Minimizing Carbon Dioxide Contamination in Anion Reagent-Free™ Ion Chromatography

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Introduction

The ubiquitous presence of carbon dioxide in air (typically 390 ppm and increasing[1]) results in dissolved carbon dioxide being the most common anionic contaminant in laboratory water. In deionized water, dissolved carbon dioxide exists as nonionic carbonic acid and bicarbonate. Carbonic acid is both a blessing and a curse in suppressed ion chromatography (IC). When it was recognized that solutions of sodium carbonate and sodium bicarbonate were useful eluents and could be suppressed to low conductance carbonic acid,[2] carbonate-based eluents became the mainstay for suppressed anion IC. With the advent of hydroxide-selective, anion-exchange columns and the subsequent development of Reagent-Free™ IC (RFIC™) systems and electrolytic eluent generation using water as the pumped phase, carbonate became a contaminant, instead of an eluent. Because potassium hydroxide suppresses to water, the presence of carbonate in the eluent water or ambient carbon dioxide absorbed into the basic eluent causes an increase in the suppressed background conductivity.

Because most anion RFIC system separations using potassium hydroxide are based on gradient elution, trace carbonate accumulates at lower eluent concentration and elutes at higher eluent concentrations. The elution of the carbonate causes a baseline shift as well as a carbonate peak. In samples, dissolved carbon dioxide may constitute the highest concentration analyte and compromise separation and detection of trace analytes. The carbonate peak, whether from the eluent or the sample, can be quite large relative to analytes and thus can interfere with integration.

This work describes processes for minimizing carbonate contamination in gradient anion RFIC systems. Devices for in-line purification of water and eluent are described as well as decarbonation techniques for post-suppressor carbonate removal. Examples demonstrating the benefits of reducing carbon dioxide contamination in anion RFIC system separations are shown.

Experimental

Instrumentation

Water Purification—Trovion *iWP* Electrolytic Water Purification system consisting of:

- Reagent Pump Controller
- CIRA EP or CIRA 10 Electrolytic Water Purifier

Thermo Scientific Dionex ICS-2100 RFIC system with:

- Dionex EGC II KOH Eluent Generator Column (EGC)
- Dionex Continuously Regenerated Anion Trap Column (CR-ATC)
- Dionex CRD 300 Post Suppression Carbonate Removal Device (CRD)
- Thermo Scientific Dionex IonPac™ AEP-ER1 (for water recycle)

Chromatography Conditions

Columns:	Dionex IonPac AS18, AS19, or AS20, as specified
Flow Rate and Gradients:	as specified
Suppressors:	Thermo Scientific Dionex ASRS™ 300 Anion Self-Regenerating Suppressor (4 mm)
Detection:	Conductivity

Results and Discussion

Anion Analysis of Deionized Water

The primary source of carbonate is from the deionized water used for electrolytic eluent generation eluent. A Dionex ICS-3000 system was used to analyze deionzed water from a bench top lab water system. A Dionex IonPac AS18 separator column was used isocratically (25 mM KOH) with a large loop (1.5 mL) injection method. The deionized water was injected as a sample every 30 min and for approximately 21 h (42 runs). Next the deionzed water was passed through the Trovion *iWP* system prior to analysis (Figure 1). The Trovion *iWP* system is a point-of-use electrolytic water purification system that produces ionically pure water for direct feed to a Dionex RFIC system.[3] Figure 2 compares the anion chromatogram for the deionzed water sample and the same water passed through the *iWP* system. Not only was the carbonate reduced 90%, but the *iWP* system also reduced other sub-ppb anions such as fluoride acetate, formate, chloride, and sulfate. Figures 3a and 3b show the trend in carbonate over the 21 h. Note for the deionzed water, the carbonate peak continues to rise as carbon dioxide from the air is absorbed into the water. With the *iWP* system, the carbonate peak is not only an order of magnitude smaller, but continues to decrease as the CIRA EP electrolytic water purifier becomes “cleaner” as a result of continuous electrolytic regeneration.

FIGURE 1. Trovion *iWP* System with the CIRA EP shown at top.

FIGURE 2. Comparison of deionized water and Trovion *iWP* water. (Conditions: Dionex IonPac AS18 separator, [4 mm] 25 mM KOH at 1.0 mL/min, Dionex ASRS 300 suppressor.)

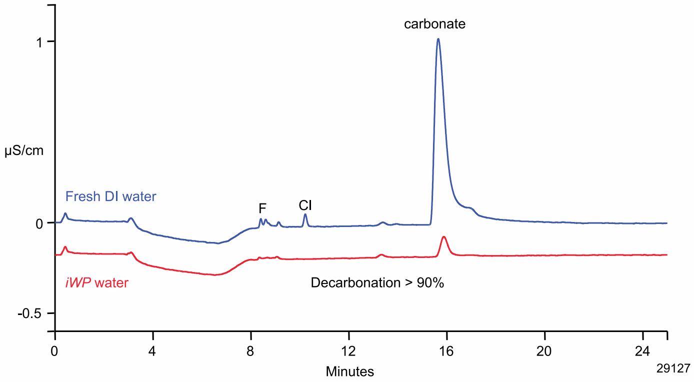
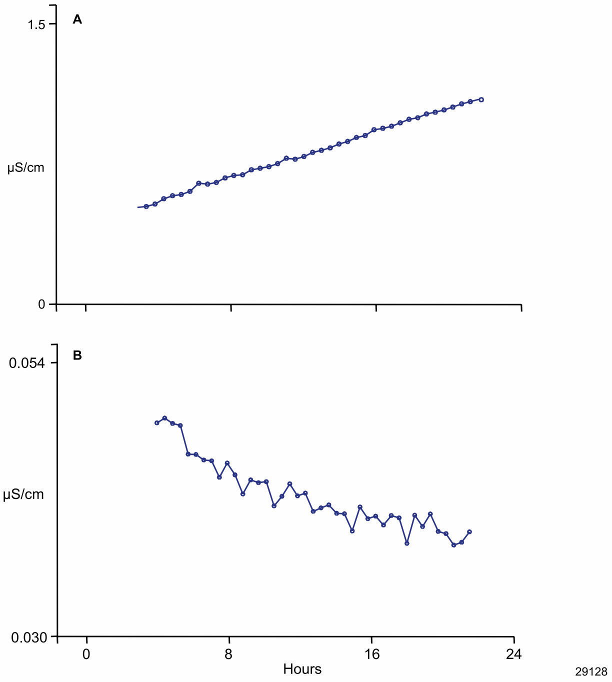


FIGURE 3. A) Measured carbonate (peak height) by anion RFIC system in deionized water (20 h). B) Measured carbonate (peak height) by anion RFIC system in *iWP* water (20 h). Conditions used as in Figure 2.



While it is important to remove carbonate from the deionzed feed water used in the Dionex RFIC system for electrolytic eluent generation, there are others sources of carbonate in the system. Once the potassium hydroxide is formed in the eluent generator, the basic eluent is even more effective at absorbing carbonate than deionzed water. The Dionex CR-ATC column (Figure 4) is designed to remove anionic contamination from the potassium hydroxide eluent.[4] The task of removing ionic contamination such as carbonate from the eluent is more difficult than removing the carbonate or other anionic contamination from the feed water. Thus, by using electrolytic water purification for the feed water, the carbonate load in the eluent is reduced which improves the performance of the Dionex CR-ATC. Further reduction in carbonate that originates after electrolytic eluent generation (including sample injection) can be accomplished with the Dionex CRD 200 or 300 device (Figure 5). The Dionex CRD is a post-suppressor device,[5] which removes carbonic acid (as carbon dioxide) from the suppressed eluent. In gradient operation, trace carbonate in the potassium hydroxide concentrates in the early portion of the gradient, and then elutes as a peak in the later portion of the gradient. The large carbonate peak compromises integration of analytes (sulfate and phosphate) in the region of the carbonate and also affects analyte response since the analytes are being measured on a higher carbonate background rather than a “water” background.

FIGURE 4. Dionex CR-ATC schematic.

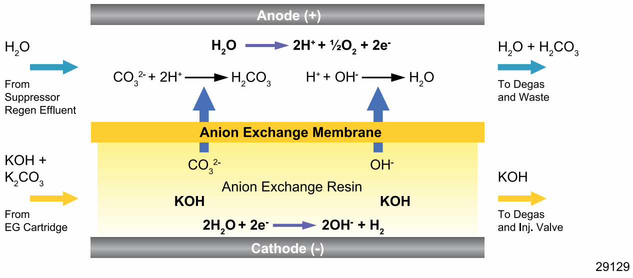
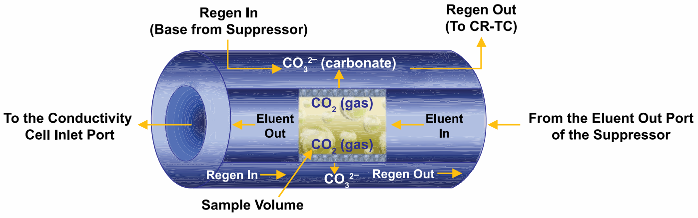


FIGURE 5. Dionex CRD 200 device schematic.



- Self-sustained source of base
- No need for any external reagents
- Formats: 2 mm microbore and 4 mm standard bore available

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Controlling Carbonate in an Anion RFIC System

A Dionex ICS-2100 RFIC system was optimized for controlling carbonate contamination. Figure 6 shows the major components of the RFIC system and components used for minimizing carbonate. The Dionex ASRS suppressor was operated in the external water mode at 1.0 mL/min. To minimize ambient contamination of the feed DI water, the 2 L eluent bottle was pressurized with 7—10 psi nitrogen. A Trovion CIRA 10 purifier was placed between the pressurized eluent bottle and the analytical pump. The CIRA 10 is a single-channel electrolytic water purifier which consists of an anion and composite ion-exchange layer as shown in Figure 7. In the CIRA 10, the majority of the anionic contamination is retained by the homogenous anion-exchange layer and any residual anionic contamination is removed in the composite layer. From the CIRA 10, the water enters the Dionex ICS-2100 pump degasser where dissolved gasses such as nitrogen and oxygen are removed so that the analytical pump does not lose prime.

The in-line degasser has a volume 480 µL, so the residence time of the eluent is about 30 seconds at 1 mL/min. This residence time is sufficient for effective removal of nitrogen and oxygen, but not carbon dioxide. At this point, the feed water is essentially ionically pure and from the pump, enters the Dionex EGC II column where the potassium hydroxide eluent is formed. Next, the potassium hydroxide passes to the Dionex CR-ATC column which acts as a final anionic polisher before the eluent enters the analytical column. Removing the majority of the carbonate from the feed water prior to eluent generation ensures that the Dionex CR-ATC column can remove residual anionic impurities from the eluent.

FIGURE 6. Dionex ICS-2100 RFIC system optimized for controlling carbonate contamination.

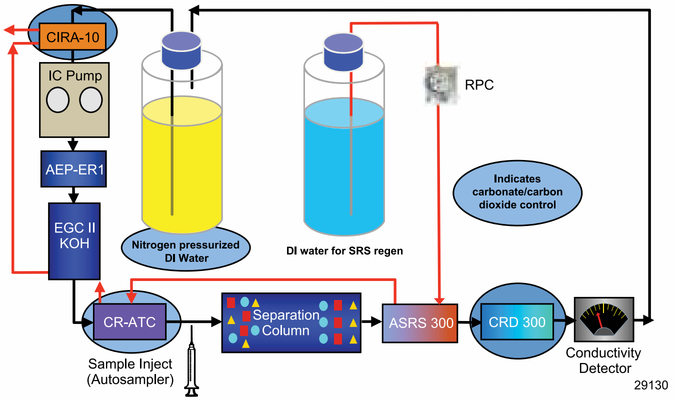
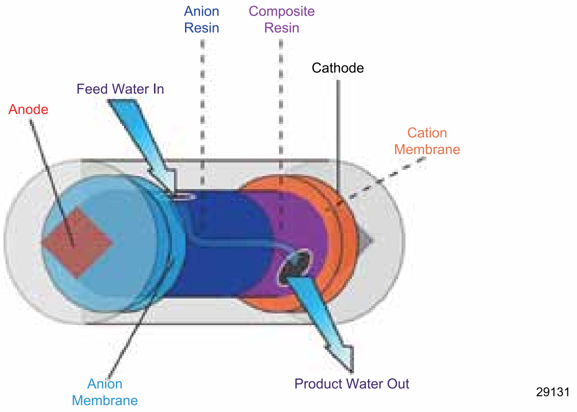


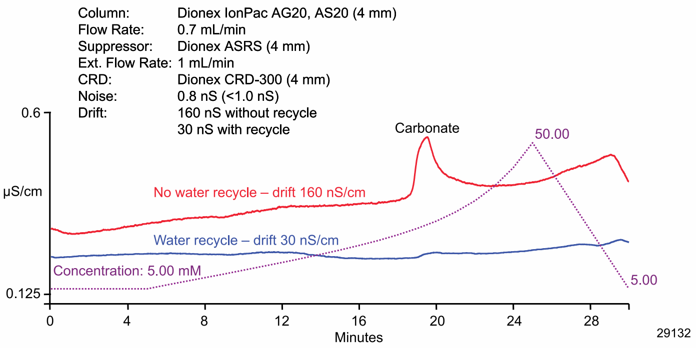
FIGURE 7. Cross-section drawing of the CIRA 10 electrolytic water purifier.



From the Dionex CR-ATC column, the eluent passes through the Dionex EGC degasser which removes the electrolytically formed hydrogen from the eluent generation process. The eluent then passes to the injection valve and analytical column. From the Dionex ASRS suppressor, the suppressed eluent (water) passes into the CRD 300 where residual carbon dioxide (carbonic acid) from the eluent and sample is reduced prior to conductivity detection. Using the system described above, a gradient from 5.0 to 50 mM potassium hydroxide was run over 20 minutes at 0.70 mL/min as shown in Figure 8. The baseline shift in this gradient was approximately 160 nS/cm. The carbonate peak is from residual carbonate in the eluent. This experiment demonstrates the difficulty of controlling carbonate in gradient anion Reagent-Free IC.

To further investigate reduction of carbonate, suppressed eluent was recycled back to the feed water container. The Trovion Reagent Pump Controller (RPC) was used to deliver deionized water for the Dionex ASRS regenerant (SRS external water mode). From the conductivity cell, the suppressed eluent (water) was directed back to the nitrogen pressurized eluent bottle. The 2 L eluent bottle was replaced with a 250 mL bottle (filled with 200 mL of DI water) to decrease the recycle time for the eluent (about a five hour recycle time). A Dionex IonPac AEP-ER1 trap column was placed between the pump and the eluent generator to reduce ionic organic contamination. This closed loop system not only has the advantage of recycling the eluent feed water, but multiple passes of the feed water through the CIRA 10 should further reduce carbonate contamination. Sample anions are removed by the CIRA 10 prior to electrolytic eluent generation.

FIGURE 8. Typical anion RFIC system gradient blank obtained when controlling carbonate contamination.


Column: Dionex IonPac AG20, AS20 (4 mm)
Flow Rate: 0.7 mL/min
Suppressor: Dionex ASRS (4 mm)
Ext. Flow Rate: 1 mL/min
CRD: Dionex CRD-300 (4 mm)
Noise: 0.8 nS (<1.0 nS)
Drift: 160 nS without recycle
30 nS with recycle

A gradient from 5 to 100 mM potassium hydroxide was run over 45 min. After approximately two cycles of the feed water, the gradient blank in Figure 9 was obtained. Not only was the gradient drift reduced (30 nS/cm) as a result of the recycle, but the carbonate blank peak was also greatly reduced. Using the water recycle method, Figure 10 shows a typical run is shown for an 8 to 50 mM gradient. Note the extremely small carbonate peak and the gradient drift is less than 25 nS/cm. Figure 11 shows the analysis of trace bromate in drinking water using a small sample loop (25 μL) with the water recycle system of Figure 6.

FIGURE 9. Typical background of gradient elution of 5–100 mM KOH using the water recycle method.

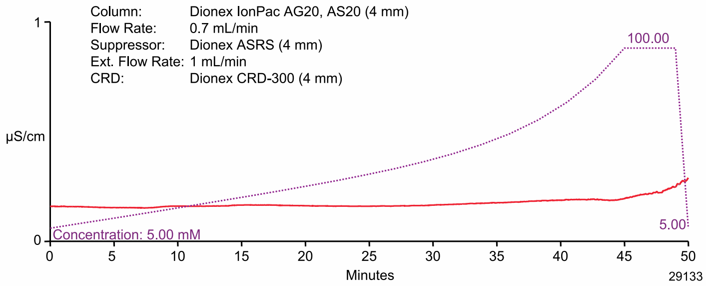
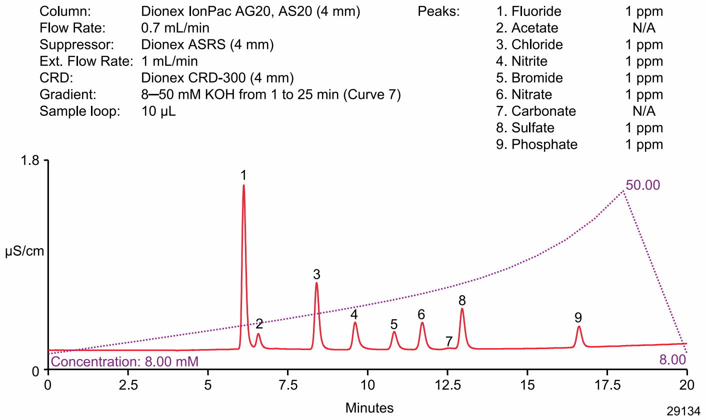

Column: Dionex IonPac AG20, AS20 (4 mm)
Flow Rate: 0.7 mL/min
Suppressor: Dionex ASRS (4 mm)
Ext. Flow Rate: 1 mL/min
CRD: Dionex CRD-300 (4 mm)

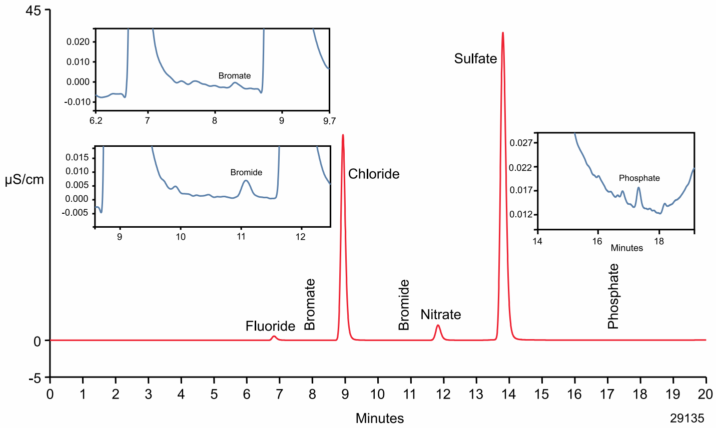
FIGURE 10. Optimized anion RFIC system gradient separation.


Column: Dionex IonPac AG20, AS20 (4 mm)
Flow Rate: 0.7 mL/min
Suppressor: Dionex ASRS (4 mm)
Ext. Flow Rate: 1 mL/min
CRD: Dionex CRD-300 (4 mm)
Gradient: 8—50 mM KOH from 1 to 25 min (Curve 7)
Sample loop: 10 μL

Peaks:	
1. Fluoride	1 ppm
2. Acetate	N/A
3. Chloride	1 ppm
4. Nitrite	1 ppm
5. Bromide	1 ppm
6. Nitrate	1 ppm
7. Carbonate	N/A
8. Sulfate	1 ppm
9. Phosphate	1 ppm

FIGURE 11. Determination of bromate (4 ppb) in drinking water using a small loop injection (25 µL) with water recycle. System as shown in Figure 6.

Column:	Dionex IonPac AG19, AS19 (4 mm)
Flow Rate:	0.7 mL/min
Suppressor:	Dionex ASRS (4 mm)
Ext. Flow Rate:	1 mL/min
CRD:	Dionex CRD-300 (4 mm)
Gradient:	5–50 mM KOH, 0 to 18 min (Curve 7)
Sample Loop:	25 µL
Sample:	Spiked 4 ppb bromate in drinking water



Conclusions

While carbon dioxide is the most common contaminant in deionized water, processes to minimize the impact of carbonate contamination in gradient anion RFIC system are readily available to the IC practitioner. No single process can remove all carbonate contamination. In anion RFIC systems, controlling carbonate in the feed water is critical (CIRA electrolytic water purifier). The use of other devices such as the Dionex CR-ATC column to remove carbonate from the eluent and the Dionex CRD device to remove carbonic acid from the suppressed eluent are all important components for reducing carbonate effects. Pressurizing the eluent container with an inert gas (nitrogen) and recycling the eluent water furthers reduces carbonate contamination. Minimizing carbonate contamination results in lower background conductivity, reduced baseline drift, and lower noise. A reduced carbonate peak improves quantitation of analytes which elute in the region of carbonate.

References

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