

Perchlorate Analysis Using Solid-Phase Extraction Cartridges

Victor F. Medina^{1,*}, Steven L. Larson¹, Barbara Extine², and Anthony Bednar¹

¹Environmental Laboratory, U.S. Army Engineer Research and Development Center, 3909 Halls Ferry Road, and ²Applied Research Associates, Inc., Southern Division, 119 Monument Place, Vicksburg MS 39180

Abstract

Perchlorate is a compound of increasing concern as an environmental contaminant and is being regulated at increasingly stringent levels. Reliable methods are needed to consistently analyze perchlorate at low concentration levels. This research investigates the use of solid-phase extraction cartridges as an alternative to large-volume injection loops to achieve low-level ($\mu\text{g/L}$ level) perchlorate quantitation. The method involves commercially available strong anion exchange (SAX) cartridges. Water samples are filtered (100 to 1000 mL) using the cartridge, which removes the perchlorate from the solution by anion exchange. Then, after the desired volume is filtered, the perchlorate is extracted using 4 mL of 1% NaOH. In addition, a cleanup method is developed to remove competing anions (chloride, sulfate, and carbonate) that are often found in environmental samples. Analyses are performed with an ion chromatograph using a 10- μL injection loop, yielding a perchlorate method detection limit (MDL) of 210 $\mu\text{g/L}$. One-liter volumes of a 2- $\mu\text{g/L}$ perchlorate spiked deionized water solution are filtered with SAX SPE. Following extraction and analysis, an MDL of 0.82 $\mu\text{g/L}$ is obtained, comparable to that found for 1-mL injection loop systems (reported as low as 0.53 $\mu\text{g/L}$). MDL studies are then conducted on perchlorate-amended groundwater (solution concentration of 70 $\mu\text{g/L}$) and surface water (solution concentration of 10 $\mu\text{g/L}$) using a filtration volume of 200 mL. The MDLs are 6.7 $\mu\text{g/L}$ for the groundwater and 2.4 $\mu\text{g/L}$ for the surface water.

Introduction

Perchlorate (ClO_4^-) occurs as a groundwater and soil contaminant, primarily caused by the use and manufacture of various pyrotechnic products. It has, therefore, become a compound of increasing concern over the past 5 years. Extensive, regional-scale contamination has been found in the Colorado River (1) and Panhandle region of Texas. Aquifer contamination has been found in both northern and southern California (2), and perchlorate contamination has recently

been identified at the Massachusetts Military Reservation (3).

Perchlorate testing has not been routinely performed even at sites where there was a high probability of its existence. For example, the majority of perchlorate detections in groundwater at the Massachusetts Military Reservation have occurred since the fall of 2001 (3), largely because it was not included as an analyte in previous groundwater studies. Improvements in analytical methods, which have lowered method detection limits from approximately 100 $\mu\text{g/L}$ to less than 1 $\mu\text{g/L}$ over the past 10 years, have also increased the number of positive detections. Perchlorate is extremely soluble (solubility of 200 g/L) and resistant to biodegradation, particularly in aerobic conditions. Therefore, it is possible that even small releases of perchlorate could cause detectable groundwater contamination.

Perchlorate has a high affinity for the human thyroid and is able to retard thyroid activity (5). Otherwise, health effects from perchlorate exposure are relatively unknown. The U.S. Environmental Protection Agency (EPA) has not issued a maximum contaminant level for perchlorate to date. However, the U.S. EPA and State regulatory agencies have set stringent regulatory and advisory levels that include the U.S. EPA preliminary drinking water limit of 1 $\mu\text{g/L}$ (6); California Department of Health Services groundwater action level of 4 $\mu\text{g/L}$ (2); California Office of Environmental Health Hazard Assessment draft public health goal ranging from 2 to 6 $\mu\text{g/L}$; U.S. EPA relevant standard for Massachusetts Military Reservation of 1.5 $\mu\text{g/L}$; and Massachusetts Department of Environmental Protection water advice for the City of Bourne of 1 $\mu\text{g/L}$ (3).

Another key aspect in the evolution of the identification and regulation of perchlorate as a contaminant has been advances in analytical methods to detect lower concentration levels. Most method development has centered on the use of ion chromatography with a conductivity detector. Although ion chromatography is effective at detecting perchlorate, it is basically used to detect anions in the mg/L range. In order to reach lower levels, large loop injection (0.5 to 1 mL) methods have been developed (7–10). These methods are able to achieve method detection limits (MDL) of as low as 0.53 $\mu\text{g/L}$.

However, the use of large injection volumes in liquid chromatography is susceptible to two critical problems (11). First,

* Author to whom correspondence should be addressed.

because the volume is increased, peaks are widened, which increases the possibility of peaks coelution, effectively masking analytes. It also allows for other peaks to broadly elute at times that overlap that of the target analyte, thereby increasing false-positive detections. A second issue with large injection volume is that matrix effects are exacerbated because the injection volumes represent a large fraction of the actual column volume. In addition, the use of large volume injection loops requires ion chromatograph users to switch columns when going from perchlorate analysis to the measurement of common anions.

Methods using mass spectrometry (MS) detectors (including electrospray MS) have also been studied (12,13). These methods have the advantage that identification is not just based on retention time and are less susceptible to interferences and false positives, but they are also much more expensive. The detection limits appear to be similar to those of conventional ion chromatography.

Solid-phase extraction (SPE) cartridges have been demonstrated to be effective at facilitating low-level detection for a variety of compounds (14–17). SPE cartridges exist for concentrating anions (15,17,18) and, therefore, might be useful for concentrating perchlorate. Ion-exchange studies indicate most anion exchange materials effectively remove perchlorate. However, in many cases, the exchange is irreversible, and recovery is not possible (19–21). Obviously, recovery would be a necessary step for SPE cartridges to be used for perchlorate analysis.

This study focused on the use of SPE cartridges for the quantitation of perchlorate at low levels using an ion chromatograph with a small, 10- μ L injection loop. The goals of the study were to develop a method for low-level detection for both spiked deionized water and for environmental samples. In order to use the method for environmental samples, a sample cleanup method was developed and tested on groundwater and surface water. Aside from developing the method, limitations of the method were evaluated so that users can make an informed decision as to whether implementing SPE cartridges is appropriate for a specific study.

Experimental

Water

The project used various water samples that were amended with perchlorate to achieve the desired concentrations. Three sources of water were used: deionized water, groundwater, and surface water. Deionized water was obtained from a Milli-Q water treatment system (Millipore, Billerica, MA). Groundwater was obtained from a water supply well in Monroe, LA. Surface water was obtained from Engineer Lake at the U.S. Army Corps of Engineers Waterways Experiment Station in Vicksburg, MS.

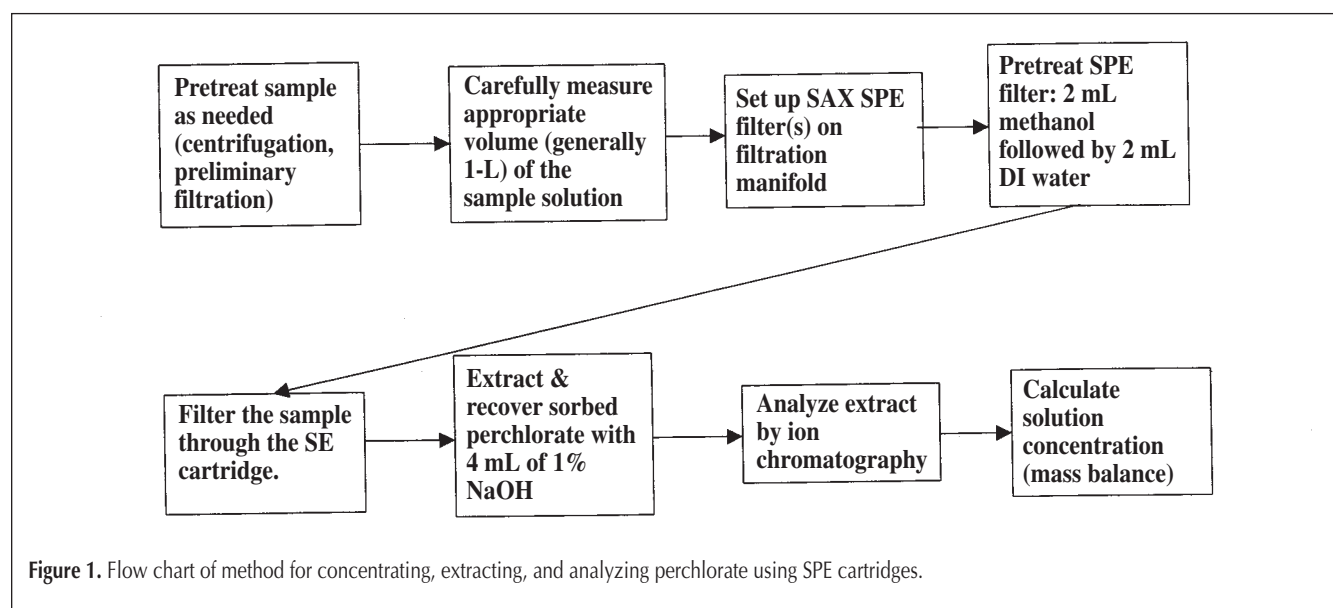
SPE filtration

There are several SPE cartridges available for the concentration of anions, including: NH₂ (Supelclean LC-NH₂, 3 mL, part number 57014) (Supelco, Bellefonte, PA), PSA (HF Bond Elut-PSA, 500 mg, 3 mL, part number 14102042) (Varian, Harbour City, CA), DEA (Varian Bond Elut-DEA, 500 mg, 3 mL, part number 12102043), and strong anion exchange (SAX, LRC-SAX, 500 mg, 10 mL, part number 12113043) (Varian). The first three of this list performed unsatisfactorily, as the perchlorate was not recovered effectively. (the NH₂ filters were initially successful, but upon obtaining a new allotment of these cartridges, it was found that these did not work effectively.) The SAX filter ended up being the most reliable cartridge.

Figure 1 summarizes the approach for filtration of the samples using SPEs. First, the sample was pretreated as needed (see Cleanup method for environmental samples section), and then the appropriate sample volume was carefully measured. The SPE was then conditioned with 2 mL of methanol followed by 2 mL of deionized (DI) water.

Next, the sample was filtered using the SPE. The filtration used a standard SPE vacuum manifold. The filtering pressure averaged 20 inches of Hg, and the filter speed was approximately 9 mL/min.

The next step was extraction of the removed perchlorate from the SPE into a small volume for analyses. The develop-



ment work focused on two parameters: extraction solution and volume of extractant. As part of this development work (not presented), two extractants were focused on: 1% NaOH and 12% NaCl. Both seemed to work equally well, so we decided to focus on 1% NaOH. Afterwards, other NaOH concentrations were tested. This showed that higher concentrations did not appear to improve performance, but lower recoveries occasionally occurred with lower NaOH concentration. In terms of extractant volume, it was found that 4 mL generally eliminated issues of unextracted perchlorate, which may occur at higher perchlorate concentrations. Thus, this was adopted as the standard.

Cleanup method for environmental samples

Preliminary studies indicated that other anions typically found in environmental samples resulted in poor perchlorate recovery when using SPE enhanced analysis. Therefore, a pretreatment method was developed to remove three key anions, chloride, carbonate, and sulfate (Figure 2). First, the sample was vacuum filtered using a 0.45- μm filter to remove particulates. Next, 1.3 g of granular barium chloride (BaCl_2 , assay > 99.8%) was added per liter of solution to be treated. The purpose of this was to remove sulfate by the following reaction:



Experiments were run with barium chloride cartridges (OnGuard II Ba, product number 057093) (Dionex, Sunnyvale, CA), but adding the granular reagent worked better.

The next step involved titrating the sample with 4% HCl until the solution pH was approximately 4. This step removed carbonate by converting it to carbon dioxide. The solution was then sparged with nitrogen gas to allow the CO_2 to escape. After sparging, the solution was allowed to settle and was filtered again with the 0.45- μm filter to remove the BaSO_4 flocculant.

Chloride, both natural and that generated by the previous treatment steps, was removed by filtration with a Dionex OnGuard AG cartridge (product number 057089), in which chloride is removed as a flocculant after reaction with silver ion. It was found that, in some cases, this flocculant would escape the filter. Thus, a third vacuum 0.45- μm filtration was conducted. At this point, the solution was ready for SAX SPE filtration (as discussed previously).

Ion chromatography

A Dionex DX 500 ion chromatograph with an AS-11 column was used to separate and quantitate perchlorate. The mobile phase was an isocratic 33.5mM NaOH solution. The flow rate was set at 1.5 mL/min, and the detector amperage was 100mA. Under these conditions, the perchlorate retention time was approximately 7.1 min, and the total run time was 12 min.

Calculation of perchlorate concentrations

Perchlorate concentrations could be calculated using a mass balance approach:

$$C_s = C_e \times V_e / V_s \quad \text{Eq. 2}$$

where C_s is the concentration in the original solution, C_e is the measured concentration of the extractant, and V_e is the extractant volume. The recovery was calculated as $C_e/C_s \times 100\%$.

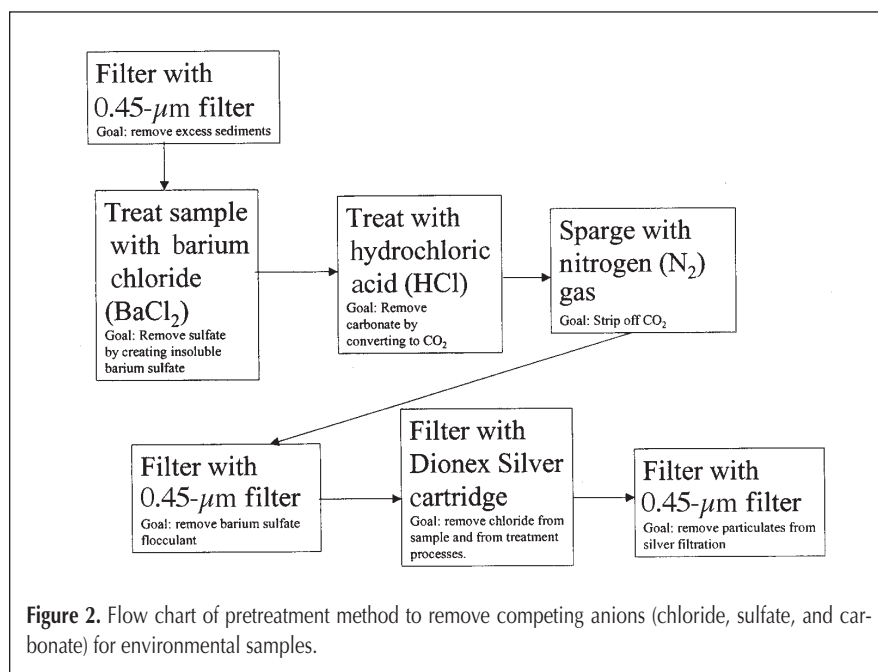
Determination and calculation of method detection limit

The method detection limit (MDL) is defined as "the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte" (22). The method for determination and calculation of the MDL followed the one that was described in the *Federal Register* (22), with the method described in *Standard Methods* (23) used as an additional reference. Seven replicate samples were carried through the pretreatment procedure (if required), then filtered, extracted, and analyzed. The standard deviation (SD) was calculated. The method detection limit was calculated as $3.14 \times \text{SD}$.

Results

Removal effectiveness of SPE cartridge

Initial experiments were conducted to demonstrate that the filters would remove 100% of perchlorate from solution until the sorptive capacity of the filter was reached. A 450- $\mu\text{g/L}$ solution was filtered in triplicate. The concentration of the filtrate was measured after 20, 50, 100, 500, and 1000 mL were filtered. Perchlorate was not detected in the leachate at volumes up to



500 mL, indicating it was sorbing on to the anion exchange media. At 1000 mL, after more than 4 meq had been filtered, the perchlorate broke through the filter.

Performance and method detection limit analysis for DI spiked samples

The method detection limit for perchlorate spiked DI water for the ion chromatograph (with 10 μL injection loop volume) without SPE concentration was 210 $\mu\text{g/L}$. This was substantially improved using SPE. Table I summarizes MDL tests on SPE concentrates of perchlorate spiked DI water ranging from 85 to 0.5 $\mu\text{g/L}$. As seen, filtration worked well on concentrations from 85 to 2 $\mu\text{g/L}$, with recoveries ranging from 93% to 108%. At 1 $\mu\text{g/L}$, the analyte was detected in all seven replicates, but the recovery had dropped to 78%. At 0.5 $\mu\text{g/L}$ high recovery occurred (107%) for five of the samples, and two had no detectable results. The 2- $\mu\text{g/L}$ set was chosen for the MDL analysis, which yielded an MDL of 0.82 $\mu\text{g/L}$.

Cleanup of environmental samples

Figure 3 summarizes the effectiveness of the cleanup method for groundwater and surface water samples, respectively. In the treatment of the groundwater (Figure 3A), the concentrations of the targeted competing anions (chloride,

sulfate, and carbonate) were reduced 68%, 93%, and 97%, respectively. The perchlorate concentration increased slightly but within the variation found among triplicate samples. Similarly, treatment of the surface water (Figure 3B) reduced chloride, sulfate, and carbonate by 89%, 94%, and 95%, and, once again, the perchlorate concentration was not substantially affected. For both environmental samples, the cleanup procedure did not appear to affect nitrate or phosphate concentrations, which were not targeted by the treatment. Nitrite was also analyzed, but was not detected in either treated or untreated samples.

The treatment approach also reduced the conductivity of the groundwater from 600 to 44 $\mu\text{S/cm}$, and reduced surface water conductivity from 392 to 12 $\mu\text{S/cm}$. Therefore, by targeting three anions (chloride, sulfate, and carbonate), the overall ionic strength of the solutions was effectively reduced by more than 92% in each case.

Although the concentrations of the targeted anions were reduced, the remaining concentrations were still in the mg/L range, which are relatively large compared with the target perchlorate concentrations (low $\mu\text{g/L}$ levels) using the SPE filtration approach. Thus, even with the treatment, there remained the opportunity for anion competition during the SAX SPE filtration.

Table I. Results of MDL Studies on Perchlorate Amended Deionized Water*

Initial concentration ($\mu\text{g/L}$)	Replicate ($\mu\text{g/L}$)							Calculations			
	1	2	3	4	5	6	7	Average ($\mu\text{g/L}$)	SD ($\mu\text{g/L}$)	MDL ($\mu\text{g/L}$)	Recovery (%)
85	94.73	94.66	83.22	89.89	89.31	90.69	87.46	91.42	2.82	8.85	107.6
5	4.10	4.37	4.18	5.29	4.51	4.77	5.37	4.65	0.51	1.60	93.1
2	2.38	2.13	1.77	2.21	1.64	1.83	1.94	1.99	0.26	0.82	99.3
1	0.57	0.84	0.68	0.75	1.01	0.80	0.80	0.78	0.14	0.43	77.8
0.5	0.63	0.74	0.61	0.49	0.68	NR [†]	NR	0.53	0.18	0.57	106.6

* For the initial concentration 0.5 $\mu\text{g/L}$ data, the 'not recovered' data were treated as zeros.
[†] Not recovered.

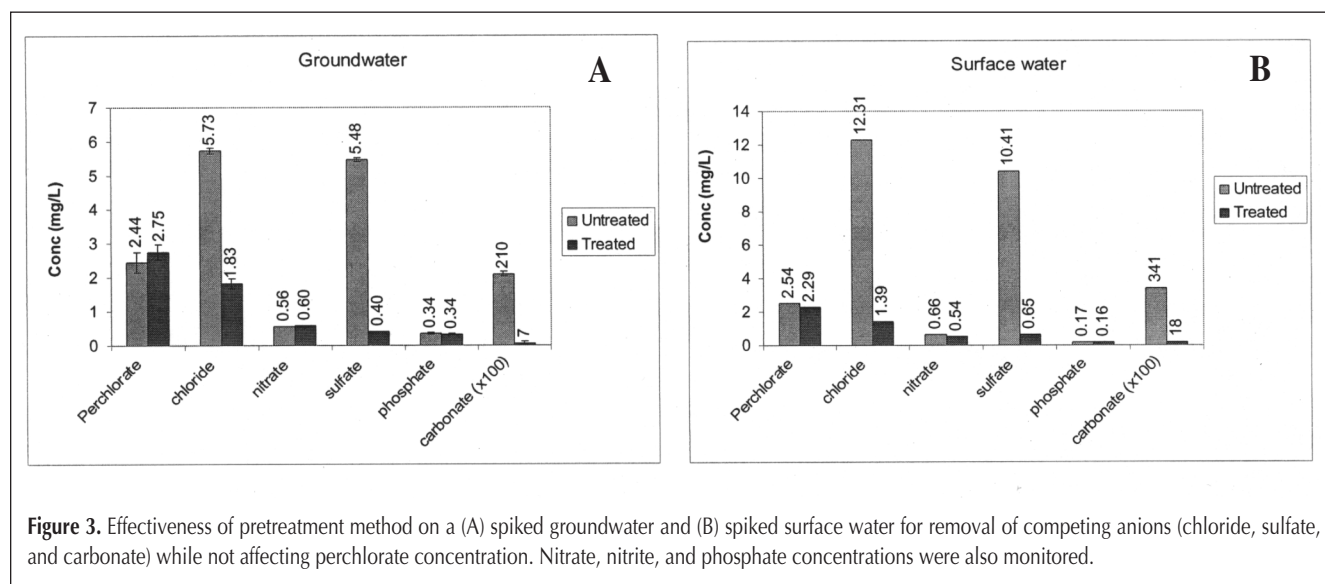


Figure 3. Effectiveness of pretreatment method on a (A) spiked groundwater and (B) spiked surface water for removal of competing anions (chloride, sulfate, and carbonate) while not affecting perchlorate concentration. Nitrate, nitrite, and phosphate concentrations were also monitored.

SPE effectiveness on pretreated environmental samples

Table II summarizes the effectiveness of SPE quantitation of perchlorate spiked groundwater and surface water at various perchlorate concentrations with filtration volumes ranging from 100 to 1000 mL. The pattern seen in each case was that, at smaller volumes, higher recovery was achieved. However, once a threshold volume was reached, the recovery dropped dramatically. In addition, as the solution concentration decreased, the threshold volume for low recovery dropped.

Ground water			
Filtration vol. (mL)	Recovery for given concentration and filtration volume		
	50 µg/L	100 µg/L	700 µg/L
100	68.1%	90.8%	99.1%
200	85.3%	94.0%	98.7%
500	NR*	98.7%	114.4%
1000	NR	NR	17.1%
Surface Water			
Filtration vol. (mL)	Recovery for given concentration and filtration volume		
	10 µg/L	50 µg/L	1000 µg/L
100	100.6%	81.6%	105.0%
200	115.3%	104.1%	111.3%
500	NR	103.9%	120.5%
1000	NR	31.2%	13.4%

* Not recovered.

Overall, recovery at lower concentrations was slightly better for the surface water sample, which is likely caused by its lower conductivity level (see previous).

Replicate filtrations and analyses were performed in order to calculate MDLs for environmental samples. The groundwater was conducted at 70 µg/L with a filtration volume of 200 mL and gave an MDL of 6.7 µg/L with a recovery of 101% (Table III). Surface water with a spiked concentration of 50 µg/L and filtration volume of 200 mL had an MDL of 2.4 µg/L and a recovery of 111%.

Discussion

The results given demonstrate that SPE cartridges can achieve low-level detections using a ion chromatography with a 10-µL injection loop for various perchlorate-spiked water samples. Although the methods worked well for the environmental samples tested (groundwater and surface water), the critical limitation to performance appears to be competition with other anions in the solution. This effect was partially ameliorated by pretreatment of the water and by controlling the volume processed. However, even after pretreatment, the residual anions were still in the mg/L range. Consequently, there would likely be limitations of the treatment process on highly saline waters, brines, and some natural waters

From a practical standpoint, the SPE method can be time consuming. Filtering a 1-L volume can take 2 or 3 h, and samples with fine particulates can take even longer. Careful pretreatment procedures can add 3 or 4 h more. However, this can be balanced, to a degree, by simultaneously preparing several samples at a time, as the time required to process 10 samples is only slightly longer than the time required for one sample.

This method may be an effective replacement for large-volume column injection for many applications. It will provide operators of existing ion chromatographs, configured to analyze mg/L levels of common anions, with an easy method to screen and quantitate low-level perchlorate concentrations in their samples.

Conclusion

The paper indicates that SPEs are an effective method to achieve low-level detection of perchlorate. Using a 10-µL injection loop, the SPE cartridges allowed for a method detection limit of 0.82 µg/L in perchlorate-spiked DI water. Even lower levels were analyzed, although at

Replicate	Ground water		Surface water	
	Extractant concentration (mg/L)	Calculated solution concentration (µg/L)	Extractant concentration (mg/L)	Calculated solution concentration (µg/L)
1	3.50	70.06	0.85	16.99
2	3.69	73.81	0.81	16.12
3	3.39	67.75	0.83	16.59
4	3.52	70.33	0.87	17.40
5	3.52	70.38	0.87	17.49
6	3.54	70.83	0.80	16.04
7	3.68	73.63	0.77	15.46
Average		70.97		16.58
Solution concentration (µg/L)		70		15
%Recovery		101%		111%
SD (µg/L)		2.13		0.75
MDL (µg/L)		6.7		2.4

* 70 mg/L solution, 200 mL filtration volume, 4 mL extraction volume.
† 50 mg/L solution, 200 mL filtration volume, 4 mL extraction volume.

some loss of accuracy and reliability. The MDLs of 6.7 and 2.4 $\mu\text{g/L}$ were obtained for perchlorate-spiked groundwater and surface water, respectively.

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