



Determination of Solvents and Additives in Lithium-Ion Battery Electrolytes Using GC/MS

Abstract

Gas chromatography – mass spectrometry (GC/MS) is a powerful instrument for analyzing complex matrices. This publication illustrates the use of Chromatec Crystal 9000 GC/MSD system for analysis of lithium-ion battery electrolyte composition. Good resolution, identification, and quantification for all compounds was obtained.

Introduction

Fossil fuels are the main source of energy. However, they create a complex series of environmental and economic problems. These reasons require a global effort to explore all the means to exploit renewable energy resources such as wind, sun, and water. Although, the use of such resources seems very attractive, there is a huge obstacle, since the energy obtained from renewable sources is not permanent. To solve this problem, the development of energy storage devices is becoming an integral part of the future transition to energy supply. Electric vehicles are an example of such a transition, where zero emission transportation is realized by moving away from combustion engines.

Lithium-ion batteries (LIBs) are the most important electrochemical energy storage devices due to their high energy density, long cycle life, and low cost. One of the critical elements of LIBs is the electrolyte, which is a solution of a lithium salt in a polar, organic, aprotic solvent.

Generally an ideal electrolyte solvent should meet the following criteria:

- be able to dissolve lithium salts to sufficient concentration,
- its viscosity should be low to enable fast ion transport and efficient (quick) filling of a commercial cell on a production line,
- be inert to all cell components especially positive and negative electrode materials,
- have sufficient wettability towards the electrodes and the separator,
- it should remain liquid in a wide temperature range.

Choosing the right solvent to meet all requirements is not an easy task. Cyclic organic carbonates, such as

ethylene carbonate and propylene carbonate, offer high dielectric constant and form low energy complexes with lithium cations. The problem is that these solvents are characterized by high viscosity and fairly high melting point, so ethylene carbonate is solid at room temperature. In order to circumvent this issue, acyclic alkyl carbonates, organic ethers and esters are usually added because they offer low viscosities and melting points. However, their dielectric constant is also low and so are their boiling and flash points, thus limiting the safety margin of the practical cell. Given the lack of better alternatives – mixtures of organic compounds are the solvents of choice for the commercial cells [1].

Electrolytes for LIBs contain various additives, e.g., vinylene carbonate or 1,3-propane sultone that promote the formation of an insoluble film between the electrolyte and the negative electrode – solid-electrolyte interface (SEI). This polymer film allows ionic conduction, but prevents electrolyte reduction at the negative electrode and contributes significantly to the long-term stability of lithium-ion batteries [2].

In this work the use of Chromatec Crystal 9000 GC/MSD system for determination of solvents and additives in LIB electrolytes is described.

Equipment

- Chromatec Crystal 9000 GC/MSD
- Autosampler AS-2M
- Liner FocusLiner™
- Capillary column DB-210 (30 m × 0.25 mm × 0.5 μm)

Instrument conditions

GC			
Analysis time	23 min		
Column			
Carrier gas	Helium		
Constant flow	1.0 mL/min		
Column temperature	45 °C	1 min	10 °C/min
	200 °C	6.5 min	
Inlet			
Temperature	200 °C		
Injection mode	Split		
Split ratio	1:20		
Septum purge flow	3 mL/min		
MSD			
Scan mode	t-SIM + Full Scan		
Mass range	35 – 350		
Ion source temperature	200 °C		
Transfer line temperature	200 °C		
AS			
Injection volume	1 µL		

Experimental

A stock solution of different solvents and additives was diluted in dichloromethane to a concentration of 1,000 mg/L. Seven calibration solutions (0.1, 1.0, 7.5,

12.5, 25, 50, and 100 mg/L) were prepared by serial dilution in dichloromethane.

It is known [3] that lithium salts, such as lithium hexafluorophosphate (LiPF₆), are destructive to the GC column; therefore, direct liquid injection of electrolyte samples should be avoided. There are two approaches for removing lithium salts. The first is centrifugation and the second is dilution to reduce column degradation and change retention times.

Samples were prepared by diluting 10 µL of LIB electrolyte in 10 mL dichloromethane. The solution was centrifuged for 10 min at 5000 rpm. The supernatant was diluted 1:10 with dichloromethane and taken for GC/MS analysis.

Results and discussion

The total ion chromatogram of the calibration mixture is shown in Figure 1. The compounds are listed in Table 1. All analytes resolved in less than 20 min. The use of a DB-210 capillary column provides excellent separations, including some critical pairs. The resolution *R*_s of propyl propionate and diethyl carbonate is 3.8, ethylene carbonate and propylene carbonate is 6.5.

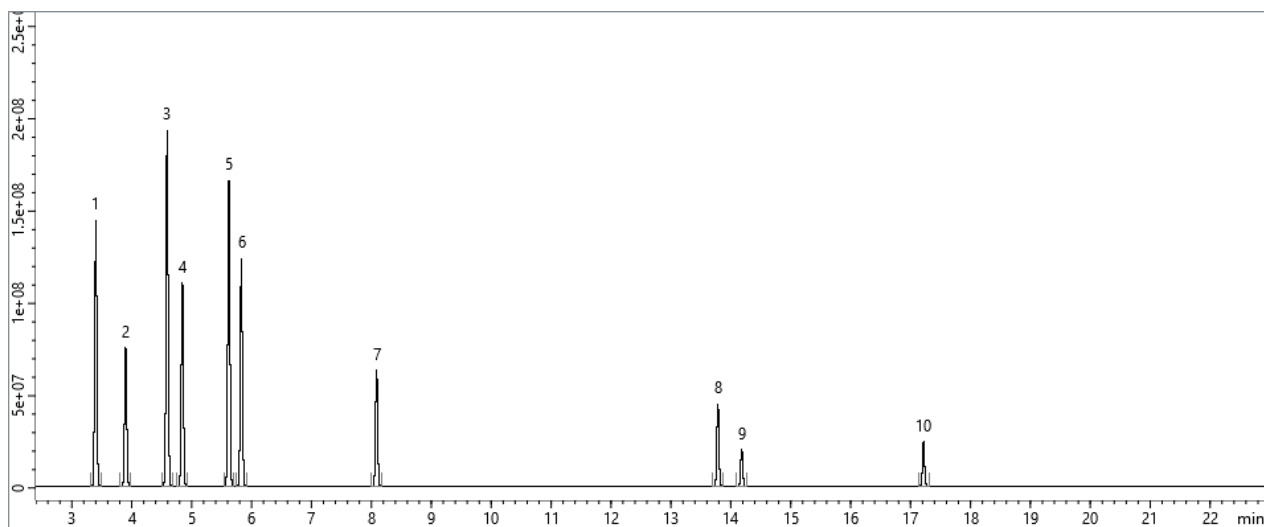


Figure 1. Total ion chromatogram of the LIB electrolyte standard at 100 mg/L

Table 1. Retention time, quantitation and qualitative ions, linearity for the analytes

Compound	Retention time (min)	Quantitation ion	Qualitative ions	Linear range (mg/L)	Coefficient of determination (R ²)
1. Ethyl acetate	3.39	43	61, 88	0.1 – 50	0.9989
2. Dimethyl carbonate	3.89	59	45, 90	0.1 – 100	0.9997
3. Propyl acetate	4.58	61	43, 73	0.1 – 50	0.9986
4. Ethyl methyl carbonate	4.84	77	45, 59	0.1 – 100	0.9997
5. Propyl propionate	5.61	57	75, 87	0.1 – 100	0.9993
6. Diethyl carbonate	5.83	91	45, 63	0.1 – 100	0.9991
7. Vinylene carbonate	8.07	86	42, 58	0.1 – 100	0.9994
8. Ethylene carbonate	13.78	88	43, 58	0.1 – 100	0.9987
9. Propylene carbonate	14.18	57	43, 87	0.1 – 100	0.9996
10. 1,3-Propane sultone	17.21	58	57, 122	0.1 – 100	0.9984

Calibration curves for carbonates and additives showed good linearity for concentrations ranging from 0.1 to 100 mg/L, for ethyl acetate and propyl acetate between

0.1 and 50 mg/L. Table 1 summarizes determination coefficients (R^2) for each component. The R^2 value for all compounds was above 0.998. Figure 2 displays the calibration curves of some compounds.

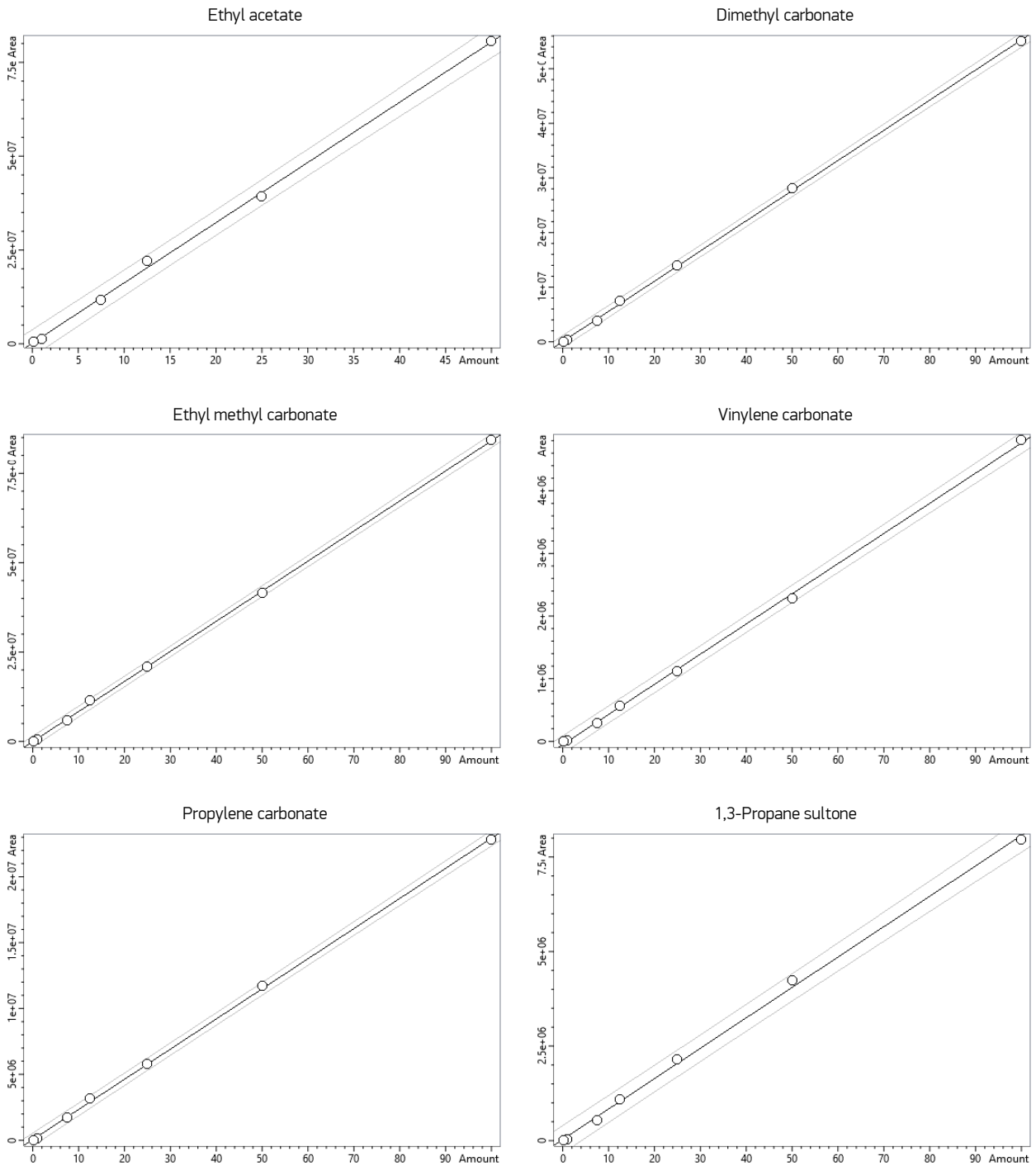


Figure 2. Calibration curves for some compounds in this study

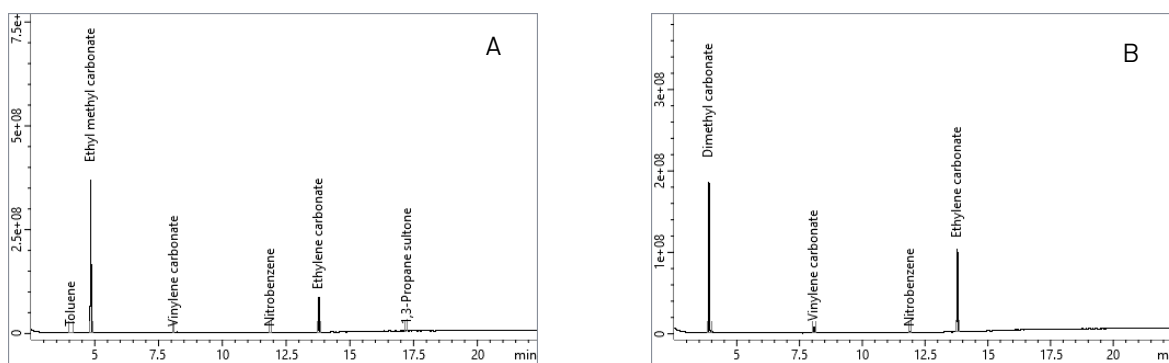


Figure 3. Total ion chromatograms of LIB electrolyte samples

Analysis of two LIB electrolyte samples demonstrated ethylene carbonate as the major compound (Figure 3). The difference between the two samples is in linear alkyl carbonates, one contains dimethyl carbonate, the other ethyl methyl carbonate. Vinylene carbonate and 1,3-propane sultone were found as additives in the samples.

Using GC/MS in full scan mode enable identification of unknown solvents, additives, and impurities in commercial products. Thus, toluene and nitrobenzene were found in the studied electrolyte samples (Figure 3).

Conclusion

This application demonstrates the capability of the Chromatec Crystal 9000 GC/MSD system to analyze lithium-ion battery electrolyte composition. The method demonstrates excellent resolution, sensitivity and linearity. The GC/MS is a powerful tool for qualitative and quantitative analysis of solvents and additives in electrolyte solutions.

References

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