Coping with Dissolved Carbon Dioxide Gas in Suppressed Ion Chromatography

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ABSTRACT

In ion chromatographic analysis with hydroxide eluents, the presence of dissolved carbon dioxide gas in the eluent impacts the background and, in turn, affects the chromatographic performance by lowering the absolute peak response and reproducibility of the retention time and peak response. The introduction of the eluent generator (EG) system and the continuously regenerated trap column (CR-TC) addresses the above limitations and an automated means of generating high purity eluent for IC is now possible. However, the presence of dissolved carbon dioxide gas in the sample is also a pathway for introducing carbon dioxide into the IC system. The peak constituting to carbon dioxide in some instances interferes with the chromatographic integration and quantitation of some analytes.

In this poster we investigate means of addressing the dissolved carbon dioxide gas from the sample and in the eluent. In one example a carbonate removal device (CRD) will be used for the purpose of inline removal of carbon dioxide after the separation and suppression of the eluent. In another example a CRD device will be used directly on the sample stream. This poster discusses the merits and limitations of these approaches. Analysis of both simulated test samples and real samples containing varying levels of carbon dioxide is shown here.

EXPERIMENTAL

Effect of Carbon Dioxide in the Sample

- Dissolved CO_2 in the sample manifests itself as a peak constituting carbonate during anion analysis with hydroxide eluents and, depending on the concentration, can lead to:
  - Poor quantitation of some analytes
  - Poor resolution
- Due to the carbonate background, the CO_2 peak at low levels is not detected with carbonate eluents
- When the level of CO_2 from the sample increases higher than the CO_2 level in the suppressed eluent:
  - Outgassing can occur causing issues with pump flow (for example, with beverage or soda samples)
  - Solution: Remove the CO_2 prior to injection (will only work for acidic samples)

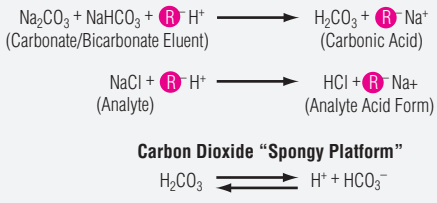
Ion Chromatography with Hydroxide Eluents

- Hydroxide eluents provide the lowest suppressed background leading to:
  - Highest sensitivity
  - Excellent linearity and dynamic range
  - Fully compatible with gradients
- Dissolved carbon dioxide in the sample manifests as a peak and, depending on the concentration, may affect resolution and quantitation of some peaks of interest

Ion Chromatography with Carbonate Eluents

- Suppressed background is carbonic acid leading to:
  - Higher background (14–23 µS/cm)
  - Lower sensitivity due to the "carbon dioxide spongy platform" effect*
  - Nonlinear response due to a weakly dissociated background
- Able to handle a relatively higher level of CO_2 dissolved in the sample
  - CO_2 peak is not detected at low levels
- Dissolved carbon dioxide in the sample at high levels manifests as a peak and, depending on the concentration, may affect resolution and quantitation of some peaks of interest

Figure 1. Suppression Reactions



Due to the presence of acidic analytes, the carbonic acid equilibrium is driven to the left causing a lower background in the analyte zone leading to a lower response.

* H. Small, *Ion Chromatography,* Plenum Press, New York (1989), chapter 7, p 176.

Previous Work on Use of Gas Permeable Tubings in IC

- Removing CO_2 from the suppressed carbonate and/or bicarbonate eluents
  - $H_2CO_3 \rightleftharpoons H_2O + CO_2$
- Silicone rubber based tubings, perfluoro based tubings such as porous PTFE tubings (Gore-Tex®) and Teflon® AF
  - Removing CO_2 from carbonate/bicarbonate eluents resulted in lower background and improved sensitivity

Literature References

- HPLC application for removal of oxygen
  - Reim *Anal. Chem,* **1983,** *55,* 1188–1191.
    Silicone rubber, Teflon, 4-methyl-1-pentene, Tygon® and Nafion® were evaluated for oxygen permeability
- Post suppressor devices for removal of CO_2 from suppressed carbonate eluents
  - Sunden, et. al. *Anal. Chem.* **1984**, *56,* 1085–1089.
    Described the use of porous PTFE tubings (Gore-Tex)
  - Siemer and Johnson, *Anal. Chem.* **1984,** *56,* 1033–1034.
    Silicone rubber tubing for carbon dioxide removal from carbonate/bicarbonate eluents, 0.1 M KOH @ 79 °C was used for the exterior solution
  - Shintani and Dasgupta, *Anal. Chem.* **1987**, *59*, 802–808.
    Polypropylene tubings coated with silicone rubber or asymmetric coated membrane. 10x coatings on the surface lead to thick coatings (>90 µm thick)
  - Saari-Nordhaus R.; Anderson, J. M., Jr. *J. Chromatogr., A,* **2002,** *956,* 15–22.
    Teflon AF tubing used for post suppressor removal of CO_2
  - Dasgupta, et. al. *Anal. Chem.* **2004,** *76,* (*23),* 7084–7093.
    Asymmetric coated membrane used for CO_2 removal

Carbonate Removal Device

- CRD—Post suppressor removal
  - Added delay volume leading to lower efficiency for early eluting peaks
- CRD—Preinjection removal
  - No issues with delay volume
  - Will work only with acidic samples
  - Basic samples will require a suppressor device in order to convert the stream to an acidic stream

Figure 2. Asymmetric Coated Membrane

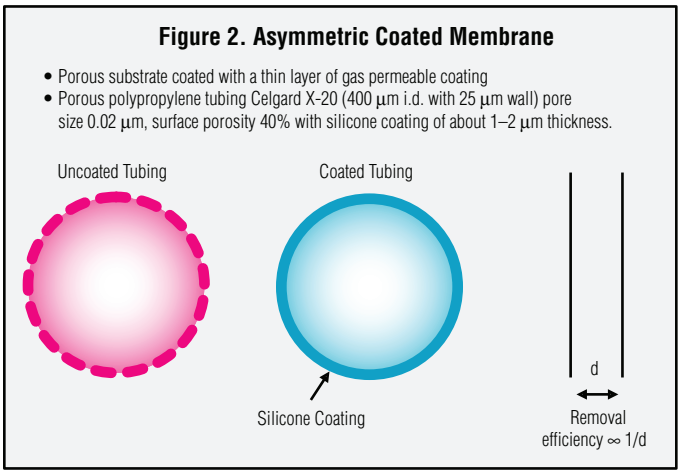


Figure 3. CRD Schematic

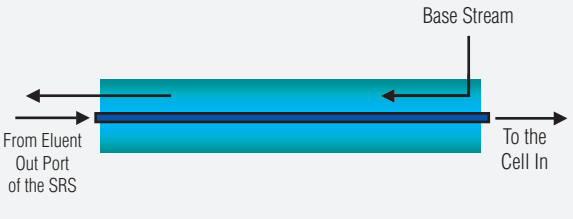


Figure 4. CRD Pumbing

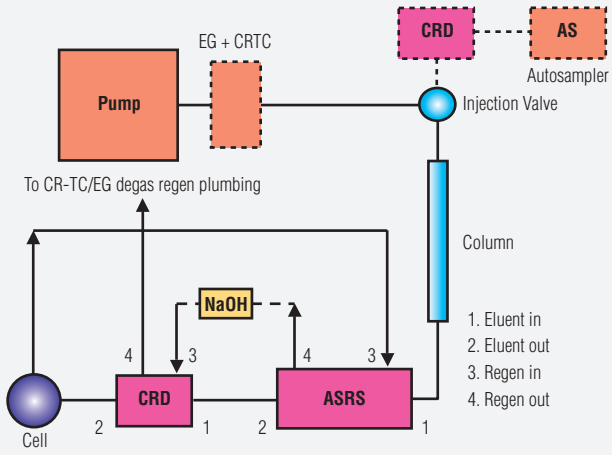


Figure 4. The installation of the CRD is shown in the above schematic. The solid lines of the CRD indicate a post suppressor installation. The dotted lines of the CRD indicate a preinjection installation. The eluent channel of the CRD is plumbed inline with the suppressor eluent channel and is connected to the cell. The regenerant channel of the CRD is swept with a base stream from an external reservoir or by routing the base stream from the suppressor regenerant channel.

Column: IonPac® AS15 4 mm
Eluent: 38 mM NaOH
Flow Rate: 1.2 mL/min
Suppressor: ASRS® ULTRA II, 4 mm
Current: 100 mA
Injection Loop: 1 mL
Temperature: 30 °C

Peaks:	Concentration (ppb)
1. Fluoride	20
2. Chloride	30
3. Carbonate	NA
4. Nitrite	100
5. Sulfate	150
6. Bromide	100
7. Nitrate	100
8. Phosphate	150

Chloride Peak Efficiency	
	Plates
Control	11736
CRD	11292

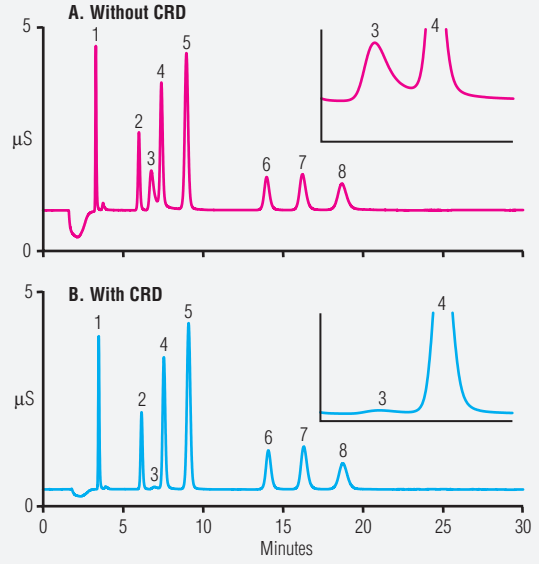


Figure 5. Analysis of a seven anion test mixture under isocratic conditions is shown here. In inset A the carbonate peak is marginally resolved from nitrite leading to poor quantitation of nitrite. In inset B, the carbonate peak is substantially removed by the CRD leading to improved quantitation of nitrite. The efficiency of the early elutors such as chloride suffers due to the added delay volume of the CRD device.

Column: IonPac AS15, 4 mm
Flow Rate: 1.2 mL/min
Suppressor: ASRS ULTRA II, 4 mm
Current: 150 mA
Injection Loop: 25 µL
Temperature: 30 °C

Peaks:	Concentration (ppb)
1. Fluoride	10
2. Chloride	15
3. Nitrite	50
4. Carbonate	30000
5. Sulfate	75
6. Bromide	50
7. Nitrate	50
8. Phosphate	75

Time	EG Gradient (mM)
0	1
1	1
21	50
26	50
26.1	1
31	1

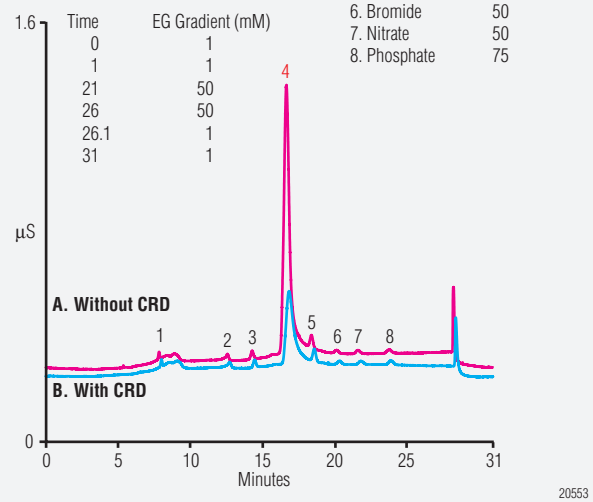


Figure 6. Analysis of a seven-anion test mixture under AS15 gradient conditions is shown here. Trace A shows the integration and quantitation of sulfate is compromised due to the presence of 30 mg/L of carbonate in the sample. Due to the significant removal of the carbonate peak with the CRD installed, integration of sulfate is significantly improved as shown in trace B.

Column: IonPac AS16, 4 mm
Eluent: 65 mM KOH (EG)
Flow Rate: 1.2 mL/min
Suppressor: ASRS ULTRA II, 4 mm
Current: 300 mA

Injection Loop: 1.0 mL
Temperature: 30 °C

Matrix	Concentration (ppm)
Chloride	100
Carbonate	100
Sulfate	100
Peaks:	
1. Perchlorate	0.01

Perchlorate Peak Area	
Without CRD:	0.0226
With CRD:	0.0246

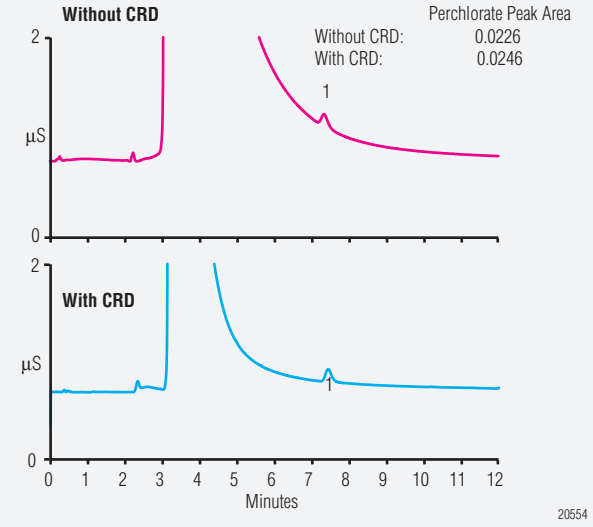


Figure 7. Analysis of a perchlorate standard in a simulated sample matrix comprising 100 mg/L of chloride, bicarbonate, and sulfate was done using AS16 chemistry under isocratic conditions. With the CRD present the baseline disturbance from the matrix peak is considerably diminished leading to improved sensitivity and quantitation for perchlorate.

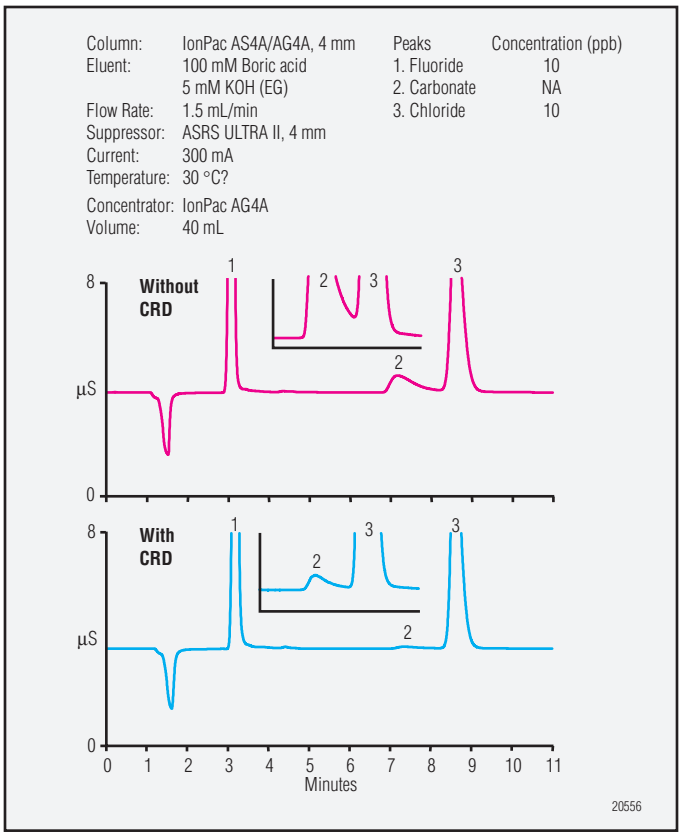


Figure 8. Analysis of a simulated water sample from a PWR power station is shown here using EGC generated borate eluents. Due to the removal of the carbonate peak improved quantitation of chloride became possible with the CRD installed.

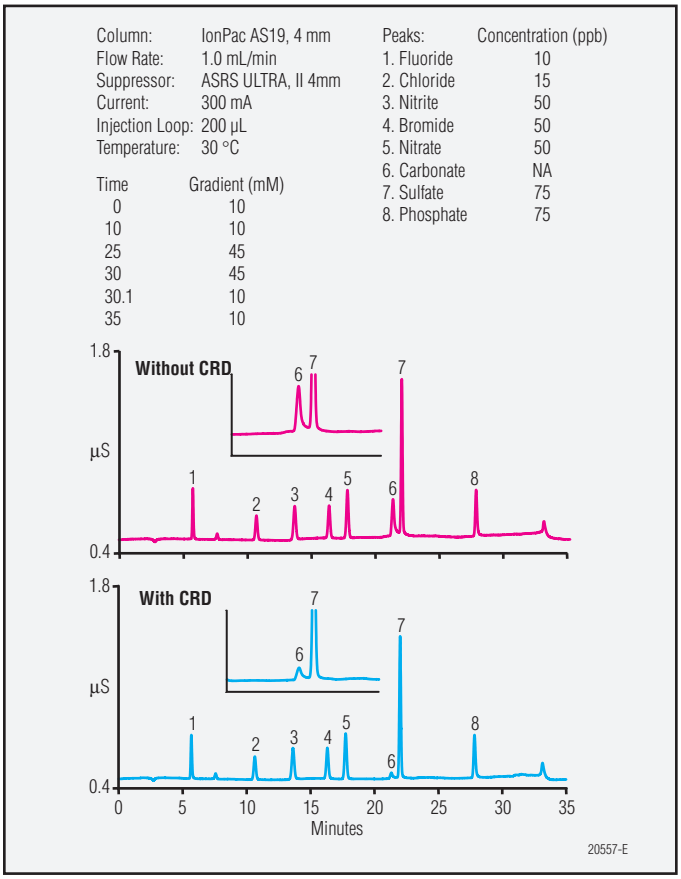


Figure 9. Analysis of a seven-anion test mixture under AS19 gradient conditions is shown here. The integration for sulfate is improved when the carbonate peak was significantly removed by installing the CRD.

Column: IonPac AS9-HC, 4 mm
Flow Rate: 1.0 mL/min
Eluent: 9.0 mM Carbonate
Suppressor: ASRS ULTRA II 4mm
Current: 50 mA (Recycle)
Injection Loop: 25 µL
Temperature: 30 °C

Background
No CRD: 23.0 µS/cm
W Prototype CRD: 0.87 µS/cm

Peak	No CRD Area Counts	Prototype CRD Area Counts
Fluoride	0.2711	0.4333
Chloride	0.2594	0.3782
Nitrate	0.4816	0.7210
Phosphate	0.3769	0.5707
Sulfate	0.9932	1.5056

Peaks: Concentration (ppm)
1. Fluoride 1.0
2. Chloride 1.5
3. Nitrate 5.0
4. Phosphate 7.5
5. Sulfate 7.5

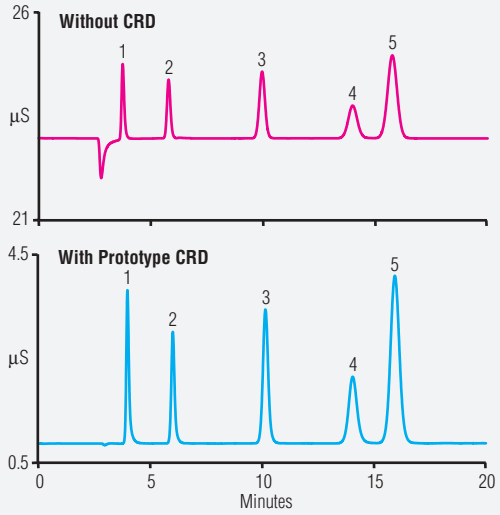


Figure 10. Analysis of a five-anion test mixture under AS9-HC isocratic conditions is shown here. The background was significantly reduced as shown in the figure and the sensitivity improved as shown in the above table when a prototype CRD device was installed.

Column: IonPac AS9-HC, 4 mm
Flow Rate: 1.0 mL/min
Eluent A: 9.0 mM Bicarbonate
Eluent B: 9.0 mM Carbonate
Suppressor: ASRS ULTRA II 4 mm
Current: 50 mA (Recycle)
Injection Loop: 25 µL
Temperature: 30 °C

Time	Gradient A	Gradient B
0.00	50	50
4.99	50	50
5.00	0	100
25.00	0	100

Peaks: Concentration (ppm)
1. Fluoride 0.1 mg/L
2. Chloride 0.15
3. Nitrate 0.5
4. Phosphate 0.75
5. Sulfate 0.75

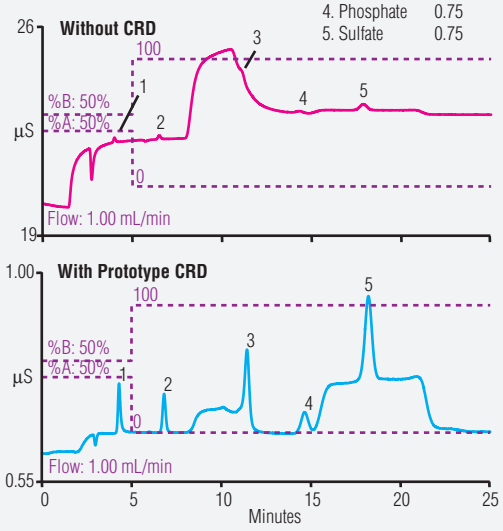
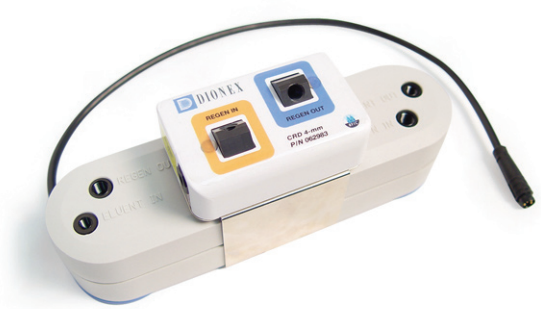


Figure 11. Analysis of a five-anion test mixture under AS9-HC gradient conditions is shown here. Although improvement in sensitivity can be inferred, the results also show significant shifts in the baseline possibly due to incomplete removal of CO_2 suggesting that the prototype CRD device is not compatible with carbonate gradients. Such anomalous baseline shifts are not observed with RFIC™ hydroxide gradients.

CONCLUSIONS

- CRD is useful for CO_2 removal from the sample stream
  - Preinjection removal for acidic samples
- The use of CRD as a post suppressor device minimizes the peak constituting CO_2 leading to:
  - Improved quantitation for some analytes
  - Improved resolution
  - Improved sensitivity
- CRD can be used to reduce the carbonic acid background from carbonate eluents leading to:
  - Improved sensitivity
  - Due to large shifts in the background, compatibility with gradient runs is questionable and warrants further investigation



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