

# Determination of Dissolved Manganese in Lithium/Manganese Oxide Battery Electrolyte

Chanita Chantarasukon,<sup>1</sup> Suparek Tukkeeree,<sup>1</sup> and Jeff Rohrer<sup>2</sup>

<sup>1</sup>Thermo Fisher Scientific, Bangkok, Thailand; <sup>2</sup>Thermo Fisher Scientific, Sunnyvale, CA USA

## Key Words

Lithium-Ion Battery, Cathode, Dionex IonPac CS12A Column, Reagent-Free Ion Chromatography System

## Introduction

Lithium-ion batteries are widely used in products such as portable consumer electronic devices and electric vehicles. Many different materials are used to make the cathode in lithium batteries, including those that are manganese-, cobalt-, and nickel-based. Lithium-ion batteries that are manganese-based are more environmentally friendly, have a good safety record, and can be made at a lower cost; however, they have a shorter lifetime than other types of lithium-ion batteries. One of the reported causes of lifetime loss is the dissolution of manganese from the cathode into the electrolyte during cycling (i.e., charging/discharging). Lithium/lithium manganese oxide (Li/LiMn<sub>2</sub>O<sub>4</sub>) is a type of battery that has a manganese-based cathode.

In Thermo Scientific Application Note (AN) 258, ion chromatography (IC) was applied to determine the anions tetrafluoroborate, perchlorate, and hexafluorophosphate in a simulated electrolyte solution for lithium-ion batteries.<sup>1</sup> AN 258 used a Reagent-Free™ IC (RFIC™) system, and it is also possible to use an RFIC system to determine manganese in a simulated electrolyte solution for lithium-ion batteries. There is one report of an IC method that uses manually prepared eluents and direct conductivity detection to determine dissolved manganese in the electrolyte of a Li/LiMn<sub>2</sub>O<sub>4</sub> battery.<sup>2</sup> However, that method has poor sensitivity, which is inherent with direct conductivity detection. Even with a three-component (tartaric acid, dipicolinic acid, and ascorbic acid) mobile phase, the manganese peak exhibits extreme tailing on the chosen column. A better IC cation column will improve peak shape and therefore improve integration precision and method accuracy, while suppressed conductivity detection will improve method sensitivity.



The work shown here uses an RFIC system with suppressed conductivity detection to quantify dissolved manganese in the simulated electrolyte of a Li/LiMn<sub>2</sub>O<sub>4</sub> battery. The method uses the Thermo Scientific™ Dionex™ IonPac™ CS12A column set, which was designed to deliver good peak shapes for cations such as manganese(II) (Mn<sup>2+</sup>), with a simple methanesulfonic acid (MSA) eluent produced by an eluent generator. The combination of the RFIC system and a quality IC column yields a method that is sensitive, accurate, reproducible, and easy to execute, requiring only the addition of deionized water to the RFIC system.

## Goal

To develop an IC method that accurately determines dissolved manganese in the electrolyte of a Li/LiMn<sub>2</sub>O<sub>4</sub> battery using an RFIC system

## Equipment

- Thermo Scientific Dionex ICS-2100 Integrated RFIC system,\* including a Thermo Scientific Dionex AS-AP Autosampler
- Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data System (CDS) software version 6.80, SR9 or higher

\*Any Thermo Scientific RFIC system may be used.

## Reagents and Standards

- Deionized (DI) water (H<sub>2</sub>O), Type I reagent grade, 18 M -cm resistivity or better
- Ethylene Carbonate (C<sub>3</sub>H<sub>4</sub>O<sub>3</sub>), 99% (Fisher Scientific P/N 50-700-5617)
- Ethyl Methyl Carbonate (C<sub>4</sub>H<sub>8</sub>O<sub>3</sub>), 99% (Sigma-Aldrich® P/N 754935)
- Vinylene Carbonate (C<sub>3</sub>H<sub>2</sub>O<sub>3</sub>), 97% (Fisher Scientific P/N 50-751-1840)
- Lithium Hexafluorophosphate (LiPF<sub>6</sub>), 98% (Fisher Scientific P/N 21324-40-3)
- Manganese(II) Sulfate, Monohydrate (MnSO<sub>4</sub>·H<sub>2</sub>O) (Fisher Scientific P/N 10034-96-5)

## Preparation of Solutions and Reagents

### Mixture of Ethylene Carbonate and Ethyl Methyl Carbonate, 1:1 (w/v)

Dissolve 10 g of ethylene carbonate in 10 mL of ethyl methyl carbonate.

### Manganese Stock Standard Solution, 1000 mg/L

Place 0.308 g of manganese(II) sulfate monohydrate in a 100 mL volumetric flask, dissolve in DI water, bring to volume with DI water, and mix.

### Working standard solution

Add the appropriate volumes of 1000 mg/L manganese stock standard solution into separate 100 mL volumetric flasks, bring to volume with DI water, and mix. The volumes of manganese stock standard solution used for the preparation of working standard solutions are shown in Table 1.

Table 1. Preparation of working standards.

Level	Volume of Manganese Stock Solution (1000 mg/L) Used for a 100 mL Preparation (mL)	Concentration (mg/L)
1	0.010	0.10
2	0.020	0.20
3	0.040	0.40
4	0.080	0.80
5	0.100	1.00

## Sample Preparation

### Preparation of a Simulated Sample

Prepare 1.12 M of LiPF<sub>6</sub> and 2 wt % of vinylene carbonate in the mixture of ethylene carbonate and ethyl methyl carbonate by placing 1.7 g of LiPF<sub>6</sub> and 0.2 g of vinylene carbonate in a 10 mL volumetric flask; dissolve, then bring to volume with the mixture of ethylene carbonate and ethyl methyl carbonate. Prepare a 1 to 50 dilution of this simulated sample using DI water prior to injection. This is the same dilution used in the published method.<sup>2</sup>

### Spiked Sample Simulation

Prepare 5 mg/L of manganese, 1.12 M of LiPF<sub>6</sub>, and 2 wt % of vinylene carbonate in the mixture of ethylene carbonate and ethyl methyl carbonate by placing 1.7 g of LiPF<sub>6</sub>, 0.2 g of vinylene carbonate, and 50 µL of 1000 mg/L manganese stock standard solution in a 10 mL volumetric flask; dissolve, then bring to volume with the mixture of ethylene carbonate and ethyl methyl carbonate. Prepare a 1 to 50 dilution of this spiked simulated sample using DI water prior to injection.

## Chromatographic Conditions

Columns:	Dionex IonPac CG12A Guard, 4 × 50 mm (P/N 046074) Dionex IonPac CS12A Analytical, 4 × 250 mm (P/N 046073)
Eluent Source:	Thermo Scientific Dionex EGC III MSA Eluent Generator Cartridge (P/N 074535) with Thermo Scientific Dionex CR-CTC II Continuously Regenerated Cation Trap Column (P/N 066262)
Eluent Concentration:	20 mM MSA
Flow Rate:	1.0 mL/min
Inj. Volume:	20 µL
Temperature:	35 °C
Detection:	Suppressed Conductivity, Thermo Scientific™ Dionex™ CSRS™ 300 Cation Self-Regenerating Suppressor, 4 mm (P/N 064556), Recycle Mode, Current 60 mA
Total Conductivity:	~0.34 µS

Analyte	Concentration (mg/L)					Calibration Results			
	Level 1	Level 2	Level 3	Level 4	Level 5	Points	r <sup>2</sup>	Offset	Slope
Manganese	0.1	0.2	0.4	0.8	1.0	15	0.9997	-0.0046	0.1617

## Results and Discussion

### Separation

Manganese is a divalent cation that can be separated from six common cations using the Dionex IonPac CS12A column set with isocratic elution. As shown in Figure 1, manganese is well separated from the other common divalent cations—magnesium and calcium—using a 20 mM MSA eluent. Figure 1 also shows that manganese is well resolved from other common cations. Note the good peak shape for manganese and the other cations. The MSA eluent is automatically produced by pumping DI water through the eluent generator cartridge with the concentration controlled by Chromeleon CDS software.

### Method Calibration

The method was calibrated before sample analysis using five concentrations of manganese ranging from 0.1 to 1.0 mg/L. The method showed a linear relationship between analyte concentration and peak area of manganese. The coefficient of determination ( $r^2$ ) for the line was 0.9997. Figure 2 shows the overlay of chromatograms of the working (calibration) standards, and Table 2 shows the concentrations of the working standards and the calibration result. Note that a 20  $\mu$ L injection of the 0.1 mg/L standard produced a peak of significant size and good peak shape, whereas the nonsuppressed method in Reference 2 produced a small tailing peak for a 1 mg/L standard (though only a 10  $\mu$ L injection). This highlights the expected sensitivity benefit of using suppressed rather than nonsuppressed conductivity detection.

Columns: Dionex IonPac CS12A Guard, 4  $\times$  50 mm  
 Dionex IonPac CG12A Analytical, 4  $\times$  250 mm  
 Eluent Source: Dionex EGC III MSA Cartridge with Dionex CR-CTC Column  
 Eluent: 20 mM MSA  
 Flow Rate: 1.0 mL/min  
 Inj. Volume: 20  $\mu$ L  
 Temperature: 35  $^{\circ}$ C  
 Detection: Suppressed Conductivity, Dionex CSRS 300 Suppressor,  
 4 mm, Recycle mode, Current 60 mA  
 Sample: Standard Mixture

Peaks: 1. Lithium 1.0 mg/L  
 2. Sodium 1.0  
 3. Ammonium 1.0  
 4. Potassium 1.0  
 5. Magnesium 1.0  
 6. Manganese 1.0  
 7. Calcium 1.0

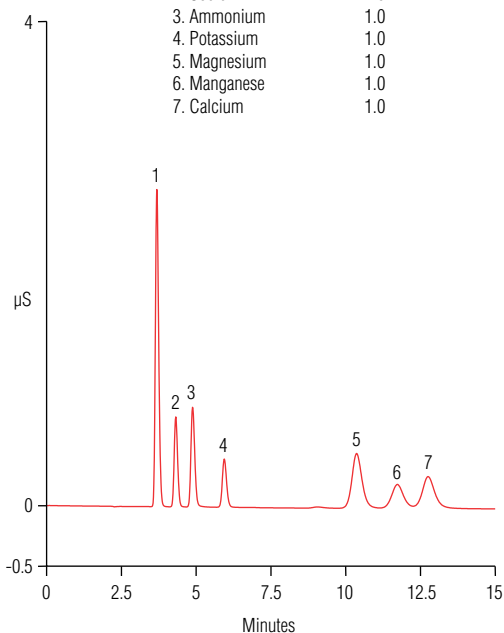


Figure 1. Chromatogram of a standard containing six common cations and manganese.

Columns: Dionex IonPac CS12A Guard, 4  $\times$  50 mm  
 Dionex IonPac CG12A Analytical, 4  $\times$  250 mm  
 Eluent Source: Dionex EGC III MSA Cartridge with Dionex CR-CTC Column  
 Eluent: 20 mM MSA  
 Flow Rate: 1.0 mL/min  
 Inj. Volume: 20  $\mu$ L  
 Temperature: 35  $^{\circ}$ C  
 Detection: Suppressed Conductivity, Dionex CSRS 300 Suppressor,  
 4 mm, Recycle mode, Current 60 mA  
 Sample: Calibration Standard

Peak: 1. Manganese 0.1, 0.2, 0.4, 0.8, and 1.0 mg/L

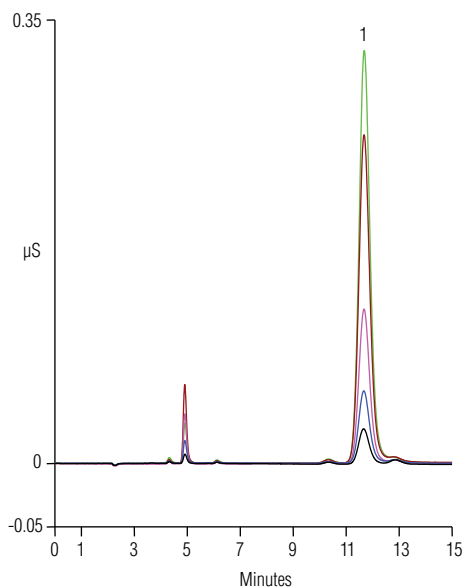


Figure 2. Overlay of chromatograms of the calibration standards.

## Sample Analysis

An electrolyte sample was simulated as described in the Sample Preparation section and diluted 1 to 50 with DI water. Five sample injections were made and, as expected, no manganese was found in the simulated sample. A sample was then prepared to simulate manganese cathode dissolution in the electrolyte. This simulated sample had a manganese concentration of 0.1 mg/L after dilution. Five injections of the diluted spiked simulated sample were made to quantify manganese. The measured concentrations were then compared to the prepared concentration. This analysis yielded a manganese recovery of 103% with an RSD of 0.15% (Table 3).

Figure 3 shows the overlay of chromatograms of the simulated and spiked simulated samples. Note that the magnesium and calcium peaks—eluting before and after manganese, respectively—do not interfere with the quantification of manganese. Overall, the results indicate that this is an accurate and reproducible method for determining manganese in Li/LiMn<sub>2</sub>O<sub>4</sub> battery electrolyte.

## Conclusion

This study demonstrates an accurate and reproducible IC method that uses suppressed conductivity detection to determine manganese in the simulated electrolyte of a Li/LiMn<sub>2</sub>O<sub>4</sub> battery. The method uses an RFIC system and requires only 15 min per analysis with a simple isocratic separation using an MSA eluent. The eluent is produced by an eluent generator to preclude the labor and potential error associated with eluent preparation.

## References

1. Thermo Scientific Application Note 258: Determination of Tetrafluoroborate, Perchlorate, and Hexafluorophosphate in a Simulated Electrolyte Sample from Lithium Ion Battery Production. Sunnyvale, CA, 2010. [Online] [www.dionex.com/en-us/webdocs/88116-AN258-IC-Lithium-Battery-AN70399\\_E.pdf](http://www.dionex.com/en-us/webdocs/88116-AN258-IC-Lithium-Battery-AN70399_E.pdf) (accessed Apr. 5, 2013).
2. Doh, C.; Lee, J.; Lee, D.; Jin, B.; Moon, S. The Quantitative Analysis of the Dissolved Manganese in the Electrolyte of Li/LiMn<sub>2</sub>O<sub>4</sub> Cell Using by Ion Chromatography. *Bull. Korean Chem. Soc.* **2009**, *30* (10), 2429–2432.

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Dionex IonPac CG12A Analytical, 4 × 250 mm  
Eluent Source: Dionex EGC III MSA Cartridge with Dionex CR-CTC Column  
Eluent: 20 mM MSA  
Flow Rate: 1.0 mL/min  
Inj. Volume: 20 µL  
Temperature: 35 °C  
Detection: Suppressed Conductivity, Dionex CSRS 300 Suppressor, 4 mm, Recycle mode, Current 60 mA  
Samples: Sample  
Spiked Sample

Peak: 1. Manganese 0.1033 mg/L

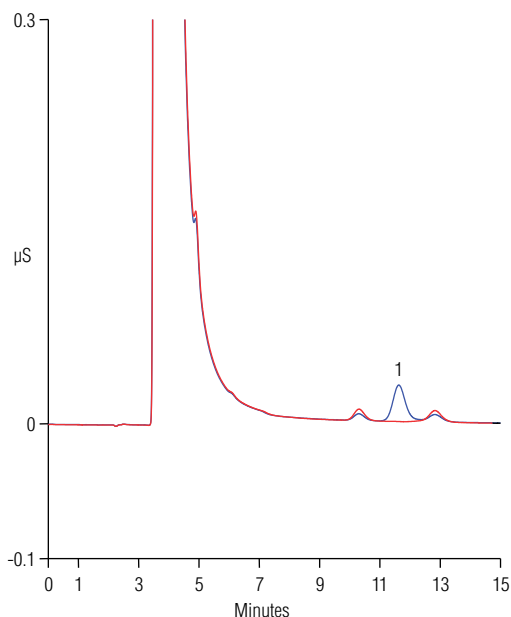


Figure 3. Overlay of chromatograms of unspiked and spiked samples.

Table 3. Sample and spiked sample results.

Injection No.	Amount in Sample (mg/L)	Amount in Spiked Sample, Spiked Conc 0.1 mg/L (mg/L)
1	ND	0.1030
2	ND	0.1034
3	ND	0.1033
4	ND	0.1034
5	ND	0.1033
<b>Average</b>	ND	<b>0.1033</b>
<b>RSD (%)</b>	—	<b>0.15</b>
<b>Recovery (%)</b>	—	<b>103</b>

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