

Battery solutions

Determination of inorganic anions in saturated lithium carbonate solution

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Keywords

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RFIC system, lithium-ion batteries

Goal

To demonstrate the determination of inorganic anions in saturated lithium carbonate solution

Introduction

Lithium carbonate is an important compound for industry. It is used in many applications including lithium-ion and lithium polymer batteries. Rechargeable batteries are an increasing part of our daily life as we use more portable electronic devices, including mobile phones. These batteries are also important for the electric car industry. Lithium-ion batteries are the most commonly used rechargeable batteries because of their high volumetric energy density.¹ Lithium carbonate is a precursor to make lithium compounds used in lithium-ion batteries. Determination of inorganic anions in saturated lithium carbonate solution and using those values to determine the amounts in the solid, is desired by both battery recyclers and chemical suppliers.

This application note demonstrates the determination of inorganic anions in saturated lithium carbonate solution using the Thermo Scientific™ Dionex™ ICS-5000+ Reagent-Free™ Ion Chromatography (RFIC™) system² with a Thermo Scientific™ Dionex™ IonPac™ AS23 anion-exchange column.³

Equipment and consumables

- A Dionex ICS-5000+ Ion Chromatography (RFIC) system* was used in this work which includes:
 - Thermo Scientific™ Dionex™ ICS-5000+ SP/DP Pump module
 - Thermo Scientific™ Dionex™ ICS-5000+ EG Eluent Generator module with high-pressure degasser module
 - Thermo Scientific™ Dionex™ ICS-5000+ DC Detector/Chromatography module with conductivity detector and dual temperature zones
- Thermo Scientific™ Dionex™ AS-AP Autosampler with 250 µL syringe, 1.2 mL buffer line assembly, and 10.0 µL injection loop
- VP Vacuum Pump Kit (P/N 60-064194)
- Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software, version 7.2

* Equivalent results can be achieved using a Thermo Scientific™ Dionex™ ICS-6000 HPIC™ System.

Consumables

- Thermo Scientific™ Dionex™ EGC 500 K₂CO₃ Potassium Carbonate Eluent Generator Cartridge (EGC), (P/N 088453)
- Thermo Scientific™ Dionex™ Eluent pH Modifier (EPM 500), (P/N 088471)
- Dionex EGC 500 Carbonate Mixer Kit, 2 mm, (P/N 088467)

- Thermo Scientific™ Dionex™ AERS™ 500 Carbonate Anion Electrolytically Regenerated Suppressor (2 mm), (P/N 085028)
- Thermo Scientific™ Dionex™ IonPac™ AS23 IC Guard Column (2 × 50 mm), (P/N 064143)
- Thermo Scientific™ Dionex™ IonPac™ AS23 IC Analytical Column (2 × 250 mm), (P/N 064145)
- Thermo Scientific™ Dionex™ CRD 300 with VP Vacuum Pump Kit (4 mm), (P/N 064638) or Thermo Scientific™ Dionex™ CRD 300 Carbonate Removal Device (2 mm), (P/N 068475)
- Thermo Scientific™ Nalgene™ Syringe filter (0.2 µm, PES membrane)**, (P/N 7252520)
- Dionex AS-AP Autosampler Vial Kit with vials, caps, and blue septa. Package of 100, 10 mL, polystyrene, (P/N 074228)

** Fisher Scientific P/N 09-740-113

System preparation and setup

Figure 1 shows the flow diagram of the IC system. The IC system is plumbed as a RFIC system using eluent generation following the Dionex Eluent Generator Cartridges product manual.⁴ The suppressor is installed in recycle mode.⁵ A carbonate removal device, Dionex CRD 300 (2 mm)⁶, is installed after the suppressor in the vacuum mode (Figure 2). This device removes carbonic acid generated by the suppression of carbonate to reduce the carbonate peak from the lithium carbonate sample and the background caused by the residual conductivity of suppressed carbonate/bicarbonate eluent. The end result is an increase in the sensitivity to allow lower detection limits for the sample's anions.

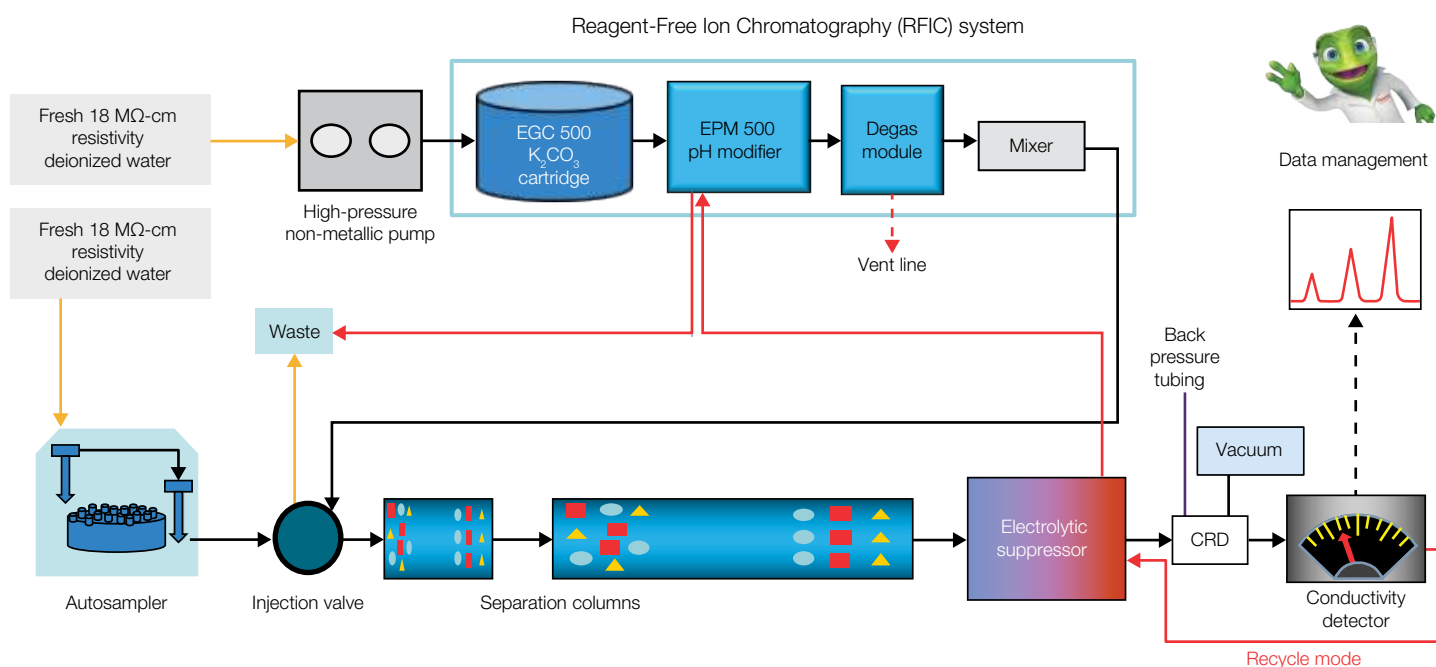


Figure 1. Flow schematic: Dionex CRD 300 vacuum mode (the CRD 300 is pictured on top of the suppressor)

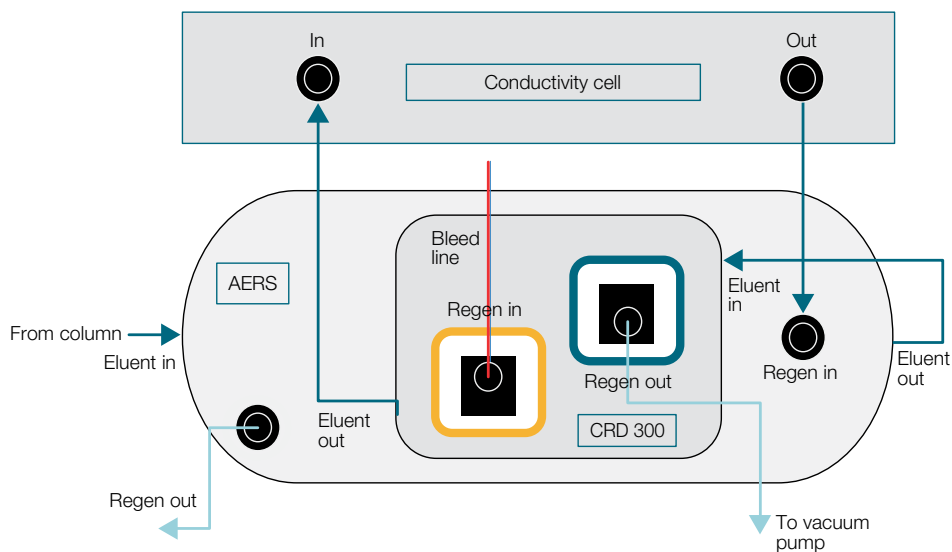


Figure 2. Dionex CRD 300 vacuum mode flow schematic

Conditions

Table 1. Chromatography conditions

Columns	Dionex IonPac AS23 IC analytical column, 2 × 250 mm Dionex IonPac AG23 IC guard column, 2 × 50 mm
Eluent	4.5 mM potassium carbonate, 0.8 mM potassium bicarbonate
Eluent source*	Dionex EGC 500 K ₂ CO ₃ cartridge with an EPM 500 pH modifier and a mixer
Flow rate	0.25 mL/min
Injection volume	5.0 µL (full loop)
Column temperature	30°C
Detection	Suppressed conductivity, Thermo Scientific™ Dionex™ AERS 500 Carbonate Anion Electrolytically Regenerated Suppressor, recycle mode, 8 mA current
Detection/suppressor compartment	30°C
Cell temperature	30°C
Background conductance	≈1.3 µS/cm
System backpressure	≈2300 psi (100 psi = 0.689 MPa)
Noise	≈2 nS/cm
Run time	25 min

* Manually prepared eluent can be used, but the detection limits will be inferior to those reported in this document. If using manual eluents, any Dionex ICS system can be used.

Reagent and standards

- Degassed deionized (DI) water, 18 MΩ-cm resistance or better
- Lithium carbonate (Powder, ACS Certified, L119-500, Fisher Chemical)
- Thermo Scientific™ Dionex™ Seven Anion Standard II (P/N 057590)

Preparation of solutions and reagents

Calibration standard solutions

Calibration standards were prepared by diluting the Dionex Seven Anion Standard II with DI water.

Table 2. Calibration standards (mg/L)

	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7
Fluoride	0.02	0.05	0.1	0.2	0.4	1	2
Chloride	0.1	0.25	0.5	1	2	5	10
Nitrite	0.1	0.25	0.5	1	2	5	10
Bromide	0.1	0.25	0.5	1	2	5	10
Nitrate	0.1	0.25	0.5	1	2	5	10
Phosphate	0.2	0.5	1	2	4	10	20
Sulfate	0.1	0.25	0.5	1	2	5	10

Sample preparation

Saturated lithium carbonate

Saturated lithium carbonate samples were prepared by adding excess lithium carbonate solid in DI water. Two simulated saturated lithium carbonate samples were prepared as below:

- **Saturated lithium carbonate A:** Weight 2.0 g of lithium carbonate solid into a 20 mL bottle, add 1st 20.0 g of DI water, mix, and let it dissolve overnight to reach saturation. Filter the supernatant through a syringe filter.
- **Saturated lithium carbonate B:** Take the lithium carbonate solid that did not dissolve in above procedure, add 20.0 g of DI water, mix, and let it dissolve overnight. Filter the supernatant through syringe filter.

Note: During method development, it was found that a saturated lithium carbonate solution cannot be analyzed directly due to column overload. With the injection volume used in the IC method reported here, the column is not overloaded when lithium carbonate concentration is less than or equal to 0.4 g/100 mL. Lithium carbonate solubility is 1.31 wt % at 20°C and its solubility decreases with temperature increase.⁷ Therefore, these two samples were then prepared for analysis by mixing one part of the saturated lithium carbonate sample with 3 parts of DI-water by volume.

Lithium carbonate

A lithium carbonate solution was prepared at a known concentration (less than saturation). Weigh 0.2 g of lithium carbonate solid into a 20 mL bottle, add 20.0 g of DI water, and mix to dissolve. Solid should be all dissolved at this concentration (1.0 g/100 mL). Filter this solution through a syringe filter.

Dilute with DI-water to 0.4 g/100 mL for sample analysis.

Method detection limit standards and spiked samples

Saturated lithium carbonate solution B contains almost no anions and was used as sample matrix to prepare the method detection limit (MDL) standards. The Dionex Seven Anion Standard II was spiked into the 1 to 4 diluted saturated lithium carbonate solution B for the MDL determinations, and the concentrations for each MDL determination are listed in Table 3.

Two types of spiked samples were prepared by adding a known amount of mixed inorganic anion standard into the lithium carbonate solutions: High level spiked solutions were used for method development and low-level spiked solutions were for method accuracy evaluation (Table 3).

Table 3. Samples for method development, MDL determination, and recovery

	Spiked samples for method development			MDL determination	MDL validation	Spiked recovery sample
	in 0.4 g/100 mL lithium carbonate (mg/L)	in ¼ diluted saturated lithium carbonate B (mg/L)	in ½ diluted saturated lithium carbonate B (mg/L)	in ¼ diluted saturated lithium carbonate B (mg/L)	in 0.4 g/100 mL lithium carbonate (mg/L)	in 0.4 g/100 mL lithium carbonate (mg/L)
Fluoride	1	1	1	0.02	0.02	0.05
Chloride	5	5	5	0.025	0.1	0.25
Nitrite	5	5	5	0.05	0.1	0.25
Bromide	5	5	5	0.05	0.1	0.25
Nitrate	5	5	5	0.05	0.1	0.25
Phosphate	10	10	10	0.1	0.2	0.5
Sulfate	5	5	5	0.1	0.1	0.25

Results and discussion

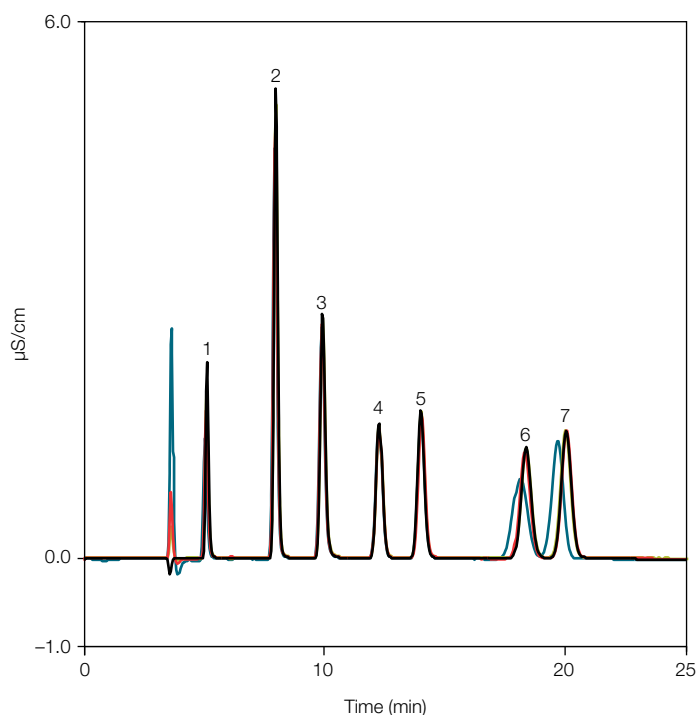
Separation

The Dionex IonPac AS23 column is a high-capacity anion-exchange column designed for the determination of inorganic anions in aqueous samples using suppressed conductivity detection. The column is designed to be used with an isocratic carbonate/bicarbonate eluent, which can be easily prepared from concentrated eluent stock or produced by an electrolytic eluent generator. Using manually prepared eluent during method development, a dip in the baseline was observed for lithium carbonate samples at the retention time of sulfate. Subsequent experimentation revealed that the dip was caused by the impurity sulfate in the eluent concentrate being higher than the amount of sulfate in the sample. Two lots of eluent concentrate were tested and the amount of contaminating sulfate varied. A RFIC system generates high purity eluent and thus eliminates this problem. Therefore, a RFIC system is recommended for this application.

Figure 3 shows a separation of inorganic anions within 25 min using the Dionex IonPac AS23 column in different matrices (DI water, 0.4 g/100 mL lithium carbonate, $\frac{1}{2}$ and $\frac{1}{4}$ saturated

lithium carbonate). This figure shows that the seven common inorganic anions are well resolved. A dip (in DI water) or a peak (in lithium carbonate) at ≈ 3.5 min is observed depending on the sample matrix.

Direct injection of 5.0 μL of concentrated lithium carbonate samples, e.g., saturated lithium carbonate, will overload the 2 mm Dionex IonPac AS23 column. Figure 3 shows that a 1 to 2 dilution (chromatogram in teal color) is insufficient to prevent overload as the retention times of phosphate and sulfate are shifted significantly. Figure 3 also shows that the column is not overloaded when lithium carbonate concentration is less than or equal to 0.4 g/100 mL (chromatogram in red color). Lithium carbonate solubility is 1.31 wt. % at 20°C and its solubility decreases with temperature increase.⁷ Therefore, a 1 to 4 dilution of saturated lithium carbonate (lithium carbonate concentration at ≈ 0.33 g/100 mL) can be used for the determination of inorganic anions in saturated lithium carbonate solution, and it was used here. Figure 4 shows the chromatograms of the lithium carbonate samples.

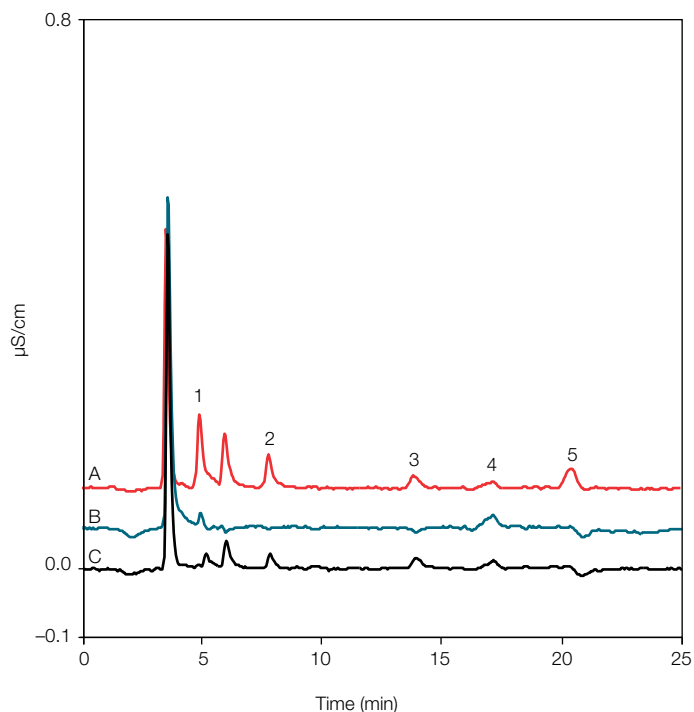


Columns: Dionex IonPac AG23, 2 × 50 mm
and Dionex IonPac AS23, 2 × 250 mm
Eluent: 4.5 mM K_2CO_3 /0.8 mM KHCO_3
Flow rate: 0.25 mL/min
Inj. volume: 5.0 μL (full loop)
Column temp.: 30°C
Detection: Suppressed conductivity,
Dionex AERS 500 carbonate suppressor, (2 mm),
30°C, 8 mA, recycle mode

Sample: A mixed inorganic anion standard at the
concentration below in:
Teal: $\frac{1}{2}$ saturated lithium carbonate solution
Red: 0.4 g/100 mL lithium carbonate solution
Green: $\frac{1}{4}$ saturated lithium carbonate solution
Black: DI-water

Peaks:		Min	mg/L
1	Fluoride	5.0	1.0
2	Chloride	7.9	5.0
3	Nitrite	9.9	5.0
4	Bromide	12.2	5.0
5	Nitrate	14.0	5.0
6	Phosphate	18.3	10.0
7	Sulfate	20.0	5.0

Figure 3. Chromatograms of a mixed inorganic anion standard in different matrices



Columns: Dionex IonPac AG23, 2 × 50 mm and Dionex IonPac AS23, 2 × 250 mm
 Eluent: 4.5 mM K₂CO₃ / 0.8 mM KHCO₃
 Flow rate: 0.25 mL/min
 Inj. volume: 5.0 µL (full loop)
 Column temp.: 30°C
 Detection: Suppressed conductivity, Dionex AERS 500 carbonate suppressor, (2 mm), 30°C, 8 mA, recycle mode

Sample: A: ¼ saturated lithium carbonate solution A
 B: ¼ saturated lithium carbonate solution B
 C: 0.4 g/100 mL lithium carbonate solution

Peaks:		mg/L		
		A	B	C
1	Fluoride	0.07	0.02	0.02
2	Chloride	0.07	0.0	0.04
3	Nitrate	0.12	0.0	0.12
4	Carbonate	N/A	N/A	N/A
5	Sulfate	0.13	0.0	0.0

Figure 4. Chromatograms of lithium carbonate samples

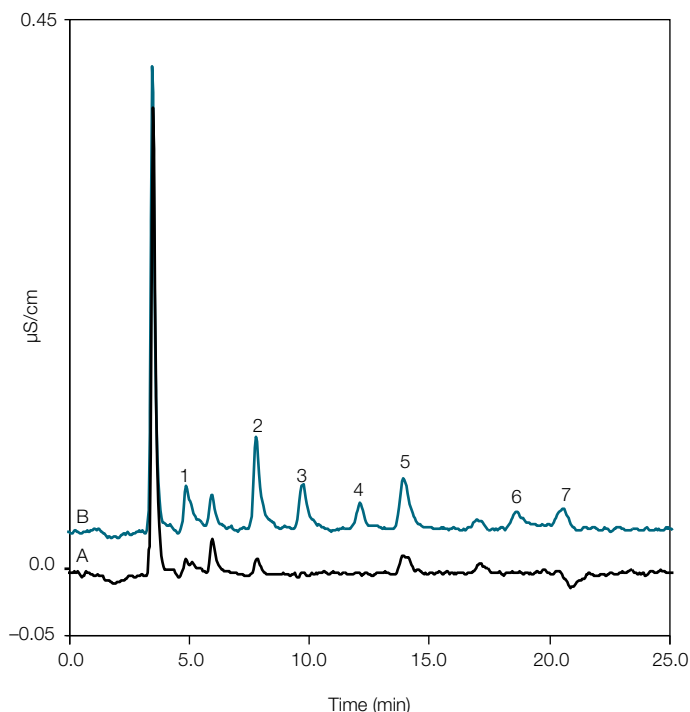
Retention time, linearity, and MDLs

Here, seven-point calibrations were studied (Table 2). For determining low concentrations, a calibration curve with the lower five concentrations can be used.

MDLs were determined by performing seven replicate injections of standards at a concentration less than ten times the estimated method detection limits. To take the sample matrix into account, standards for MDL determination were prepared with a seven-anion standard spiked into the 1 to 4 dilution of saturated lithium carbonate B. Compared to saturated lithium carbonate A, the B is a much cleaner sample matrix only containing a low concentration of fluoride (Figure 4). The three spiked solutions described in the sample preparation section were used to

measure MDLs, so the MDL of each anion was determined at a concentration less than ten times the estimated method detection limit (Table 4). These MDL standards are alkaline and therefore will absorb acids from the air. Therefore, they need to be prepared freshly and analyzed soon after preparation. The MDLs for saturated lithium carbonate were determined by multiplying the MDL determined in the 1 to 4 dilution of saturated lithium carbonate by four.

Because the exact concentration of the 1 to 4 dilution of saturated lithium carbonate solution B is not known, the validity of these values was evaluated by spiking a low concentration anion standard into 0.4 g/mL lithium carbonate (Table 3 MDL Validation column, Figure 5).



Columns: Dionex IonPac AG23, 2 × 50 mm and Dionex IonPac AS23, 2 × 250 mm
 Eluent: 4.5 mM K₂CO₃/0.8 mM KHCO₃
 Flow rate: 0.25 mL/min
 Inj. volume: 5.0 μL (full loop)
 Column temp.: 30°C
 Detection: Suppressed conductivity, Dionex AERS 500 carbonate suppressor, (2 mm), 30°C, 8 mA, recycle mode

Sample: A (Black): 0.4 g/100 mL lithium carbonate solution sample
 B: A spiked with a mix anions standard at the concentration below

Peaks:	Min	mg/L
1 Fluoride	5.0	0.02
2 Chloride	7.9	0.10
3 Nitrite	9.8	0.10
4 Bromide	12.1	0.10
5 Nitrate	13.9	0.10
6 Phosphate	18.5	0.20
7 Sulfate	20.7	0.10

Figure 5. Chromatograms of a 0.4 g/100 mL lithium carbonate sample and spiked with a low-level anion standard

Table 4 shows the retention times, linear concentration ranges, the coefficients of determination (r^2), and calculated MDLs for seven anions. The method shows linear relationships (Figure 6) of peak area to concentration in the chosen calibration ranges with coefficients of determination (r^2) from 0.997 to 0.998. The method is sensitive for the determination of seven inorganic anions in saturated lithium carbonate with low MDLs (0.02 to 0.22 mg/L).

Table 4. Linearity, method detection limits (MDL), and retention time obtained using a Dionex IonPac AS23 IC column with a 5.0 μL injection

Analyte	Retention time	Range (mg/L)	Coefficient of determination (r^2) (n = 3)	Calculated *MDL (mg/L)	Concentration for MDL determination (mg/L in 1 to 4 dilution of saturated lithium carbonate B)	Calculated MDL in saturated lithium carbonate (mg/L)
Fluoride	5.0	0.02–2	0.9998	0.004	0.02	0.02
Chloride	7.9	0.1–10	0.9998	0.006	0.025	0.02
Nitrite	9.8	0.1–10	0.9998	0.026	0.05	0.11
Bromide	12.1	0.1–10	0.9998	0.042	0.05	0.17
Nitrate	13.9	0.1–10	0.9997	0.023	0.05	0.09
Phosphate	18.5	0.2–20	0.9998	0.056	0.1	0.22
Sulfate	20.7	0.1–10	0.9998	0.043	0.1	0.17

*MDL = (t) × (S). t = Student's t value for a 99% confidence level and a standard deviation estimates with n-1 degrees of freedom (t = 3.14 for seven replicates), S = standard deviation of the replicate analyses.

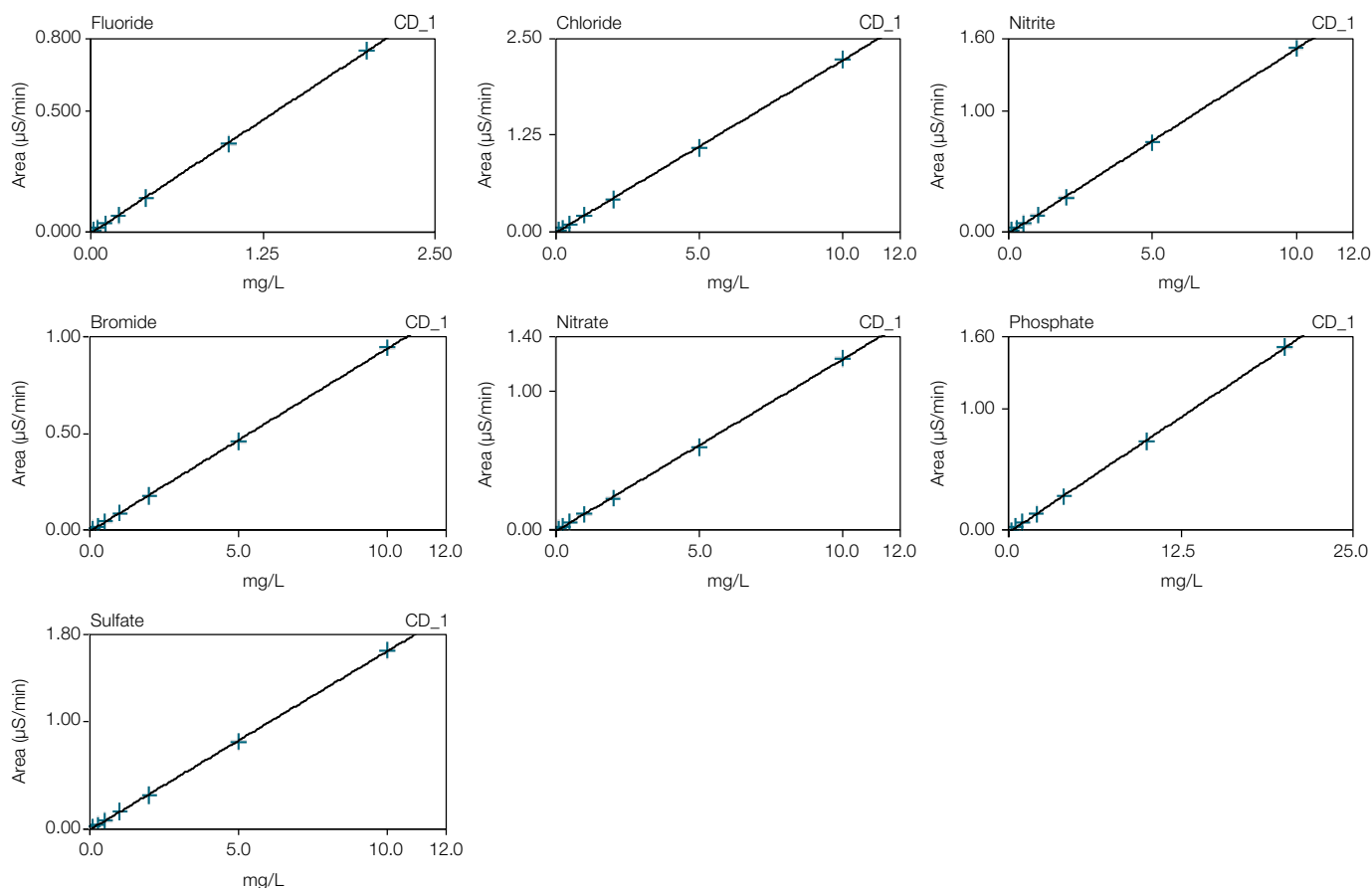


Figure 6. Calibration plots

Inorganic anions in lithium carbonate

Inorganic anions were determined in saturated lithium carbonate solutions and the lithium carbonate solution prepared at a known concentration (Figure 4 and Table 5). The known concentration solution was used to determine the anion concentrations in the solid. Observe that saturated solution B only contains a low concentration of fluoride, as discussed earlier.

Using the values obtained from 0.4 g/100 mL lithium carbonate solution, the inorganic anion impurities in the lithium carbonate solid are 0.47 mg/kg fluoride, 0.94 mg/kg chloride, and

2.9 mg/kg nitrate, which agree with the analysis label for the sample (Chloride <0.005% (50 mg/kg), nitrate <5.0 ppm). The RSDs > 10% correspond to the samples that were analyzed at concentrations where the anions were close to their MDLs.

It was observed that the first solution, saturated lithium carbonate solution A, shows more inorganic anions than the second solution, saturated lithium carbonate solution B. This is likely because that inorganic anion impurities are low, and thus are all dissolved in saturated lithium carbonate solution A.

Table 5. Determination of inorganic anions in saturated lithium carbonate solutions and lithium carbonate solid (calculated from 0.4 g/100 mL solution)

Analyte	RT (min)	Saturated A			Saturated B			Solid		
		Inorganic anions (mg/L)	RSD		Inorganic anions (mg/L)	RSD		Inorganic anions (mg/kg)	RSD	
			A*	B*		A*	B*		A*	B*
Fluoride	2.4	0.28	1–3	4	0.09	3–7	48	0.47	2–15	25
Chloride	3.3	0.26	3–5	9	ND	N/A	N/A	0.94	3–5	18
Nitrite	3.7	ND	N/A	N/A	ND	N/A	N/A	ND	N/A	N/A
Bromide	4.3	ND	N/A	N/A	ND	N/A	N/A	ND	N/A	N/A
Nitrate	4.6	0.50	4–12	9	ND	N/A	N/A	2.9	12	12
Phosphate	7.0	ND	N/A	N/A	ND	N/A	N/A	ND	N/A	N/A
Sulfate	8.1	0.53	5–8	14	ND	N/A	N/A	ND	N/A	N/A

* The samples were prepared on separate days, n = 3/each day. A is intraday RSD range, B is interday RSD for all samples.

Method precession and accuracy

The method precision and accuracy were evaluated by spiking inorganic anions in 0.4 g/100 mL lithium carbonate (Table 6). The method is precise (RSD range 1–6%) and accurate (recovery range 95–107%).

Table 6. Spiked recovery of inorganic anions in 0.4 g/100 mL lithium carbonate

	Added (mg/L)	Recovery (%)	RSD	Added (mg/L)	Recovery (%)	RSD
Fluoride	0.05	103	3	0.2	107	1
Chloride	0.25	97	2	1	95	1
Nitrite	0.25	102	3	1	99	2
Bromide	0.25	96	1	1	99	1
Nitrate	0.25	95	3	1	97	2
Phosphate	0.5	105	6	2	99	2
Sulfate	0.25	96	6	1	97	3

Conclusion

This application note described a method for the determination of inorganic anions (fluoride, chloride, nitrite, bromide, nitrate, phosphate, and sulfate) in saturated lithium carbonate solution using a RFIC system with a Dionex IonPac AS23 column, carbonate eluent suppressor, and carbonate removal device. The method is sensitive (MDL 0.02–0.22 mg/L in saturated lithium carbonate solution), precise (RSD range 1–6%, and accurate (recovery range 95–107%).

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