota (Grass)	50	µg/kg	48	96.0%	52	104.0%	50	100.0%
SGW (7,700µS)	0.2	µg/L	0.22	110.0%	0.22	110.0%	0.2	100.0%
SGW (7,700µS)	1	µg/L	0.88	88.0%	0.84	84.0%	0.89	89.0%
SGW (7,700µS)	4	µg/L	4.1	102.5%	4.2	105.0%	4.3	107.5%
GSL (21,000µS)	0.2	µg/L	0.19	95.0%	0.2	100.0%	0.23	115.0%
GSL (21,000µS)	1	µg/L	0.9	90.0%	1.1	110.0%	1.2	120.0%
GSL (21,000µS)	5	µg/L	5	100.0%	4.9	98.0%	5	100.0%
DW = Drinking Water (Conductivity = 1uS)								
SGW = Simulated Groundwater 1,000 mg/L of Chloride, Sulfate, Carbonate (Conductivity = 7,700 µS)								
GSL= Great Salt Lake Water diluted 10X (Conductivity = 21,000 µS)								