

Industrial

Determination of chloride and sulfate in saturated lithium hydroxide solution

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Goal

To demonstrate the determination of chloride and sulfate in saturated lithium hydroxide solution

Introduction

Lithium hydroxide is an important compound for industry. It is used in many applications, such as battery manufacturing (lithium-ion and lithium polymer batteries), welding, electroplating painting (pigments, binders, and biocides), cleaning products, and household care.¹

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.² Lithium hydroxide and lithium carbonate are precursors to make lithium compounds used in lithium-ion batteries. Determination of chloride and sulfate in saturated lithium hydroxide and lithium carbonate solutions, and using those values to determine the amounts in the solid, is desired by both battery recyclers and chemical suppliers.

A method was developed for lithium carbonate.³ This application note demonstrates the determination of chloride and sulfate in saturated lithium hydroxide solution using a Thermo Scientific™ Dionex™ Reagent-Free Ion Chromatography™ (RFIC™) system⁴ with a Thermo Scientific™ Dionex™ IonPac™ AS29-Fast-4µm anion-exchange column⁵. The method includes sample preparation using Thermo Scientific™ Dionex™ OnGuard™ II H cartridges⁶.

Experimental

Equipment and consumables

- A Dionex ICS-5000+ Ion Chromatography (RFIC) system* was used in this work, which includes:
 - Dionex ICS-5000+ SP/DP Pump module
 - Dionex ICS-5000+ EG Eluent Generator module with high-pressure degasser module
 - 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 5.0 µL injection loop
- Thermo Scientific™ Chromeleon™ 7.2 Chromatography Workstation

Equivalent results can be achieved by using any Thermo Scientific™ Dionex™ RFIC system capable of electrolytically generating carbonate and bicarbonate-based eluents.

Consumables

- Thermo Scientific™ Dionex™ EGC 500 K₂CO₃ Potassium Carbonate Eluent Generator Cartridge (EGC) (P/N 088453)
- Thermo Scientific™ Dionex™ EPM 500 Electrolytic pH Modifier (P/N 088471)
- Thermo Scientific™ Dionex™ EGC Carbonate Mixer Kit, 2 mm (P/N 088467)
- Thermo Scientific™ Dionex™ AERS™ 500 Carbonate electrolytically regenerated suppressor (2 mm) (P/N 085028)
- Thermo Scientific™ Dionex™ IonPac™ AG29-Fast-4µm, Guard Column (2 × 30 mm) (P/N 302836)
- Thermo Scientific™ Dionex™ IonPac™ AS29-Fast-4µm, Analytical Column (2 × 150 mm) (P/N 302835)
- Thermo Scientific™ Dionex™ OnGuard™ II H cartridges, 1 mL (P/N 057085)
- Thermo Scientific™ Nalgene™ Syringe filter (0.2 µm, PES membrane) (P/N 725-2520, Fisher Scientific P/N 09-740-113)
- Thermo Scientific™ Dionex™ AS-AP Autosampler vials. Package of 100, 10 mL polystyrene vials with caps and blue septa (P/N 074228)

System preparation and setup

Figure 1 shows the flow diagram of the IC system used for the determination of chloride and sulfate in lithium hydroxide solution.

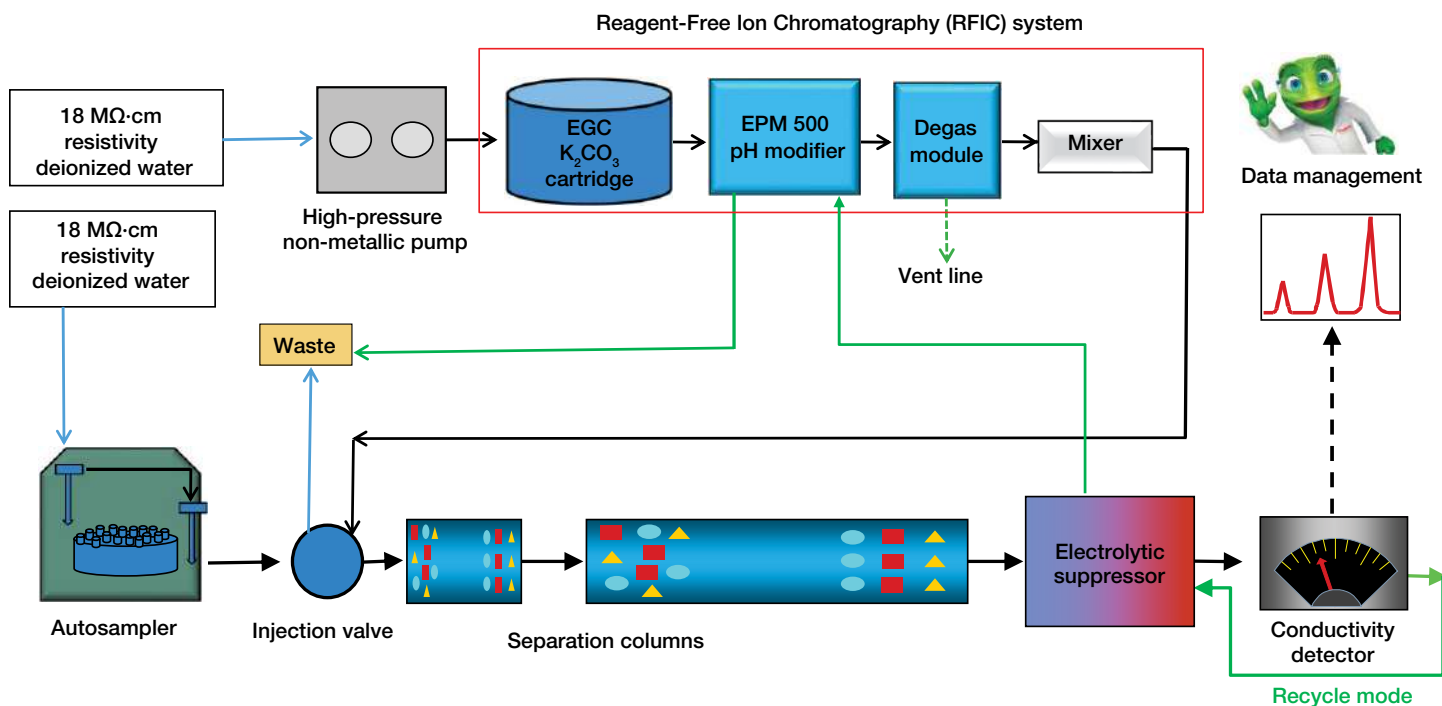


Figure 1. Illustration of the IC system flow diagram

A high-capacity anion-exchange column, the Dionex IonPac AS29-Fast-4 μ m column, was used.⁵ This column was selected because it was designed for fast determinations of inorganic anions in a variety of challenging samples, including high pH, low pH, and high ionic strength samples using carbonate/bicarbonate eluents. The IC system is plumbed as an RFIC system using eluent generation following the Dionex Eluent Generator Cartridges product manual⁷. The suppressor is installed in recycle mode⁸.

Chromatography conditions

Parameter	Value
Columns	Dionex IonPac AS29-Fast-4 μ m analytical column, 2 $\times$ 150 mm Dionex IonPac AG29-Fast-4 μ m guard column, 2 $\times$ 30 mm
Eluent	4.5 mM potassium carbonate, 2.0 mM potassium bicarbonate
Eluent source*	Dionex EGC 500 K ₂ CO ₃ cartridge with a Dionex EPM 500 pH modifier and Dionex EGC carbonate mixer
Flow rate	0.25 mL/min
Injection volume	5.0 μ L (full loop)
Column temperature	30 °C
Detection	Suppressed conductivity, Dionex AERS 500 Carbonate electrolytically regenerated suppressor, recycle mode, 9 mA current
Detection/Suppressor compartment temp.	30 °C
Cell temp.	30 °C
Background conductance	~24 μ S/cm
System backpressure	~2,600 psi (100 psi = 0.689 MPa)
Run time	12 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 M Ω -cm resistance or better
- Lithium hydroxide, Monohydrate (Powder, ACS Certified, e.g., Thermo Scientific Chemicals [P/N AC413321000](#))
- Sodium chloride (ACS, $\geq$ 99%, Ultrapure, e.g., Thermo Scientific Chemicals [P/N J21618.36](#))
- Sodium sulfate (99+%, for HPLC, anhydrous, e.g., Thermo Scientific Chemicals [P/N 194100500](#))

Preparation of solutions and reagents

Stock standard solutions (1,000 mg/L)

Stock standard solutions were prepared by dissolving the appropriate amounts of the required analytes in 100 mL of DI water, according to Table 1. The 1,000 mg/L standard solutions are also available from Thermo Fisher Scientific, and their part numbers are also listed in Table 1. Stock standards were stored at 4 °C.

Table 1. Masses of compounds used to prepare 100 mL of 1,000 mg/L anion standards

Analyte	P/N	Compound	Amount* (mg)
Chloride	037159	Sodium chloride (NaCl)	164.9
Sulfate	037160	Sodium sulfate (Na ₂ SO ₄)	147.9

*Compound must be dry.

Calibration standard solutions

Calibration standards were prepared by diluting the 1,000 mg/L stock standards with DI water (Table 2).

Table 2. Calibration standards (mg/L)

	Level					
	1	2	3	4	5	6
Chloride	0.02	0.1	0.5	1	5	10
Sulfate	0.02	0.1	0.5	1	5	10

Method detection limit (MDL) standards

The mixed standards containing low concentrations of chloride and sulfate were prepared for their estimated MDLs. The MDLs were determined using a mixed standard containing 0.01 mg/L chloride and 0.01 mg/L sulfate.

Sample preparation

Saturated lithium hydroxide

Saturated lithium hydroxide sample was prepared by adding excess lithium hydroxide monohydrate solid to DI water (~10 g/50 mL) and allowing it to dissolve overnight to reach saturation. The solubility of lithium hydroxide in water is 12.8 g/100 mL at 20 °C.¹

Lithium hydroxide sample

Saturated lithium hydroxide cannot be analyzed directly. It must be diluted before analysis. In-line sample preparation using a Thermo Scientific™ Dionex™ Guardcap™ H vial cap did not work due to the capacity of the cap.⁹ Here, we used a Dionex OnGuard II H cartridge as follows.

1. Before application of the sample, slowly (<2 mL/min) flush the Dionex OnGuard II H cartridge first with 10 to 15 mL of deionized (DI) water using a 5 mL syringe.
2. Push 5 to 10 mL of air to remove the DI water from the cartridge.
3. Prepare 10x diluted sample by mixing 1 part saturated lithium hydroxide with 9 parts DI water.
4. Push 4 mL of the 10x diluted sample from step 3 slowly (<2 mL/min) through the previously prepared Dionex OnGuard II H cartridge. Discard the first 2 mL. Collect the second 2 mL fraction for analysis.

Spiked samples

To evaluate method accuracy, two spiked samples were prepared by adding a known amount of mixed chloride and sulfate standard into the saturated lithium hydroxide solution. The spiked samples were also prepared through steps 1 to 4 above before analysis.

Results and discussion

Separation

The Dionex IonPac AS29-Fast-4 μ m column⁴ is a high-capacity anion-exchange column designed for the determination of anions, including chloride and sulfate, in aqueous samples using suppressed conductivity detection. It can be used in a variety of sample matrices including high pH, low pH, and high ionic strength matrices. The column is designed to be used with an isocratic carbonate/bicarbonate eluent, which can be prepared from concentrated eluent stock or produced by an electrolytic eluent generator.

Figure 2 shows a separation of chloride and sulfate within 12 min using a Dionex IonPac AS29-Fast-4 μ m column. Chloride and sulfate are well resolved. A carbonate dip at ~6 min is observed. The carbonate can appear as a dip or a peak depending on the relative carbonate concentration in the sample compared to the eluent. The dip observed here indicates that the carbonate concentration in the sample is lower than in the eluent. One of the advantages for the Dionex IonPac AS29-Fast-4 μ m column is that carbonate is well separated from all common anions, including chloride and sulfate.

Columns: Dionex IonPac AG29-Fast-4 μ m, 2 $\times$ 30 mm and Dionex IonPac AS29-Fast-4 μ m, 2 $\times$ 150 mm
Eluent: 4.5 mM K₂CO₃ / 2.0 mM KHCO₃
Flow rate: 0.25 mL/min
Inj. volume: 5.0 μ L (full loop)
Column temp.: 30 °C
Detection: Suppressed conductivity, Dionex AERS 500 Carbonate suppressor (2 mm), 30 °C, 9 mA, recycle mode

Sample: A. Mixed standard (blue trace)
B. 10x diluted saturated lithium hydroxide (gray trace)

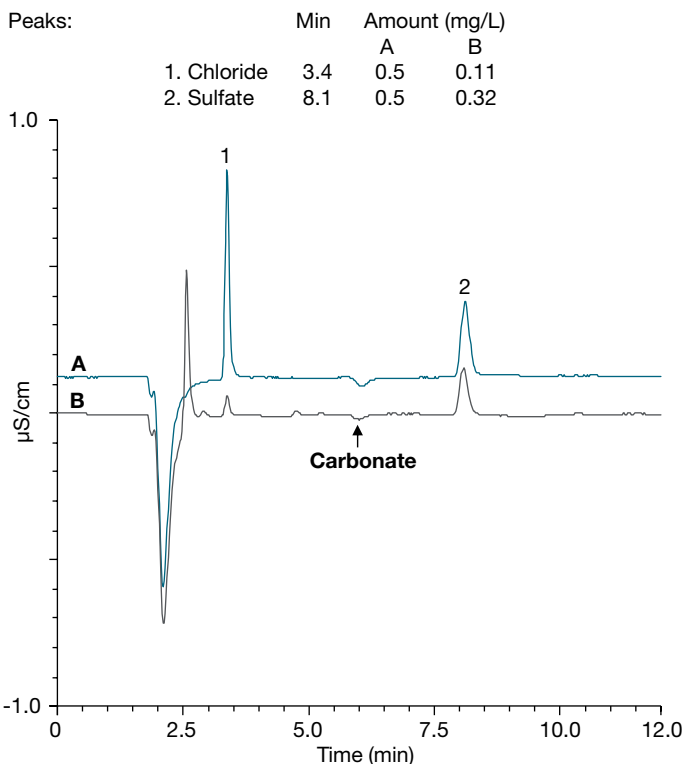


Figure 2. Chromatograms of a mixed standard and a lithium hydroxide sample

Using manually prepared eluent, the anion impurities in the concentrated eluent stock will cause interference, a dip or peak at the retention time of the impurity. To avoid the interferences caused by chloride and sulfate impurities in the eluent, a RFIC system to generate high purity eluent is recommended for this application.

Linearity and method detection limits (MDLs)

The six-point calibrations for chloride and sulfate were evaluated (Table 2). MDLs were determined by performing seven replicate injections of standards at a concentration less than ten times the estimated MDLs. The MDLs for saturated lithium hydroxide were determined by multiplying the method MDLs by ten.

Table 3 shows the retention times, linear concentration ranges, the coefficients of determination (r^2), and calculated MDLs for chloride and sulfate. The method shows linear relationships (Figure 3) of peak area to concentration in the chosen calibration ranges with coefficients of determination (r^2) of 0.9992 for chloride and 0.9999 for sulfate. The method is sensitive for the determination of chloride and sulfate in saturated lithium hydroxide with low MDLs (0.09 mg/L for chloride and 0.13 mg/L for sulfate).

Chloride and sulfate in lithium hydroxide

Chloride and sulfate were determined in the saturated lithium hydroxide solution (Figure 2 and Table 4). This saturated lithium hydroxide solution contains 1.1 mg/L chloride and 3.2 mg/L sulfate.

Method precision and accuracy

The method precision and accuracy were evaluated by spiking chloride and sulfate in the saturated lithium hydroxide solution (Table 5). The method is precise (RSD range 1–6%) and accurate (recovery range 91–102%).

Table 3. Linearity, method detection limit (MDL), and retention time obtained using a Dionex IonPac AS29-Fast-4 μ m column with a 5.0 μ L injection

Analyte	Retention time (min)	Range (mg/L)	Coefficient of determination (r^2) (n=3)	Calculated * MDL (mg/L)	Calculated MDL in saturated lithium hydroxide (mg/L)
Chloride	3.4	0.02–10	0.9992	0.009	0.09
Sulfate	8.1	0.02–10	0.9999	0.013	0.13

* MDL = (t) $\times$ (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

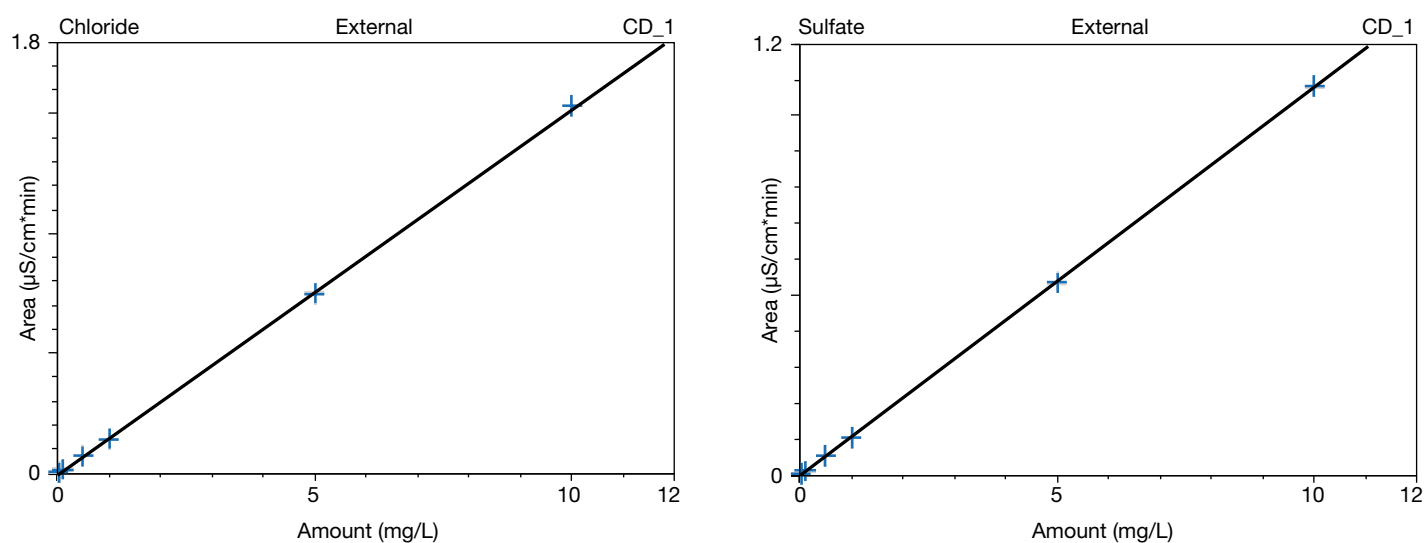


Figure 3. Calibration plots

Table 4. Chloride and sulfate in the saturated lithium hydroxide solution

Analyte	RT (min)	Average (mg/L)	RSD
Chloride	3.3	1.1	4
Sulfate	8.1	3.2	2

* n=3

Table 5. Spike recovery of chloride and sulfate in saturated lithium hydroxide

	Added (mg/L)	Recovery (%)	RSD	Added (mg/L)	Recovery (%)	RSD
Chloride	2	91	2	10	102	1
Sulfate	2	97	6	10	99	3

Conclusion

This application note describes a method for the determination of chloride and sulfate in saturated lithium hydroxide solution using an RFIC system with a 2 mm version of a Dionex IonPac AS29-Fast-4 μ m column. The method is sensitive (MDL = 0.09 mg/L for chloride and 0.13 mg/L for sulfate in saturated lithium hydroxide solution), precise (RSD range = 1–6%), and accurate (recovery range = 91–102%).

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