

# Improved Determination of Trace Perchlorate in Drinking Water Using 2D-IC

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## Key Words

EPA, Dionex IonPac AS20 Column, Dionex IonPac AS16 Column, Dionex IonSwift MAC-200 Column

## Introduction

Perchlorate is identified as an environmental contaminant found in drinking, ground, and surface waters. The origins of perchlorate are both natural and anthropogenic. In its natural origin, perchlorate originates from atmospheric deposition, possibly from chloride aerosol by electrical discharge and ozone exposure.<sup>1</sup> Another possible natural source is from the nitrate deposits of the Atacama Desert in Chile.<sup>2</sup>

Perchlorate contamination is attributed to the manufacture and use of ammonium perchlorate in solid propellant for rockets, missiles, fireworks, and elsewhere (e.g., production of matches, flares, pyrotechnics, ordnance, and explosives).<sup>3</sup> Research on perchlorate in the environment has received attention because perchlorate poses a human health concern. Perchlorate impairs normal thyroid function by interfering with iodine uptake by the thyroid.<sup>4</sup>

Ion chromatography (IC) is recognized as an effective tool for the determination of perchlorate in drinking water and other samples.<sup>5-8</sup> The U.S. Environmental Protection Agency (EPA) Methods 314.0, 314.1, and 314.2 describe the determination of trace perchlorate in drinking water. All of these methods use IC with suppressed conductivity detection. The method detection limits (MDLs) of Methods 314.0 and 314.1 are 0.53 µg/L<sup>9</sup> and 0.03 µg/L,<sup>10</sup> respectively. These methods are also described in Thermo Scientific™ Application Update 148 and Thermo Scientific™ Application Note (AN) 176, which demonstrate MDLs of 0.10 µg/L<sup>11</sup> and 0.02 µg/L,<sup>12</sup> respectively.

Method 314.2, an improvement of Methods 314.0 and 314.1, was specifically developed for the determination of perchlorate in high ionic strength samples using a two-dimensional (2D) IC system. Method 314.2 has a lower MDL that ranges from 0.012 to 0.018 µg/L, depending on the sample volume analyzed.<sup>13</sup> Dionex AN 178 was produced based on an EPA collaboration during the development of Method 314.2. This method has a reported MDL of 0.016 µg/L with an injection volume of 4 mL.<sup>14</sup>

In Method 314.2 and AN 178, perchlorate is partially resolved on a 4 mm Thermo Scientific™ Dionex™ IonPac™ AS20 Analytical Column in the first dimension, collected onto a concentrator column, and then resolved in the second dimension using a 2 mm Thermo Scientific™ Dionex™ IonPac™ AS16 Analytical Column. Because the second dimension column has a smaller cross-sectional area relative to the first dimension, detection sensitivity is enhanced. Because this 2D method combines two columns with two different column chemistries, the selectivity of this method is also improved.

This study reports an improvement to AN 178. The 4 mm and 2 mm columns used in AN 178 are replaced with 2 mm and 0.4 mm columns, respectively. The system operates using a smaller-diameter column and at a lower flow rate, thus reducing reagent consumption and system maintenance. From the first to the second dimension, there is a greater decrease in the cross-sectional area in this method as compared to Method 314.2, thereby improving sensitivity. There is a 25-fold increase in sensitivity when going from a 2 mm column in the first dimension to a 0.4 mm column in the second dimension, as compared to a four-fold increase when using a 4 mm column to a 2 mm column. Sufficient sensitivity of the 2 mm/0.4 mm configuration obviates the need to use a 4 mm/0.4 mm configuration. This study demonstrates an MDL of 0.005 µg/L and good perchlorate recoveries with different sample matrices.

## Goal

To develop an improved 2D-IC method for the determination of perchlorate in drinking water using a hybrid system (analytical/capillary) with suppressed conductivity detection

## Equipment

- Thermo Scientific Dionex ICS-5000 Hybrid IC (Analytical/Capillary) system\*\*\*, including:
  - DP Dual Pump
  - EG Eluent Generator
  - DC Detector/Chromatography Compartment
  - Thermo Scientific™ Dionex™ AS-AP Autosampler\* with Sample Syringe, 5.0 mL (P/N 074308) and 8.5 mL buffer line assembly (P/N 075520)
- Thermo Scientific™ Dionex™ Potassium Hydroxide Eluent Generator Cartridge (EGC III KOH, P/N 074532)
- Thermo Scientific™ Dionex™ EGC KOH, Capillary Cartridge (P/N 072076)
- Thermo Scientific™ Dionex™ CR-ATC Continuously Regenerated Anion Trap Column (P/N 060477)
- Dionex CR-ATC Continuously Regenerated Anion Trap Column, Capillary (P/N 072078)
- Thermo Scientific™ Dionex™ CRD 200 Carbonate Removal Device, 2 mm (P/N 062986)
- Dionex Capillary CRD 200 Carbonate Removal Device, Capillary (P/N 072054)
- Thermo Scientific™ Dionex™ IonSwift™ MAC-200 Monolith Anion Concentrator Column (P/N 075461)
- Vial Kit, Polystyrene with Caps and Blue Septa, 10 mL (P/N 074228)
- Thermo Scientific™ Dionex™ IC Cube™ Cartridge with six-port valve (P/N 078841)
- Corning™ Syringe Filter, surfactant-free cellulose acetate (SFCA), 0.2 µm pore, 26 mm (Fisher Scientific P/N 09-754-13)
- Disposable syringe, 20 mL (24 mL) Luer Lock, Sterile (Fisher Scientific P/N 14-817-33)
- Sterile sample container, 125 mL, I-Chem™ Sterile Nalgene™ Bottles (Fisher Scientific P/N N411-0125)
- PEEK tubing, 38 cm (15 in.) piece of 0.025 mm (0.001 in.) i.d. (P/N 074582) for conditioning a new capillary Dionex EGC cartridge

\*A Thermo Scientific™ Dionex™ AS or AS-DV Autosampler can also be used for sample delivery.

\*\*A Thermo Scientific™ Dionex™ ICS-6000 IC system can be used for equivalent results.

## Reagents and Standards

- Deionized water (DI), Type I reagent grade, 18 MΩ-cm resistance or better
- Sodium perchlorate, 98%, extra pure (Fisher Scientific P/N AC34218)
- Sodium chloride, crystalline, 99.0% (Fisher Scientific P/N S671)
- Sodium sulfate, anhydrous (Fisher Scientific P/N S429)
- Sodium bicarbonate, certified ACS (Fisher Scientific P/N S233)

## Conditions

### First Dimension

Columns:	Dionex IonPac AG20 Guard, 2 × 50 mm (P/N 063066)
	Dionex IonPac AS20 Analytical, 2 × 250 mm (P/N 063065)
Eluent Source:	Dionex EGC III KOH Eluent Generation Cartridge with Dionex CR-ATC Continuously Regenerated Anion Trap Column
Eluent:	35 mM KOH 0–30 min, step to 60 mM at 30.1 min, 60 mM 30.1–40 min, step to 35 mM at 40.1 min, 35 mM 40.1–45 min
Flow Rate:	0.25 mL/min
Injection Volume:	500 µL
Temperature:	15 °C (upper compartment) 30 °C (lower compartment)
Detection:	Suppressed conductivity, Thermo Scientific™ Dionex™ ASRS™ 300 Anion Self-Regenerating Suppressor™, 2 mm, 38 mA, external water mode
System Backpressure:	~2185 psi
Background Conductance:	~0.500 µS
Noise:	~0.3 nS/min peak-to-peak
Run Time:	45 min

## Second Dimension

Columns:	Dionex IonPac AG16 Capillary Guard, 0.4 × 50 mm (P/N 082316)  Dionex IonPac AS16 Capillary Analytical, 0.4 × 250 mm (P/N 082315)
Eluent Source:	Dionex EGC-KOH (Capillary) Cartridge with Dionex CR-ATC Continuously Regenerated Anion Trap Column (Capillary)
Eluent:	65 mM KOH
Flow Rate:	0.01 mL/min
Injection Volume:	1 mL (on the concentrator column from first dimension)
Temperature:	15 °C (upper compartment) 30 °C (Dionex IC Cube Cartridge)
Detection:	Suppressed conductivity, Dionex ACES™ 300 Anion Capillary Electrolytic Suppressor (P/N 072052), 12 mA, external water mode
System Backpressure:	~1230 psi
Background Conductance:	~0.400 µS
Noise:	~0.5 nS/min peak-to-peak
Run Time:	45 min

## Preparation of Solutions and Reagents

### Stock Perchlorate Standard Solution

Dissolve 0.1231 g sodium perchlorate in 100 mL of DI water for a 1000 mg/L standard solution. When stored in an opaque plastic storage bottle, this stock solution can be stable for up to one year.

### Perchlorate Primary Dilution Standard

Prepare 10 mg/L perchlorate solution by adding 1 mL of the 1000 mg/L stock standard in a 100 mL volumetric flask and dilute to volume with DI water. When stored in an opaque plastic storage bottle, the resulting solution will be stable for at least one month.

### Perchlorate Second Dilution Standard

Prepare 1 mg/L perchlorate solution by adding 10 mL of the primary dilution solution to a 100 mL volumetric flask and dilute to volume with DI water. When stored in an opaque plastic storage bottle, the resulting solution will be stable for at least one month.

### Perchlorate Calibration Standards

Prepare perchlorate calibration standards by adding the appropriate volumes of the perchlorate secondary dilution solution to separate 100 mL volumetric flasks.

## Common Anion Stock Solution

Prepare 25,000 mg/L each of chloride, sulfate, and bicarbonate. Dissolve 4.121 g sodium chloride in DI water and dilute to 100 mL. Dissolve 3.696 g sodium sulfate in DI water and dilute to 100 mL. Dissolve 3.442 g sodium bicarbonate in DI water and dilute to 100 mL.

## High Ionic Strength Water (HIW) Fortified with Perchlorate

Transfer 4 mL of each of the 25,000 mg/L chloride, sulfate, and bicarbonate stock solutions to a 100 mL volumetric flask and add the appropriate volumes of the perchlorate secondary dilution solution. Dilute to volume with DI water to prepare simulated HIW containing 1000 mg/L each of chloride, sulfate, and bicarbonate.

## Sample Preparation

All samples must be sterile filtered with a Corning syringe filter (SFCA, 0.2 µm pore, 26 mm) to remove any potential microorganisms. Perchlorate is susceptible to microbiological degradation by anaerobic bacteria. Use a disposable sterile syringe (20 mL Luer Lock) to draw ~20 mL of the sample and then attach a sterile syringe filter. Discard the first 3–5 mL of sample and then filter the remaining sample into a 125 mL sample container (I-Chem Sterile Nalgene Bottle). Discard the syringe and filter after each use.

## System Preparation and Configuration

For the analytical system, install and configure the EG by first installing the backpressure tubing in place of the columns to produce a total backpressure of 2000–2500 psi at a flow rate of 1 mL/min. Install a Dionex EGC III KOH cartridge and condition the cartridge by setting the KOH concentration to 50 mM at 1 mL/min for 30 min. After the conditioning process is complete, disconnect the backpressure tubing temporarily installed in place of the column set. Install a Dionex CR-ATC trap column between the Dionex EGC III KOH cartridge and the Dionex EGC degasser. Hydrate the Dionex CR-ATC trap column prior to use by following the instructions outlined in the Dionex EluGen Cartridge (EGC) KOH, NaOH, LiOH & MSA Quickstart guide (Document No. 065037-03).

For the capillary system, connect the 38 cm (15 in.) piece of 0.025 mm (0.001 in.) i.d. PEEK tubing between the pump pulse damper and the Dionex EGC cartridge inlet port to provide the backpressure for the Dionex EGC cartridge configuration procedure. Set the pump flow rate to 0.02 mL/min and flush the capillary Dionex EGC cartridge for 20 min. After flushing is complete, connect the capillary Dionex CR-ATC trap column at the outlet of the Dionex EGC cartridge, then flush the Dionex CR-ATC trap column at 0.02 mL/min for 15 min. To condition the Dionex EGC cartridge and Dionex CR-ATC trap column, set the KOH concentration to 50 mM at 0.02 mL/min for 15 min. Detailed instructions for plumbing the capillary system can be found in the Dionex ICS-5000 Ion Chromatography System Installation Instructions (Document No. 065343).

Install and configure the Dionex AS-AP Autosampler in Push Mode. Follow the instructions in the Dionex AS-AP Autosampler Operator's Manual (Document No. 065361) to calibrate the sample transfer line to ensure accurate and precise sample injections. Due to the large sample injection volumes in this application, install a sample syringe size of 5 mL. An 8.2 mL buffer line assembly is required. Prepare a 500  $\mu$ L sample loop by measuring ~43.25 in. of 0.030 in. i.d. tubing. To verify the volume of the loop, weigh the empty tubing, fill the tube with DI water, then reweigh the filled tube and calculate the volume. The total sample volume must be 500  $\mu$ L  $\pm$  5%. Install the sample loop on Injection Valve #1 of the DC. A six-port valve (P/N 061961) is required on the Dionex IC Cube cartridge to replace the 4-port valve for System #2.

Install the Dionex IonPac AG20 (2  $\times$  50 mm) and the Dionex IonPac AS20 (2  $\times$  250 mm) columns on System #1 in the lower compartment of the DC. For System #2, install the Dionex IonPac Capillary AG16 (0.4  $\times$  50 mm) and the Dionex IonPac AS16 (0.4  $\times$  250 mm) columns in the column cartridge and install the cartridge in the Dionex IC Cube module in the upper compartment of the DC. Connect a piece of 0.01 in. i.d. tubing from the conductivity detector cell out on System #1 to the sample inlet port on the injection valve of the Dionex IC Cube cartridge. Keep the length of this tubing to a minimum. Install a Dionex IonSwift MAC-200 concentrator column (0.72  $\times$  80 mm) in place of the sample loop on the injection valve of the Dionex IC Cube cartridge. The direction of sample loading must be opposite the direction of the capillary flow (refer to the diagram printed on the Dionex IC Cube cartridge, which indicates the plumbing for the injection valve and shows that the flow direction of the Dionex IonSwift MAC-200 concentrator column is from Port 1 to Port 4).

Hydrate the Dionex ASRS 300 and Dionex ACES 300 suppressors and the Dionex CRD 200 devices (2 mm and capillary) according to the instructions in the operating manuals. Prior to installing the suppressors, rinse the columns with 65 mM KOH while diverting to waste for 30 min. Operate both suppressors in the external water mode by connecting the external water source to the Regen In of the suppressor, the Regen Out of the suppressor to the Regen In of the Dionex CRD device, the Regen Out of the Dionex CRD device to the Regen In of the Dionex CR-ATC trap column, and the Regen Out of the the Dionex CR-ATC trap column to the Regen In of the EG degasser. The schematic diagram of the system configuration is shown in Figure 1.

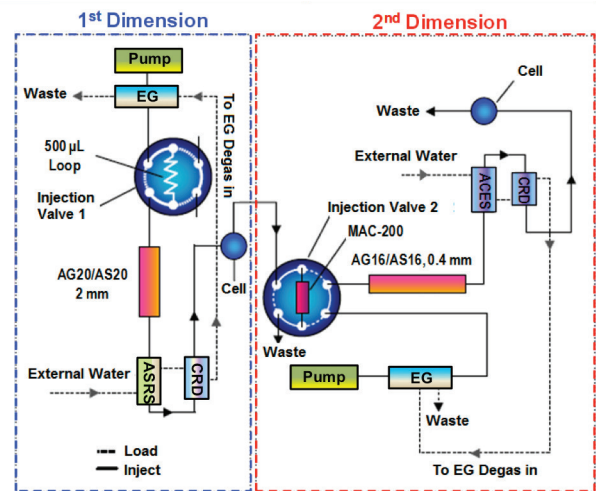


Figure 1. Schematic diagram of the analytical/capillary 2D system: perchlorate is resolved from the matrix on a 2 mm Dionex IonPac AS20 column set, concentrated on a monolithic capillary concentrator, separated on a 0.4 mm Dionex IonPac AS16 column set, and detected by suppressed conductivity detection.

Equilibrate the Dionex IonPac AS20 column set with 35 mM KOH and the Dionex IonPac Capillary AS16 column set with 65 mM KOH at their respective flow rates (shown in the Conditions section) for ~60 min. Analyze a water blank by injecting DI water. An equilibrated system has a background conductance of ~0.5  $\mu$ S and ~0.4  $\mu$ S for the analytical and capillary systems, respectively. Determine the cut time (pre-concentration time) of the sample to be transferred from the first dimension to the second dimension, as described in the next section, before determining perchlorate in samples.

### Determination of Cut Time for the Second Dimension

Due to possible slight variations in system plumbing, column capacity, and tubing lengths, individual laboratories must determine the optimum cut time (from the first dimension) before determining perchlorate in the second dimension. The large injection volume in the first dimension system will result in an increase in retention time of perchlorate, compared to that in the quality assurance report of the column. Therefore, perform duplicate 500  $\mu$ L injections of 5  $\mu$ g/L perchlorate in DI water to determine the average perchlorate retention time on the Dionex IonPac AS20 column. Verify the retention time of perchlorate on the Dionex IonPac AS20 column weekly to ensure good trapping efficiency on the Thermo Scientific™ Dionex™ IonSwift™ MAC-200 concentrator column.

In this study, the perchlorate retention time ( $t_{\text{ClO}_4}$ ) was ~21 min. In the high ionic strength matrix, the retention of perchlorate is reduced to ~19 min. Therefore, the start and end times for the cut window were 18 min ( $t_{\text{ClO}_4} - 3$  min) and 22 min ( $t_{\text{ClO}_4} + 1$  min), respectively. The normal position for the six-port valve in System #2 is the inject position; at 18 min, the Dionex IC Cube valve switches to the load position in which perchlorate is trapped in the preconcentration column. At 22 min, the Dionex IC Cube valve switches back to the inject position, bringing the preconcentrated perchlorate into the second dimension. In this configuration, the perchlorate eluted at ~35 min (~ 13 min from the start of the second dimension) from the Dionex IonPac Capillary AS16 column.

Figure 2 shows the chromatograms of 2  $\mu\text{g/L}$  perchlorate from the first and second dimensions. In the first dimension, there are two baseline deflections associated with the switching of the valve in System #2. In the second dimension, a significant increase in the perchlorate signal relative to the first dimension is observed.

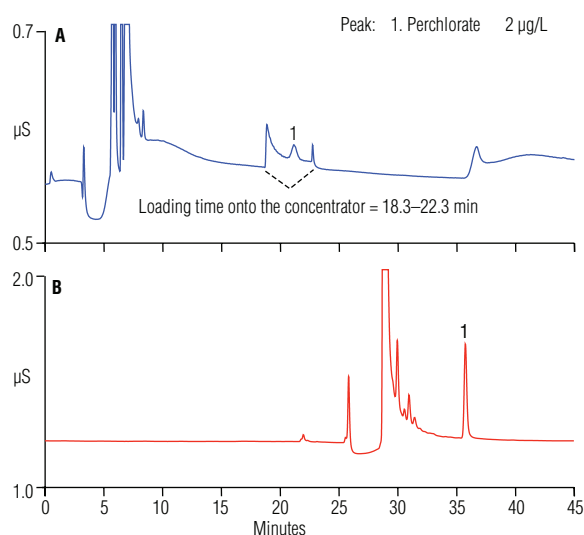


Figure 2. Chromatogram of a 2  $\mu\text{g/L}$  perchlorate standard in reagent water in (A) first dimension and (B) second dimension.

## Results and Discussion

A DI water blank was injected into the 2D system to ensure that there was no interference or contamination. The second-dimension system was calibrated by injecting duplicates of seven calibration standards to cover the desired concentration range. For the same amount of analyte injected, the analyte concentration is inversely proportional to the cross-sectional area of the column; therefore, the peak height is enhanced when using columns with smaller cross-sectional areas. Thus, a larger increase in sensitivity can be obtained using the 2 mm/0.4 mm 2D system in this study when compared to the 4 mm/2 mm 2D system described in AN 178.

This allows a smaller injection volume into the first-dimension system, possibly exposing the columns to less contaminating sample, and thus increasing column lifetime. Instead of injecting 1 mL of sample into the 2 mm first dimension, which is the equivalent of injecting 4 mL into the 4 mm first dimension in AN 178, only 500  $\mu\text{L}$  were injected. The system was more sensitive than that in AN 178; therefore, the system was calibrated from 0.01  $\mu\text{g/L}$  instead of 0.3  $\mu\text{g/L}$ . The peak area response generated by the calibration standards was plotted against the perchlorate concentration using a quadratic regression curve, producing a correlation coefficient of 0.9998.

Section 9.2.6 of Method 314.2 states that the determination of the detection limit is not a specific requirement of this method but may be required by various regulatory bodies associated with compliance monitoring. The limit of detection (LOD) was determined for perchlorate using the 2D method by performing seven replicate injections of DI water fortified with 0.02  $\mu\text{g/L}$  perchlorate and calculating the LOD using the following equation:

$$\text{LOD} = St_{(n-1, 1-\alpha = 0.99)}$$

Where:

$t_{(n-1, 1-\alpha = 0.99)}$  = Student's  $t$ -value for a 99% confidence level with  $n - 1$  ( $t = 3.14$  for seven replicate injections)

$n$  = number of replicates

$S$  = standard deviation of replicate analyses

The results from this equation produced a calculated LOD of 5 ng/L. Table 1 summarizes the results of the calibration and calculated MDL.

The lowest concentration minimum reporting level (LCMRL) was also determined. The U.S. EPA provides a

Table 1. Calibration data and method detection limit (MDL) of perchlorate.

Analyte	Range ( $\mu\text{g/L}$ )	Linearity ( $r^2$ )	MDL Standard ( $\mu\text{g/L}$ )	SD ( $\mu\text{g/L}$ )	Calculated MDL** ( $\mu\text{g/L}$ )
Perchlorate	0.01–10	0.9998	0.02	0.002	0.005

\*Quadratic fit, peak area vs. concentration

\*\*MDL = (SD)  $\times$  ( $t_s$ ), where ( $t_s$ ) is Student's  $t$ -value for a 99% confidence level ( $t = 3.14$  for seven replicate injections)



statistical approach for determining a single-laboratory LCMRL using linear regression and prediction intervals. The LCMRL is the lowest true concentration at which the future recovery is predicted to have a 99% confidence between 50 and 150% recovery. Although the EPA encourages all laboratories to determine the LCMRL to aid in evaluating the performance of spiked recoveries at or below the MRL, it does not mandate LCMRL determinations.

In this study, seven individually prepared replicates of 0.01, 0.02, 0.05, 0.10, and 0.20  $\mu\text{g/L}$  perchlorate were analyzed. The data from these injections were inserted into the statistical program provided on the EPA website, which produced an LCMRL of 0.05  $\mu\text{g/L}$ . Figure 3 shows an example second dimension chromatogram of a 0.1  $\mu\text{g/L}$  perchlorate standard.

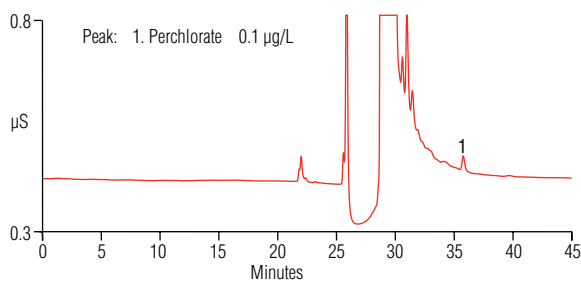


Figure 3. Chromatogram of a 0.1  $\mu\text{g/L}$  perchlorate standard in reagent water in the second dimension.

The MRL was chosen to be 0.2  $\mu\text{g/L}$ . To confirm that 0.2  $\mu\text{g/L}$  was an appropriate MRL, seven replicates at this concentration were analyzed. The mean and standard deviations of the seven replicate injections were calculated. The equations used to determine the upper and lower limits for the Half Range Prediction Interval of Results ( $\text{HR}_{\text{PIR}}$ ) are described in Section 9.2.4 in Method 314.2. Using those equations, the upper and lower limits were calculated to be 108.5% and 97.0%, respectively. The results are well within the  $\pm 50\%$  requirement of Method 314.2. Therefore, 0.2  $\mu\text{g/L}$  was confirmed as an acceptable MRL for this application.

Some drinking water sources contain high concentrations of common anions such as chloride, sulfate, and carbonate. This can pose a challenge in determining perchlorate at  $\mu\text{g/L}$  concentrations with accuracy and precision. EPA Method 314.2 describes a 2D method that uses a 4 mm Dionex IonPac AS20 column in the first dimension where the matrix is diverted to waste. At the same time, 5 mL of the suppressed effluent containing perchlorate is trapped on a Thermo Scientific™ Dionex™ IonPac™ TAC-ULP1 Trace Anion Concentrator – Ultralow Pressure column and then separated in the second dimension on a 2 mm Dionex IonPac AS16 column.

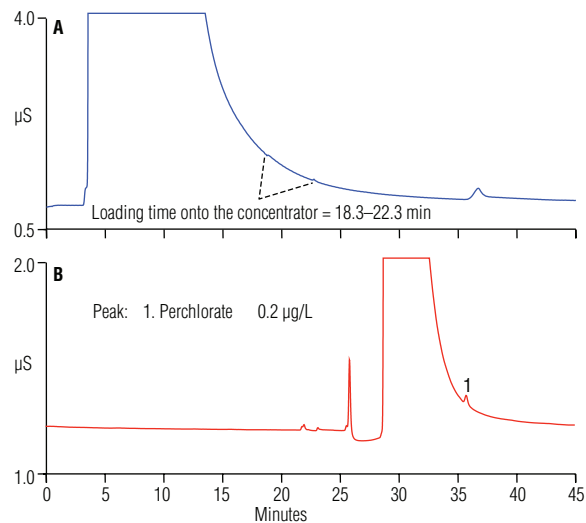


Figure 4. Chromatograms of synthetic high inorganic water containing 1000 mg/L each of chloride, sulfate, and bicarbonate fortified with 0.2  $\mu\text{g/L}$  perchlorate in (A) first dimension and (B) second dimension.

In this study, a similar approach is demonstrated, but the first dimension uses the 2 mm column and the second dimension uses a 0.4 mm capillary column, which together provide improved sensitivity for perchlorate relative to the configuration described in Method 314.2. To evaluate the performance of this 2D system, synthetic HIW—which contained 1000 mg/L each of chloride, sulfate, and bicarbonate—was fortified with different concentrations of perchlorate. Figure 4 shows an example of a synthetic HIW sample fortified with 0.2  $\mu\text{g/L}$  perchlorate. In the first dimension separation shown in Figure 4A, the detection of perchlorate is impossible due to extensive tailing from the matrix anions. In the second dimension (Figure 4B), most of the matrix has been diverted, and therefore, good recovery of perchlorate is obtained.

To validate this method, recoveries of perchlorate from five different samples—including reagent water, synthetic HIW, and drinking water from three different sources—were studied. Each sample was fortified with 0.2 and 2  $\mu\text{g/L}$  perchlorate. To ensure accuracy, the quality control standards prepared at 0.2, 2, and 10  $\mu\text{g/L}$  were analyzed at the beginning, middle, and end of each sample analysis batch. Seven replicate injections were made for each sample.

Table 2. Perchlorate recoveries from laboratory fortified samples.

Sample	Amount Found ( $\mu\text{g/L}$ )	Amount Added ( $\mu\text{g/L}$ )	Replicates	Peak Area Precision (RSD)	Recovery (%)
Reagent Water	—	0.2	7	2.61	102
		2.0	7	0.91	103
HIW*	—	0.2	7	1.70	110
		2.0	7	0.34	106
Drinking Water A	0.056	0.2	7	1.20	92.8
		2.0	7	0.85	103
Drinking Water B	0.128	0.2	7	2.93	93.6
		2.0	7	0.69	103
Drinking Water C	0.992	0.2	7	0.64	94.4
		2.0	7	0.40	101

\* HIW = High ionic strength water containing 1000 mg/L each of chloride, sulfate, and bicarbonate.

Table 2 summarizes the results for the recovery study. Calculated recoveries for samples fortified with 0.2  $\mu\text{g/L}$  perchlorate were in the range of 93–110%, well within the  $\pm 50\%$  requirement specified in Method 314.2. Similarly, the recoveries for samples fortified with 2  $\mu\text{g/L}$  perchlorate ranged from 101 to 106%, within the  $\pm 20\%$  requirement. The peak area precisions of all samples were  $<3\%$ . Figure 5 shows overlaid chromatograms of three drinking water samples fortified with 0.2  $\mu\text{g/L}$  perchlorate. No interfering peaks were observed in the sample matrices examined in this study.

## Conclusion

This study demonstrates a 2D-IC system for determining trace concentrations of perchlorate in drinking waters. This method was developed based on AN 178 and EPA Method 314.2. Improvements were made by using a hybrid system in which perchlorate was resolved from the matrix on a 2 mm Dionex IonPac AS20 column, concentrated on a monolithic capillary concentrator, separated on a 0.4 mm Dionex IonPac AS16 column, and detected by suppressed conductivity detection.

The reduction of column diameter from the first to the second dimension results in a significant increase in sensitivity. This configuration also greatly reduces reagent consumption compared to a 4 mm/2 mm configuration. Resolving the analyte from the sample matrix in the first dimension, immediately followed by preconcentrating the analyte before the separation in the second dimension using a Reagent-Free™ IC (RFIC™) system, enhances the level of automation and improves precision. Significant enhancement in sensitivity is achieved due to a large increase in the concentration factor using the capillary format in the second dimension. This also allows smaller injection volumes of high ionic strength matrix samples, benefiting column lifetime. Compared to AN 178, improved sensitivity is also obtained.

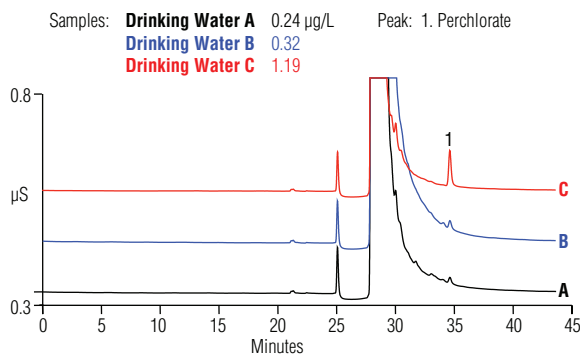


Figure 5. Second dimension chromatograms of drinking water samples fortified with 0.2  $\mu\text{g/L}$ .

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