Application Note 121

Analysis of Low Concentrations of Perchlorate in Drinking Water and Ground Water by Ion Chromatography

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Introduction

Perchlorate (as ammonium perchlorate), which is widely used in solid rocket propellants, has recently been found in drinking water wells in areas where aerospace materials and munitions were manufactured and tested.[1] Perchlorate is a health concern because it interferes with the production of thyroid hormones. Current data suggest that an exposure level range of 4 to 18 µg/L (ppb) is acceptable.[2] Although perchlorate is not yet regulated in the U.S. under the Federal Safe Drinking Water Act, the State of California requires remedial action for drinking water sources containing greater than 18 µg/L of perchlorate.

This application note details a new method developed to quantify low levels of perchlorate. A large loop injection (1000 µL) is used with a Thermo Scientific™ Dionex™ IonPac™ AS11 column and suppressed conductivity detection to quantify perchlorate in drinking water down to approximately 2.5 µg/L.

Equipment

- Thermo Scientific Dionex DX-500 Ion Chromatography System*:
  - GP40 Gradient Pump
  - CD20 Conductivity Detector
  - AS40 Automated Sampler
  - LC20 Chromatography Enclosure with a rear-loading valve
- 4 L plastic bottle assemblies (two for external water mode)
- Thermo Scientific Dionex PeakNet™ Chromatography Workstation

*Equivalent or improved results can be achieved using the Thermo Scientific Dionex ICS-1100 or the Thermo Scientific ICS-1600 system.

Reagents and Standards

- Deionized water (DI H_2O), Type I reagent grade, 18 MΩ-cm resistance or better
- Sodium hydroxide, 50% (w/w) aqueous solution
- Sodium perchlorate, 99% A.C.S. reagent grade or better
- Potassium sulfate, 1000 mg/L aqueous solution

Conditions	
Columns:	Dionex IonPac AS11 Analytical, 4 × 250 mm Dionex IonPac AG11 Guard, 4 × 50 mm
Eluent:	100 mM sodium hydroxide
Run Time:	12 min
Flow Rate:	1.0 mL/min
Sample Volume:	1000 µL
Detection:	Suppressed conductivity, Thermo Scientific™ Dionex™ ASRS™ ULTRA II Suppressor, 4 mm, auto-suppression, external water mode
System Backpressure:	600–900 psi (3.95–5.93 MPa)
Background Conductance:	2–5 µS

Preparation of Solutions and Reagents

Standard Solution

Stock Perchlorate Standard Solution (1000 mg/L)

Dissolve 1.231 g of sodium perchlorate in 1000 mL of deionized water to prepare a 1000 mg/L standard. The standard is stable for at least one month when stored at 4 °C.

Working Standard Solutions

Dilute 1000 mg/L standard solution as required with deionized water to prepare the appropriate working standards.

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Eluent Solution

100.0 mM Sodium Hydroxide

Weigh 992.0 g of deionized water into an eluent bottle. Degas water for approximately 5 min. Carefully add 8.0 g of 50% sodium hydroxide directly to the bottle. Mix, then quickly transfer the eluent bottle to the instrument and pressurize the bottle with helium at 8 psi (0.055 MPa).

Results and Discussion

For the best perfomance at low ppb levels, it is critical that baseline noise be kept to a minimum. To minimize baseline noise, it is necessary to use the Dionex ASRS ULTRA II Suppressor in external water mode rather than recycle mode. An equilibrated system will produce a background conductance of 2–5 µS. Peak-to-peak noise is typically 10 nS and system backpressure is 600–900 psi (3.95–5.93 MPa). A system blank is determined by using deionized water as a sample. This blank establishes the baseline and confirms the lack of contamination in the system. The linear concentration range was determined to ensure accurate quantification of perchlorate in the 2.5–100 µg/L range. Figure 1 shows the results of a linearity study.

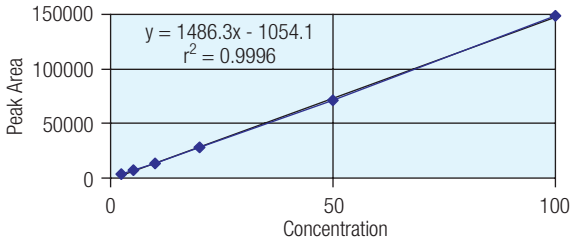

Figure 1. Perchlorate calibration.

This plot demonstrates that calibration of perchlorate is linear in the low-ppb range. Figure 2 shows a typical chromatogram of a 20 µg/L perchlorate standard. To determine the method detection limit (MDL), seven injections of the 2.5 µg/L perchlorate standard were made. Table 1 shows the results of an MDL study. The 1000 µL injection is large enough to achieve the desired detection limit without overloading the column. Note that this method is not intended for use with high (ppm) levels of perchlorate. The calculated MDL equals 880 ng/L (ppt).

Column: Dionex IonPac AG11, AS11
Eluent: 100 mM sodium hydroxide
Flow Rate: 1 mL/min
Inj. Volume: 1000 µL
Detection: Suppressed conductivity, Dionex ASRS ULTRA II suppressor, auto-suppression, external water mode

Peaks:
1. Void peak
2. Unidentified peak
3. Unidentified peak
4. Perchlorate

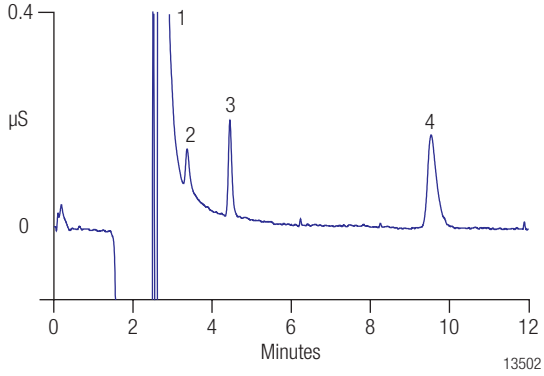

Figure 2. 20 µg/L perchlorate standard.

Table 1. MDL for perchlorate based on a 1000 µLinjection volume.

Injection #	Area Counts	Retention Time (min)
1	3391	9.48
2	3405	9.57
3	3504	9.50
4	3503	9.45
5	3435	9.47
6	3301	9.52
7	3315	9.43
Average	3408	9.49
SD	81	0.05
RSD	2.38	0.49

MDL = 880 ng/L (ppt), MDL = SD*$t_{s,99}$ where $t_{s,99}$ =3.14 for n = 7

Figures 3 through 5 show chromatograms obtained for 2.5 µg/L perchlorate in three different matrices. Figure 3 shows the chromatogram of 2.5 µg/L perchlorate in deionized water. Figure 4 shows 2.5 µg/L perchlorate in tap water. Note that all other anions present in tap water elute in the void volume and do not interfere with perchlorate determination. Some environmental samples may contain low levels of perchlorate in the presence of a large amount of sulfate. Figure 5 shows the determination of 2.5 µg/L perchlorate in the presence of 700 mg/L sulfate. The high concentration of sulfate does not affect perchlorate recovery or the detection limit.

Column: Dionex IonPac AG11, AS11
Eluent: 100 mM sodium hydroxide
Flow Rate: 1 mL/min
Inj. Volume: 1000 µL
Detection: Suppressed conductivity, Dionex ASRS ULTRA II suppressor, auto-suppression, external water mode
Peaks: 1. Void peak
2. Unidentified peak
3. Perchlorate

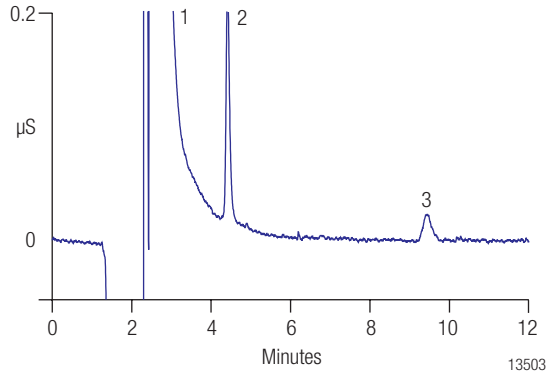

Figure 3. 2.5 µg/L perchlorate in deionized water.

Column: Dionex IonPac AG11, AS11
Eluent: 100 mM sodium hydroxide
Flow Rate: 1 mL/min
Inj. Volume: 1000 µL
Detection: Suppressed conductivity, Dionex ASRS ULTRA II suppressor, auto-suppression, external water mode
Peaks: 1. Anions in tap water
2. Perchlorate

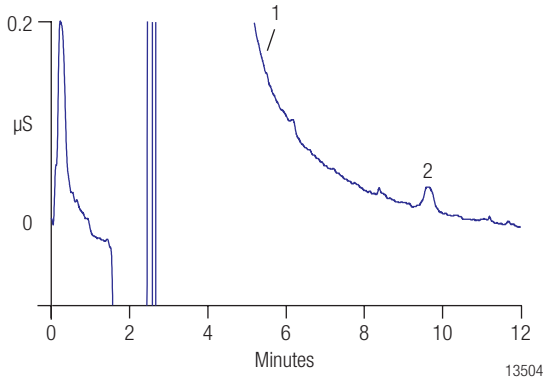

Figure 4. 2.5 µg/L perchlorate in tap water.

Column: Dionex IonPac AG11, AS11
Eluent: 100 mM sodium hydroxide
Flow Rate: 1 mL/min
Inj. Volume: 1000 µL
Detection: Suppressed conductivity, Dionex ASRS ULTRA II suppressor, auto-suppression, external water mode
Peaks: 1. Sulfate
2. Perchlorate

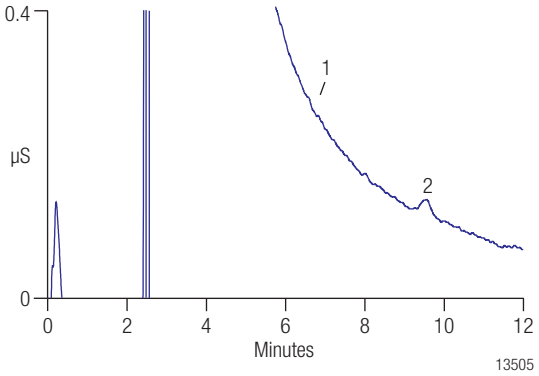

Figure 5. 2.5 µg/L perchlorate and 700 mg/L sulfate.

Summary

The method outlined in this application note allows the determination of low-µg/L (ppb) levels of perchlorate. A linear concentration range has been established to accurately quantify perchlorate in drinking water and ground water samples.

References

1. "Perchlorate in California Drinking Water"; California Department of Health Services, September 1997.
2. Correspondence from Joan S. Dollarhide, National Center for Environmental Assessment, Office of Research and Development, to Mike Girrard, Chairman, Perchlorate Study Group, U.S. EPA, 1995.

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