

Determination of Low Concentrations of Perchlorate in Drinking and Groundwaters Using Ion Chromatography

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Introduction

Ammonium perchlorate is a key ingredient in solid rocket propellants. Perchlorate has recently been found in drinking water wells in regions of the U.S. where aerospace material, munitions, or fireworks were developed, tested, or manufactured.¹ Perchlorate poses a human health concern because it can interfere with the thyroid gland's ability to utilize iodine to produce thyroid hormones. Current data suggest that 4 to 18 µg/L (ppb) is an acceptable exposure level.¹ The State of California requires remedial action for drinking water sources containing more than 18 µg/L perchlorate.

The determination of perchlorate at trace levels is a difficult analytical task and ion chromatography (IC) represents the only viable means for the quantification of such low concentrations of perchlorate. In 1997, the California Department of Health Services (CDHS) developed an IC method to support the California action level of 18 µg/L.² The CDHS method uses a Thermo Scientific™ Dionex™ IonPac™ AS5 column and an eluent of 120 mM sodium hydroxide containing 2 mM p-cyanophenol, which is added to minimize hydrophobic interactions with the resin.³ In 1998, we developed an updated method for determining low perchlorate concentrations using a Dionex IonPac AS11 column with an eluent of 100 mM sodium hydroxide and suppressed conductivity detection.^{4,5}

This application note describes an improved method to quantify low levels of perchlorate. This method uses a Dionex IonPac AS16 column to separate perchlorate from the other anions typically found in drinking and groundwaters. The Dionex IonPac AS16 is a high-capacity, very hydrophilic, hydroxide-selective column designed for the fast separation of polarizable anions (for example, thiosulfate, iodide, and perchlorate). Compared to other anion-exchange columns, the polarizable anions are eluted with higher efficiency and improved peak shape, without the addition of organic solvents. The Dionex IonPac AS16 column is the column specified in U.S. EPA Method 314.0,

which is the analytical method to be prescribed for the analysis of perchlorate in the assessment phase of the Unregulated Contaminant Monitoring Rule.⁶

Because perchlorate is well separated from other inorganic anions using the Dionex IonPac AS16 column at a lower hydroxide eluent concentration than needed for the IonPac AS11, the EG40 eluent generator can be used. This application note shows that perchlorate can be quantified at the 2 µg/L level using a Dionex IonPac AS16 column, EG40-generated hydroxide eluents, a large-loop injection, and suppressed conductivity detection.

Equipment

- Thermo Scientific Dionex DX-500 Ion Chromatography System
 - GP50 Gradient Pump
 - CD20 Conductivity Detector
 - AS40 Autosampler
 - LC30 Chromatography Oven
 - EG40 Eluent Generator with a Thermo Scientific Dionex EluGen™ Hydroxide Cartridge
- Two 4 L plastic bottle assemblies (for external water mode suppression)
- Thermo Scientific Dionex PeakNet™ Chromatography Workstation

Reagents and Standards

- Deionized water (DI H₂O), Type I reagent grade, 18 MΩ-cm resistance or better
- Sodium perchlorate, 99% A.C.S. reagent grade or better (Sigma-Aldrich)
- A.C.S. reagent grade sodium salts (Fisher, Sigma-Aldrich, Fluka, EM Science) were used to make standards of other anions for interference studies.

Conditions	
Columns:	Dionex IonPac AS16 Analytical, 4 × 250 mm (P/N 055376) Dionex IonPac AG16 Guard, 4 × 250 mm (P/N 055377)
Eluent:	65 mM potassium hydroxide
Eluent Source:	EG40
Flow Rate:	1.2 mL/min
Temperature:	30 °C
Sample Volume:	1000 µL
Detection:	Suppressed conductivity, Thermo Scientific Dionex ASRS™ ULTRA, auto-suppression, external water mode; Power setting – 300 mA
System Backpressure:	2600 psi
Background Conductance:	1–4 µS
Run Time:	12 min

Preparation of Solutions and Reagents

Stock Perchlorate Standard Solution

Dissolve 1.4120 g of sodium perchlorate monohydrate in 1000 mL of deionized water to prepare a 1000 mg/L standard solution. This standard is stable for at least one month when stored at 4 °C.

Working Standard Solutions

Appropriate dilutions of the 1000 mg/L perchlorate standard solution were made for studies of method linearity and the method detection limit (MDL). Method linearity was determined by diluting 2, 10, 20, 50, and 100 µL of the 1000 mg/L perchlorate standard to 1 L to prepare working standard solutions at 2, 10, 20, 50, and 100 µg/L and making two injections of each working standard. Seven injections of the 2 µg/L standard were made for the MDL study.

Interference Studies

To determine if other anions interfere with perchlorate determinations, 1 mL samples containing 100 ppb of the chosen anion and 20 ppb of perchlorate were injected. Arsenate, arsenite, bromate, bromide, carbonate, chlorate, chloride, chromate, cyanide, humic acid, iodate, iodide, molybdate, nitrate, nitrite, phosphate, phthalate, selenate, sulfate, sulfite, thiocyanate, and thiosulfate were tested as possible interferences.

To ascertain the effect of high levels of common anions on perchlorate recovery, solutions containing 50, 200, 600, and 1000 mg/L carbonate, chloride, or sulfate and 20 µg/L perchlorate were prepared. The effect of sulfate on perchlorate recovery was further investigated by preparing solutions containing 50, 200, 600, and 1000 mg/L sulfate and either 2 or 200 µg/L perchlorate. One-milliliter aliquots of each of these samples were analyzed. To determine the effect of very high chloride concentrations, a sample was prepared that contained 10,000 mg/L chloride and 100 µg/L perchlorate. An aliquot of this sample was treated with a Thermo Scientific Dionex OnGuard™ Ag cartridge (P/N 39637) followed by a Dionex OnGuard H cartridge (P/N 39596).

Prepare the Dionex OnGuard cartridges by passing 10 mL of deionized water through them at 2 mL/min. (For details on cartridge preparation, refer to the Dionex OnGuard cartridge manual, P/N 032943.) After the cartridges have been prepared, pass 5 mL of the undiluted sample through the cartridge. Discard the first 3 mL and collect the remainder for injection.

System Preparation and Setup

For determinations of target anions at trace concentrations, it is essential to have low baseline noise. To ensure a quiet baseline, the following steps must be taken during the system setup. The Dionex ASRS ULTRA is operated in the external water mode rather than the recycle mode. A 1000 psi backpressure coil must be added to the degas module on the eluent generator. Refer to the Dionex EG40 Eluent Generator manual (P/N 031373) for details on adding backpressure to the degas module. The final system backpressure should be in the range of 2400–2600 psi when using the EG40 eluent generator. Prior to sample analysis, determine a system blank by analyzing 1 mL of deionized water using the method described above. An equilibrated system has a background conductance between 1 and 4 µS with the peak-to-peak noise should not exceed ions 5–10 nS, and no peaks eluting with the same retention time as perchlorate (9.6 ± 0.2 min).

Results and Discussions

Figure 1 shows a chromatogram of a 20 µg/L perchlorate standard. Perchlorate elutes at 9.6 min. The method linearity range was determined to ensure accurate quantification of perchlorate. Figure 2 shows that the method is linear from 2 to 100 µg/L, a concentration range appropriate for this application. This method is also linear in a larger concentration range (2–100 ppm, $r^2 = 0.9999$). The excellent linearity over a wide concentration range is a result of the high capacity for perchlorate and its symmetrical peak shape using the Dionex IonPac AS16 column. The MDL was established by making seven

Column: Dionex IonPac AG16, AS16
 Eluent: 65 mM potassium hydroxide
 Eluent Source: EG40
 Temperature: 30 °C
 Flow Rate: 1.2 mL/min
 Inj. Volume: 1000 µL
 Detection: Suppressed conductivity, Dionex ASRS ULTRA,
 auto-suppression, external water mode
 Peaks: 1. Perchlorate 20 µg/L

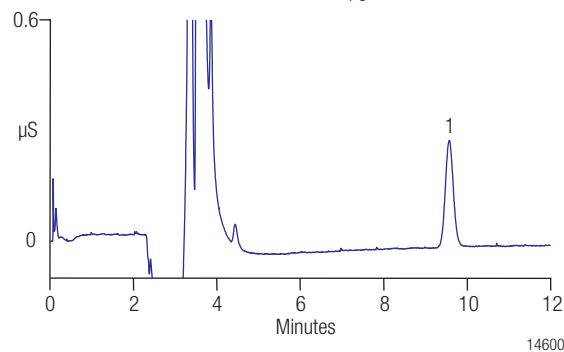


Figure 1. Perchlorate standard at 20 µg/L.

replicate injections of a 2 µg/L perchlorate standard. Table 1 shows the results of this study. The MDL calculated using the method described in U.S. EPA Method 300.0 is 151.4 ng/L.⁷ Figure 3 shows a chromatogram of a 2 µg/L perchlorate standard.

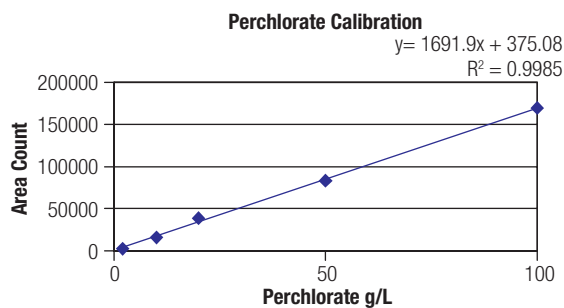


Figure 2. Perchlorate calibration.

Table 1. Determination of the method detection limit for perchlorate.

Injection #	Peak Area	Retention Time (min)
1	2416	9.82
2	2314	9.82
3	2313	9.83
4	2323	9.85
5	2414	9.73
6	2317	9.82
7	2384	9.72
Average	2354	9.80
SD	48.22	0.05
RSD	2.05	0.53
MDL*	151.4 ng/L	

*MDL = SD * $t_{s,99}$, where $t_{s,99} = 3.14$ for $n = 7$

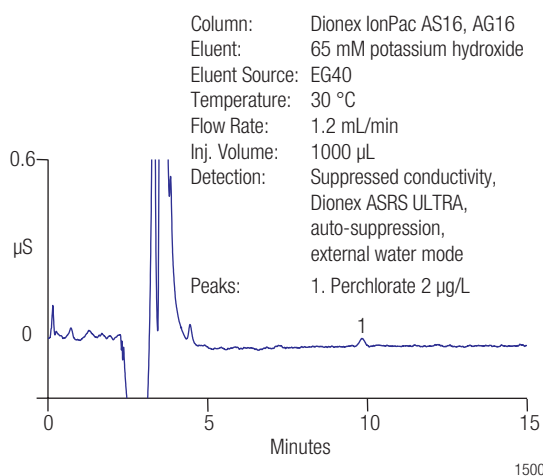


Figure 3. Perchlorate standard at 2 µg/L.

Interference Studies

Common Anions

Twenty-two anions were injected using the conditions described in this application note to study whether they interfere with the determination of perchlorate. Included in these 22 anions were polarizable anions that are typically well retained on anion-exchange columns. The results of this study are shown in Table 2. All 22 anions elute well before perchlorate, most in less than 4 min, and therefore do not interfere with the determination of perchlorate.

Table 2. Comparison of the retention times of 22 anions and perchlorate on the Dionex IonPac AS16 column (1000 µL injected)*.

Anion	Anion Retention Time (min)	Perchlorate Retention Time (min)
Arsenate	<4	9.78
Arsenite	<4	9.75
Bromate	<4	9.72
Bromide	<4	9.73
Carbonate	<4	9.72
Chlorate	<4	9.72
Chloride	<4	9.68
Chromate	<4	9.68
Cyanide	<4	9.65
Humic acid	<4	9.67
Iodate	<4	9.65
Iodide	5.28	9.65
Molybdate	<4	9.63
Nitrate	<4	9.65
Nitrite	<4	9.63
Phosphate	<4	9.63
Phthalate	<4	9.62
Selenate	<4	9.60
Sulfate	<4	9.60
Sulfite	<4	9.60
Thiocyanate	7.72	9.60
Thiosulfate	<4	9.58

* An eluent of 50 mM hydroxide at 1.5 mL/min was used for this study.

Groundwater samples may contain high concentrations of common anions, particularly carbonate, chloride, or sulfate. The method outlined in this application note can be used to determine low concentrations of perchlorate in the presence of high concentrations of these common anions. The effect of mg/L levels of these anions on perchlorate recovery was investigated by injecting solutions of 20 µg/L perchlorate in the presence of 50, 200, 600, and 1000 mg/L carbonate, chloride, or sulfate. Quantitative recoveries were obtained for perchlorate at the 20 µg/L level in all cases, as shown in Table 3.

Table 3. Effect of mg/L levels of common anions on perchlorate recovery (20 µg/L) on the Dionex IonPac AS16 column (1000 µL injected)*.

Anion	Anion Concentration (mg/L)	Perchlorate Recovery
Carbonate	50	97.6%
Carbonate	200	94.4%
Carbonate	600	95.4%
Carbonate	1000	93.5%
Chloride	50	96.1%
Chloride	200	96.7%
Chloride	600	109.6%
Chloride	1000	97.4%
Sulfate	50	94.4%
Sulfate	200	96.3%
Sulfate	600	94.7%
Sulfate	1000	95.5%

* An eluent of 50 mM hydroxide at 1.5 mL/min was used for this study.

Because sulfate is the most likely interference in groundwaters, the effect of sulfate on perchlorate recovery was further investigated. Perchlorate (200 µg/L) was determined in the presence of 50, 200, 600, and 1000 mg/L sulfate. The recovery of perchlorate from these samples was 78, 89, 77, and 90%, respectively. The same study was also done with 2 µg/L perchlorate. For that experiment, the recoveries were 115, 107, 109, and 110%, respectively. Figure 4 shows an overlay of chromatograms of 200 µg/L perchlorate in the presence of 50 to 1000 mg/L sulfate, demonstrating that high concentrations of sulfate do not significantly affect the retention time or peak shape for perchlorate.

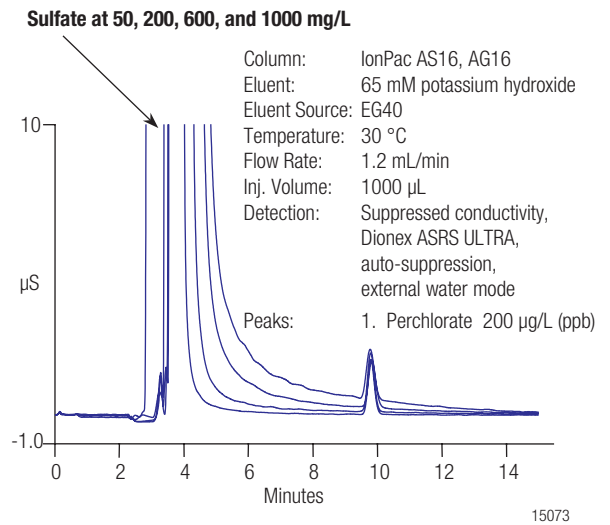


Figure 4. Effect of sulfate on perchlorate recovery on the Dionex IonPac AS16 column.

Extreme Chloride Matrices

Low concentrations of perchlorate are sometimes found in matrices containing a very high chloride concentration (for example, brines). The sample used for this study had a chloride concentration of 10,000 mg/L and a perchlorate concentration of 100 µg/L. One approach for determining perchlorate in an extreme chloride matrix is to reduce the sample's chloride concentration. This can be achieved by pretreating the sample with a Dionex OnGuard Ag cartridge. The cartridge packing is a high-capacity, strong acid, cation-exchange resin in the Ag⁺ form that is designed to remove chloride from the sample by precipitating it as silver chloride. Figure 5B shows an analysis of the sample (10,000 mg/L chloride and 100 µg/L perchlorate) after treatment with a Dionex OnGuard Ag cartridge. This treatment allows perchlorate to be quantified with good recovery (92.6%). Analysis of the untreated sample is shown in Figure 5A.

Another approach for determining perchlorate in an extreme chloride matrix is to dilute the sample and/or reduce the eluent concentration. The same sample containing chloride at 10,000 mg/L and perchlorate at 100 µg/L was diluted 10-fold and the diluted solution was analyzed using two different eluent strengths, 35 mM and 65 mM KOH. Figure 6A shows that when using 65 mM KOH, perchlorate is difficult to quantify because it elutes on the tail of the large chloride peak. When the weaker eluent (35 mM KOH) is used, perchlorate elutes at 14 min and is easier to quantify (Figure 6B).

When choosing an approach for analyzing perchlorate in samples containing high concentrations of chloride, the perchlorate concentration must be considered. For a sample containing low levels of perchlorate (<40 µg/L), use the Dionex OnGuard Ag cartridge. In samples where the concentration of perchlorate is higher, sample dilution and a 35 mM KOH eluent is recommended.

Column: Dionex IonPac AG16, AS16
 Eluent: 65 mM potassium hydroxide
 Eluent Source: EG40
 Flow Rate: 1.2 mL/min
 Temperature: 30 °C
 Inj. Volume: 1000 μ L
 Detection: Suppressed conductivity,
 Dionex ASRS ULTRA, auto-suppression,
 external water mode

Sample Prep.: (A) Direct injection
 (B) Dionex OnGuard - Ag

Recovery: (B) 92.6%

Peaks: 1. Perchlorate spiked at 100 μ g/L

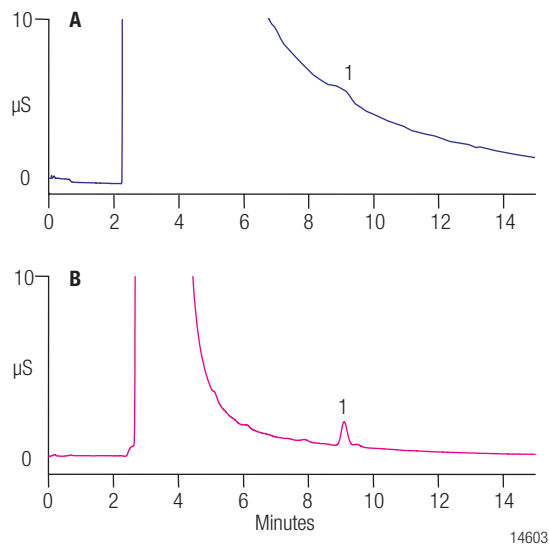


Figure 5. Determination of perchlorate in high chloride (10,000 mg/L) matrices.

Column: Dionex IonPac AS16, AG16
 Eluent: (A) 65 mM potassium hydroxide
 (EG40)
 (B) 35 mM potassium hydroxide
 (EG40)
 Eluent Source: EG40
 Flow Rate: 1.2 mL/min
 Temperature: 30 °C
 Inj. Volume: 1000 μ L
 Detection: Suppressed conductivity,
 Dionex ASRS ULTRA,
 auto-suppression,
 external water mode

Sample Prep.: 1:5 dilution
 Recovery: (A) 88.3%
 (B) 88.0%

Peaks: 1. Perchlorate spiked at 100 μ g/L

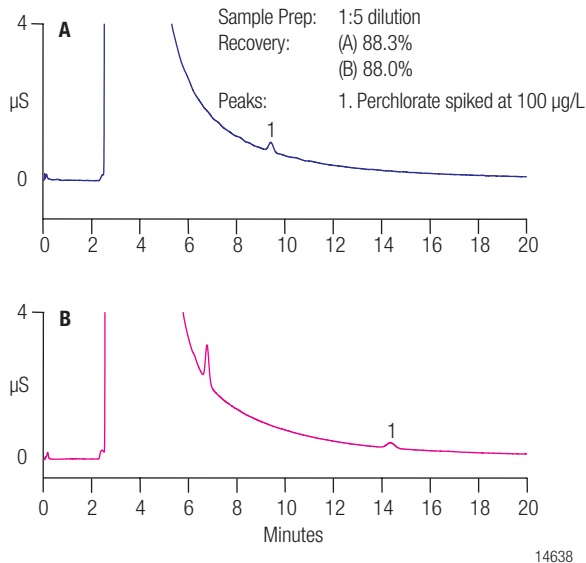


Figure 6. Determination of perchlorate in high chloride (10,000 mg/L) matrices.

Conclusion

The method described in this application note can be used to determine low μ g/L concentrations of perchlorate in drinking and ground waters. The use of IC with the Dionex IonPac AS5 or AS11 columns has previously been shown to provide an interference-free method for the analysis of perchlorate in modest-ionic-strength drinking water and groundwater samples⁸; the AS16 column provides similar results. The Dionex IonPac AS16 also is compatible with the EG40 eluent generator, and its higher capacity makes it most appropriate for the analysis of perchlorate in higher- ionic-strength samples.

Suppliers

EM Science, P.O. Box 70, 480 South Democrat Road,
 Gibbstown, NJ 08027 USA, Tel: 800-222-0342, www.
 emscience.com.

Fisher Scientific, 2000 Park Lane, Pittsburgh, PA 15275-
 1126 USA, Tel: 800-766-7000, www.fishersci.com.

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 Louis, MO 63178 USA, Tel: 1-800-325-3010, www.
 sigmaldrich.com.

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