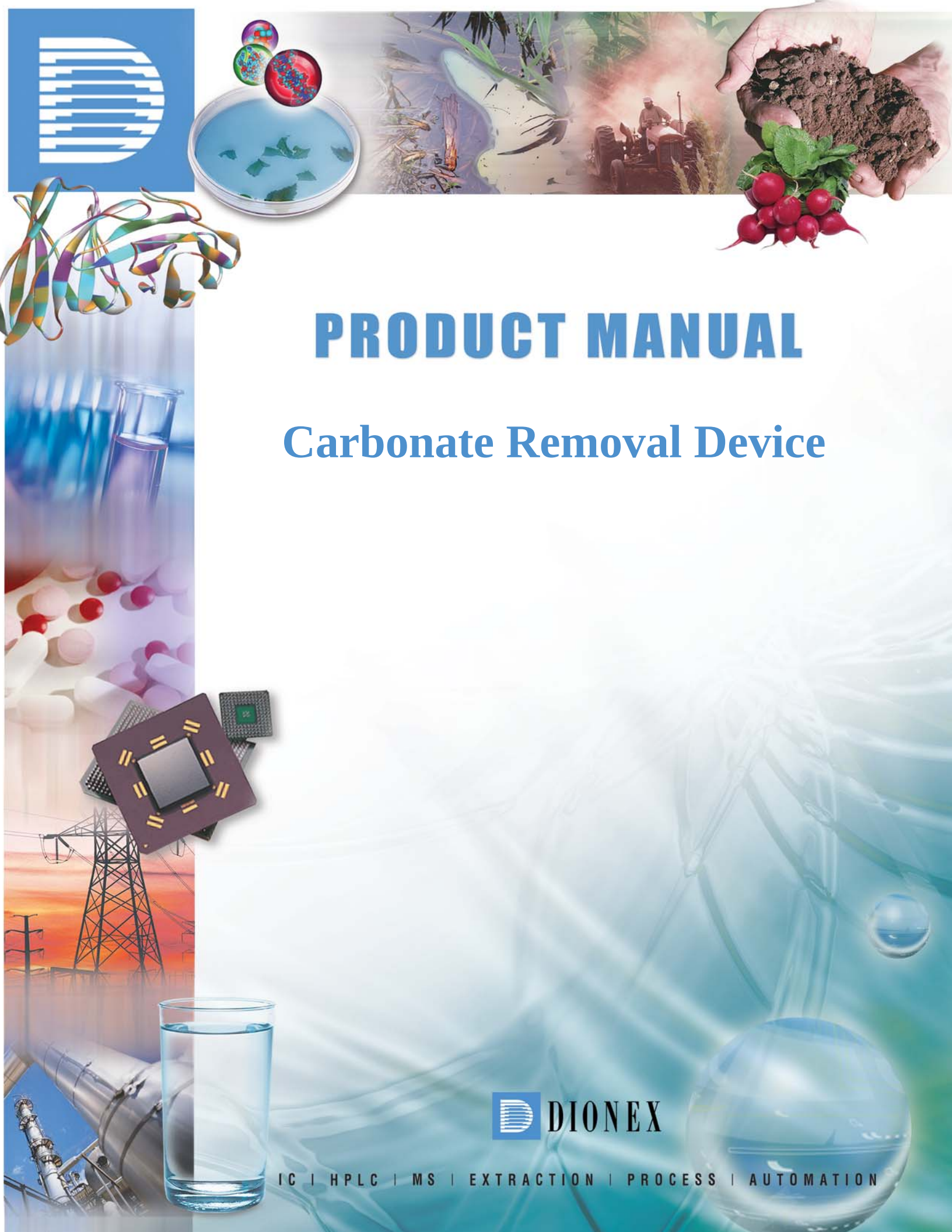


PRODUCT MANUAL

Carbonate Removal Device

DIONEX

IC | HPLC | MS | EXTRACTION | PROCESS | AUTOMATION

PRODUCT MANUAL

FOR

CARBONATE REMOVAL DEVICE

CRD 4-mm (P/N 062983)
CRD 2-mm (P/N 062986)

Dionex® Corporation, 2005
Document No. 065068
Revision 02
June 2005

TABLE OF CONTENTS

1. INTRODUCTION

The Carbonate Removal Device (CRD) is a membrane-based module that transports CO_2 from the suppressed eluent stream into the outer regenerant waste stream for removal (Figure 1). The CRD is installed between the suppressor and the detector cell (e.g. conductivity cell). This placement reduces the carbonate peak contributed by the sample during anion analysis by suppressed anion chromatography with hydroxide eluents.

For optimal performance, Dionex recommends using the CRD with a Reagent-Free Ion Chromatography (RFIC™) system comprised of a Dionex Ion Chromatograph (IC) system equipped with an Eluent Generator (EluGen®), Continuously Regenerated Anion Trap Column (CR-ATC), and a hydroxide eluent compatible column (such as IonPac AS11, AS15, AS16, AS17, AS18, AS19, AS20, or AS21). The CRD can also be used with RFIC systems pursuing borate chemistry with AS4A, AS14, or AS14A chemistries.

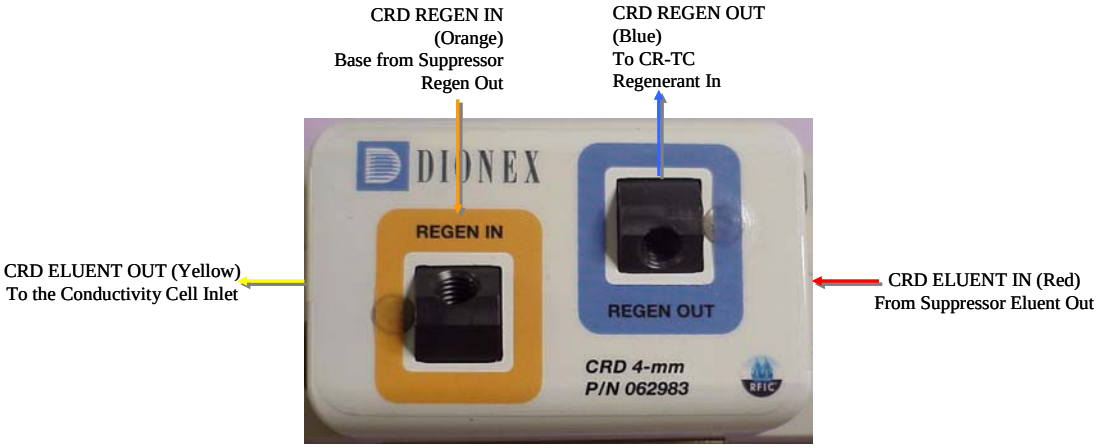


FIGURE 1
CRD Basic Plumbing

Assistance is available for any problem during the shipment or operation of Dionex instrumentation, columns, and consumables through the Dionex North America Technical Call Center at 1-800-DIONEX-0 (1-800-346-6390) or through any of the Dionex Offices listed in "Dionex Worldwide Offices" on the Dionex Reference Library CD-ROM.

1.1. CRD Design and Operation

The CRD consists of a gas permeable membrane with a silicone coating that is selective to CO_2 (Figure 2). The CRD is plumbed between the suppressor module and the cell. The regenerant channel that encloses the CRD membrane is flushed with the suppressor waste (base) and aids removal of the CO_2 as carbonate.

The carbonate peak after suppression is converted to carbonic acid. Carbonic acid is in equilibrium with carbon dioxide gas dissolved in water. The CRD removes the carbonate peak as CO_2 from the suppressed eluent.

$$\mathbf{H_2CO_3} \quad \Longleftrightarrow \quad \mathbf{H_2O + CO_2}$$

EQUATION 1
CRD EQUILIBRIUM

As the CO_2 peak is removed by the CRD membrane, the equilibrium shifts to the right, thereby facilitating further removal of the CO_2 and reducing the net carbonic acid concentration. Additionally, the basic environment in the regenerant channel allows a quick conversion of the removed CO_2 to carbonate anion. The net result of the above steps is a reduction of the peak resulting from carbonate.

The CRD can remove high levels of the peak resulting from carbonate (>1000 mg/L of carbonate with >90% apparent removal efficiency (see Equation 2). It should be noted that high levels of CO_2/carbonate in the sample may affect chromatographic peak shapes and recovery.

$$\text{Apparent \% } \textit{Removal Efficiency} = 100 - \left[\frac{\textit{Response}_{w/CRD}}{\textit{Response}_{w/oCRD}} \text{ X } 100 \right]$$

$Response_{w/CRD}$ = Peak area or height with CRD installed
$Response_{w/oCRD}$= Peak area or height without CRD installed

EQUATION 2
APPARENT REMOVAL EFFICIENCY

It should be noted that the true CO_2 removal efficiency is based on the chemical equilibrium outlined in Equation 1. Equation 2 underestimates this removal efficiency and therefore is the apparent removal efficiency. It is included here for reference purpose only. For example, using a known level of carbonate for a peak height of 23 µS/cm when the peak is reduced to 2.3 µS/cm, the true removal efficiency based on the chemical equilibrium described in Equation 1 is calculated as 99% whereas Equation 2 calculates this removal efficiency as 90%.

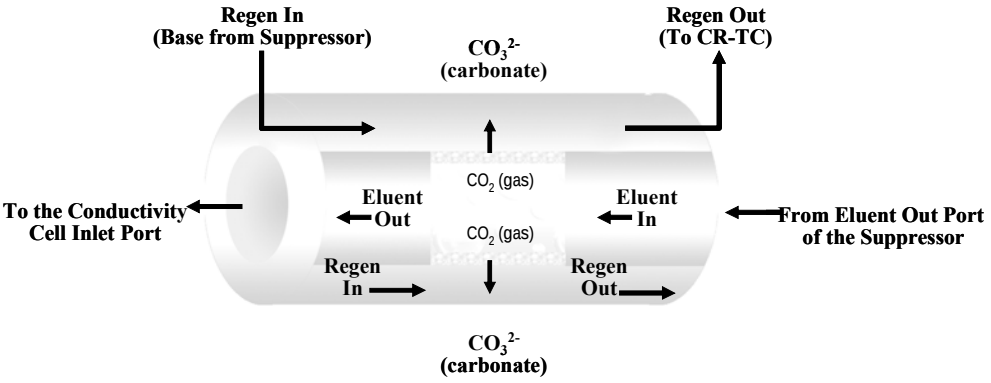


FIGURE 2
CRD Design and Operation

1.2. CRD Configuration

The CRD is available in both 2-mm and 4-mm formats for use with 2, 3, 4, and 5-mm Ion chromatography columns. The 4-mm CRD has a typical delay volume of 200 µL and is recommended for 4 or 5-mm column applications. The 2-mm CRD has a typical delay volume of 40 µL and is recommended for 2 or 3-mm column applications.

2. GETTING STARTED

The CRD must be handled with care to ensure proper operation. Fittings only need to be finger tightened.

WARNING

Do not attempt to disassemble the CRD; it may result in irreversible damage.

2.1. CRD Quickstart

2.1.1. Hydrating the CRD

Step 1.

Using a 5 cc disposable plastic syringe (P/N 016640) and the 10-32 Luer adaptor (P/N 046888), push approximately 3 mL of degassed DI water through the ELUENT IN port. Using a 5 cc disposable plastic syringe (P/N 016640) and the 1/4-28 Luer adaptor (P/N 024305), push 5 mL of degassed DI water through the REGEN IN port (Figure 3).

NOTE

Step 1 can be accomplished by installing the CRD in the system and connecting the ELUENT OUT port to the REGEN IN port on the CRD by using suitable tubing and pumping 5 mL of deionized water through the CRD ELUENT IN port. In the above step, it is recommended to bypass the guard and analytical columns.

Step 2.

Allow the CRD to sit for approximately 10 minutes to fully hydrate the CRD membrane.

P/N	Description
016640	5 cc plastic syringe
024305	¼ - 28 Luer Adaptor
046888	10 - 32 Luer Adaptor

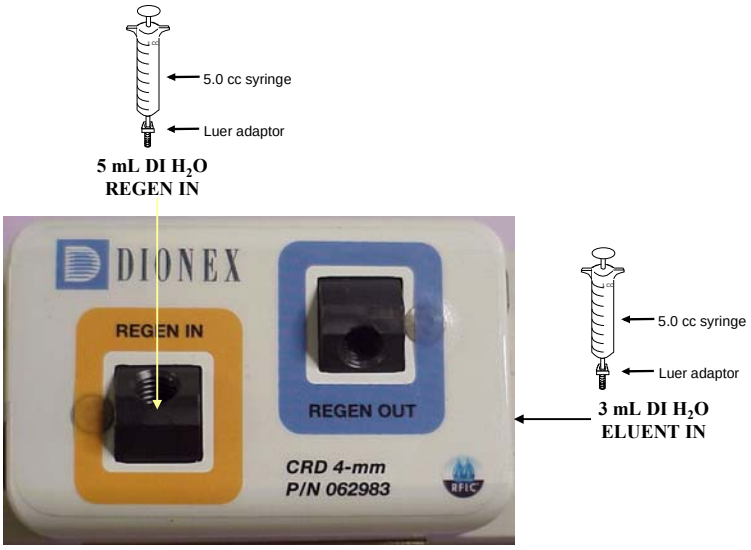


Figure 3
Hydrating the CRD

2.1.2. Backpressure Instructions

The total backpressure to the suppressor eluent channel should be less than 100 psi. This includes the CRD, the cell, and the backpressure coil. Trim the backpressure coil if required to achieve <100 psi total backpressure. Refer to Section 3.3 for backpressure measurement instructions.

WARNING

Total backpressure amounts exceeding >100 psi may cause irreversible damage to the CRD and the suppressor.

3. INSTALLATION

3.1. Installing the CRD

NOTE ***Always minimize tubing lengths for obtaining efficient peaks. For 4-mm or 5-mm applications (standard bore format) use 0.010" ID x 0.016" OD Black tubing. For 2-mm applications (microbore format) or 3-mm applications, use 0.005" ID x 0.016" OD Red tubing.***

1. The CRD is installed on the top of the SRS module. The CRD is shipped with an attached mounting clip that allows easy installation on the SRS module.

2. To install, remove the suppressor from the Chromatography Module and remove all connections to the suppressor with the possible exception of the ELUENT IN line coming from the column.

3. Attach the CRD mounting clip to the suppressor as shown in Figure 4. When seated properly, a "click" will be heard as the mounting clip locks into place on the suppressor.

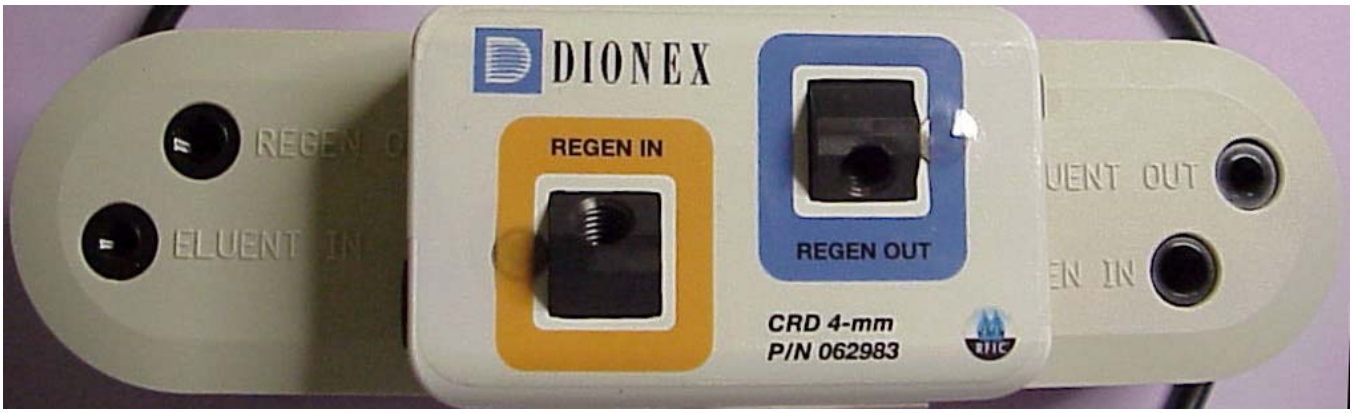


FIGURE 4
CRD Mounted on SRS

3.2. Plumbing the CRD

NOTE

For 4-mm or 5-mm applications (standard bore format) use 0.010" ID x 0.016" OD Black tubing. For 2-mm or 3-mm applications (microbore format) use 0.005" ID x 0.016" OD Red tubing. Connecting the wrong tubing dimensions for a given application may damage the CRD and suppressor modules.

1. The CRD is installed on the top of the SRS module as shown in Figure 4.
2. To begin plumbing of the CRD, refer to the plumbing schematic as shown in Figure 5.
   a) Turn off the pump and the Self-Regenerating Suppressor (SRS) before making any connections.
   b) Remove the plugs from the CRD ports.
   c) Connect an approximately 2 inch length of 0.016" OD Black or Red tubing from the ELUENT OUT port of the suppressor to the ELUENT IN port of the CRD (Red label).
   d) Connect an approximately 6 inch length of 0.016" OD Black or Red tubing from the conductivity cell inlet port to the ELUENT OUT port of the CRD (Yellow label).
   e) Connect a short piece of 1/8" OD tubing (opaque) from the backpressure coil at the cell outlet port to the REGEN IN port of the suppressor.
   f) Connect an approximately 5 inch length of 1/8" OD tubing (opaque) from the REGEN OUT port of the suppressor to the REGEN IN port of the CRD (Orange label).
   g) Divert the REGEN OUT port of the CRD (Blue label) to the waste or use it as a regenerant stream for other modules such as continuously regenerated –trap column (CR-TC) and the Eluent generator (EG) degas assembly.
   h) Reinstall the suppressor and the CRD into the chromatography module. An example of a typical installation of a CRD in a chromatography module is shown in Figure 6.
   i) CRD is now installed. Before using the CRD for analysis, proceed to Section 3.3, "CRD Backpressure Measurement".

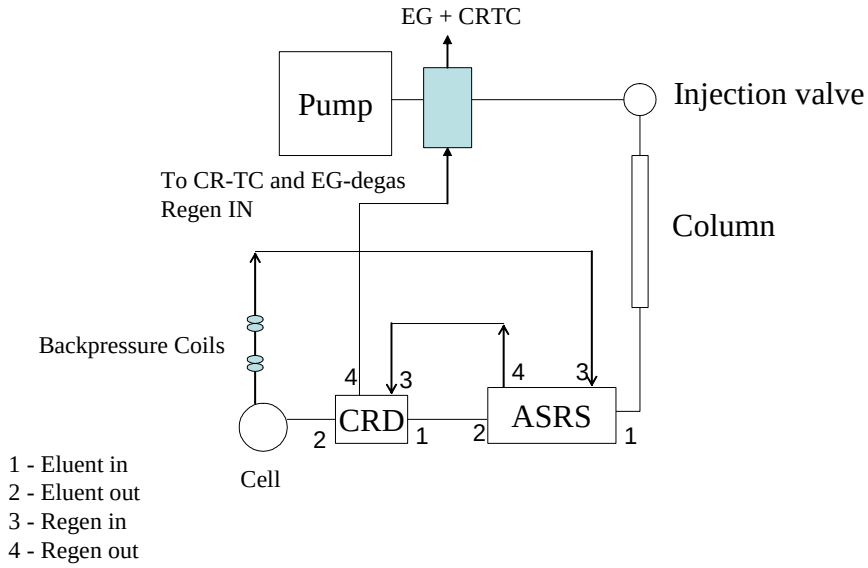


FIGURE 5
CRD Plumbing Schematic

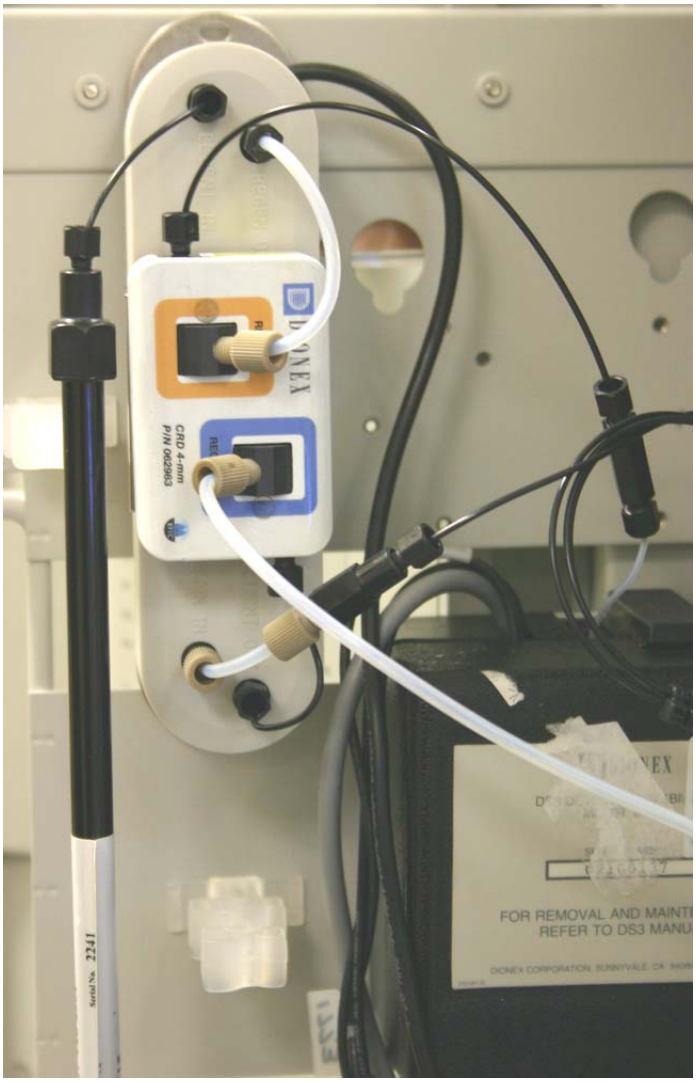


FIGURE 6
CRD Installed in the System

External water setup: When pursuing the external water or chemical regenerant mode of operation, the CRD is plumbed similar to what was previously described. However, in Step e, the fluid from the cell outlet port is diverted to waste and the suppressor REGEN IN port is plumbed to the external water source. It is recommended that the external water flow rate is 1-2 ml/min for 2 or 3-mm applications and 3-5 ml/min for 4 or 5-mm applications.

3.3. CRD Backpressure Measurement

The backpressure to the suppressor module needs to be measured and adjusted if needed. This will ensure optimal performance of the system. Failure to complete the following steps may result in a leaking suppressor and/or CRD.

a) After installing the CRD, measure the total system pressure (P1).
b) Remove the line from the ELUENT OUT port of the suppressor and measure the system pressure (P2).

$$P1 - P2 = P3 \leq 100$$

c) If P3 is higher than 100 psi, then trim the backpressure coil (line out of the conductivity cell) to achieve a total pressure of less than 100 psi.

WARNING ***Total backpressure exceeding >100 psi may cause irreversible damage to the CRD and suppressor.***

NOTE ***Always use 1/8" tubing when connecting lines for the regenerant side of the Self – Regenerating Suppressor or Atlas Electrolytic Suppressor (SRS/AES), Carbonate Removal Device (CRD), Continuously Regenerated – Trap Column (CR-TC), and Eluent Generator (EG) Degas modules.***

4. APPLICATIONS

The Carbonate Removal Device (CRD) has been optimized for removing the peak resulting from carbonate (as CO_2) in ion chromatography systems for anion analysis using Eluent Generation modules.

4.1. Recommended Applications

The CRD is recommended for both routine and trace level work with hydroxide and borate eluents when the presence of CO_2/carbonate from the sample interferes with the anion analytes of interest. By simply being exposed to carbon dioxide in the air, samples can become contaminated with carbonate. In some samples, depending on the column and separation conditions, the presence of high levels of carbonate originating from dissolved carbon dioxide interferes with the accurate determination of analytes of interest, such as sulfate and nitrite. Under the above conditions, minimizing carbonate using the CRD leads to improved peak integration and quantification for analytes such as sulfate and nitrite in hydroxide RFIC systems. The CRD is particularly useful for analyzing drinking water, groundwater, wastewater, ultra pure water, and caustic solutions where carbonate is a major component in the samples, especially when pursuing large-volume injections or preconcentration techniques.

4.2. Negative Dip at the Carbonate Peak Location

A negative peak may be observed at the location where the peak resulting from carbonate is removed. We hypothesize that the trace level of carbonic acid at the carbonate peak location consumes the trace hydroxide in the background and this lowers the background response at that location.

Some applications may not benefit from the CRD module due to the following reasons.

a) Even after CO_2 removal the peaks of interest continue to co-elute with the residual CO_2 peak. If possible, it is recommended under these conditions to investigate other columns or eluent conditions that exhibit different selectivity for the peaks of interest.
b) The presence of CO_2 does not interfere with peaks of interest. Under these conditions, there is no need for a CRD device.

WARNING ***The CRD is designed to perform optimally with hydroxide and borate eluents only. It is not recommended for carbonate and/or bicarbonate, or acid (cation) applications.***

NOTE ***The CRD will remove CO_2 from the carbonate peak thus minimizing the peak, but complete removal of CO_2 may not occur.***

NOTE ***Due to the added delay volume of the device, the early eluting peaks will show a decline in peak efficiency and all peaks will show a small change in retention time.***

5. OPERATION

5.1. Example Chromatograms

Analysis using borate eluents is typically pursued in the nuclear power industry for analyzing borated waters. In the example below, the CRD is useful in reducing the carbonate peak and improving the quantitation of chloride.

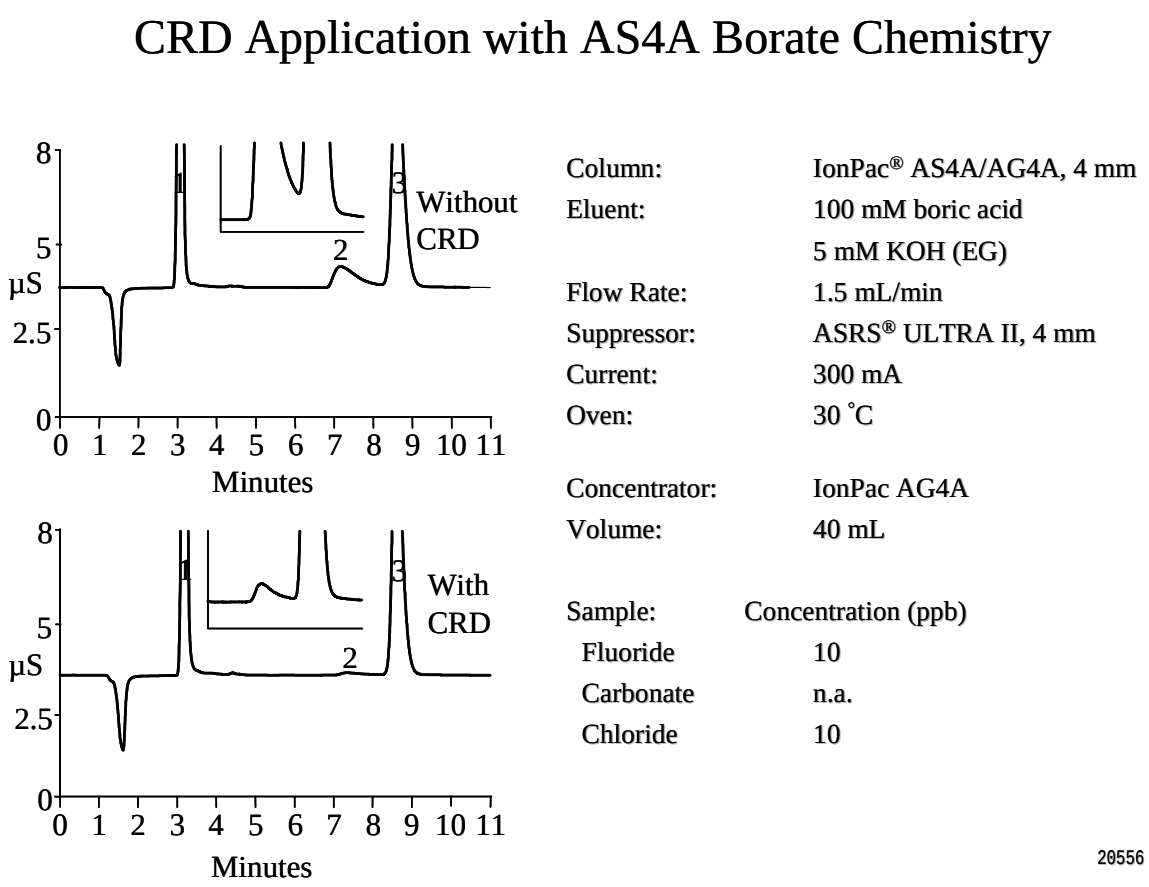
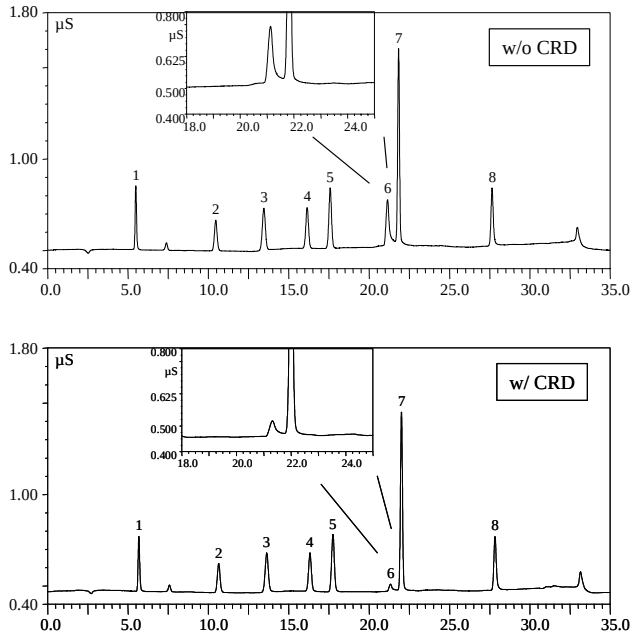


FIGURE 7
CRD with AS4A Borate Chemistry

A typical anion application at ppb level shown below demonstrates the utility of the CRD to remove CO_2 and aid in the improved quantitation of sulfate.

CRD Application with AS19 Gradient Chemistry



Conditions:

Column	AS19 4-mm
Flow rate	1.0 ml/min
Suppressor	ASRS Ultra II 4-mm
Current	300 mA
Loop	200 µl
Oven	30 °C

Time	Gradient (mM)
0	10
10	10
25	45
30	45
30.1	10
35	10

Sample	Concentration (ppb)
Fluoride	10
Chloride	15
Nitrite	50
Bromide	50
Nitrate	50
Carbonate	n/a
Sulfate	75
Phosphate	75

20557-E

FIGURE 8
CRD with AS19 Gradient Chemistry

6. TROUBLESHOOTING

WARNING

High backpressure may cause irreversible damage to the CRD and suppressors. The total pressure from the cell, the CRD, and the backpressure coil should not exceed 100 psi.

6.1. Leakage Due to High Backpressure

a) High backpressure will cause irreversible damage to the CRD.
b) Measure the backpressure to the suppressor (i.e. cell + CRD + the backpressure coil) following the instructions in Section 3.3. The backpressure should not exceed 100 psi. Trim the backpressure coil, if needed.
c) Check the waste lines and ensure these do not contribute to the overall backpressure. Replace and trim tubings if needed.
d) When operating in external water mode, ensure that the external water flow is 1 – 2 mL/min for 2-mm and 3-mm applications and 3 - 5 mL/min for 4-mm and 5-mm applications. Lower the external water flow rate if recommended rates were exceeded.

6.2. Poor CO_2 Removal Efficiency

a) Ensure that the CRD is installed correctly with suppressor waste (base) flowing into the external regenerant channel.
b) Check for leaks and reconnect.

6.3. No Peaks

a) Ensure that the CRD is connected as outlined in the plumbing instructions.
b) Check for leaks and reconnect.
c) CRD may have an internal leak due to damage; replace the CRD.

6.4. High Noise in the Baseline and on Top of the Peaks

a) Ensure that the recommended RFIC system pressure is maintained (optimal operating pressure is 2300 psi). If needed, add the backpressure coil for raising the total system pressure by installing 0.003" ID Yellow tubing between the EG degas module and the injection valve.
b) Release any trapped gases in the cell, suppressor, or the CRD by systematically opening the lines from:
   - ELUENT OUT port of the suppressor
   - The ELUENT IN and ELUENT OUT ports of the CRD
   - The cell outlet port.

6.5. Negative Dips Before All the Analyte Peaks

a) The CRD may have an internal leak due to damage. Replace the CRD if a leak is detected. Ensure the suppressor is fully regenerated by pursuing a sulfuric acid treatment.

6.6. Negative Peak or Dip at the Carbonate Peak Location

a) Refer to Section 4.2.

6.7. How to Check for CRD Leaks

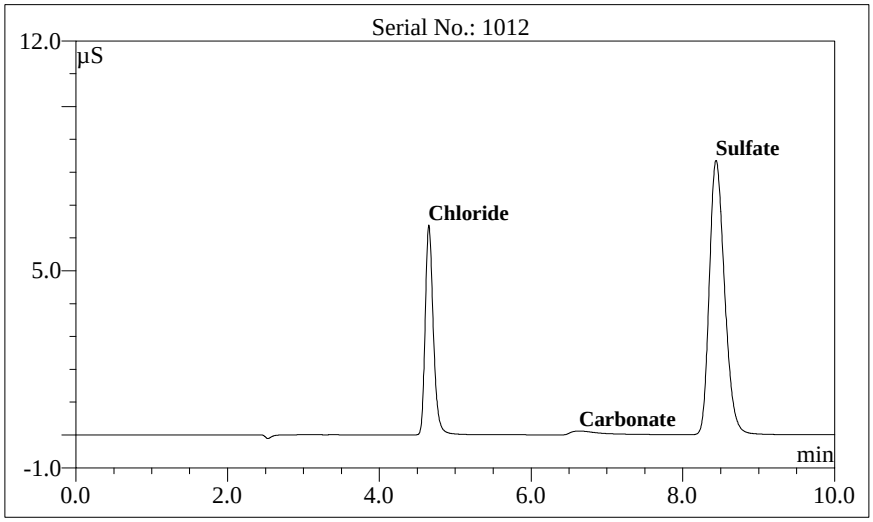
a) Visually inspect for liquid drops or leakage at the CRD eluent and regen ports. Reconnect the lines and tighten the fittings if needed. Do not overtighten as damage may occur.
b) Disconnect the lines from the regen ports of the CRD and, with the eluent flowing in the eluent channel of the CRD, observe for fluid flow out of the regen channel. A continuous flow of liquid from the regen ports of the CRD indicates an internal leak. Replace the CRD.

Assistance is available for any problem during the shipment or operation of Dionex instrumentation, columns, and consumables through the Dionex North America Technical Call Center at 1-800-DIONEX-0 (1-800-346-6390) or through any of the Dionex Offices listed in "Dionex Worldwide Offices" on the Dionex Reference Library CD-ROM.

Carbonate Removal Device
CRD 2-mm
Product No. 062986

Date: 04-Jun-05 09:49
Serial No. : 001012

Eluent:	23 mM KOH
Eluent Source	EGC II KOH Cartridge
Flow Rate:	0.25 mL/min
Temperature:	30 °C
Detection:	Suppressed Conductivity using a CD25
Suppressor:	Anion Self-Regenerating Suppressor (ASRS® ULTRA II, 4mm) AutoSuppression® Recycle Mode
Applied Current:	50 mA
Injection Volume:	5 µL
Storage Solution:	Deionized Water



QA Results:

Test Parameter	Specification	Results
Leak	Pass/Fail	Passed
Eluent Back Pressure	Pass/Fail	Passed
Regen Back Pressure	Pass/Fail	Passed
CO2 Removal	Pass/Fail	Passed

Production Reference:
Datasource: SPD_local
Sequence: C62983-VAL-02_CRD_4mm
Sample No.: 63

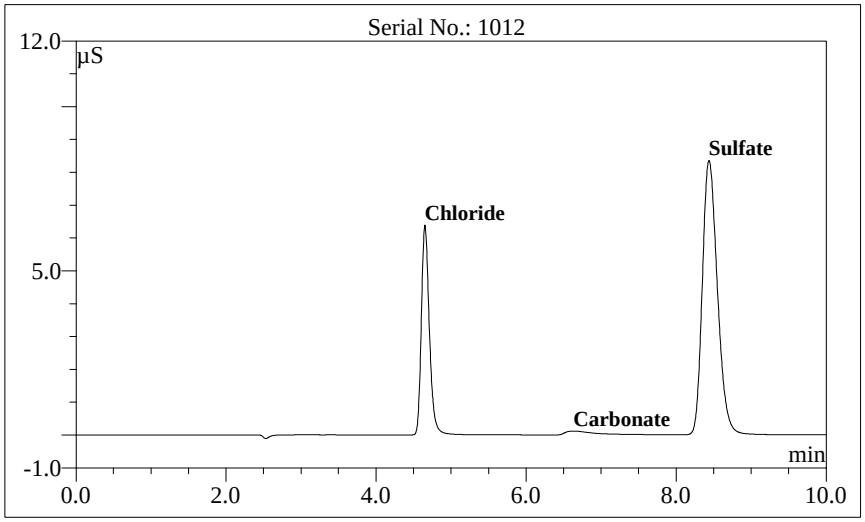
6.60 SP3 Build 1485 (Demo-Installation)

Carbonate Removal Device
CRD 4-mm
Product No. 062983

Date: 04-Jun-05 09:49

Serial No. : 001012

Eluent:	23 mM KOH
Eluent Source	EGC II KOH Cartridge
Flow Rate:	1.00 mL/min
Temperature:	30 °C
Detection:	Suppressed Conductivity using a CD25
Suppressor:	Anion Self-Regenerating Suppressor (ASRS® ULTRA II, 4mm) AutoSuppression® Recycle Mode
Applied Current:	300 mA
Injection Volume:	20 µL
Storage Solution:	Deionized Water



QA Results:

Test Parameter	Specification	Results
Leak	Pass/Fail	Passed
Eluent Back Pressure	Pass/Fail	Passed
Regen Back Pressure	Pass/Fail	Passed
CO2 Removal	Pass/Fail	Passed

Production Reference:

Datasource: SPD_local

Sequence: C62983-VAL-02_CRD_4mm

Sample No.: 63

6.60 SP3 Build 1485 (Demo-Installation)