Reducing Carbonate Interference in Anion Determinations with the Carbonate Removal Device (CRD)

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Reagents and Standards

Carbonate, a naturally occurring anion in water and aqueous solutions, results from the dissolution of carbon dioxide gas in these solutions. In some beverages, carbon dioxide is purposely added for flavor or effervescence and also acts as a preservative. When samples are analyzed by ion chromatography (IC) with hydroxide and tetraborate eluents, the sample carbonate may coelute and interfere with the quantification of anions of interest (for example, nitrite, bromide, sulfate, or perchlorate).

Carbonate contamination in IC with hydroxide and tetraborate eluents can be introduced by the eluent or the sample. Because the carbonate acts as an eluent, variable carbonate levels in the mobile phase due to variation in eluent preparation steps cause poor retention time and peak area reproducibilities. This type of carbonate contamination is largely eliminated using a Thermo Scientific™ Dionex™ Reagent-Free™ Ion Chromatography (RFIC™) system.[1] The RFIC system electrolytically generates the hydroxide eluent in situ, thereby eliminating the exposure to air and subsequent carbon dioxide absorption. Carbonate introduced into the IC system with the deionized (DI) water (used to supply the RFIC system) is essentially eliminated by the Thermo Scientific™ Dionex™ CR-ATC Continuous Regenerating Anion Trap Column. The Dionex CR-ATC column is installed before the injection valve and after the Thermo Scientific™ Dionex™ EluGen™ EGC Cartridge and EG degas module.

Until recently, carbonate could not be eliminated from the sample without a sample preparation step that could potentially contaminate the sample. The carbonate peak can now be removed from the chromatogram by the Thermo Scientific™ Dionex™ CRD 200 Carbonate Removal Device without compromising the sample or adding sample preparation steps.[2]

This technical note discusses the theory, operation, and installation of the Dionex CRD 200 device, and highlights its advantages for anion determinations. This note also demonstrates the benefits of using the Dionex CRD 200 device for three different applications:

a) Determination of low µg/L concentrations of anions and organic acids in ultrapure water using a Thermo Scientific™ Dionex™ IonPac™ AS15 column (3 × 150 mm, 5 µm) and a gradient separation with a 1 mL injection (Dionex [now part of Thermo Scientific] Application Update (AU) 142)[3],

b) Determination of low µg/L perchlorate in drinking water using a Dionex IonPac AS16 column (4 × 250 mm) with a 1 mL injection Thermo Scientific AU 148[4],

c) Determination of anions in carbonated mineral water using a Dionex IonPac AS18 (2 × 250 mm) column (Dionex [now part of Thermo Scientific] Application Note (AN) 154)[5].

AU 142 describes the determination of µg/L concentrations of anions and organic acids in ultrapure water. This is an important application for the semiconductor, disk drive, electronic components, and nuclear power industries. In ultrapure water, carbonate is the most abundant anion, more than 10× the concentration of any other anion. In this application, the analytical challenge is to accurately identify and quantify ng/L or low µg/L concentrations of adipate, sulfate, oxalate, and bromide that elute on the tail of a much larger carbonate peak.

AU 148 describes the determination of single-digit µg/L concentrations of perchlorate in very high mg/L concentrations of chloride, sulfate, and carbonate. The challenge is to accurately identify and quantify perchlorate as it elutes on the tail of the combined peak for chloride, carbonate, and sulfate.

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AN 154 describes the determination of anions in environmental waters using an RFIC system. We selected a carbonated mineral water sample for this application. Carbonated mineral water is a challenging sample when bromide and chlorate must be determined. For this and the other two applications, the Dionex CRD 200 device successfully removes carbonate just prior to conductivity detection after it exits the anion self-regenerating suppressor (Thermo Scientific™ Dionex™ ASRS™ ULTRA II). This permits the easy quantification of the target analytes.

Experimental

Equipment

- Thermo Scientific™ Dionex™ ICS-2500 system or ICS-3000 equivalent system:
  - Gradient pump (GP50 or DP/SP) with degas option and gradient mixer (GM-4, P/N 049136)
  - Eluent generator (EG50 or EG) with Dionex EluGen II potassium hydroxide (Dionex, P/N 058900),
  - Dionex CR-ATC Continuous Regenerating Anion Trap Column (P/N 060477) and degas module
  - Conductivity detector (CD25A with AS50T thermal compartment or DC with CD, P/N 079829)
  - Thermo Scientific™ Dionex™ Autosampler (AS50 or AS)
  - Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Workstation with Chromeleon 6.6 Chromatography Management Software

(Note: The Dionex CRD 200 device can be used with any RFIC system.)

- Filter unit, 0.2 µm nylon (Nalgene Media-Plus with 90 mm filter, P/N 164-0020 or equivalent nylon filter)
- Vacuum pump
- 300 cm of green 0.75 mm i.d. (0.030 in.) PEEK™ tubing to make 1100 µL loop (P/N 044077, ordered per in.)
- Black 0.25 mm i.d. (0.01 in.) PEEK tubing to make 5 µL loop (P/N 052306 for 5 ft.)
- Low pressure Teflon® tubing (1.6 mm or 0.063 in. i.d., P/N 014157) for the Dionex CRD 200 and degas waste lines
- 10 mL polystyrene vials (for AS50 or AS Autosampler), with caps and slit septa (P/N 055058)
- Micropipettor and tips for preparing samples, standards, and pipetting samples into vials
- Application 1: Corning or other brands of similar quality (Corning®, Corning, NY, USA, P/N 431081 or VWR, P/N 29186-199) 225 mL polystyrene sterile flasks.

Reagents and Standards

DI water, Type 1 reagent grade, 18 MΩ-cm resistivity or better

(Note: Use only A.C.S. reagent grade chemicals for all reagents and standards).

Application 1: Anions and Organic Acids in Ultrapure Water

- Thermo Scientific™ Dionex™ Combined Seven Anion Standard II (P/N 57590)
- Acetic acid (J.T. Baker®, P/N JT9515-03)
- Adipic acid (Aldrich, P/N A26357-100G)
- Glycolic acid (or hydroxyacetic acid) (Sigma, P/N G8284)
- Hydroxyisobutyric acid (HIBA) (Aldrich, P/N 32,359-4)
- Methanesulfonic acid (P/N 033478)
- Oxalic acid, dihydrate (Fisher, P/N A219-500)
- Phthalic acid (Aldrich, P/N 402915))
- Sodium formate (Fisher, P/N S648-500)

Application 2: Perchlorate in Drinking Water

- Sodium carbonate, monohydrate (Fisher, P/N S262-3)
- Sodium chloride, crystalline (J.T. Baker ULTRAPURE BIOREAGENT, P/N JT3624-1)
- Sodium perchlorate, anhydrous crystal (EM Science, P/N EM-SX0692-1)
- Sodium sulfate, granular (EM Science, P/N EM-SX0760-1)

Application 3: Carbonated Mineral Water

- Acetic acid (J.T. Baker, P/N JT9515-03)
- Citric acid, monohydrate (J.T. Baker, P/N JT0110-1)
- Oxalic acid, dihydrate (Fisher, P/N A219-500)
- Sodium bromide (Aldrich, P/N 31,050-6)
- Sodium carbonate, monohydrate (Fisher, P/N S262-3)
- Sodium chlorate (Aldrich ReagentPlus™, P/N 24,414-7)
- Sodium chloride, crystals (J.T. Baker ULTRAPURE BIOREAGENT, P/N JT3624-1)
- Sodium fluoride (Fisher, P/N S299-100)
- Sodium formate (Fisher, P/N S648-500)
- Sodium nitrate, crystalline (Fisher, P/N S343-500)
- Sodium nitrite (J.T. Baker, P/N JT3780-1)
- Sodium phosphate, dibasic anhydrous (J.T. Baker ULTRAPURE BIOREAGENT, P/N JT4062-1)
- Sodium sulfate, granular, (EM Science, P/N EM-SX0760-1)

Samples

- Application 1: Type 1 deionized water
- Application 2: City of Sunnyvale, CA, drinking water
- Application 3: Brand A carbonated mineral water, purchased from a grocery store

Conditions	
Application 1: Anions and Organic Acids in Ultrapure Water	
Columns:	Dionex IonPac AS15-5 µm Analytical, 3 × 150 mm (P/N 057594) Dionex IonPac AG15-5 µm Guard, 3 × 30 mm (P/N 057597)
Flow Rate:	0.7 mL/min
Eluent (EG50 or EG):	7–60 mM potassium hydroxide for 5–12 min
Inj. Valve:	Reset to the "Load" position at 4 min
Temperature:	30 °C
Inj. Loop Size:	1100 µL
Inj. Volume:	1000 µL partial loop injection of 1100 µL loop
Detection:	Suppressed conductivity with Dionex ASRS ULTRA II, recycle mode, 2 mm (P/N 061562) Current setting, 104 mA
CRD:	Microbore 2 mm (P/N 062986)
Background:	0.8 µS at 7 mM potassium hydroxide
Typical Backpressure:	~2300 psi
Typical Noise:	<3 nS
Run Time:	20 min
Application 2: Perchlorate in Drinking Water	
Columns:	Dionex IonPac AS16 Analytical, 4 × 150 mm (P/N 055376) Dionex IonPac AG16 Guard, 4 × 50 mm (P/N 055377)
Flow Rate:	1.2 mL/min
Eluent (EG50 or EG):	65 mM potassium hydroxide
Temperature:	30 °C
Inj. Loop Size:	1100 µL
Inj. Volume:	1000 µL partial loop injection of 1100 µL loop
Detection:	Suppressed conductivity with Dionex ASRS ULTRA II, external water mode, 4 mm (P/N 061561) Current setting, 193 mA
CRD:	Standard bore, 4 mm (P/N 062983)
Background:	0.4 µS
Typical Backpressure:	~2300 psi
Typical Noise:	<1.0 nS
Run Time:	15 min
Application 3: Carbonated Mineral Water	
Columns:	Dionex IonPac AS18 Analytical, 2 × 150 mm (P/N 060553) Dionex IonPac AG18 Guard, 2 × 50 mm (P/N 060555)
Flow Rate:	0.25 mL/min
Eluent (EG50 or EG):	22–40 mM potassium hydroxide for 7–8 min
Injection Valve:	Reset to the "Load" position at 4 min
Temperature:	30 °C
Inj. Volume:	5 µL full loop injection (PEEK sample loop)
Detection:	Suppressed conductivity with Dionex ASRS ULTRA II, recycle mode, 2 mm (P/N 061562) Current setting, 25 mA
CRD:	Microbore, 2 mm (P/N 062986)
Background:	0.4 µS at 22 mM potassium hydroxide
Typical Backpressure:	~2100 psi
Typical Noise:	<2 nS
Run Time:	15 min

Preparation of Solutions and Reagents

Eluent Preparation

It is essential to use high quality, Type 1 water, >18 MΩ-cm. Degas if needed.

Standard Preparation

Application 1: Anions and Organic Acids in Ultrapure Water

Prepare individual stock solutions of 1000 mg/L acetate, formate, glycolate, adipate, oxalate, and phthalate. Dissolve the amount of reagent grade compound (Table 1) in DI water in a 100 mL Class A volumetric flask and dilute to 100 mL mark with DI water.

Table 1. Amount of compound used to prepare 100 mL of individual 1000 mg/L stock solutions.

Anion	Compound	Mass (g)
Glycolate	Glycolic acid ($CH_2OHCOOH$)	0.101
Acetate	Glacial acetic acid (CH_3COOH)	0.102
Formate	Sodium formate (HCOONa)	0.151
Hydroxyisobutyrate	2-Hydroxyisobutyric acid (HIBA) ($CH_3CHOHCH_2COOH$)	0.101
Methanesulfonate	Methanesulfonic acid (CH_3SO_3H)	0.101
Adipate	Adipic acid ($COOH(CH_2)_4COOH$)	0.101
Oxalate	Oxalic acid dihydrate ($HOOCCOOH•2H_2O$)	0.143
Phthalate	Phthalic acid ($C_6H_4(COOH)_2$)	0.101

Prepare separate intermediate standards of 1.0 mg/L from each of the stock solutions. Pipette 100 µL of the individual stock solution into a 120 mL polypropylene bottle. Dilute with deionized water to 100.00 g total weight. Prepare an intermediate standard from the Dionex Combined Seven Anion Standard II. Pipette 1000 µL into the 120 mL polypropylene bottle. Dilute with deionized water to 100.00 g total weight.

Prepare the Corning 225 mL polystyrene sterile flasks for the µg/L standards two days or more prior to the standard preparation. Rinse each flask five times with deionized water, fill it to the top with deionized water, and let it soak overnight. Repeat this daily until flasks are needed for the µg/L standards. (See AU 142 for additional precautions needed for determinations of µg/L anion concentrations[6].)

Prepare working standards of combined anion and organic standards from the intermediate standards. Pipette 1000 µL and 3000 µL of the intermediate standards of Combined Seven Anion Standard and organic acids, respectively, into a 225 mL polystyrene sterile flask. Dilute this working standard with DI water to 100.00 g total weight. The final concentrations are 1.0 µg/L nitrite, chloride, sulfate, nitrate, and bromide, 0.2 µg/L of fluoride; 2.0 µg/L of phosphate, and 3.0 µg/L of glycolate, acetate, formate, hydroxyisobutyrate, methanesulfonate, adipate, oxalate, and phthalate. Prepare working standards of 0.5, 2.0, 4.0, and 5.0 µg/L of anions with 2.0, 4.0, 5.0, and 10 µg/L of organic acids, in a similar manner as the first working standard. Prepare low µg/L standards daily, higher µg/L standards weekly, and mg/L standards monthly.

Application 2: Perchlorate in Drinking Water

Prepare stock solutions of 1000 mg/L perchlorate and 25,000 mg/L each of carbonate, chloride, and sulfate. Dissolve the amount of reagent grade compound (Table 2) in deionized water and dilute with DI water to 100.00 g total weight.

Prepare an intermediate standard of 1.0 mg/L perchlorate. Pipette 100 µL of the 1000 mg/L perchlorate stock into a 120 mL polypropylene bottle and dilute with deionized water to 100.00 g total weight.

Prepare working standards of 0, 5, and 25 µg/L perchlorate in water, 100MA, and 500MA. One hundred MA (100MA) is defined as a matrix solution of 100 mg/L each of chloride, carbonate, and sulfate, and 500MA is 500 mg/L each of the same anions. Pipette the amount shown in Table 3 of perchlorate, carbonate, chloride, and sulfate from the stock solutions into a 120 mL polypropylene bottle and dilute with deionized water to 100.00 g total weight.

Prepare 100 and 500 mg/L carbonate spiked samples in deionized water to evaluate carbonate removal. Pipette the amount of carbonate shown in Table 3 from the stock solutions into a 120 mL polypropylene bottle and dilute with deionized water to 100.00 g total weight.

Table 2. Amount of compound used to prepare 100 mL stock solutions.

Anion	Compound	Mass (g)	Concentration of Anion in Stock Solution (mg/L)
Perchlorate	Sodium perchlorate ($NaClO_4$)	0.123	1,000
Carbonate	Sodium carbonate monohydrate ($Na_2CO_3 \cdot H_2O$)[a]	5.166	25,000
Chloride	Sodium chloride (NaCl)	4.121	25,000
Sulfate	Sodium sulfate (Na_2SO_4)	3.697	25,000

[a] Or 4.4160 g of anhydrous sodium carbonate

Table 3. Amount (µL) of stock solutions used to prepare 100 mL of working standards.

	1.0 mg/L Perchlorate	25,000 mg/L Carbonate	25,000 mg/L Chloride	25,000 mg/L Sulfate
5 µg/L perchlorate in water	500	—	—	—
25 µg/L perchlorate in water	2500	—	—	—
100MA[b]	—	400	400	400
5 µg/L perchlorate in 100MA	500	400	400	400
25 µg/L perchlorate in 100MA	2500	400	400	400
500MA[c]	—	2000	2000	2000
5 µg/L perchlorate in 500MA	500	2000	2000	2000
25 µg/L perchlorate in 500MA	2500	2000	2000	2000
100 mg/L carbonate	—	400	—	—
500 mg/L carbonate	—	2000	—	—

[a] 1 mg/L perchlorate is an intermediate standard.
[b] 100MA is a matrix solution of 100 mg/L each of chloride, carbonate, and sulfate.
[c] 500MA is a matrix solution of 500 mg/L each of chloride, carbonate, and sulfate.

Application 3: Carbonated Mineral Water

Prepare individual stock solutions of 1000 mg/L of fluoride, acetate, formate, nitrite, bromide, nitrate, chlorate, oxalate, phosphate, and citrate, and 2 5,000 mg/L of chloride, sulfate, and carbonate. Dissolve the amount of reagent grade compound (Table 4) in DI water in a 120 mL polypropylene bottle and dilute with deionized water to 100.00 g total weight.

Table 4. Amount of compound used to prepare 100 mL of individual stock solutions.

Anion	Compound	Mass (g)	Concentration of Anion in Stock Solution (mg/L)
Fluoride	Sodium fluoride (NaF)	0.221	1000
Acetate	Glacial acetic acid (CH_3COOH)	0.102	1000
Formate	Sodium formate (HCOONa)	0.151	1000
Chloride	Sodium chloride (NaCl)	4.121	25,000
Nitrite	Sodium nitrite ($NaNO_2$)	0.150	1000
Bromide	Sodium bromide (NaBr)	0.129	1000
Carbonate	Sodium carbonate monohydrate ($Na_2CO_3 \cdot H_2O$)[a]	5.166	25,000
Sulfate	Sodium sulfate (Na_2SO_4)	3.697	25,000
Nitrate	Sodium nitrate ($NaNO_3$)	0.137	1000
Chlorate	Sodium chlorate ($NaClO_3$)	0.128	1000
Oxalate	Oxalic acid dihydrate ($HOOCCOOH \bullet 2H_2O$)	0.143	1000
Phosphate	Sodium phosphate, dibasic (Na_2HPO_4)	0.150	1000
Citrate	Citric acid monohydrate ($HOOCCH_2C(OH)(COOH)CH_2COOH \bullet H_2O$)	0.110	1000

[a] Or 4.4160 g of anhydrous sodium carbonate.

Prepare combination working standards of 0.05, 0.10, 1.0, and 5.0 mg/L of fluoride, acetate, formate, nitrite, bromide, chlorate, oxalate, phosphate, and citrate with 2.5, 5.0, 10, and 50 mg/L of nitrate, and 50, 100, 200, and 500 mg/L of chloride, sulfate, and carbonate. Pipette the amount shown in Table 5 from the stock solutions into a 120 mL polypropylene bottle and dilute with deionized water to 100.00 g total weight.

Table 5. Amount (µL) of stock solutions used to prepare 100 mL of working standards.

Stock Solution (mg/L)	Working Standard			
	1	2	3	4
Fluoride, acetate, formate, nitrite, bromide, chlorate, oxalate, phosphate, and citrate	5	10	100	500
Chloride, carbonate, and sulfate	200	400	800	2000
Nitrate	250	500	1000	5000

Sample Preparation

Application 1: Anions and Organic Acids

Type I DI water was analyzed directly without any sample treatment. Trace anion determinations in ultrapure water require additional steps to maintain a contamination-free system. Powder-free vinyl or nitrile gloves should be worn during all sample preparation and sample handling steps. Sample vials should be rinsed three to five times and soaked 24 h prior to use with Type 1, DI water. The DI water in the syringe flush container should be replaced daily with fresh DI water. (See Dionex [now part of Thermo Scientific] AU 142 for additional precautions needed for determinations of µg/L anion concentrations.)

Application 2: Perchlorate in Drinking Water

The City of Sunnyvale drinking water was analyzed directly without any dilution or sample preparation. The drinking water was spiked with perchlorate at 5, 10, 15, and 20 µg/L. To prepare these samples, pipette 500, 1000, 1500, and 2000 µL of the 1.0 mg/L perchlorate stock into separate 120 mL polypropylene bottles and dilute to 100.00 g with drinking water.

Application 3: Carbonated Mineral Water

Brand A carbonated mineral water sample was diluted five-fold with degassed DI water prior to analysis. Samples were prepared fresh daily from a previously unopened bottle of the same lot.

System Setup

Install the GM-4 Eluent Gradient Mixer, Dionex EluGen II potassium hydroxide cartridge, Dionex CR-ATC column, Dionex ASRS ULTRA II suppressor, columns, and backpressure loops for the suppressor and the eluent generator. Install the GM-4 Eluent Gradient Mixer between the pump and the Dionex EluGen cartridge according to the start-up instructions in the EG50 product manual.[7] Follow the Quickstart instructions for the Dionex CR-ATC column[8] to hydrate the CR-ATC column and install it after the EGC cartridge and before the injection valve and the degas module. Install the columns after the injection valve according to the product manuals.[9–11] Install a backpressure loop on the "cell out" position of the conductivity cell. Follow the Quickstart instructions in the suppressor product manual[12] to hydrate the suppressor and install it between the columns and the conductivity cell. The suppressor should be installed in recycle mode for Applications 1 and 3, and external water mode for Application 2. Measure the system pressure with and without the backpressure coil at the experiment's flow rate.[13] This must be ~40 psi to prevent suppressor damage. After the installations are completed, check the total system pressure. The total system pressure should be >2000 psi for the eluent generator with the optimum operating pressure of 2300 psi. If the system pressure is <2000 psi, install yellow (0.003 in. i.d.) PEEK tubing between the degas module and the injection valve to increase the system pressure to ~2300 psi.[14] Do not allow the system pressure to exceed 3000 psi, because it could damage the degas module.

Application 1: Preparation of an 1100 µL Sample Loop

To make a 1000 µL injection with the Dionex AS50 Autosampler, use an 1100 µL sample loop to make a partial loop injection. To prepare an 1100 µL sample loop, cut a 242 cm length of green 0.75 mm i.d. (0.030 in.) PEEK tubing. The sample loop volume must be calibrated by weight using an analytical balance because the tubing inside diameter can vary by as much as 20%. The sample loop volume is the difference between the loop filled with deionized water and the empty loop. (SeeDionex [now part of Thermo Scientific] AN 166 for an example of this calculation.[15]) For this application, the calculated sample loop should be at least 1090 µL.

Application 1: Dionex AS50 Autosampler Parameters and Program Parameters

For partial loop injection, enter this sample loop volume as the "sample loop size," on Dionex AS50 module under Module Setup Menu, Plumbing Configuration. Enter the program parameters listed in Table 6 during program creation with the Chromeleon Program Wizard.

The flush volume should be 3–5× the sample loop volume. On the Dionex AS50 Autosampler, the flush occurs through the injection needle and injection port but not through the sample loop. During the run, the sample loop is open to elute both at the low concentration and high concentration eluent. A high eluent concentration in the loop at the time of sample loading will affect early eluting organic acids, especially at trace anion concentrations. Therefore, the injection valve is reset to the load position prior to the gradient ramp, and after the eluent flow has swept the sample loop 2–10×. In this case, with a flow of 0.7 mL/min, every 1.57 min the 1100 µL sample loop is completely swept with eluent and the gradient ramp starts at 5 min. Therefore, the injection valve (see Table 6, Relay & State Device Options) is programmed to reset to the load position at 4 min. The injection valve command can also be entered manually into the program file, using "Control," "Command." The Dionex AS autosampler operates in a similar manner. More information can be found in the operator's manuals for the Dionex AS50 and AS autosamplers.[16,17]

Application 2: Preparation of an 1100 µL Sample Loop

The 1100 µL loop is prepared in the same manner as described in Application 1.

Table 6. Program wizard entries for determinations of trace anions in ultrapure water.

Parameter	Factor		Section	Action
Gradient type Flow	Multistep gradient 0.6		Pump options	
Retention time –5.1 –5.0 0 5.0 12.0 20.0	Concentration 60.0 7.0 7.0 7.0 60.0 60.0	Gradient curve 5.0 5.0 5.0 5.0 5.0 5.0	Flow gradient options	Equilibration Start and inject Start gradient End gradient High concentration, end
Column temperature Syringe speed Sample needle height Cut volume Flush volume	30 4 2 30 3000		Sampler options	3–5× sample volume
Acquisition time	0 to 20		Acquisition options	
Data collection rate Oven temperature Suppressor Hydroxide	5.0 off ASRS _2mm 60		ECD_1 options	Enter high concentration
Retention time Sampler_inject valve Load position Add	4.0 Select Select Select		Relay & state device option	Reset to load at 4.0 min

Application 2: AS50 Autosampler Parameters and Program Parameters

For partial loop injection, enter the sample loop volume as the "sample loop size" on the Dionex AS50 module under Module Setup Menu, Plumbing Configuration. Enter the program parameters listed in Table 7 with the Chromeleon program wizard. The flush volume should be 3–5× the sample loop volume.

Application 3: Preparation of a 5 µL Sample Loop

Prepare a 5 µL loop from black PEEK 0.25 mm i.d. (0.010 in) tubing. Cut a 10 cm length and calibrate the sample volume by measuring the weight difference of the tubing filled with DI water and empty tubing. (See AN 166 for an example of this calculation.[15])

Application 3: AS50 Autosampler Parameters and Program Parameters

In this application, the injection is a full loop injection of 5 µL. Enter the sample loop volume on the Dionex AS50 Autosampler module under Plumbing Configuration, and the Cut Volume of "0" in the System Parameters for a full loop injection. We used a flush volume of 250 µL.

The injection valve was reset to the load position at 4 min (~10× the volume of the sample loop and before the gradient concentration ramp). Enter the program parameters listed in Table 8 with the Chromeleon program wizard.

Table 7. Program wizard entries for determining perchlorate in mg/L chloride, carbonate, and sulfate.

Parameter	Factor		Section	Action
Gradient type Flow	Isocratic 1.2		Pump options	
Retention time –0.1 0.0 15.0	Concentration 65.0 65.0 65.0	Gradient curve 5.0 5.0 5.0	Flow gradient options	Start, Inject End
Column temperature Syringe speed Sample needle height Cut volume Flush volume	30 4 2 30 3000		Sampler options	3–5× sample volume
Acquisition time	0 to 15		Acquisition options	
Data collection rate Oven temperature Suppressor Hydroxide	5.0 off ASRS _4mm 65		ECD_1 options	

Table 8. Program wizard entries for determination of inorganic anions in carbonated mineral water.

Parameter	Factor		Section	Action
Gradient type Flow	Multistep gradient 0.25		Pump options	
Retention time –5.1 –5.0 0 7.0 8.0 15.0	Concentration 40.0 22.0 22.0 22.0 40.0 40.0	Gradient curve 5.0 5.0 5.0 5.0 5.0 5.0	Flow gradient options	Equilibration Start and inject Start gradient End gradient High concentration, End
Column temperature Syringe speed Sample needle height Cut volume Flush volume	30 4 2 30 3000		Sampler options	3–5× sample volume
Acquisition time	0 to 15		Acquisition options	
Data collection rate Oven temperature Suppressor Hydroxide	5.0 off ASRS _2mm 40		ECD_1 options	Enter high concentration
Retention time Sampler_inject valve Load position Add	4.0 Select Select Select		Relay and state device option	Reset to load at 4.0 min

CRD

Theory and Operation of the Dionex CRD 200 Device

The Dionex CRD 200 device is a membrane-based module that transports carbon dioxide across a gas-permeable membrane (Figure 1).[18] Carbonate ion is removed as carbon dioxide from the sample after suppression and just prior to detection, resulting in improved separation and quantification of select anions.

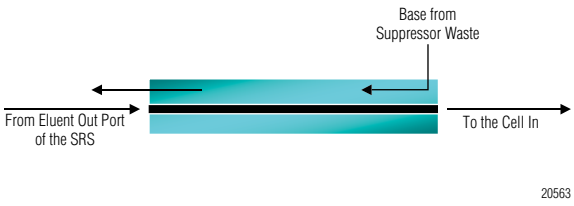

Figure 1. Carbonate removal device schematic.

The Dionex CRD 200 device contains a narrow-bore capillary membrane tube that is thinly coated with a carbon dioxide permeable silicone film (Figure 2)[19] that takes advantage of the carbonic acid-carbon dioxide equilibrium (Equation 1) chemistry to remove carbon dioxide, thus removing the carbonate peak.

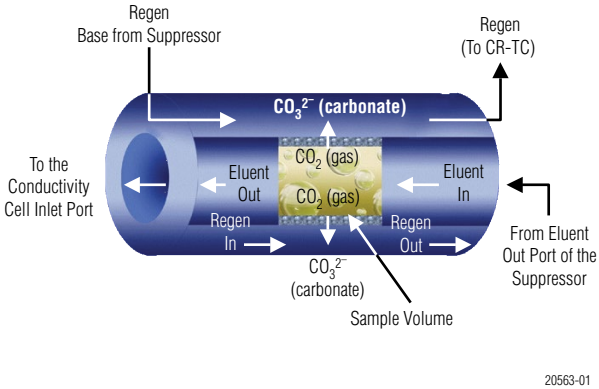

Figure 2. Carbonate Removal Device schematic.

$$H_2CO_3 \longleftrightarrow H_2O + CO_2$$

Equation 1. Carbonate Removal Device equilibrium.

The efficiency of the carbonate peak removal will be called "Apparent % Removal Efficiency" (Equation 2).

$$\text{Apparent \% Removal Efficiency} = 100 - \left(\frac{\text{Response}_{wCRD}}{\text{Response}_{w/oCRD}} \times 100 \right)$$

Equation 2. Apparent removal efficiency.

The Dionex CRD 200 device is positioned between the Dionex ASRS ULTRA II suppressor and the conductivity cell. The eluent and separated sample flow out of the column and into the suppressor. The suppressor converts carbonate ion to carbonic acid (H_2CO_3) in equilibrium with carbon dioxide. As the suppressed eluent flows into the Dionex CRD 200 device and through the inner Dionex CRD 200 device membrane tube, carbon dioxide flows across the membrane. This drives the equilibrium to form more carbon dioxide. Concurrently, regenerant waste from the suppressor flowing through the exterior surface of the Dionex CRD 200 device membrane tube converts carbon dioxide to carbonate ion. The carbonate ion is carried to waste.

Dionex CRD 200 Device Installation

The Dionex CRD 200 device is easily installed on top of the Dionex ASRS ULTRA II suppressor (Figure 3)[20] and is intended for use with hydroxide and borate chemistries, and a Dionex RFIC system. To install, spread the bottom metal clips open and place the Dionex CRD 200 device over the Dionex ASRS ULTRA II suppressor with the Eluent In port of the Dionex CRD 200 device facing the Eluent Out port of the suppressor. Connect the 1.6 mm i.d. (0.063 in.) Teflon tubing to the regenerant lines and PEEK tubing (red for 2 mm, P/N 052310; black for 4 mm, P/N 052306) on the eluent lines.

Application of pressures higher than those recommended will damage the Dionex CRD 200 device. Always remove all plugs from the Dionex CRD 200 device before connecting it to the suppressor or the conductivity cell. Ensure that the pressure drop is between 30 and 40 psi for the cell with the backpressure tubing installed. This measurement was discussed in the System Setup section.

The 2 mm and 4 mm Dionex CRD 200 devices cannot be used interchangeably. The 2 mm Dionex CRD 200 device should only be used with 2 mm and 3 mm column sets; the 4 mm Dionex CRD 200 device with the 4 mm column sets. We recommend that the Dionex CRD 200 device be hydrated before operation. See the Dionex CRD 200 device product manual for the hydration and backpressure measurement instructions.

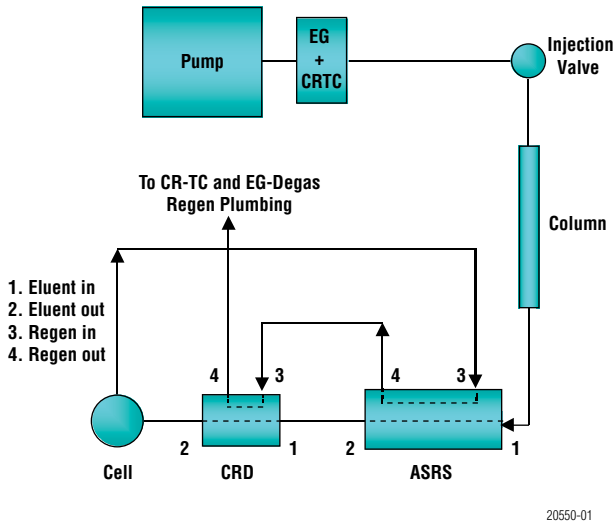

Figure 3. Carbonate Removal Device plumbing.

Results and Discussion

Application 1: Anions and Organic Acids

Trace anion analysis in ultrapure water is intended for detection of ng/L to low µg/L levels of anions. Carbonate, which is easily and readily absorbed in this very clean matrix, is the most abundant anion present, and interferes or coelutes with sulfate, adipate, oxalate, and other anions. AU 142 describes trace anion concentrations in ultrapure water using a Dionex IonPac AS15-5µm, 3 mm column set, gradient separation, a 1 mL injection, and suppressed conductivity detection.

We chose this application to demonstrate that the Dionex CRD 200 device significantly reduces the sample carbonate peak and improves trace-level anion determinations, especially for sulfate and adipate. We first determined the retention times of seven inorganic anions and eight organic acids with 10 µg/L single anion standards and then analyzed anions in a combined standard containing 1 µg/L chloride, nitrite, bromide, nitrate, and sulfate, 0.2 µg/L fluoride, 2 µg/L phosphate, and 3 µg/L of glycolate, acetate, formate, hydroxyisobutyric acid (HIBA), methanesulfonate, adipate, oxalate, and phthalate. This standard was analyzed with and without the Dionex CRD 200 device installed. Figure 4 shows the effect of the Dionex CRD 200 device on removing the carbonate peak from the combined anion and organic acid standard. Carbonate remains the most abundant peak in these samples, but most of the carbonate peak was removed by the Dionex CRD 200 device (85 ± 4.5%, Apparent % Removal Efficiency, Table 9). Adipate was only detected with the Dionex CRD 200 device installed (Table 10). The results show that there is an increase in retention times for all anions, +0.08 min to +0.15 min. This is expected because the Dionex CRD 200 device adds to the delay volume.

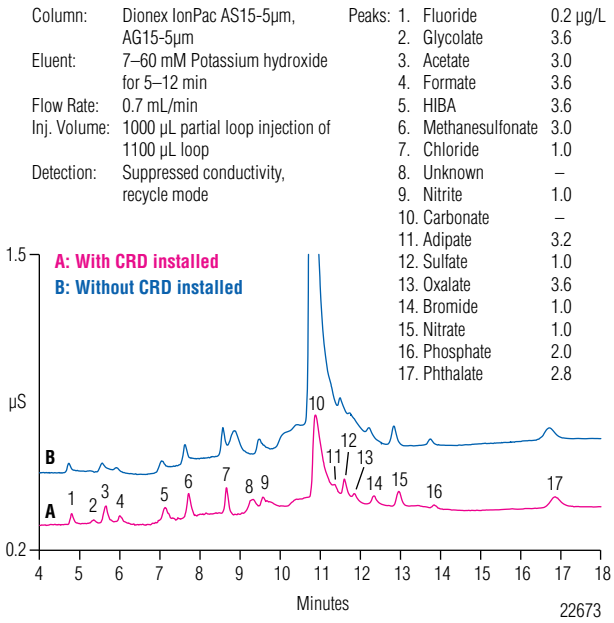

Figure 4. Determination of mixed anion and organic acid standard with (A) and without (B) a Dionex CRD 200 device.

Table 9. Carbonate peak removal by the Dionex CRD 200 device from ultrapure water.

Sample	Without CRD Carbonate Peak Area (µS-min)	With CRD Carbonate Peak Area (µS-min)	Apparent % Removal Efficiency
Combined anion and organic acid standard	10.89 ± 0.01	0.123 ± 0.029	85.6 ± 4.5

n=10 for each data point.

Table 10. Effect of the Dionex CRD 200 device on retention times of µg/L anions in ultrapure water.

Combined Anion and Organic Acid Standard	Without CRD Retention Time (min)	With CRD Retention Time (min)
Fluoride	4.73 ± 0.01	4.81 ± 0.03
Glycolate	5.26 ± 0.00	5.35 ± 0.03
Acetate	5.57 ± 0.01	5.65 ± 0.02
Formate	5.92 ± 0.01	6.01 ± 0.02
HIBA[a]	7.06 ± 0.01	7.14 ± 0.01
Methanesulfonate	7.63 ± 0.00	7.72 ± 0.01
Chloride	8.57 ± 0.00	8.67 ± 0.02
Nitrite	9.47 ± 0.01	9.63 ± 0.02
Carbonate	10.79 ± 0.01	10.88 ± 0.01
Adipate	Not detected	11.30 ± 0.01
Sulfate	11.48 ± 0.07	11.60 ± 0.01
Oxalate	11.72 ± 0.07	11.86 ± 0.01
Bromide	12.20 ± 0.01	12.33 ± 0.01
Nitrate	12.83 ± 0.01	12.96 ± 0.01
Phosphate	13.75 ± 0.01	13.85 ± 0.02
Phthalate	16.72 ± 0.02	16.87 ± 0.03

n=10 for each data point.
[a] Hydroxyisobutyric acid

Application 2: Perchlorate in Drinking Water

Perchlorate is typically determined at single-digit µg/L concentrations in the presence of 100–1000 mg/L levels of carbonate, chloride, and sulfate, a 1:100,000 to 1:1,000,000 ratio. Chloride, sulfate, and carbonate elutes as a large peak and perchlorate elutes on the tail of that peak at 9.6 min. AU 148 describes the determination of µg/L concentrations of perchlorate levels in a matrix containing high concentrations of carbonate, chloride, and sulfate using a Dionex IonPac AS16 column set (4 mm), a 1 mL partial loop injection, and suppressed conductivity detection.

Table 11. Summary of perchlorate peak retention times, peak widths, and peak efficiencies.

	Perchlorate Without CRD			Perchlorate With CRD		
Perchlorate Sample	Perchlorate Retention Time (min)	Perchlorate Peak Width (min)	Efficiency (USP)	Perchlorate Retention Time (min)	Perchlorate Peak Width (min)	Efficiency (USP)
5 µg/L in water	9.71 ± 0.02	0.454 ± 0.005	7347 ± 185	9.76 ± 0.01	0.452 ± 0.004	7408 ± 95
5 µg/L in 100MA[a]	9.72 ± 0.03	0.455 ± 0.007	7297 ± 211	9.73 ± 0.01	0.453 ± 0.005	7435 ± 120
5 µg/L in 500MA[a]	9.55 ± 0.02	0.601 ± 0.027[b]	4067 ± 387[b]	9.71 ± 0.01	0.602 ± 0.003[b]	4157 ± 46[b]
25 µg/L in water	9.77 ± 0.01	0.460 ± 0.000	7430 ± 28	9.79 ± 0.00	0.450 ± 0.000	7591 ± 89
25 µg/L in 100MA[a]	9.60 ± 0.01	0.457 ± 0.009	7106 ± 250	9.71 ± 0.01	0.460 ± 0.000	7186 ± 63
25 µg/L in 500MA[a]	9.63 ± 0.01	0.618 ± 0.004[b]	3883 ± 52[b]	9.76 ± 0.00	0.604 ± 0.011[b]	4184 ± 165[b]

n=10 for each data point.

[a] MA indicates a mixed common anion solution of chloride, sulfate, and carbonate included in the sample matrix at the parenthetical mg/L concentration for each anion.

[b] Both the peak widths and the efficiencies are manually calculated. In these samples, perchlorate is a rider peak on the combined peak of chloride and sulfate.

This application demonstrates that the 4 mm Dionex CRD 200 device can reduce the carbonate peak and improve perchlorate quantifications. Samples of 5 µg/L and 25 µg/L perchlorate spiked in water (100MA and 500MA) were analyzed with and without the Dionex CRD 200 device installed (Table 11). As expected, perchlorate elutes later with the Dionex CRD 200 device installed. Peak efficiency (USP) is defined as:

$$16\left(\frac{\text{Retention time}}{\text{Peak width}}\right)^2$$

and therefore it is expected that the efficiencies will decrease with the longer delay time added by the Dionex CRD 200 device. However, in this case, the perchlorate peak efficiencies remained about the same with the Dionex CRD 200 device installed. Due to the presence of large concentrations of chloride and sulfate, it is difficult to measure the carbonate peak removal, but the chromatograms show significant reduction in the combined chloride-sulfate-carbonate peak (Figure 5). Figure 5 shows that large amounts of carbonate were removed from 500MA samples. The large peak is reduced in size and its tail approaches the baseline earlier.

To better assess carbonate removal, 100 mg/L and 500 mg/L carbonate were spiked into DI water and the samples analyzed with and without the Dionex CRD 200 device (Table 12). These data show that >86% of the carbonate peak was removed from the two samples.

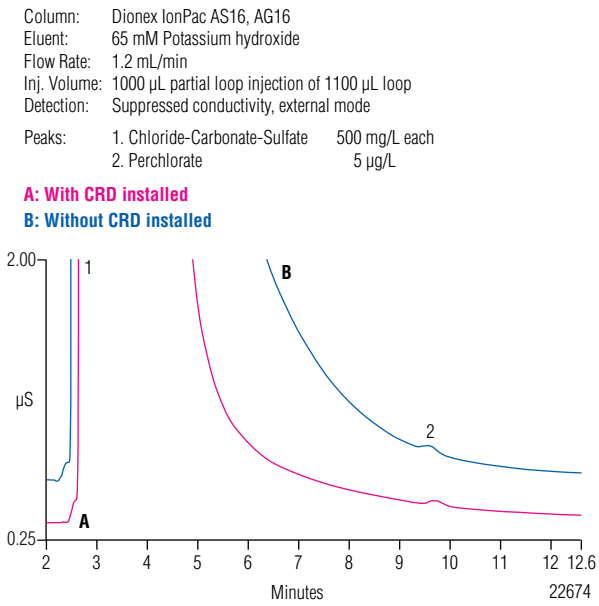

Figure 5. Chromatograms of 5 µg/L perchlorate in 500MA, with (A) and without (B) a Dionex CRD 200 device.

Table 12. Effect of the Dionex CRD 200 device on carbonate peak retention times, peak areas, and apparent % removal efficiencies.

Carbonate Spiked Deionized Water Sample	Retention Time (min)	Peak Area (µS-min)	Apparent % Removal Efficiency
100 mg/L without CRD	3.61 ± 0.01	10.8 ± 0.2	N/A
100 mg/L with CRD	3.69 ± 0.01	1.51 ± 0.11	86.0 ± 0.9
500 mg/L without CRD	3.89 ± 0.01	25.1 ± 0.4	N/A
500 mg/L with CRD	4.01 ± 0.01	3.42 ± 0.13	86.4 ± 0.6

n=6 for each data point.

The City of Sunnyvale drinking water spiked with 5 µg/L increments of perchlorate was analyzed with this method. Good spike recovery was obtained with and without the Dionex CRD 200 device installed. The City of Sunnyvale drinking water spiked with 5, 10, 15, and 20 µg/L of perchlorate without the Dionex CRD 200 device installed had 104 ± 3%, 106 ± 2%, 110 ± 2%, and 112 ± 1% recoveries, respectively. The same samples with the Dionex CRD 200 device installed had similar recoveries: 105 ± 1%, 108 ± 2%, 106 ± 1%, and 108 ± 1%, respectively (Table 13). Carbonate peak tailing was reduced with the Dionex CRD 200 device (Figure 6).

Table 13. Spike recovery (%) of perchlorate in City of Sunnyvale drinking water.

City of Sunnyvale Water	+ 5 µg/L	+ 10 µg/L	+ 15 µg/L	+ 20 µg/L
Without CRD	104 ± 3	106 ± 2	110 ± 2	112 ± 1
With CRD	105 ± 1	108 ± 2	106 ± 1	108 ± 1

Column: Dionex IonPac AS16, AG16 Peaks: 1. Carbonate-Sulfate —
Eluent: 65 mM Potassium hydroxide 2. Perchlorate 5 µg/L
Flow Rate: 1.2 mL/min
Inj. Volume: 1000 µL partial loop injection of 1100 µL loop
Detection: Suppressed conductivity, external mode

A: With CRD installed
B: Without CRD installed

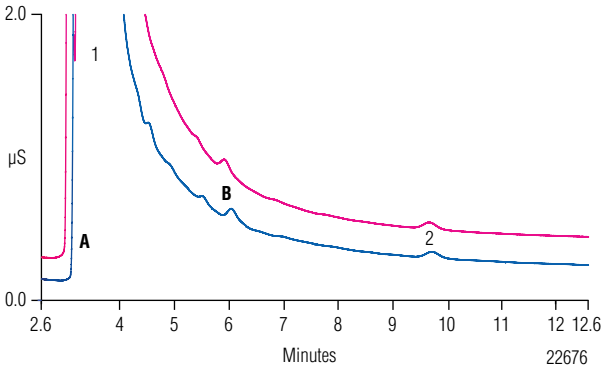

Figure 6. City of Sunnyvale drinking water with 5 µg/L perchlorate spike, with (A) and without (B) a Dionex CRD 200 device.

Application 3: Carbonated Mineral Water and Artificial Drinking Water

Carbonated mineral water contains high levels of carbonate that interfere with routine anion determinations. Typically, the sample must be degassed prior to analysis in order to obtain acceptable results. The concern in any sample preparation is potential contamination or degradation of the sample. A sample preparation also requires several control samples to monitor the process.

Carbonated mineral water samples typically have high µg/L levels of fluoride, nitrite, bromide, chlorate, and phosphate in mg/L levels of nitrate, carbonate, chloride, and sulfate. These samples can be analyzed using a Dionex IonPac AS18 column set (2 mm), and suppressed conductivity detection. We designed these experiments to show that the Dionex CRD 200 device reduced carbonate concentrations and improved low-level anion determinations in carbonated drinking water. Artificial Drinking Water Standards were created to simulate high µg/L concentrations of fluoride, nitrite, bromide, chlorate, and phosphate, and low mg/L concentrations of nitrate in high mg/L concentrations of chloride, carbonate, and sulfate. Anion peak retention times and peak efficiencies results were compared with and without the Dionex CRD 200 device installed (Table 14). The results show similar carbonate removal by the Dionex CRD 200 device, 91.7 ± 0.0% to 98.8 ± 0.4% Apparent % Removal Efficiency (Table 15). Figure 7 shows that with the Dionex CRD 200 device installed, it is now easier to quantify bromide. The results again showed small increases in retention time and small peak efficiency losses, ~60 to 160 USP plates, with the Dionex CRD 200 device installed.

Table 14. Effect of the Dionex CRD 200 device on retention times and peak efficiencies for artificial drinking water sample #1.

Simulated Drinking Water #1[a]	Without CRD Retention Time (min)	With CRD Retention Time (min)	Without CRD Efficiency (USP)	With CRD Efficiency (USP)
Fluoride	3.30 ± 0.00	3.46 ± 0.00	9605 ± 610	7339 ± 319
Chloride	5.10 ± 0.00	5.29 ± 0.00	11334 ± 27	9289 ± 26
Nitrite	6.38 ± 0.00	6.59 ± 0.00	14814 ± 111	13011 ± 403
Carbonate	7.55 ± 0.01	7.91 ± 0.01	985 ± 31	223 ± 35
Bromide	9.30 ± 0.00	9.58 ± 0.00	19276 ± 440	15653 ± 623
Sulfate	9.93 ± 0.01	10.3 ± 0.01	5542 ± 133	5360 ± 26
Nitrate	11.2 ± 0.00	11.5 ± 0.00	15690 ± 198	15487 ± 51
Chlorate	12.0 ± 0.00	12.3 ± 0.00	28382 ± 1551	26301 ± 2720
Phosphate	14.8 ± 0.01	15.1 ± 0.01	47614 ± 1960	44655 ± 1526

n=10 for each data point.
[a] Artificial Drinking Water #1: 0.05 mg/L of fluoride, nitrite, chlorate, bromide, and phosphate; 2.5 mg/L nitrate; 25 mg/L sulfate; 50 mg/L chloride and carbonate.

We then applied the Dionex CRD 200 device to a carbonated mineral water sample. Brand A carbonated mineral water was labeled as a "low sodium, sparkling mineral water with lime essence and other natural flavors." The ingredients list stated that it contains mineral water, natural flavors, and CO_2. A 5 µL injection of this sample overloaded the column, therefore we diluted the sample five-fold with degassed DI water. Due to the fluctuations in the initial carbonate concentration in the sample, carbonate peak removal is difficult to measure, but our data suggests that over 98% of the carbonate peak was removed (Figure 8).

Table 15. Carbonate peak removal results from using a Dionex CRD 200 device on artificial drinking water.

Standard	Without CRD Carbonate Peak Area (µS-min)	With CRD Peak Area (µS-min)	Apparent % Removal Efficiency
Drinking water #1[a]	1.28 ± 0.00	0.11 ± 0.01	91.7 ± 0.0
Drinking water #2[b]	1.64 ± 0.04	0.11 ± 0.01	93.5 ± 0.3
Drinking water #3[c]	2.65 ± 0.01	0.12 ± 0.00	95.4 ± 0.0
Drinking water #4[d]	3.82 ± 0.01	0.05 ± 0.02	98.8 ± 0.4

n=10

[a] Artificial Drinking Water #1: 0.05 mg/L of fluoride, nitrite, chlorate, bromide, and phosphate; 2.5 mg/L nitrate; 25 mg/L sulfate; 50 mg/L chloride and carbonate.

[b] Artificial Drinking Water #2: 0.1 mg/L of fluoride, nitrite, chlorate, bromide, and phosphate; 5 mg/L nitrate; 50 mg/L sulfate; 100 mg/L chloride and carbonate.

[c] Artificial Drinking Water #3: 0.2 mg/L of fluoride, 1.0 mg/L of nitrite, chlorate, bromide, and phosphate; 10 mg/L nitrate; 100 mg/L sulfate; 200 mg/L chloride and carbonate.

[d] Artificial Drinking Water #4: 0.4 mg/L of fluoride, 5 mg/L of nitrite, chlorate, bromide, and phosphate; 50 mg/L nitrate; 200 mg/L sulfate; 500 mg/L chloride and carbonate.

Conclusion

The Dionex CRD 200 device removes most of the carbonate introduced by the sample, 86.0–98.8% in the three applications described here. This reduces carbonate interference when quantifying neighboring anions, including sulfate, adipate, and bromide. Due to the added delay volume, the Dionex CRD 200 device causes a slight increase in retention times and a slight decrease in efficiencies but these changes do not negate the significant advantages afforded by the removal of carbonate.

The Dionex CRD 200 device is easily installed on top of the Dionex ASRS ULTRA II suppressor and works efficiently in both the recycle and external modes of the suppressor. The applications presented here demonstrated the removal of carbonate from samples containing a wide range of carbonate concentrations and a wide range of analyte concentrations from µg/L to mg/L. The Dionex CRD 200 device is suitable for hydroxide applications with our systems using EluGen eluent generation, CR-ATC column, and ASRS ULTRA II suppressor. The Dionex CRD 200 device has also been shown suitable for borate applications, but borate applications were not reviewed in this technical note.

More information on all these applications and products, including application notes and updates, technical notes, and product and installation manuals, can be found on the Thermo Scientific website, www.thermoscientific.com.

Precautions

As described in the Dionex CRD 200 Carbonate Removal Device Product Manual, the internal parts of the device can be damaged by overtightening. All fittings on the Dionex CRD 200 device should be tightened by hand to "finger-tight."

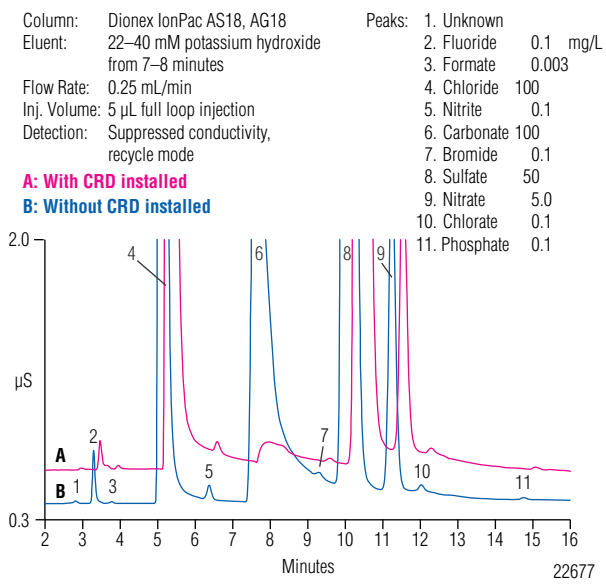

Figure 7. Dionex CRD 200 device removal of carbonate from an artificial drinking water sample #2.

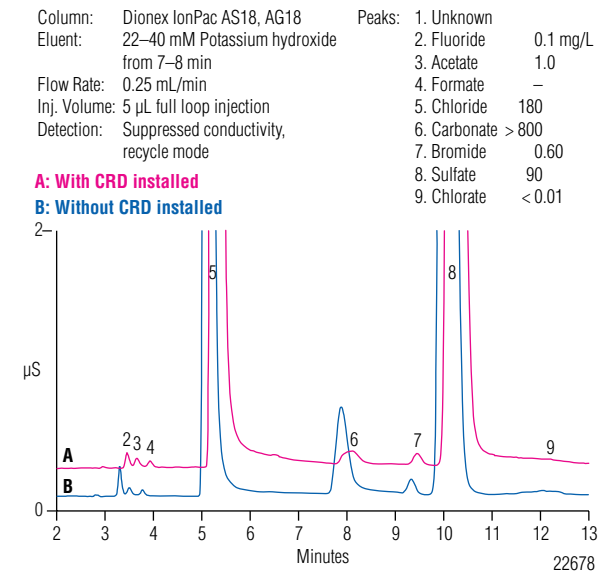

Figure 8. Dionex CRD 200 removal of carbonate from a five-fold dilution of "Brand A" carbonated mineral water.

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Suppliers

1. Fisher Scientific International Inc., Liberty Lane, Hampton, NH 03842, USA. Tel: (800) 766-7000, www.fisherscientific.com.
2. VWR International, Inc., Goshen Corporate Park West, 1310 Goshen Parkway, West Chester, PA 19380, USA Tel: (800) 932-5000, www.vwrsp.com.
3. Sigma-Aldrich, Inc., P.O. Box 951524, Dallas, TX 75395-1524, USA Tel: (800) 325-3010, www.sigmaaldrich.com.

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