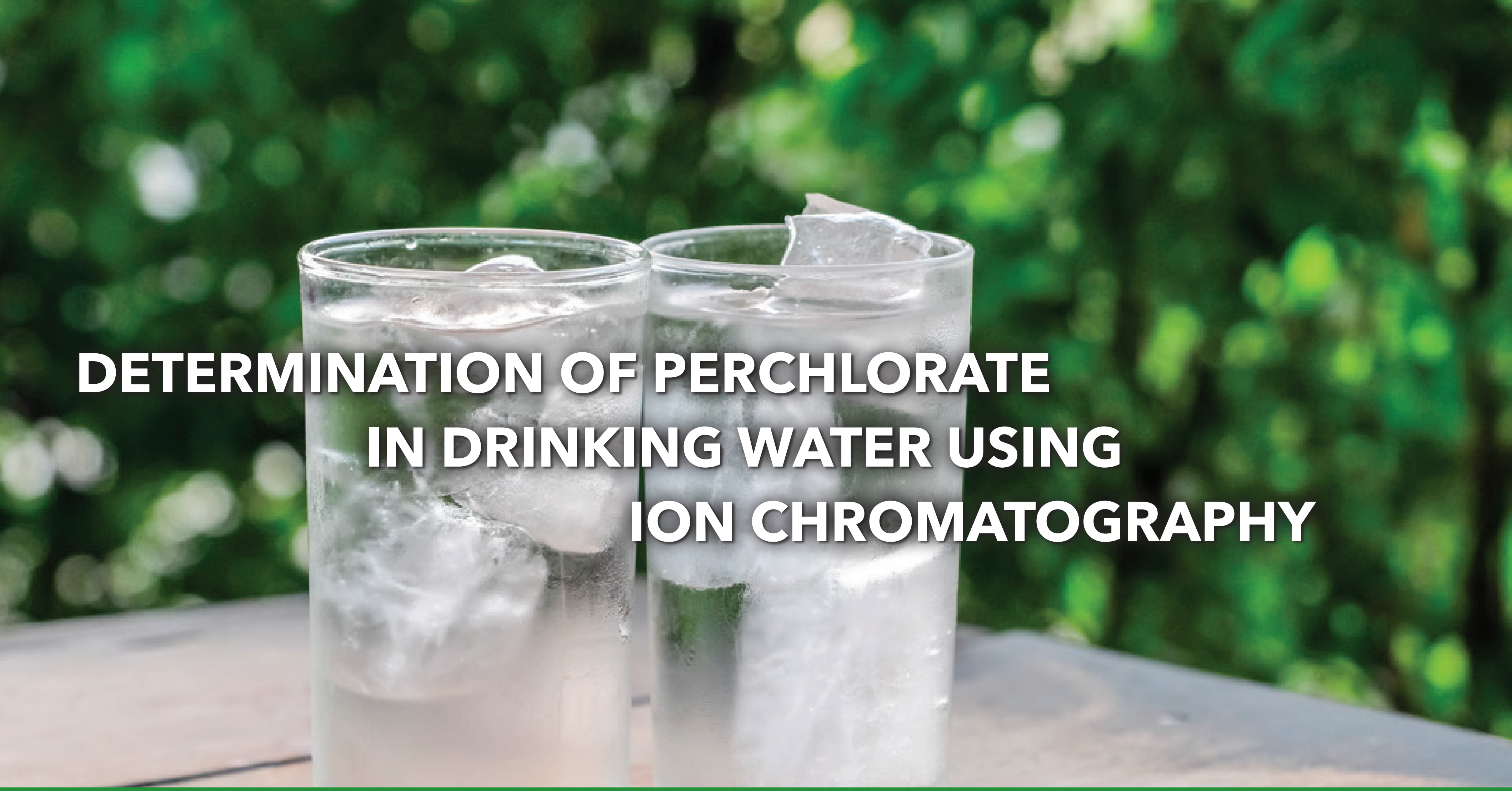


DETERMINATION OF PERCHLORATE IN DRINKING WATER USING ION CHROMATOGRAPHY

Goal

To develop a fast method for the determination of perchlorate in drinking water using a high-resolution Thermo Scientific™ Dionex™ IonPac™ AS16-4µm column

Introduction

Perchlorate is widely used as the oxidizing component in solid propellants for rockets, munitions, and fireworks.[1] However, perchlorate can contaminate soil, groundwater, and drinking water, leading to adverse health effects.

Perchlorate in high doses can disrupt thyroid function and hormone production, and therefore negatively affect the growth and development of fetuses and children and healthy metabolism in adults. Children who have been treated with perchlorate for their overactive thyroids are often found to have neurological and behavioral problems.

California started to regulate perchlorate in drinking water in October 2007, setting the Maximum Contaminant Level (MCL) at 6 µg/L. In 2015, the state also established the Public Health Goal (PHG) for perchlorate at 1 µg/L, superseding the PHG of 6 µg/L established in 2004.[2] More than ten other states have similar health-based goals or advisory levels for perchlorate in drinking water. The U.S. Environmental Protection Agency (EPA) placed perchlorate on the first Contaminant Candidate List (CCL1) in 1998 and determined that perchlorate meets the Safe Drinking Water Act's criteria for regulation as a contaminant in February 2011. However, perchlorate is still not federally regulated.

Multiple analytical methods are available for perchlorate analysis. U.S. EPA Method 314.0 uses ion chromatography with suppressed conductivity detection.[3] The EPA method 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. Thermo Scientific™ Application Update 148 describes an updated method for perchlorate determination in drinking water with an improved suppressor.[4] This article updates the approach with a high-resolution Dionex IonPac AS16-4µm 2 mm column. In comparison to the conventional Dionex IonPac AS16 column, the Dionex IonPac AS16-4µm column exhibits higher peak efficiency while maintaining chromatographic selectivity. This article shows that using the Dionex IonPac AS16-4µm column increases the sample throughput by 20% and saves three minutes per injection, thereby improving productivity for perchlorate determinations in drinking water. Key performance parameters were evaluated including separation, linearity, limits of detection, accuracy, and precision. Perchlorate concentrations were determined in three drinking water samples.

Experimental

Equipment

- Thermo Scientific™ Dionex™ ICS-5000$^+$ HPIC™ system including*:
  - Dionex ICS-5000$^+$ DP Pump module
  - Dionex ICS-5000$^+$ DC Detector/Chromatography module with Conductivity Detector
  - Thermo Scientific™ Dionex™ AS-AP Autosampler with sample tray cooling, 5000 µL sample syringe (P/N 074308), 8500 µL buffer line (P/N 075520) and 10 mL vial trays
- Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software, version 7.2.9

**This method can be run on any Thermo Scientific Dionex HPIC instrument using a Thermo Scientific™ Dionex™ AXP pump to add the suppressor regenerant.*

Consumables

- Thermo Scientific™ Dionex™ EGC 500 KOH Cartridge (P/N 075778)
- Thermo Scientific™ Dionex™ CR-ATC 500 Continuously Regenerated Anion Trap Column (P/N 075550)
- Thermo Scientific™ Dionex™ ADRS 600 Anion Dynamically Regenerated Suppressor, 2 mm (P/N 088667)
- Dionex AS-AP Autosampler Vials 10 mL (P/N 074228)

Reagents and standards

- Degassed deionized (DI) water, 18 MΩ·cm resistance or better
- Sodium and potassium salts, A.C.S. reagent grade or better, for preparing anion standards

Samples

Three residential tap waters were collected from three cities in the San Francisco Bay Area in California. (DW #1-3)

Chromatographic conditions	
Columns:	Dionex IonPac AG16-4µm Guard Column, 2 × 50 mm (P/N 302756) Dionex IonPac AS16-4µm Analytical Column, 2 × 250 mm (P/N 302755)
Eluent:	65 mM KOH
Eluent source:	Dionex EGC 500 KOH cartridge with Dionex CR-ATC 500
Flow rate:	0.38 mL/min
Injection volume:	250 µL in Push-Full mode
Column temperature:	30 °C
Detection:	Suppressed conductivity
Suppressor:	Dionex ADRS 600 (2 mm) Suppressor, external water mode (flow rate = 0.38 mL/min), 62 mA current
Detection/suppressor compartment:	20 °C
Cell temperature:	35 °C
Background conductance:	<0.5 µS/cm
System backpressure:	~4100 psi (28.3 MPa)
Noise:	<0.5 nS/cm
Run time:	12 min

Preparation of solutions and reagents

Perchlorate stock standard solution

Dissolve 123.1 mg of sodium perchlorate in DI water in a 125 mL polypropylene bottle. Adjust the volume to 100 mL to prepare a 1000 mg/L standard solution. This stock standard is stable for at least a month at 4 °C.

Perchlorate calibration standard solutions

Dilute perchlorate 1000 mg/L stock standard with DI water in a 125 mL polypropylene bottle to prepare a 1 mg/L secondary stock solution. Further dilute the 1 mg/L secondary stock solution with DI water to prepare calibration standards at 1, 2, 5, 10, 25, and 50 µg/L.

Common anions stock solutions

Prepare stock standard solutions (1000 mg/L) by dissolving the appropriate amounts of the required analytes in 100 mL of DI water according to Table 1. Prepare individual chloride, sulfate, and carbonate stock solutions (25,000 mg/L) according to Table 2. Stock standards for most anions are stable for at least 6 months at 4 °C.

Mixed common anions solution

Prepare a mixed common anions solution according to Table 3. Prepare the stock standard mixture by adding the appropriate volume of each stock standard (1000 mg/L) in DI water and adjust the volume to 100 mL. Further dilute the stock mixture solution 100-fold to prepare a 13-anion standard mixture.

Prepare 200 mg/L and 1000 mg/L solutions of mixed anions (MA) standards of chloride, sulfate, and carbonate (MA 200 and MA 1000) using the 25,000 mg/L stock solutions. For example, prepare MA 1000 by adding 4 mL each of chloride, sulfate, and carbonate stocks (25000 mg/L) in DI water, and adjust the volume to 100 mL. Spike 25 µg/L of perchlorate in MA 200 and MA 1000.

Results and discussion

Separation

The Dionex IonPac AS16-4µm column is a high-resolution and high-capacity, hydroxide-selective anion exchange column designed for the isocratic separation of polarizable anions including iodide, thiocyanate, thiosulfate, and perchlorate in a variety of samples. The high resolution provides better peak identification and the high capacity allows the injection of more concentrated samples without overloading the column. The Dionex IonPac AS16-4µm column's capacity and selectivity is similar to the Dionex IonPac AS16 column. Compared to the Dionex IonPac AS16 column, this anion-exchange column uses smaller resin particles for more efficient separations, resulting in more accurate peak integration and more reliable results.³

Figure 1 shows a separation of perchlorate and common anions within 12 min using a Dionex IonPac AS16-4µm column. As this figure shows, perchlorate is well resolved from common inorganic anion peaks such as chloride, sulfate, and carbonate. 4-chlorobenzene sulfonate can be found in leachates from some hazardous waste sites. As Figure 1 shows, 4-chlorobenzene is resolved from perchlorate.

Compared to the Dionex IonPac AS16 column, the Dionex IonPac AS16-4µm column demonstrates better resolution between perchlorate and the inorganic anion peaks under the same conditions. In addition, 4-chlorobenzene is not resolved from the perchlorate peak on the Dionex IonPac AS16 column. Thus, a shorter method (12 min), which still resulted in excellent separation of perchlorate was used in this study compared to the 15 min method described in AU148. In this shorter method, the eluent was 65 mM at a flow rate 0.38 mL/min using a 2 mm diameter Dionex IonPac AS16-4µm column.

Table 1. Masses of compounds used to prepare 100 mL of 1000 mg/L ion standards

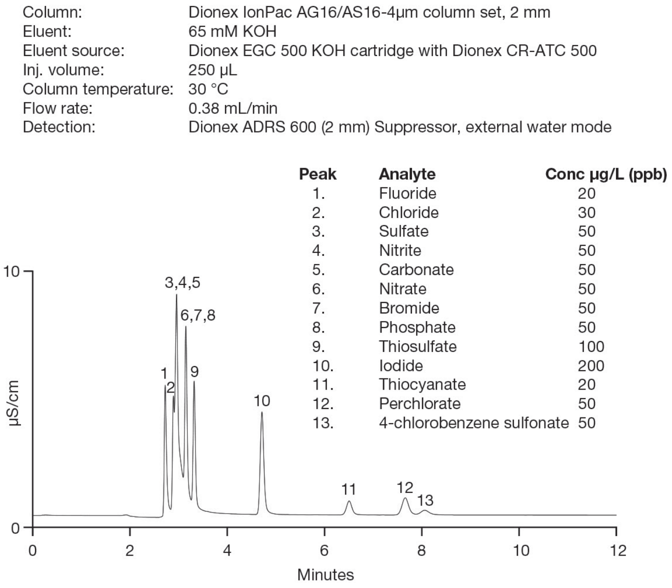
Analyte	Compound	Amount (mg)
Fluoride	Sodium fluoride (NaF)	221.0
Chloride	Sodium chloride (NaCl)	164.9
Nitrite	Sodium nitrite ($NaNO_2$)	150.0
Bromide	Sodium bromide (NaBr)	128.8
Nitrate	Sodium nitrate ($NaNO_3$)	137.1
Sulfate	Sodium sulfate (Na_2SO_4)	147.9
Phosphate	Potassium phosphate, monobasic (KH_2PO_4)	143.3
Carbonate	Sodium carbonate (Na_2CO_3)	176.6
Perchlorate	Sodium perchlorate ($NaClO_4$)	123.1
Iodide	Sodium iodide (NaI)	118.1
4-chlorobenzene sulfonate	Sodium 4-chlorobenzenesulfonate ($C_6H_4ClNaO_3S$)	112.0
Thiosulfate	Sodium thiosulfate ($Na_2S_2O_3$)	141.0
Thiocyanate	Sodium thiocyanate (NaSCN)	139.6

Table 2. Masses of compounds used to prepare 100 mL of 25,000 mg/L ion standards

Analyte	Compound	Amount (g)
Chloride	Sodium chloride (NaCl)	4.123
Sulfate	Sodium sulfate (Na_2SO_4)	3.698
Carbonate	Sodium carbonate (Na_2CO_3)	4.415

Table 3. Mixture of 13 anions standard

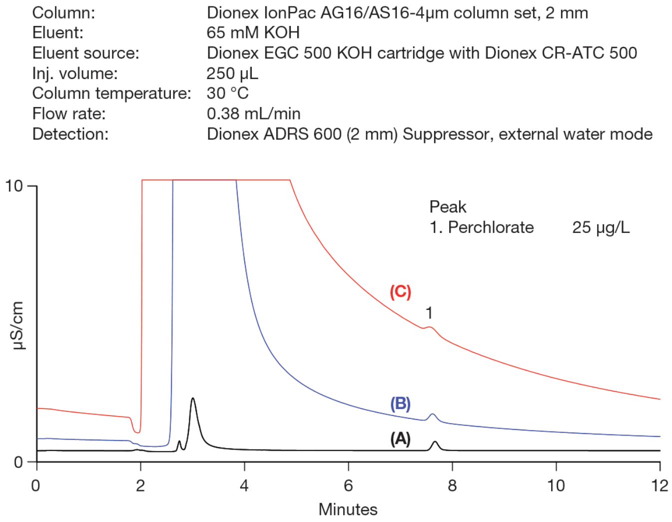
Analyte	13-anion stock standard mixture concentration (mg/L)	1000 ppm stock volume (µL)	13-anion standard mixture concentration (µg/L)
Fluoride	2	200	20
Chloride	3	300	30
Sulfate	5	500	50
Nitrite	5	500	50
Carbonate	5	500	50
Nitrate	5	500	50
Bromide	5	500	50
Phosphate	5	500	50
Thiosulfate	10	1000	100
Iodide	20	2000	200
Thiocyanate	2	200	20
Perchlorate	5	500	50
4-chlorobenzene sulfonate	5	500	50



Column: Dionex IonPac AG16/AS16-4µm column set, 2 mm
Eluent: 65 mM KOH
Eluent source: Dionex EGC 500 KOH cartridge with Dionex CR-ATC 500
Inj. volume: 250 µL
Column temperature: 30 °C
Flow rate: 0.38 mL/min
Detection: Dionex ADRS 600 (2 mm) Suppressor, external water mode

Peak	Analyte	Conc µg/L (ppb)
1.	Fluoride	20
2.	Chloride	30
3.	Sulfate	50
4.	Nitrite	50
5.	Carbonate	50
6.	Nitrate	50
7.	Bromide	50
8.	Phosphate	50
9.	Thiosulfate	100
10.	Iodide	200
11.	Thiocyanate	20
12.	Perchlorate	50
13.	4-chlorobenzene sulfonate	50

Figure 1. Separation of perchlorate and common anions using a Dionex IonPac AS16-4µm column



Column: Dionex IonPac AG16/AS16-4µm column set, 2 mm
Eluent: 65 mM KOH
Eluent source: Dionex EGC 500 KOH cartridge with Dionex CR-ATC 500
Inj. volume: 250 µL
Column temperature: 30 °C
Flow rate: 0.38 mL/min
Detection: Dionex ADRS 600 (2 mm) Suppressor, external water mode

Figure 2. Determination of 25 µg/L perchlorate in (A) DI water, (B), MA 200, and (C) MA 1000

Figure 2 shows chromatograms of 25 µg/L perchlorate in DI water, MA 200, and MA 1000. Chromatographic performance of perchlorate can deteriorate at high anionic concentrations, primarily due to the presence of high concentrations of chloride, sulfate, and carbonate.

Method linearity

The linearity of perchlorate was investigated in the concentration range of 1–50 µg/L (1, 2, 5, 10, 25, and 50 µg/L). Figure 3 shows the calibration curve; the coefficient of determination (r^2) is 0.9997 using linear fitting. Figure 4 shows a chromatogram of a 1 µg/L low-level calibration standard.

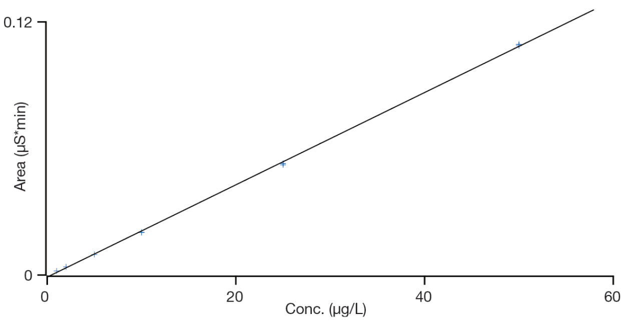


Figure 3. Perchlorate calibration curve

Column:	Dionex IonPac AG16/AS16-4µm column set, 2 mm
Eluent:	65 mM KOH
Eluent source:	Dionex EGC 500 KOH cartridge with Dionex CR-ATC 500
Inj. volume:	250 µL
Column temperature:	30 °C
Flow rate:	0.38 mL/min
Detection:	Dionex ADRS 600 (2 mm) Suppressor, external water mode

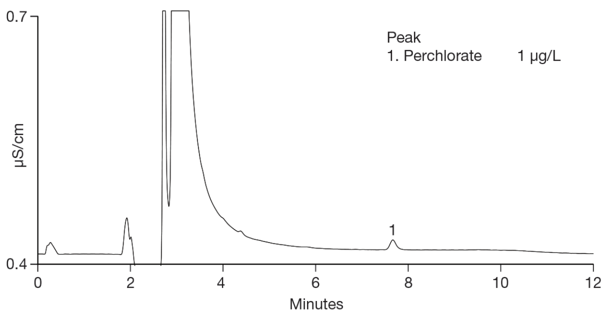


Figure 4. Determination of 1 µg/L perchlorate in DI water

Method detection limit

Several approaches for determining the detection limit are possible. Here two methods were used. The LOD method is based on the signal-to-noise (S/N) ratio. Determination of the S/N ratio is performed by comparing measured signal from a standard with low concentrations of analyte with those of blank samples and establishing the minimum concentration at which the analyte can be reliably detected. A S/N=3 is used for estimating the detection limit (LOD) and a S/N=10 is used for estimating the quantification limit (LOQ)[5]. In this study, the baseline noise was first determined by measuring the peak-to-peak noise in a representative 1 min segment of the baseline where no peaks elute, but close to the peak of interest. The signal was determined from the average height of three injections of standard (0.2 µg/L). The calculated LOD is 0.073 µg/L.

The MDL method is based on the standard deviation of the response. MDLs were determined by performing seven replicate injections of standards at a concentration of three to five times the estimated instrument detection limits (0.3 µg/L). The MDL was calculated as follows: MDL=(*t*) x (S), where *t*= Student's value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom (*t*=3.14 for seven injections), S=standard deviation of the replicate analysis. Figure 5 shows a chromatogram of a 0.3 µg/L perchlorate standard in DI water. The calculated MDL is 0.062 µg/L, which is more than three times lower than what is reported in AU148 (0.2 µg/L). The MDL is expected to change as the ionic strength of the sample increases. Figure 6 shows a chromatogram of a 0.5 µg/L perchlorate standard in DI water. Perchlorate is more sensitively detected compared to the chromatogram of 0.5 µg/L perchlorate in AU148.

Column:	Dionex IonPac AG16/AS16-4µm column set, 2 mm
Eluent:	65 mM KOH
Eluent source:	Dionex EGC 500 KOH cartridge with Dionex CR-ATC 500
Inj. volume:	250 µL
Column temperature:	30 °C
Flow rate:	0.38 mL/min
Detection:	Dionex ADRS 600 (2 mm) Suppressor, external water mode

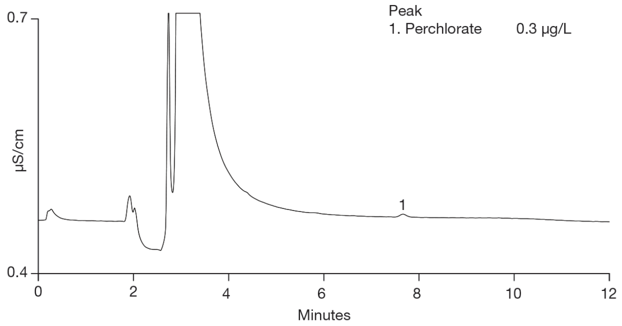


Figure 5. Determination of 0.3 µg/L perchlorate in DI water

Column:	Dionex IonPac AG16/AS16-4µm column set, 2 mm
Eluent:	65 mM KOH
Eluent source:	Dionex EGC 500 KOH cartridge with Dionex CR-ATC 500
Inj. volume:	250 µL
Column temperature:	30 °C
Flow rate:	0.38 mL/min
Detection:	Dionex ADRS 600 (2 mm) Suppressor, external water mode

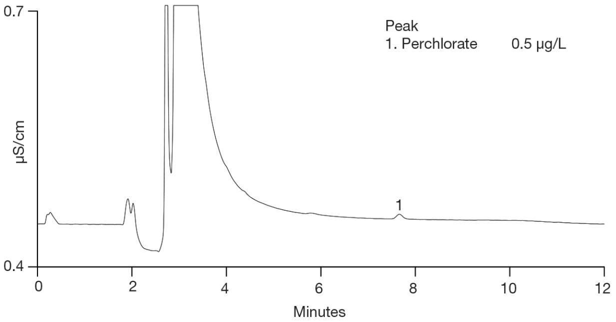


Figure 6. Determination of 0.5 µg/L perchlorate in DI water

Sample analysis

Three residential tap waters were collected from three cities in the San Francisco Bay Area, California. Figure 7 shows the chromatograms of the three drinking water samples.

Perchlorate is detected in drinking water #1 at 0.84 µg/L. Perchlorate is not detected in drinking waters #2 and #3.

Column:	Dionex IonPac AG16/AS16-4µm column set, 2 mm
Eluent:	65 mM KOH
Eluent source:	Dionex EGC 500 KOH cartridge with Dionex CR-ATC 500
Inj. volume:	250 µL
Column temperature:	30 °C
Flow rate:	0.38 mL/min
Detection:	Dionex ADRS 600 (2 mm) Suppressor, external water mode

Peak	**A** **DW #1**	**B** **DW #2**	**C** **DW #3**	
1. Perchlorate	0.84	NA	NA	µg/L

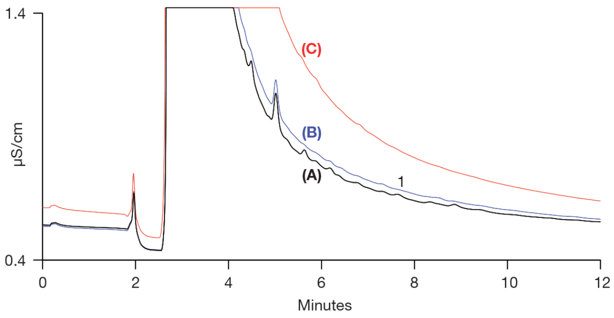


Figure 7. Determination of perchlorate in three drinking water samples

Method accuracy

Method accuracy was evaluated through recovery studies using spiked drinking water samples. Table 4 shows recovery of perchlorate spiked in water samples. The recovery for perchlorate in the three samples is in the range of 98.8% to 104%. Figure 8 shows an overlay chromatogram of unspiked and spiked drinking water #1.

Column:	Dionex IonPac AG16/AS16-4µm column set, 2 mm
Eluent:	65 mM KOH
Eluent source:	Dionex EGC 500 KOH cartridge with Dionex CR-ATC 500
Inj. volume:	250 µL
Column temperature:	30 °C
Flow rate:	0.38 mL/min
Detection:	Dionex ADRS 600 (2 mm) Suppressor, external water mode

Peak	**A** **DW #1**	**B** **Spiked DW #1**	
1. Perchlorate	0.84	4.83	µg/L

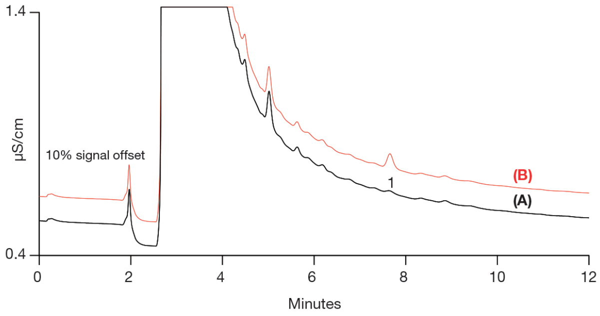


Figure 8. Overlay of chromatograms of (A) DW #1 and (B) spiked DW #1

Table 4. Recoveries of perchlorate spiked in drinking waters

Drinking Water	Amount Found (µg/L)	Amount Added (µg/L)	Recovery (%)
#1	0.840	4	99.6
#2	NA	4	104
#3	NA	4	98.8

Conclusions

This study demonstrates that perchlorate can be determined sensitively and accurately in municipal drinking water using a Dionex IonPac AS16-4µm column. The excellent resolution of the 4-µm-column allows for faster analysis (12 min) without compromising data quality.

The Reagent-Free ion chromatography system provides excellent reproducibility, thereby yielding greater quantification accuracy and consistently reliable results.

References

1. Jackson, P.E.; Gokhale, G.T.; Streib, T.; Rohrer, J.S.; Pohl, C.A. *J. Chromtogr.* A **2000,** *888,* 151.

2. California Water Boards, Perchlorate in Drinking Water, https://www.waterboards.ca.gov/drinking_water/certlic/drinkingwater/Perchlorate.html (accessed October 9, 2019).

3. U.S. EPA Method 314.0; U.S. Environmental Protection Agency; Cincinnati, OH, 1997

4. Thermo Scientific Application Update 148: Determination of perchlorate in drinking water using a reagent-free ion chromatography system. https://assets.thermofisher. com/TFS-Assets/CMD/Application-Notes/AU-148-IC-Perchlorate-Drinking-Water- AU71713-EN.pdf

5. Thermo Scientific Dionex IonPac AS16-4µm column manual. https://assets.thermofisher.com/TFS-Assets/CMD/manuals/Man-065723- IonPac-AS16-4um-Man065723-EN.pdf

6. ICH Guideline Q2B, Validation of Analytical Procedures, Methodology (CPMP/ ICH/281/95), Geneva, Switzerland, November 1996.

Author Contact Details
Jingli Hu and Jeff Rohrer, Thermo Fisher Scientific • Sunnyvale, CA, USA • **Web: www.thermofisher.com**