Trace borate determination in high-purity waters

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Keywords: Dionex IonPac ICE Borate column, Dionex ICS-6000 system, Dionex ACRS-ICE 500 suppressor, boric acid, TBC-1, trace borate concentrator column

Goal

To develop a simple and robust IC method for the determination of trace borate in high-purity water

Introduction

Borate is one of the most weakly retained anions on anion-exchange materials and is the first to break through many water purification systems. In the power generation and semiconductor industries, monitoring trace levels of boron as borate in high-purity waters is a measure of the efficiency of the water purification systems. The presence of borate is a sign that the water purification system requires service.

In this application note, we demonstrate and evaluate an ion-exclusion method for the determination of trace-level borate in high-purity water. This ion-exclusion method coupled with suppressed conductivity detection offers an integrated solution for the determination of trace-level boron as borate. We used a Thermo Scientific™ Dionex™ IonPac™ ICE-Borate analytical column and a Thermo Scientific™ Dionex™ IonPac™ TBC-1 Trace Borate concentrator column, specifically designed for this application.[1,2] The experimental approach shown combines large sample volume/preconcentration with ion exclusion chromatography. This approach achieves sensitive detection at low to sub-µg/L levels.

Experimental

Equipment

- Thermo Scientific™ Dionex™ ICS-6000 HPIC system including:
  - Dionex ICS-6000 DP Pump module
  - Dionex ICS-6000 Low Temperature DC Detector/ Chromatography module with two injection valves
  - CD Conductivity Detector
- Thermo Scientific™ Dionex™ AXP Auxiliary pump (single-piston, isocratic metering pump, P/N 063973)
- Thermo Scientific™ Dionex™ IonPac™ Trace Borate concentrator (TBC-1) column (3 × 35 mm, P/N 53944)

- Thermo Scientific™ Dionex™ IonPac™ ICE-Borate analytical column (9 × 250 mm, P/N 53945)
- Thermo Scientific™ Dionex™ ACRS-ICE 500 suppressor (9 mm) (P/N 084715)

Consumables

- Berkshire™ Gamma Wipe™ 120 cleanroom wipes, polyester (Berkshire, P/N GW120ST15; Fisher Scientific, P/N 18-999-306)
- Thermo Scientific™ Nalgene™ Rapid-Flow™ Sterile Disposable Filter Units with Nylon Membrane (1000 mL, 0.2 µm pore size, Fisher Scientific P/N 09-740-46)

Reagents and standards

- Deionized (DI) water, Type I reagent grade, 18 MΩ·cm resistance or better
- Boric acid, J. T. Baker reagent grade
- Methanesulfonic acid (MSA), 99% extra pure (ACROS Organics™, P/N 125612500)
- Tetrabutylammonium hydroxide, TBAOH, 55% aqueous solution (Sachem, P/N 355)
- D-Mannitol, >99.9999% metal basis (Sigma-Aldrich, P/N 78513)

Preparation of solutions and reagents

2.5 mM MSA/60 mM mannitol eluent

Weigh 21.860 g of mannitol. Carefully add this amount to a 1 L volumetric flask containing about 500 mL DI water. Dilute to the 1 L mark and mix thoroughly. Use a stir bar or ultrasonic bath to ensure that mannitol is completely dissolved. Filter the solution through a 0.2 µm nylon filter unit. Transfer this solution to a 2 L eluent container and add 324 µL of 99% extra pure MSA. Mix thoroughly and add DI water to the 2 L mark.

25 mM TBAOH/15 mM mannitol regenerant

Weigh 10.993 g of mannitol. Carefully add this amount to a 1 L volumetric flask containing about 500 mL DI water. Dilute to the 1 L mark and mix thoroughly. Use a stir bar or ultrasonic bath to ensure that mannitol is completely dissolved. Filter the solution through a 0.2 µm nylon filter unit. Transfer this solution to a 4 L eluent container and add 48.55 mL 55% TBAOH. Mix thoroughly and add DI water to the 4 L mark.

Standard solutions

For successful trace ion determinations, it is crucial to minimize contamination of the sample and standard containers. Refer to TN73982: Techniques for Successful Trace Anion and Trace Cation Determinations in High Purity Waters[3] for more details.

Stock borate (as boron) standard solution (1,000 mg/L)
Accurately weigh 572 mg of boric acid in a 100 mL volumetric flask. Add about 50 mL of DI water and dissolve. Dilute with DI water to volume and mix. Concentrated standards are stable for at least one month when stored at 4 °C.

25 mg/L borate standard
Dilute the stock standard 40x to make 25 mg/L borate in DI water and mix.

1,000 ng/L borate standard
Accurately measure 48 µL of 25 mg/L borate standard and add it to a 4 L bottle. Make up the volume with DI water to the 4 L mark and mix.

300 ng/L borate standard
Accurately measure 600 mL of 1,000 ng/L borate standard and add it to a 2 L bottle. Make up the volume with DI water to the 2 L mark and mix.

100 ng/L borate standard
Accurately measure 200 mL of 1,000 ng/L borate standard and add it to a 2 L bottle. Make up the volume with DI water to the 2 L mark and mix.

System preparation and setup
The Dionex ICS-6000 HPIC system is configured with a conductivity detector (CD) and a column oven. Install the concentrator, analytical column, and suppressor in the chromatography module as shown in Figure 1. Follow the instructions in the suppressor manual to install the Dionex ACRS-ICE 500 Supressor.[4]

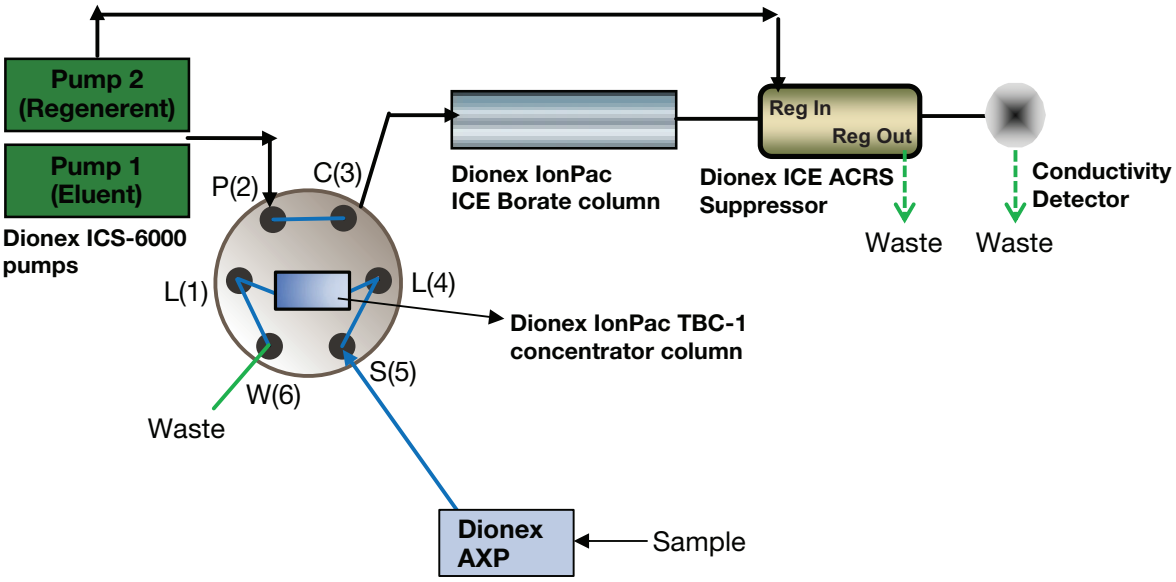


Figure 1. System configuration (valve in the LOAD position)

For the best chromatography, install the concentrator column with a short piece of tubing into Port 4 (between Ports C and S) and a longer piece of tubing as needed in Port 1 (between Ports P and W). Align the direction of the column by pointing the arrow on the label of the concentrator column from Port 1 to Port 4. It is critical to minimize the effect of band broadening when using a preconcentration technique. To minimize the dead volume that causes band broadening, use the smallest length possible of red 0.005 in (0.125 mm) PEEK tubing between the outlet of the Dionex IonPac TBC-1 column and Port 4. Connect the Dionex AXP pump to Port 5 of the injection valve as shown in Figure 1. The Dionex AXP pump is used to load the sample onto the concentrator column. Check that when the valve is in the LOAD position, liquid flows from the sample pump (Dionex AXP pump) through the concentrator Ports 1-4; when the valve is in the INJECT position, the liquid must flow from the analytical pump through the concentrator. Figure 2 shows the configuration for the 6-port injection valve and concentrator column. Prime the analytical pump with eluent and the Dionex AXP pump with DI water.

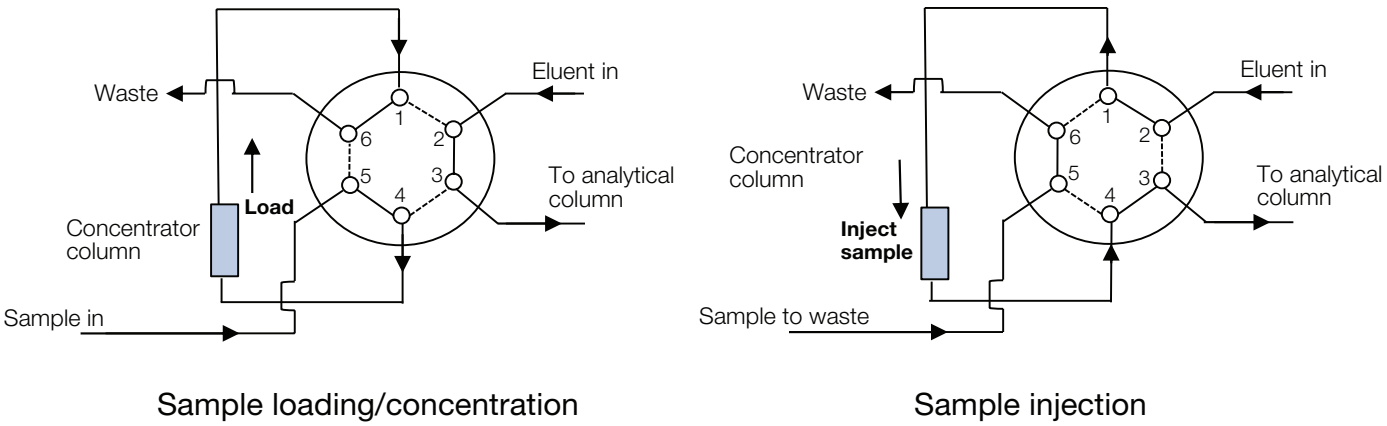


Figure 2. Configuration for the six-port valve and concentrator column

Sample delivery using a Dionex AXP pump

Use a Dionex AXP pump at 8 mL/min flow rate to deliver the sample or DI water over the concentrator for 20 min while the injection valve is in the LOAD position. An injection is made at 20.1 min, at which time data collection begins. To set up the instrument method, use the script editor and add the equilibration step before the "Start run" step, as shown in Figure 3. In the equilibration step, different equilibration times can be set for different concentration times.

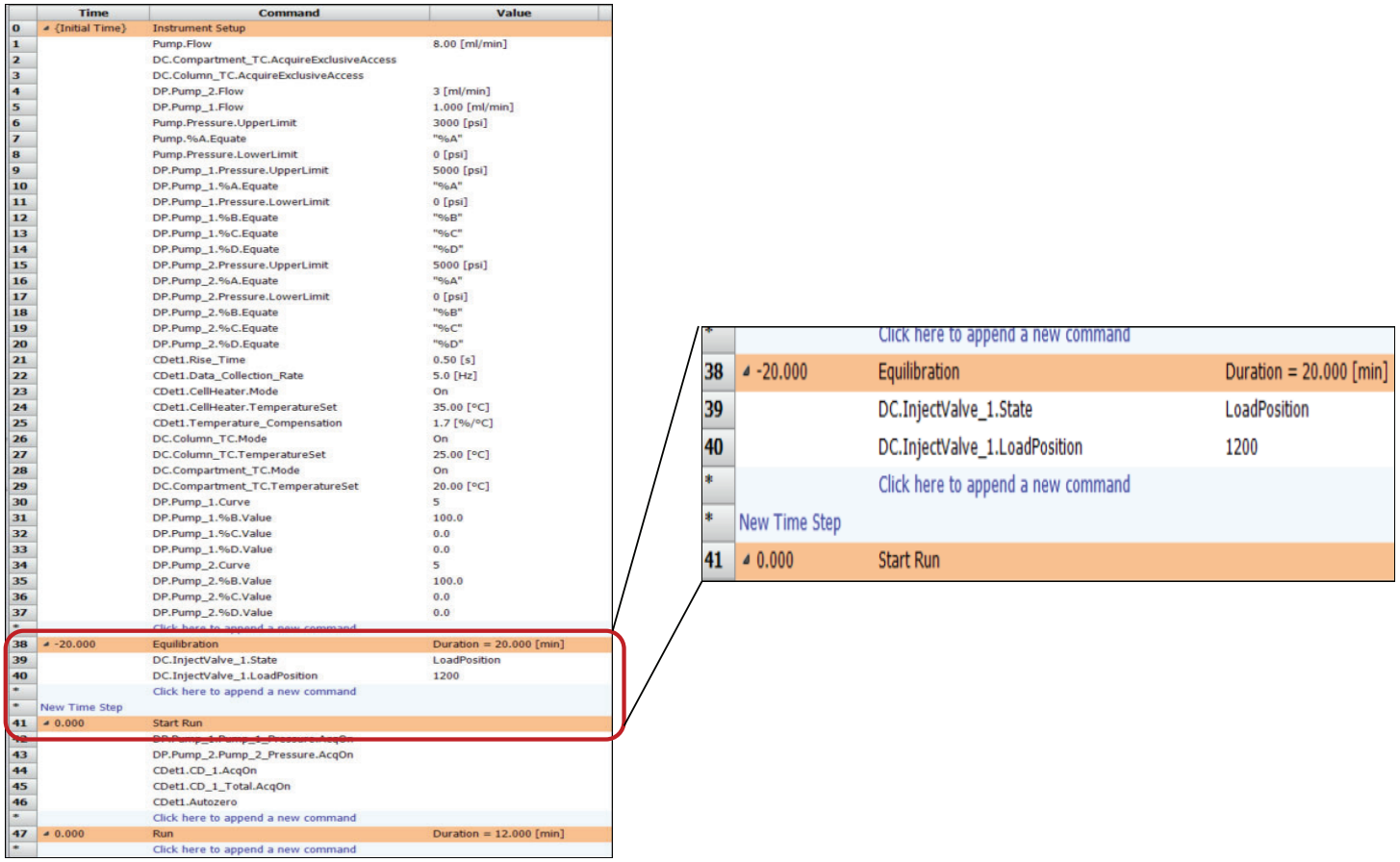


Figure 3. Script editor

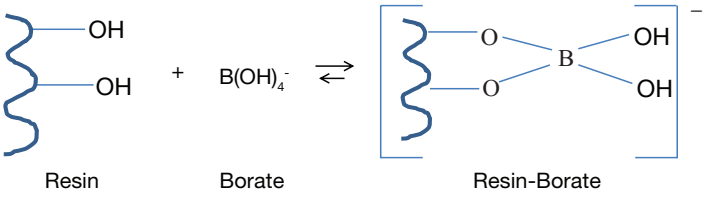
Table 1. QAR conditions

System	Dionex ICS-6000
Column	Dionex IonPac ICE-Borate column, 9 × 250 mm
Eluent	2.5 mM MSA/60 mM mannitol
Injection volume	25 µL
Column temp.	30 °C
Eluent flow rate	1 mL/min (using pump 1 of a Dionex ICS-6000 DP)
Detection	Suppressed conductivity
Suppressor	Dionex ACRS-ICE 500
Regenerant	25 mM Tetrabutylammonium hydroxide (TBAOH)/15 mM mannitol
Regenerant flow rate	3 mL/min (using pump 2 of a Dionex ICS-6000 DP)
Compartment temp.	20 °C
Run time	12 min
Background conductance	140–160 µS/cm
Noise	5–6 nS/cm

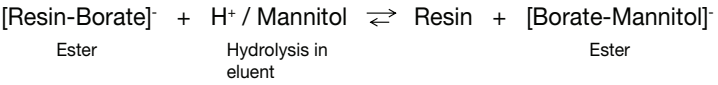
Results and discussion

Before running samples, check the performance of the column by reproducing the quality assurance report (QAR) chromatogram shipped with the column. Figure 4 displays a chromatogram of the 25 mg/L borate (as boron) standard analyzed using the conditions listed in the QAR (Table 1).

For trace-level analysis, a preconcentration technique is used. The chromatographic conditions are listed in Table 2. In this technique, a concentrator column is installed in place of the sample loop, as shown in Figure 1. Concentrator columns are short columns (typically 35–50 mm in length) containing a stationary phase that is identical or similar to the analytical column used for the analysis, or, as is the case here, selective for a specific analyte or class of analytes. The function of a concentrator column is to "strip" ions from a measured volume of a relatively clean aqueous sample matrix. This process "concentrates" the desired species, which leads to lower detection limits. The advantage of using concentrator columns is the ability to perform routine analysis for ions at µg/L (ppb) and sub-µg/L levels without extensive and laborious sample pretreatment. The concentrator column used here is the Dionex IonPac TBC-1 column. The borate chromatographic system shown in Figure 1 is easy to use and significantly improves the practicality and reliability of trace borate determinations. The sample is first passed over the Dionex IonPac TBC-1 concentrator column. The Dionex IonPac TBC-1 column packing is a 10 µm, styrene-based resin bearing hydroxyl functional groups that concentrate borate specifically (no other anions are concentrated) and can be eluted with an acid/mannitol eluent for the ion exclusion separation step.



After sample concentration is completed, the concentrator column is switched in-line with the analytical column for elution and detection.



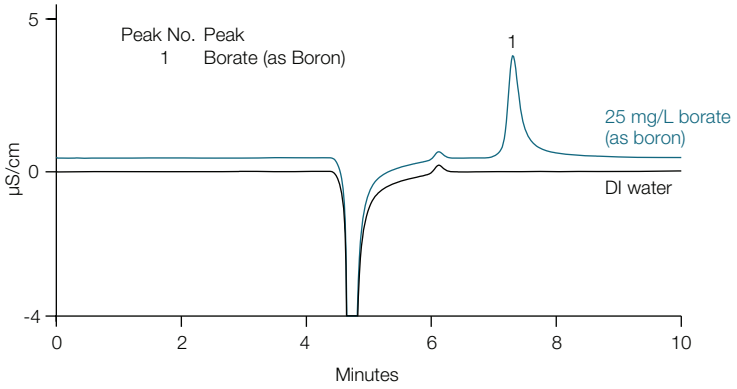


Figure 4. Chromatogram of the column QAR standard

Table 2. Chromatographic conditions for large volume/preconcentration method

System	Dionex ICS 6000
Concentrator column	Dionex IonPac TBC-1
Analytical column	Dionex IonPac ICE-Borate column, 9 × 250 mm
Column temperature	30 °C
Eluent	2.5 mM MSA/60 mM mannitol
Eluent flow rate	1 mL/min (using pump 1 of a Dionex ICS 6000 DP)
Suppressor	Dionex ACRS-ICE 500
Regenerant	25 mM TBAOH/15 mM mannitol
Regenerant flow rate	3 mL/min (using pump 2 of a Dionex ICS 6000 DP)
Compartment temperature	20 °C
Run time	12 min
Sample flow rate	8 mL/min (using AXP pump)
Sample loading/concentration time	2.5 min to 20 min
Sample volume	20–320 mL
Total run time	Depends on sample loading/concentration (12 min + sample loading time)

Separation

In ion exclusion mode, the separator resin bears anionic (negative) charge. A weak acid analyte such as borate is partitioned into the resin bed of the separator column to the extent that it is protonated. As an anion or a strong acid, the analyte is excluded due to electrostatic repulsion. The borate-mannitol anion is more conductive than borate itself and is therefore the preferred form for ion exclusion chromatography.

Figure 5 shows a typical chromatogram for a borate standard at trace levels. The typical background conductance ranges from ~140 to 160 µS/cm depending on the quality of the mannitol used in eluent preparation. The separation is performed at 30 °C to provide consistent retention times during analysis.

Calibration and method detection limit

To calibrate using a concentrator column, concentrate different volumes of the same working standard from the same bottle. Here we used 1,000 ng/L borate and concentrated with an 8 mL/min flow rate for 2.5, 5, 10, 15, and 20 min. Figure 6 shows the chromatograms of 1,000 ng/L borate std, concentrated at different times. The calibration curve for borate (Figure 7) was linear and had a coefficient of determination (r^2) greater than 0.999. Using this method, the calibration validates both the linearity of the peak response to concentration and the efficiency of the concentrator column. This method eliminates the possible errors made during the preparation of multiple standards. However, it has a systematic bias if there is any error in the working standard's concentration, so special care should be taken to ensure that its concentration is accurate.

Note: For the required method detection limit, the volume of sample concentrated can be adjusted by adjusting the sample concentration times.

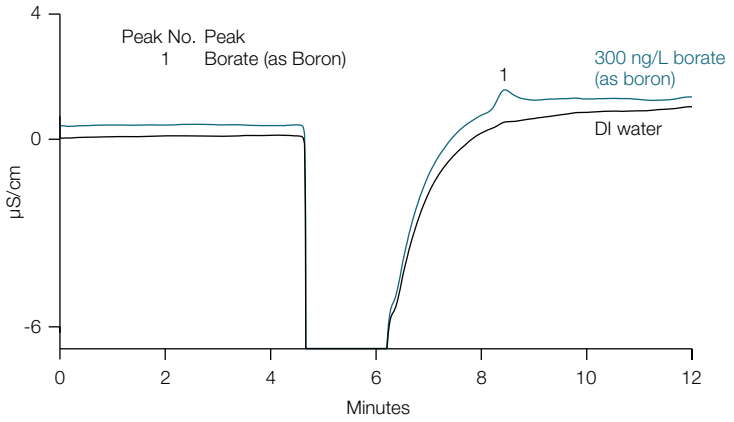


Figure 5. Chromatogram of DI water and 300 ng/L borate spike

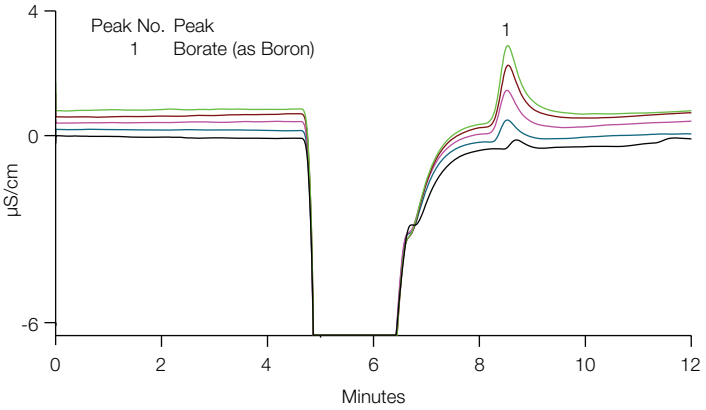


Figure 6. Chromatograms of 1,000 ng/L borate with 2.5, 5, 10, 15, and 20 min concentration times

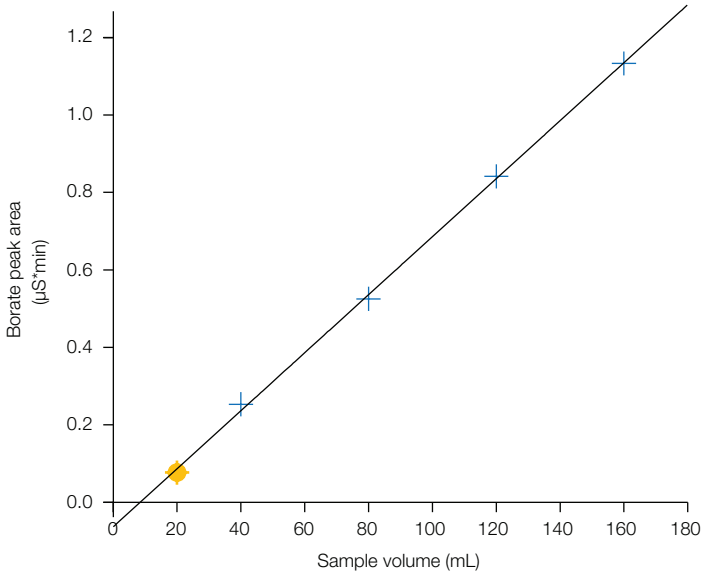


Figure 7. Borate calibration curve

Precision

Seven replicates of a DI water sample spiked with 100 ng/L borate were injected (Figure 8). The retention time and peak area precisions were less than or equal to 0.10% and 5%, respectively.

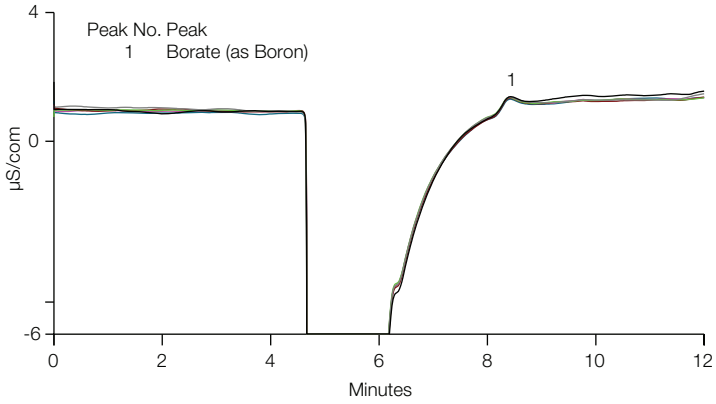


Figure 8. Chromatograms of seven replicate injections of 100 ng/L borate with a 20 min concentration time

Conclusion

This study demonstrated the determination of trace borate in high-purity waters using a large sample volume/preconcentration method with ion-exclusion chromatography and suppressed conductivity detection. The method was validated with calibration and precision studies of DI water spiked with trace levels of borate.

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