

Perchlorate in Soil and Non-Potable Water by LC-MS/MS: A Tool for Tracking Occurrence in the Environment

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Introduction

The Environmental Protection Agency published on May 23rd, 2019 the pre-proposed regulation for perchlorate. During the public comment period, the agency was interested in receiving feedback about monitoring and reporting requirements for this contaminant. To help in assessing the occurrence of perchlorate in non-potable waters and soils and hence, determine which source of potable water could be contaminated, a rapid and robust methodology was validated employing Ultra Fast Mass Spectrometry (UFMS) technology. To minimize error introduction and optimize laboratory resources, sample preparation was kept as simple as possible for both soil and water (non-potable, wastewater, and surface water) samples. The procedure for preparation and analysis was adapted from EPA method 6850. Soil samples (1 g) were extracted with water and filtered through a 0.45 µm pore size-filter; clean-up of the extract by solid phase extraction (SPE) was performed when required. Direct injection after filtration through 0.45 µm pore size-filter, was employed for the analysis of water samples. The method was validated by analyzing up to 7 samples each of water and soil environmental samples in triplicate technical replicates. Linearity, accuracy, precision, and results from environmental samples are reported.

Experimental

Perchlorate was analyzed in a 4.5-minute isocratic run on a Shimadzu LCMS 8050 triple quadrupole mass spectrometer seen in Figure 1 in MRM negative-ion mode by electrospray ionization (ESI), referencing Method EPA 6850. An automated software tool was used to optimize instrument settings in Table 1 for the monitored MRM transitions for perchlorate and its internal standard. A 10-point calibration was performed ranging from 50 ppt to 50 ppb utilizing the internal standard quantitation technique to quantitate perchlorate. Method validation for each matrix included recovery within 20% of true value, precision of 15%, and standard deviation from four laboratory control samples. Additional studies included method detection limit (MDL), limit of detection (LOD), and limit of quantitation (LOQ). Two blind performance samples for each matrix were run with acceptance criteria based on both the vendor and the participating labs in the study.

Table 1: Optimized MRM settings

Compound Name	Transition Type	Q1 m/z	Q3 m/z	Dwell Time (ms)	Q1 PreBias	CE	Q3 PreBias
Perchlorate 1	Quantitative	99	83	122.0	10.0	29.0	27.0
Perchlorate 2	Qualitative	101	85	122.0	11.0	24.0	11.0
¹⁸ O ₄ Perchlorate (IS)	IS	107	89	247.0	11.0	29.0	14.0

Figure 1: LCMS configuration used in this perchlorate study



Sample Extraction and Analysis

Water samples

A 10 mL sample aliquot was transferred to a 15 mL culture tube. 10 mL aliquots of reagent water were used for both the Method Blank (MB) and the Laboratory Control Sample (LCS). The sample was then spiked with 10 µL of 10 ppm of the instrument internal standard. For the LCS and matrix spike, 10 µL of 10 ppm spiking solution was added to each sample. All samples described above were then vortexed. The samples and QC samples were passed through a 0.45 µm PTFE filter into a labeled autosampler vial and cap prior to injection.

Soil / Solid samples

A 1g aliquot was transferred to a 15mL centrifuge tube. Approximately one gram aliquots of analyte-free matrix sand was used for the MB and LCS. All samples and QC aliquots were spiked with 10 µL of the 10 ppm perchlorate spiking solution was added to each. Sufficient volume of reagent water was added to bring the total aqueous volume to 10 mL. For samples with <90% solids, the volume of water added was adjusted to account for the moisture content of the weighed sample aliquot. All samples were vortexed, sonicated (10 minutes), and vortexed a final time. Samples were then centrifuged, when needed, for 5 minutes to separate out the solids from the extract solution. An aliquot of each extract was passed through a 0.45 µm PTFE filter into a labeled HPLC autosampler vial, followed by injection into the instrument.

When needed, solid phase extraction (SPE) was used to remove non-target organic interferences (highly colored sample extracts sometimes indicate the presence of such organic contaminants). To perform C18 cleanup, the cartridge was conditioned with 5 mL methanol followed by 5 mL HPLC grade water. Then, 6 mL of the sample extract was loaded and the final 4 mL of eluent was collected (first 2 mL was discarded). These extracts were then passed through a 0.45 µm PTFE filter and into a labeled HPLC autosampler vial.

Instrument Operating Conditions

The analysis of perchlorate was performed using an LCMS-8050 triple quadrupole mass spectrometer with optimized instrument settings in Table 2. Conditions were optimized for peak shape and length of run.

Table 2: HPLC and MS Instrument conditions

Parameter	Value
LCMS	Shimadzu LCMS-8050
Analytical Column	Phenomenex Synergi (4.6 mm ID x 250 mm L, 4 µm)
Column Oven Temperature (°C)	35 °C
Injection Volume (µL)	25 µL
Mobile Phase	Reagent A = water/0.75% formic acid Reagent B = methanol
Gradient Flow Rate (mL/min)	1.2 mL/min
Gradient	Time (min) % Reagent B
	0 5
	4.5 5
Run time (min)	4.5 min
Nebulizing gas flow (L/min)	2.0 L/min
Heating gas flow (L/min)	10 L/min
Interface temperature (°C)	300 °C
Desolvation Line temperature (°C)	250 °C
Heat Block temperature (°C)	400 °C
Drying gas flow (L/min)	10 L/min
Maximum Acquisition Loop time (sec)	0.5 sec

Calibration and Standardization

Ten calibration standards were prepared by serial dilution from purchased perchlorate stock standard solution. Each standard was diluted with reagent water to reach the desired concentration. Note the R² value of 0.9958 and R value of 0.9979.

Figure 2: Calibration curve from 0.05-50 ppb of perchlorate standard

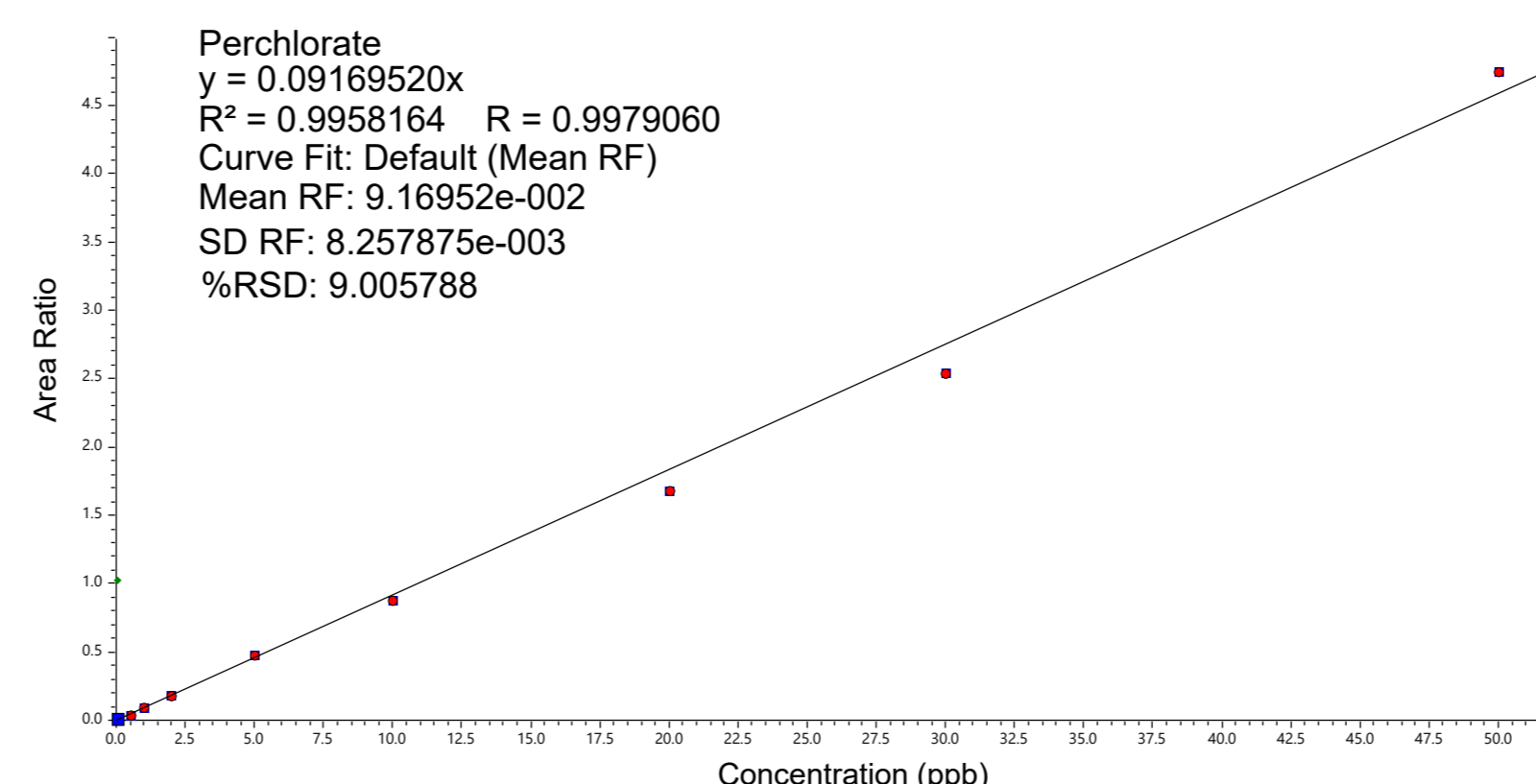


Figure 3: Chromatogram of perchlorate at 50 ppb (highest concentration in calibration curve) using optimized conditions

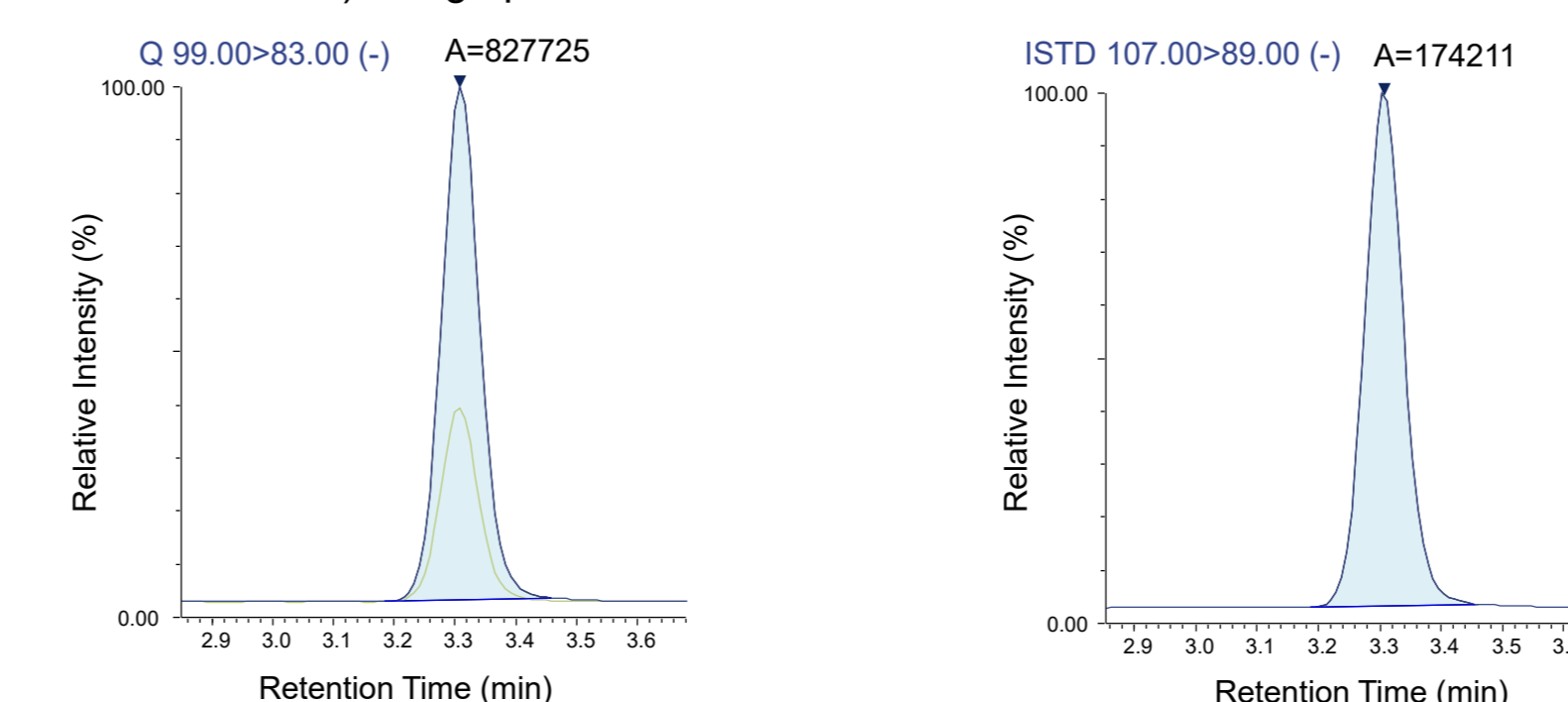
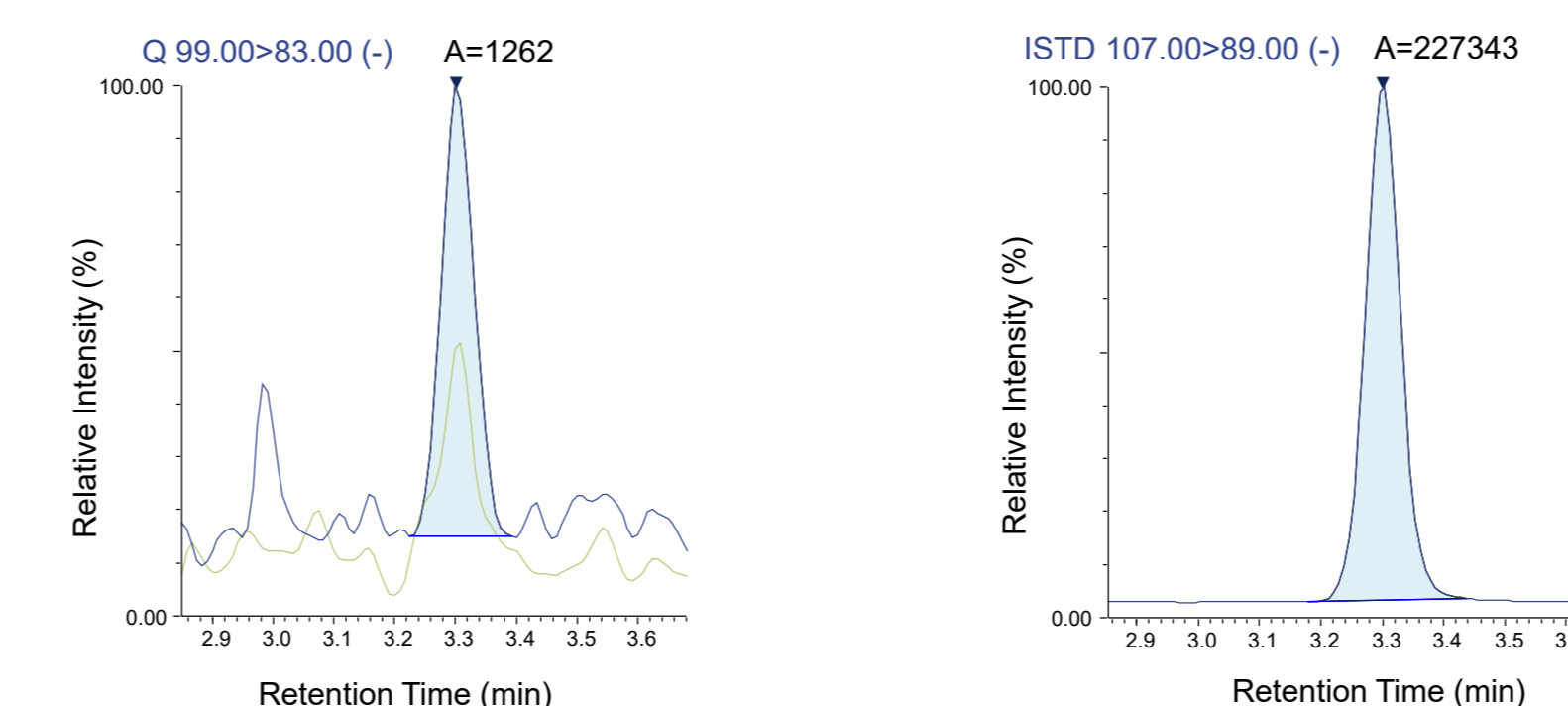


Figure 4: Chromatogram of perchlorate at 50 ppt (lowest concentration in calibration curve) using optimized conditions



Method Performance

Linearity, accuracy, precision, and method detection limits were determined from repeated injections of both water and soil samples prepared as in the Experimental and Sample Extraction sections. 4 samples of each type, injected in triplicate for technical replicates, were prepared and analyzed using outlined procedure. Results are tabulated in Tables 3 and 4.

As shown in Table 3, the mean recovery of perchlorate in soil samples was 96% (within 4% of theoretical value), the reported method detection limit (MDL) at 0.30 ug/kg, and the limit of detection (LOD) at 1.2 ug/kg. In water, comparable values are obtained for all samples with mean recovery above 100% and LOD at 0.144 ug/L. For both soil and water, RSDs were 10%.

In Table 4, the recovery of spiked perchlorate in both soil and water is approximately 88%, with standard deviation low in both cases, but even lower with water samples. The recovery percentage is within the acceptable low and high limits.

Table 3: Perchlorate in soil and water samples evaluating recovery, standard deviation, and method detection limits

	Samples							Theoretical Value	Mean Value	Mean Recovery	Std Dev	MDLc	MDLr	RSD	LOD
	A	B	C	D	E	F	G								
Soil (ug/kg)	0.915	0.774	1.067	0.993	0.947	1.015	1.015	1.0	0.96	96%	0.10%	0.302	0.300	10.01%	1.2
Water (ug/L)	0.123	0.128	0.103	0.098	0.106	0.116	0.124	0.1	0.11	114%	0.01%	0.036	0.036	10.04%	0.144

Table 4: Perchlorate in soil and water samples evaluating standard deviation, precision and recovery

Perchlorate	Spiked Value	Sample 1	Sample 2	Sample 3	Sample 4	Avg	Std Dev	Precision	Recovery	Precision Limit	Recovery Limits
Soil (ug/kg)	100	88.2	88.4	88.6	88	88.3	0.25	0.3	88.30%	±15	85-115
Water (ug/L)	10	8.83	8.97	8.9	8.86	8.89	0.06	0.7	88.90%	±15	85-115

Conclusion

This poster validated a modified method EPA 6850 for analysis of perchlorate from both non-potable water and soil samples. The implemented modifications were within those allowed by EPA's guidelines. Optimized settings for HPLC and MS enabled samples to be run in a laboratory setting with a Shimadzu LCMS 8050. Analytical data obtained were acquired, analyzed, and validated for the platform and has been in use for customer samples. Analytical data including linear calibration curve through at least three orders of magnitude, precision, accuracy, sample recovery, method detection limit, limit of detection, and limit of quantitation were obtained and validated. These parameters met and exceeded the quality criteria outlined by EPA in method 6850.

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