

Determination of Perchlorate in Drinking Water Using a Microbore Reagent-Free Ion Chromatography System

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Key Words

U.S. EPA Method 314.0, Water Analysis, Dionex IonPac AS16 Column, Dionex AERS 500 Suppressor

Goal

Describe the application of a 2 mm internal diameter column format for perchlorate determination in drinking water following U.S. EPA Method 314.0.

Introduction

Perchlorate (ClO_4^-) is an environmental contaminant released from perchlorate salts used in rocket fuel, fireworks, and other aerospace materials. Due to accidental release or improper disposal of perchlorate salt containing materials, it has been found in drinking, ground, and surface waters in several states in the U.S.¹ Perchlorate is known to inhibit thyroid gland function and affect normal growth and development.² Hence, in 1998 the U.S. EPA's Office of Groundwater and Drinking Water placed this anion on its Contaminant Candidate List (CCL) for drinking water. Currently, the U.S. EPA has not established any enforceable health regulations for perchlorate in drinking water or related matrices, although some states have set individual action levels. For example, the California Department of Public Health (CDPH) has set a maximum contaminant level (MCL) of 6 $\mu\text{g/L}$ perchlorate.³ If concentrations are detected above this level, then the CDPH recommends that utilities remove the drinking water source from service for proper treatment.

U.S. EPA Method 314.0 provides for determination of perchlorate in drinking water using ion chromatography. It allows for using an alternate column, as long as the column is capable of yielding symmetrical peak elution for perchlorate as described in Section 6.1.2.2. EPA Method 314.0 uses the Thermo Scientific™ Dionex™ ASRS™ ULTRA Suppressor but also allows for using an alternate suppressor, as long as comparable conductivity detection limits can be achieved and adequate baseline stability is attained, as measured by a combined baseline drift/noise of no more than 5 nS per minute over background conductivity (Section 6.1.3).



The previous Dionex (now Thermo Scientific) Application Update 148 (AU148) described a method for perchlorate determination in drinking waters based on EPA Method 314.0 with a Thermo Scientific™ Dionex™ IonPac™ AS16 4 mm column and suppressed conductivity detection with an improved suppressor, the Thermo Scientific™ Dionex™ ASRS™ ULTRA II Suppressor, operating in external water mode.⁴ AU148 was further updated to use the Thermo Scientific™ Dionex™ AERS™ 500 Anion Electrolytically Regenerated 4 mm suppressor.⁵ The Dionex AERS 500 suppressor is a superior suppressor to the Dionex ASRS ULTRA II suppressor, as it provides high capacity, low noise, high backpressure resilience, and fast startup. Moreover, the Dionex AERS 500 suppressor minimizes peak dispersion and improves peak efficiency particularly when coupled with 4 and 2 mm columns.

This application note further expands the scope of the U.S. EPA Method 314.0 to the 2 mm column format. The method described here uses an integrated ion chromatography system with a 2 mm Dionex IonPac AS16 column, a Thermo Scientific Dionex EGC III KOH cartridge, and suppressed conductivity detection with a Dionex AERS 500 2 mm suppressor operated in external water mode. This application note evaluates and describes the linear range and initial demonstration of capability (Section 9.2). Initial demonstration of capability includes determination of method accuracy (Section 9.2.3), precision (Section 9.2.4), method detection limit (MDL) (Section 9.2.6), and matrix conductivity threshold (MCT) (Section 9.2.8). This document also describes recovery of perchlorate in typical field samples as prescribed in EPA Method 314.0, Section 9.4.

Equipment

- A Thermo Scientific™ Dionex™ ICS-2100 Reagent-Free™ Ion Chromatography (RFIC™) system* was used in this work. The Dionex ICS-2100 system is an integrated ion chromatograph that includes:
 - Eluent Generator
 - Column Heater
 - Pump Degas
 - Dionex EG III KOH Cartridge (P/N 074532)
 - Thermo Scientific Dionex CR-ATC Continuously Regenerated Anion Trap Column (P/N 060477)
- Thermo Scientific Dionex AS-AP Autosampler (P/N 074926) with 250 µL injection loop or Thermo Scientific Dionex AS-DV Autosampler (P/N 068907) with 250 µL injection loop
- Thermo Scientific™ Autoselect™ Polyvial™ 10 mL Dionex AS-AP autosampler vials with caps and septa (P/N 055058)
- Thermo Scientific™ Polyvials™ and Filter Caps (20 µm), 250 each, for 5.0 mL vials (P/N 038141) for Dionex AS-DV autosampler
- Thermo Scientific™ Nalgene™ 2 µm Syringe Filters (P/N 194-2520)
- Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data System 7.2 Workstation
- Conductivity Meter (Thermo Scientific™ Orion™ (Model 105))
- Thermo Scientific™ Polyvials™, 250, 5 mL vials (P/N 038808) and Plain Caps without Filters (20 µm), 250, for 5.0 mL vials (P/N 039528)
- Nalgene Rapid-Flow 0.2 µm filter units, 1000 mL, nylon membrane, 90 mm diameter (Thermo Scientific P/N 164-0020)
- Nalgene Rapid-Flow 0.2 µm filter syringe filter units, polyethersulfonate membrane, 13 mm diameter (Thermo Scientific P/N 180-1320)

This method can also be run on a Thermo Scientific Dionex ICS-5000 system.

Reagent and Standards

- Deionized (DI) water, Type I reagent grade, 18 MΩ-cm resistance or better
- Sodium perchlorate (NaClO₄) (Sigma, Item No 410241)
- Sodium chloride (NaCl) (J. T. Baker, Item No 4058-05)
- Sodium sulfate (Na₂SO₄) (Mallinckrodt, Item No 8024)
- Sodium carbonate, monohydrate (Na₂CO₃•H₂O) (Fisher Scientific, Item No S262-3)

Conditions

Columns:	Dionex IonPac AS16 2 mm Analytical, 2 x 250 mm (P/N 055378) Dionex IonPac AG16 2 mm Guard, 2 x 50 mm (P/N 055379)
Eluent:	65 mM potassium hydroxide (KOH)
Eluent Source:	Dionex EGC III KOH cartridge (P/N 074532)
Flow Rate:	0.22 mL/min
Background Conductance:	<1 µS
Noise:	~1–2 nS/min peak-to-valley
Run Time:	20 min
Injection Volume:	250 µL in Push-Full mode, followed by 500 µL buffer loop wash after each injection
Column Temperature:	30 °C
Cell Temperature:	35 °C
Detection Mode:	Suppressed Conductivity with external water mode and Dionex AERS 500 suppressor, 2 mm (P/N 082541) with Thermo Scientific Dionex CRD 200 Carbonate Removal Device, 2 mm (P/N 062986)
Suppressor Current:	36 mA

Solutions, Reagents, and System Preparation

Perchlorate Standard Stock Solution

Dissolve 0.1231 g of sodium perchlorate in DI water in 125 mL polypropylene bottles. Adjust the volume to 100 mL to make a 1000 mg/L standard solution. This stock standard is stable for at least a month at 4 °C.

Working Standard Solutions

First, dilute the appropriate volume of the 1000 mg/L stock standard with DI water in a 125 mL polypropylene bottle to make a 5 mg/L secondary stock solution. The secondary stock solution is further diluted to make a 200 µg/L working stock solution. In this application, calibration standards were prepared at 1, 2, 5, 10, 25, and 50 µg/L perchlorate by appropriately diluting the working stock solution. Each calibration standard was analyzed in triplicate.

Mixed Common Anion Stock Solutions (U.S. EPA Method 314.0, Section 7.4.1)

Prepare 25 mg/mL (25,000 mg/L) each of chloride, sulfate, and carbonate in 125 mL polypropylene bottles as follows. Dissolve 4.1213 g of sodium chloride in DI water and dilute to 100 mL. Dissolve 3.6965 g of sodium sulfate in DI water and dilute to 100 mL. Dissolve 5.1658 g of sodium carbonate monohydrate (4.416 g of sodium carbonate) in DI water and dilute to 100 mL.

These solutions were used to prepare 50, 100, 200, 400, 600, 800, and 1000 mg/L (ppm) solutions of mixed anion (MA) standards of chloride, sulfate, and carbonate (MA(50), MA(100), MA(200), MA(400), MA(600), MA(800), and MA(1000), respectively). These standards were used to determine the MCT (Matrix Conductivity Threshold) (U.S. EPA Method 314.0, Section 9.2.8).

System Preparation and Setup

Install a Dionex EGC III KOH cartridge (P/N 074532). Install backpressure tubing in place of the column set to produce a total system pressure between 2000 and 2500 psi at a flow rate of 0.22 mL/min. Condition the cartridge as directed in the *Dionex EGC III Cartridge Quickstart Guide* (Document No. 031909-04) by setting the KOH concentration to 65 mM at 0.22 mL/min for 45 min. After completing the cartridge conditioning process, disconnect the backpressure tubing that was temporarily installed in place of the column set. Install a Dionex CR-ATC column between the Dionex EGC III KOH cartridge and Dionex EGC degas. For more information on installing the Dionex CR-ATC column, consult the *Dionex EGC III Cartridge Product Manual* (Document No 065018-05).

Install and configure the Dionex AS-AP or AS-DV autosampler. For the Dionex AS-AP autosampler, precision and accuracy of the autosampler will vary depending on the injection mode. The most accurate and precise injections are made with a calibrated sample loop, flushed with about five times the loop volume. The largest full-loop injection possible with the Dionex AS-AP autosampler is 7500 μ L. Install a 5 mL sample syringe and set the syringe speed to 40 μ L to make faster large-loop injections. Enter the correct "Sample Loop Size" and "Sample Syringe Volume" in the Dionex AS-AP Plumbing Configuration Screen. Refer to the *Dionex Autoselect AS-AP Autosampler Operator's Manual* (Document No. 065361) for details. The results reported here were obtained in the Push-Full mode (a full-loop injection mode).

Install 2 mm Dionex IonPac AS16 analytical and guard columns in the column oven. Use 0.005 inch diameter (red) tubing for making all the post-inject valve connections, i.e. from inject valve to the columns, then to the suppressor, then to the Dionex CRD 200 device, and finally to the detector cell. Make sure the system pressure is 2300 \pm 200 psi at the target eluent concentration and flow rate to allow the degas assembly to effectively remove electrolysis gases from the eluent. If necessary, install additional backpressure tubing between the degas assembly and the injection valve to adjust the system pressure to 2100–2500 psi. Do not allow the pressure to reach 3000 psi. Therefore, monitor the pressure periodically because pressure can gradually rise over time. To reduce pressure, trim the backpressure tubing.

Install the Dionex AERS 500 suppressor after the Dionex IonPac AS16 analytical column. The Dionex AERS 500

suppressor does not require any Quick Start using acid regenerants, and the suppressor can be installed after hydration with DI water using directions provided in *Dionex AERS 500 Suppressor Operator's Manual* (Document No. 031956-09). Configure the suppressor for external water mode according to the directions provided in the *Dionex AERS 500 Suppressor Operator's Manual*.

Install the Dionex CRD 200 (2 mm) device between the Dionex AERS 500 suppressor and the CD cell using the *Dionex CRD 200 Device Operator's manual* (Doc. No. 065068-03). Before operation, the Dionex CRD 200 device can be hydrated using instructions provided in *Quick Start Guide* (Doc. No. 065069-03). Installation of the Dionex CRD 200 device is required for this method to achieve perchlorate recovery consistent with the requirements of U.S. EPA Method 314.0 from high ionic strength matrices.

The storage solution of the Dionex IonPac AS16 column is 35 mM NaOH. Equilibrate the column with 65 mM KOH eluent at 0.22 mL/min for approximately 60 min, then analyze a system blank of DI water. An equilibrated system has a background signal of less than 1 μ S and peak-to-peak noise of less than 1 nS. No peaks should elute within the same retention time window as perchlorate. Inject a 25 μ g/L perchlorate standard. The column is equilibrated when two consecutive injections of the standard produce the same retention time for perchlorate.

Methods

Conductivity Meter Calibration

Prior to conducting the MCT study, measure the conductance of the samples with a calibrated conductivity meter that has a minimum measuring range of 1–10,000 μ S/cm. Verify the conductivity meter calibration by measuring the conductance of a commercially available reference solution or a prepared 745 mg/L KCl standard (U.S. EPA Method 314.0, Section 7.5) with a conductance of 1410 μ S/cm at 25 °C. The conductivity meter must yield a value between 1380 and 1440 μ S/cm to be considered calibrated.

MCT Study

Section 9.2.8 of U.S. EPA Method 314.0 describes the MCT as "an individual laboratory defined value" determined by preparing a series of sequentially increasing concentrations of chloride, sulfate, and carbonate fortified with a constant perchlorate concentration. Deionized water fortified with a recommended perchlorate concentration of 25 μ g/L (Laboratory Fortified Blank or LFB, Section 3.10) must be initially analyzed and followed by a series of increasing anionic solutions of chloride, sulfate, and carbonate, each containing 25 μ g/L perchlorate. The recommended 25 μ g/L perchlorate assumes that the MRL (Minimum Reporting Limit, Section 3.14) has been set between 3 μ g/L and 5 μ g/L. However, if an MRL of 1 μ g/L is required, then the MCT should be determined at a perchlorate concentration of 5 μ g/L.

We determined the MCT using 25 µg/L perchlorate. To determine the MCT with 25 µg/L perchlorate, a standard is prepared in DI water and injected in triplicate. Next, standards containing MA(50), MA(100), MA(200), MA(400), MA(600), MA(800), and MA(1000) are prepared by adding 0.2, 0.4, 0.8, 1.6, 2.4, 3.2, and 4 mL of each common anion from the stock solution (see the section *Mixed Common Anion Stock Solutions*) to separate 125 mL polypropylene bottles. Then, 2.5 mL of a 1 mg/L perchlorate secondary stock dilution standard is added to each MA solution and each standard is diluted to a final volume of 100 mL. A calibrated conductivity meter measures and records the conductance for each of these prepared solutions. Section 9.2.8.5 states that the MA(400) solution “should display a conductance of between 3200 µS/cm and 3700 µS/cm.” After analyzing each solution, the peak area to height ratio (A/H) along with quantified perchlorate concentration are recorded. The A/H values are used to calculate the A/H ratio percent difference (P/D_{AH}) between average A/H ratio of (A/H_{LFB}) and the average A/H ratios for each mixed anion solution (A/H_{MA}) using the equation provided in Section 9.2.8.8. The MCT is the matrix conductance where the P/D_{AH} exceeds 20%. As mentioned in Sections 9.2.8.9 and 9.2.8.10, there are two ways to calculate MCT using these data. The MCT can be calculated by using linear regression by plotting P/D_{AH} (as independent variable, x) and conductance (as dependent variable, y). Alternatively, instead of performing regression analysis, MCT can be set at the conductance level of the highest mixed anion solution which yielded a P/D_{AH} value below 20% threshold.

Field Sample Preparation

Compare the sample conductivity to the MCT previously determined in your laboratory (MCT determination is described above), as explained in U.S. EPA Method 314.0, Section 11. Filter all samples with a 0.2 µm syringe filter. Use a hydrophilic polypropylene or polyethersulfonate (PES) filter (e.g. Nalgene 0.2 µm PES syringe filters). Do not use a polyvinylidene fluoride (PVDF) filter. Discard the first 300 µL of the filtrate and filter the remainder into a clean, plastic autosampler vial. Qualify filters by analyzing a DI water blank and a 10 µg/L perchlorate standard that has been passed through the filter. The blank should be free of peaks within the retention time window of perchlorate and the recovery of the 10 µg/L standard should fall within 80–120%.

Samples that exceed the MCT can often be analyzed after an appropriate dilution followed by filtration with a 0.2 µm filter. U.S. EPA Method 314.0, Section 11.1.3 explains how to determine a sample’s dilution factor based on the MCT. For diluted samples, the minimum reporting level (MRL) must be raised by a proportion equivalent to the dilution.

If sample dilution does not yield the desired result or to avoid diluting samples, the concentration of the matrix ions can be reduced by treating the sample with Thermo Scientific™ Dionex™ OnGuard™ cartridges. This procedure is explained in further detail in U.S. EPA Method 314.0, Section 11.1.4 and in Dionex (now part of Thermo Scientific) Application Update 145.⁶ In this application, no pretreatment or dilution was required for the samples analyzed.

Results and Discussion

This work describes the use of 2 mm internal diameter (i.d.) column format for perchlorate determination in drinking water using U.S. EPA Method 314.0. The narrow bore column format allows for lower eluent consumption and reduces waste generation. A different column as well as eluent concentration, flow rate, and suppressor may be used for U.S. EPA Method 314.0, provided that the quality control parameters are met. Section 9.4.3 states that, “In recognition of the rapid advances occurring in chromatography, the analyst is permitted certain options, such as the use of different columns (which meet the criteria in Section 6.1.2.2), injection volumes, and/or eluents, to improve the separations or lower the cost of measurements.” U.S. EPA Method 314.0 specifies the use of a Dionex IonPac AS16 4-mm column with an eluent of 50 mM NaOH at a flow rate 1.5 mL/min, followed by suppressed conductivity detection with a Dionex ASRS ULTRA suppressor operated in the external water mode and a 1000 µL large-loop injection. Section 6.1.3 of the method further states that “An equivalent suppressor device may be utilized provided that comparable conductivity detection limits are achieved and adequate baseline stability is attained as measured by a combined baseline drift/noise of no more than 5 nS per minute over the background.” We replaced the Dionex ASRS ULTRA II suppressor used in the original AU148 with a Dionex AERS 500 suppressor. The Dionex AERS 500 suppressor provides lower background noise of 2 nS/min or less, and therefore improves the detection limits for perchlorate. In addition, we further found that for the 2 mm column method a carbonate removal device (CRD) was required for obtaining expected recovery of perchlorate from samples containing high mixed anion concentrations. The Dionex CRD 200 device combined with the flow rate and eluent concentration described here (0.22 mL/min flow rate and 65 mM eluent concentration) are required to meet all the specification described in EPA Method 314.0

Before evaluating various parameters described in the method, the system was calibrated. One blank and seven standards were injected to cover 1.5 orders of magnitude concentration range. Section 10.2.2 of the method states that the linear calibration range “should not extend over more than two orders of magnitude in concentration.” The calibration curve is linear over 1.5 orders of magnitude with a correlation coefficient of 0.999, based on data from triplicate injections of 1, 2, 4, 5, 10, 25, and 50 µg/L perchlorate standards. Figure 1 shows a chromatogram of a 1 µg/L perchlorate standard using the conditions described in this application update.

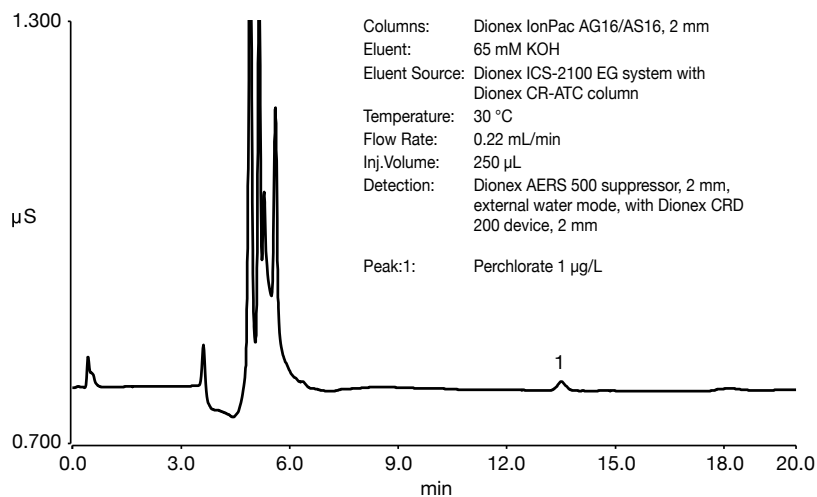


Figure 1. Determination of 1 µg/L perchlorate in DI water.

As described in Section 9.2, U.S. EPA Method 314.0 requires an initial demonstration of capability (IDC) before analyzing field samples. The IDC characterizes the instrument and laboratory performance prior to field sample analyses by the method. The IDC includes an initial demonstration of accuracy (IDA) and an initial demonstration of precision (IDP) by performing seven replicate injections of a laboratory fortified blank (LFB) fortified with 25 µg/L perchlorate. To meet the requirements of the IDA and IDP, the recovery must be within $\pm 10\%$ and the percent RSD must be less than 10%, respectively. As shown in Table 1, our results for the IDA

and IDP met the requirements described in Sections 9.2.3 and 9.2.4. As part of the IDC, a quality control standard (QCS) of 25 µg/L perchlorate was analyzed, which resulted in a recovery of 97.2%, as shown in Table 2.

This recovery meets the criteria outlined in Section 9.2.5 of the method that states the recovery of the QCS must be within $\pm 10\%$ of the stated value. We then determined the MDL, as described in Section 9.2.6, by performing seven replicate injections of DI water fortified with perchlorate at a concentration of three to five times the estimated instrument detection limit. The concentration values determined from the calibration curve were used to calculate the MDL. Figure 2 shows a chromatogram of a 0.25 µg/L perchlorate MDL standard fortified in DI water, and as shown in Table 1. The calculated MDL was 0.06 µg/L for the 2 mm column setup. This MDL value is only valid for perchlorate in a “clean” matrix, such as DI water. The MDL is expected to change as the ionic strength of the sample increases.

Table 1. Initial demonstration of capability (IDC) for perchlorate.

IDC Requirement (EPA Method 314.0 Section)	Prescribed Limit	Experimental Value
IDA (9.2.3)	Recovery within $\pm 10\%$ of true value	Recovery = 96.3%
IDP (9.2.4)	%RSD < 10	RSD = 0.54%
QCS (9.2.5)	Recovery within $\pm 10\%$ of true value	97.2%
MDL (9.2.6)	-	0.06 µg/L (perchlorate fortified at 0.25 µg/L)
MRL (9.2.7)	-	4 µg/L

Table 2. Experimental data used in the MCT determination with perchlorate fortified at 25 µg/L (N=3).

Injection Name	Conductivity (µS/cm)	Amount (µg/L)	Recovery (%)	Average Area (µS*min)	Average Height (µS)	A/H Ratio	PD _{A/H} (%)
LFB	0	25.15	100.5	0.080	0.2842	0.2821	0.0
MA 50^a	483	24.54	98.1	0.078	0.2749	0.2844	0.8
MA100	922	24.38	97.5	0.078	0.2678	0.2900	2.7
MA200	1722	24.87	99.4	0.079	0.2669	0.2971	5.3
MA400	3260	25.15	100.6	0.080	0.2571	0.3119	10.5
MA600	4520	25.48	101.9	0.081	0.2431	0.3342	18.4
MA800	5750	24.67	98.6	0.079	0.2278	0.3452	22.3
MA1000	7000	24.66	98.6	0.079	0.2170	0.3623	28.4

^aMA indicates a mixed common anion solution of chloride, sulfate, and carbonate included in the sample matrix at the parenthetical mg/L concentration for each anion.

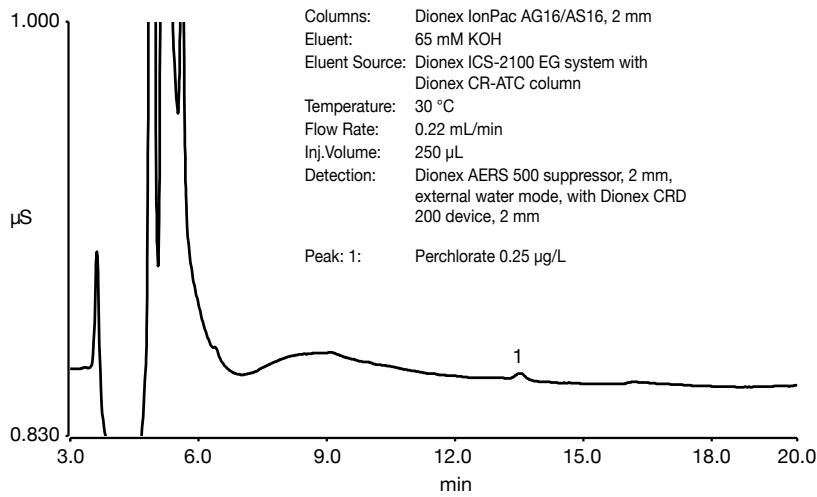


Figure 2. Determination of 0.25 µg/L perchlorate in DI water.

Next, we determined MCT (Section 9.2.8) using 25 µg/L perchlorate fortified in DI water as well as in standards containing MA(50), MA(100), MA(200), MA(400), MA(600), MA(800), and MA(1000) as described in *Methods* section above. The perchlorate concentration used for MCT determination was based on the MRL set at 4 µg/L perchlorate. MCT verification (Section 9.2.8.11) was performed by spiking MRL into a solution representing conductance equivalent to MCT. Table 2 shows the data used in this study for MCT calculation. In the results described here, the calculated MCT value was set at 4520 µS. This is the conductance value of the highest mixed anion concentration i.e. 600 mg/L that results in $PD_{A/H}$ value below 20%. The sample for MCT verification was prepared by spiking 600 mg/L mixed anions [MA(600)] into a 4 µg/L perchlorate solution. The calculated MCT value, mixed anion concentration required for MCT, and perchlorate recovery for MCT verification are included in Table 3. The calculated perchlorate recovery is 80.6%, which is within the 70–130% recovery limit prescribed for successful MCT verification. As mentioned in EPA Method 314.0, (Section 9.2.8.12), if during MCT verification, the MRL recovery fails the criteria, the MCT should be lowered by 10% and MCT verification should be repeated.

Table 3. MCT determination and verification results.

MCT Study Parameter	Value
Calculated MCT	4520 µS/cm
Mixed Anion Concentration at MCT	600 mg/L
Perchlorate Recovery for MCT Verification	80.6%

Figure 3 shows chromatograms of 25 µg/L perchlorate fortified in DI water, MA(200), and MA(1000), respectively. Chromatographic performance of perchlorate can deteriorate at high ionic concentrations, primarily due to the presence of high concentrations of chloride, sulfate, and carbonate. Before samples are analyzed, their conductance must be determined. If the conductance is greater than the determined MCT, the samples should either be appropriately diluted or pretreated to reduce the common anion concentrations (see *Field Sample Preparation* above in *Methods* section).

Sample matrix effects can bias experimental analytical results. One way to assess matrix effects is to prepare a laboratory fortified matrix (LFM, Section 3.11). A LFM is accomplished by spiking a field sample with a known amount of analyte and then determining the percent recovery from the amount added. This application analyzed five matrices: DI water and four drinking water samples from different sources. Figure 4 shows a chromatogram of drinking water samples spiked with 4 µg/L perchlorate. Each LFM sample was analyzed and the perchlorate recoveries were calculated with the equation provided Section 9.4.1.3. Figure 5 shows the results of this experiment. The calculated perchlorate recoveries were approximately 87.8 to 99.8%, which were well within the 80–120% range specified by the method (Section 9.4.1.4).

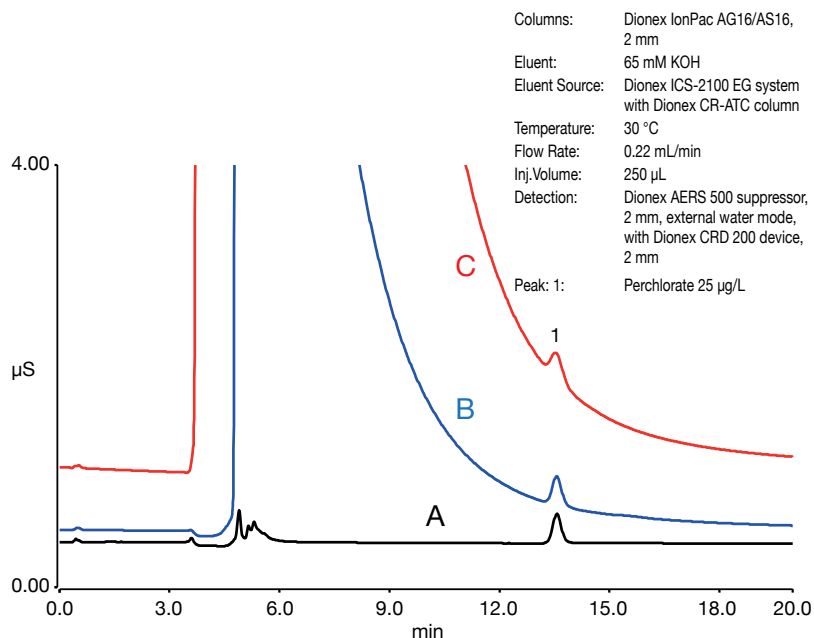


Figure 3. Determination of 25 μ g/L perchlorate in A. deionized water B. MA 200 and C. MA1000.

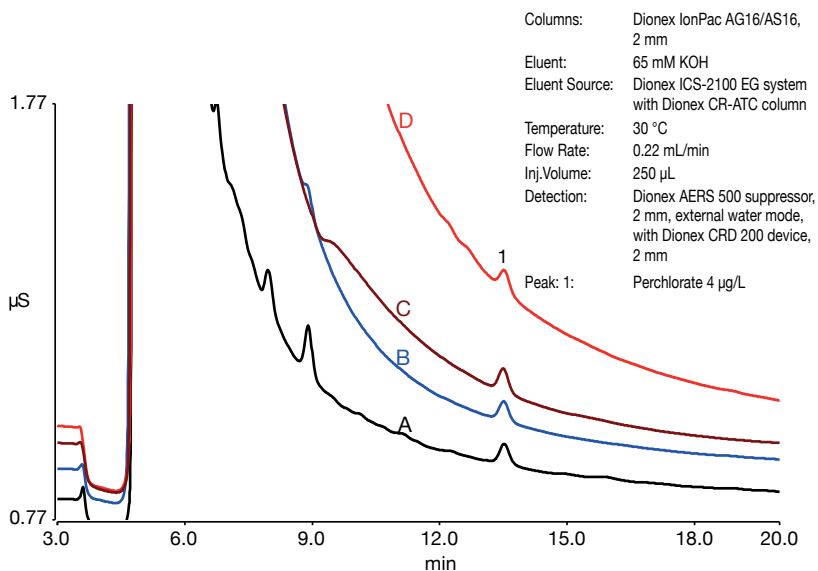


Figure 4. Determination of 4 μ g/L perchlorate in four drinking water samples.

Recovery of 4 μ g/L Perchlorate from Field Samples

(N=7, Error Bar=Stdev)

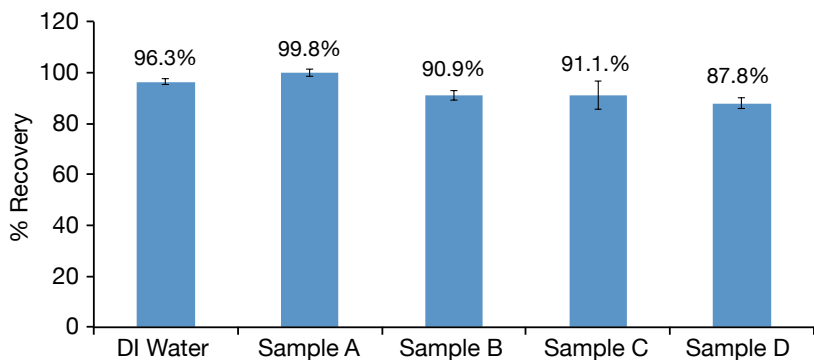


Figure 5. Calculated recoveries of 4 μ g/L perchlorate spiked into four drinking water samples.

Conclusion

This work uses a 2 mm Dionex IonPac AS16 column to demonstrate an approved approach for the determination of perchlorate in drinking water samples using U.S. EPA Method 314.0. The use of a 2 mm column format instead of 4 mm reduces eluent consumption and also waste generation. The results obtained in this work for precision and accuracy were within the limits set by U.S. EPA Method 314.0. The calculated limit of detection was 0.06 µg/L in DI water. Recovery of MRL (4 µg/L perchlorate) spiked into a solution with conductance level similar to MCT was within the 70–130% recovery limits required for successful MCT verification. Perchlorate recoveries obtained from spiked field samples were within prescribed limits indicating acceptable tolerance to matrix effects. Overall, the results presented in this application note meet or exceed the performance requirements specified in U.S. EPA Method 314.0.

Precautions for a Successful MCT Verification

1. U.S. EPA Method 314.0 prescribes external water mode to be used with the anionic suppressor device (Section 6.1.3.1). While it may be possible to use recycle mode instead for perchlorate determination, in our hands, a successful MCT verification was not possible using recycle mode. Although results may vary in individual laboratories, the recycle mode operation with the suppressor device is not recommended for perchlorate quantification.
2. A Dionex CRD 200 (2 mm) device installed after the suppressor improves perchlorate recovery from high anionic matrices used in MCT determination, verification, and field sample analysis experiments. For example, experiments without the Dionex CRD 200 device resulted in perchlorate recoveries in the MCT verification experiment that were lower than the 70–130% range prescribed in U.S. EPA Method 314.0. Hence, the Dionex CRD 200 device is required for perchlorate analysis using the microbore method described here.
3. The flow rate (0.22 mL/min) and eluent concentration (65 mM) conditions described here were found to be most suited for the MCT verification experiment. While other conditions may work, we found reproducible MCT verification was only possible using these conditions.

References

1. Jackson, P. E.; Gokhale, G. T.; Streib, T.; Rohrer, J. S.; Pohl, C. A. *J. Chromatogr. A* **2000**, *888*, 151.
2. Gilbert, M. E.; Sui, L. *Environ. Health Perspect.* **2008** June, *116*(6), 752.
3. *Perchlorate in Drinking Water*, California Department of Public Health, Effective Date October 2007: <http://www.cdph.ca.gov/services/DPOPP/regs/Pages/R-16-04-PerchlorateinDrinkingWater.aspx>
4. Dionex Corporation (now part of Thermo Scientific). *Determination of Perchlorate in Drinking Water using a Reagent Free™ Ion Chromatography System*. Application Update 148; Sunnyvale, CA.
5. Dionex Corporation (now part of Thermo Scientific). *Determination of Perchlorate in Drinking Water using a Reagent Free™ Ion Chromatography System*. Application Update 148; (2015) Sunnyvale, CA.
6. Dionex Corporation (now part of Thermo Scientific). *Determination of Perchlorate in Drinking Water by Ion Chromatography*. Application Update 145; Sunnyvale, CA.

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