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Qualitative and Quantitative Analysis of Carbonate Organic Solvents in Lithium Battery Electrolysis by LC/Q-TOF

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Introduction

In recent years, the issue of energy development has attracted worldwide attention. The development and application of lithium batteries has especially become one of the key high-tech developments in the field of new energy. Lithium batteries are mainly composed of positive and negative electrode materials, an electrolyte, and a separator. Organic solvent is also an important part of lithium battery electrolytes.

Common organic solvents in the electrolyte are mainly carbonate compounds, such as EC, PC, EMC, and DMC. Their structural formulas are shown in Figure 1. Solvent components with different ratios directly affect battery performance, so it is of great significance to analyze and study carbonate solvents in lithium batteries.

In this study, we used the Agilent 1290 Infinity II UHPLC with the Agilent 6546 LC/Q-TOF MS system to identify and analyze four carbonate organic solvents in the electrolyte, and to perform quantitative analysis of EC and PC solvents in three electrolyte samples. The method is simple, fast, efficient, and quantitatively accurate, and provides reliable technical support for qualitative and quantitative analysis of carbonate organic solvents in lithium battery electrolytes.

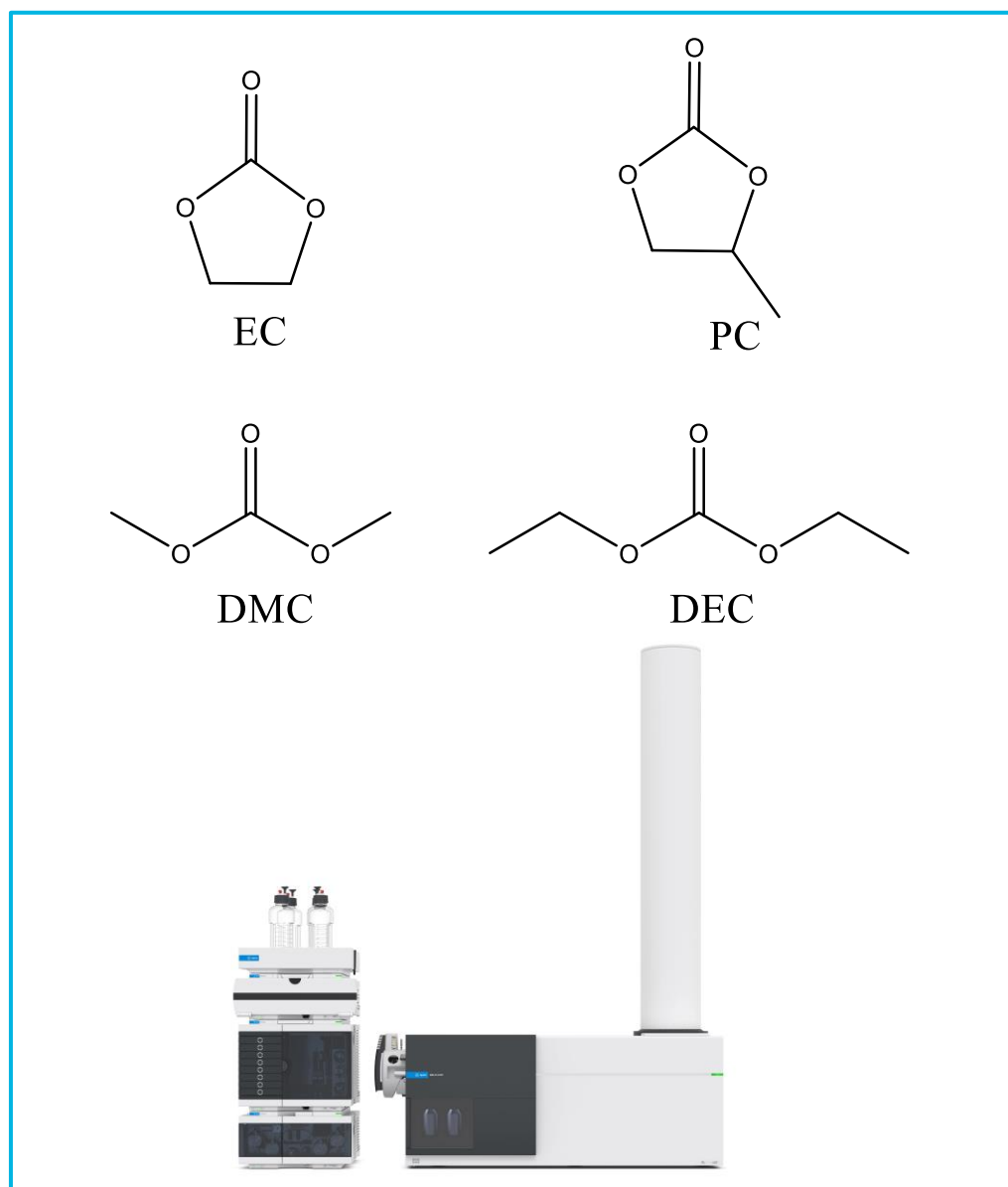


Figure 1. Structural formula of four carbonate organic solvents.

Experimental

Sample preparation

The sample is lithium battery electrolyte, provided by a user. It was diluted with acetonitrile in a certain proportion, and directly injected for analysis after filtration.

Preparation of standard curve

EC and PC stock solutions at 100 $\mu\text{g}/\text{mL}$ were accurately prepared and dissolved in pure acetonitrile. Pure acetonitrile was used to dilute the stock solution step-by-step, to prepare a series of standard working solutions with concentrations of 50, 200, 500, 1000, and 2000 ng/mL (respectively), and to make a standard curve.

Instrumentation

The UHPLC LC/Q-TOF system consists of the Agilent 1290 Infinity II binary pump, autosampler, TCC, and 6546 LC/Q-TOF with Dual Agilent Jet Stream. The UHPLC LC/Q-TOF experimental conditions are listed in Table 1.

UHPLC Q-TOF Conditions

Column	Agilent InfinityLab Poroshell 120 Bonus-RP, 3.0 \times 100 mm, 2.7 μm (p/n: 695968-301(T))	
Mobile Phase	A= Water containing 0.1% formic acid B= Methanol	
Flow Rate	0.4 mL/min	
Column Temperature	35 $^{\circ}\text{C}$	
Injection Volume	2 μL	
Gradient Program	Time (min)	B (%)
	0.00	0
	1.00	0
	8.00	50
	10.0	100
	12.0	100
Post Time	3 min	
AJS ESI source	-Ion mode: positive -Capillary voltage: 2500 V -Nozzle voltage: 500 V -Drying gas: 8 L/min at 250 $^{\circ}\text{C}$ -Sheath gas: 12 L/min at 350 $^{\circ}\text{C}$ -Nebulizer: 45 psi -Fragmentor: 70 V -MS scan: 20-1000 m/z	

Structural identification of carbonate organic solvents

The Agilent InfinityLab Poroshell 120 Bonus-RP column can withstand the 100% aqueous mobile phase system, which is beneficial for enhancing retention and separation of such polar solvents on the chromatographic column. Figure 2 shows base peak chromatograms of four carbonate compounds in lithium battery electrolyte. The Agilent 6546 time-of-flight high resolution mass spectrometer was used to acquire the primary and secondary mass spectrometry data of the main chromatographic peaks. Combined with searching the Agilent PCDL database and Agilent MassHunter Molecular Structure Correlator (MSC) software to analyze unknown substances, four main organic solvents in lithium battery samples, including EC, PC, DMC, and EMC, were identified.

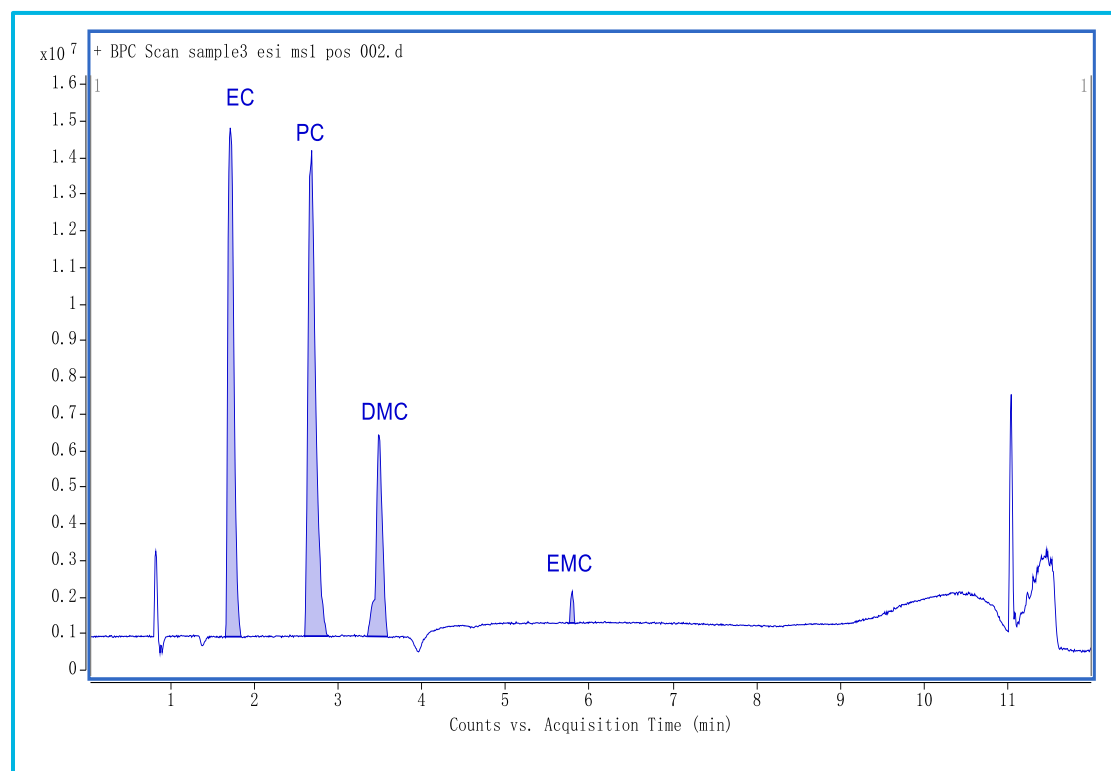


Figure 2. Base peak chromatograms of four carbonate organic solvents in lithium battery electrolyte.

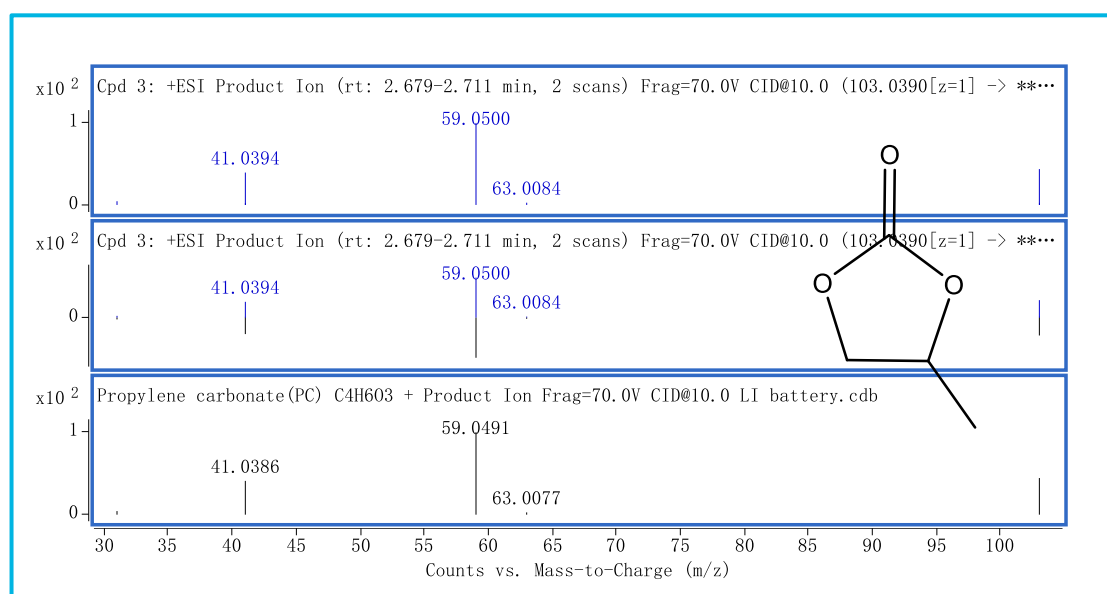


Figure 3. The matching comparison between the fragmentation spectrum of PC and the PCDL database.

Identification by searching the PCDL database

Searching the PCDL database to match compounds is an important and standard means of analyzing unknowns in high-resolution mass spectrometry. Figure 3 shows that with a collision energy of 10 eV, more than 90% of the matching score can be obtained. The image comparison chart of the measured fragment data and the PCDL fragment data is visually displayed, indicating that the result is accurate and reliable.

Identification using MSC software

Agilent MSC software can automatically generate molecular formulas based on primary and fragment data of unknowns. It can simultaneously link ChemSpider or existing PCDL databases to search and match one or more possible compound structures, to help deduce the structure of unknowns. In addition, MSC software can perform secondary fragment attribution analysis according to compound structure. Figure 4 shows the analysis results of EC identification using MSC software.

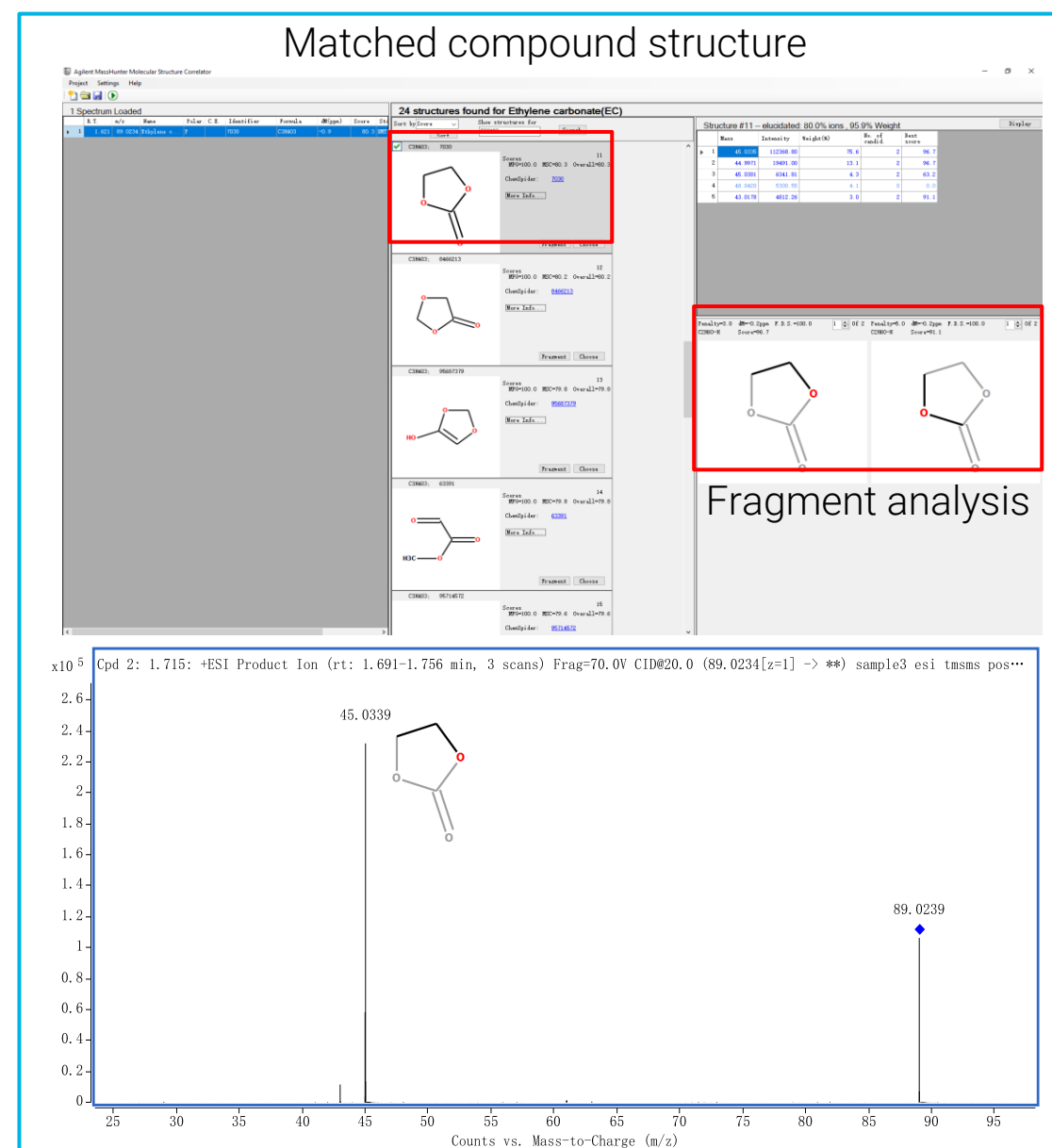


Figure 4. Identification results of EC using MSC software.

Quantitative analysis of carbonate organic solvents

High-resolution mass spectrometry captures accurate masses of compounds, reducing the effects of interfering substances. Primary mass spectrometry data was obtained in Q-TOF full-scan acquisition mode, and the characteristic ions of the corresponding compounds were extracted. These can be used for quantitative analysis of target compounds. Figure 5 shows that EC and PC have good linearity in the concentration range of 50-2000 ng/mL, and the linear correlation coefficients are $R^2 > 0.99$, respectively, indicating that this method can be accurately used for the quantitative analysis of EC and PC compounds.

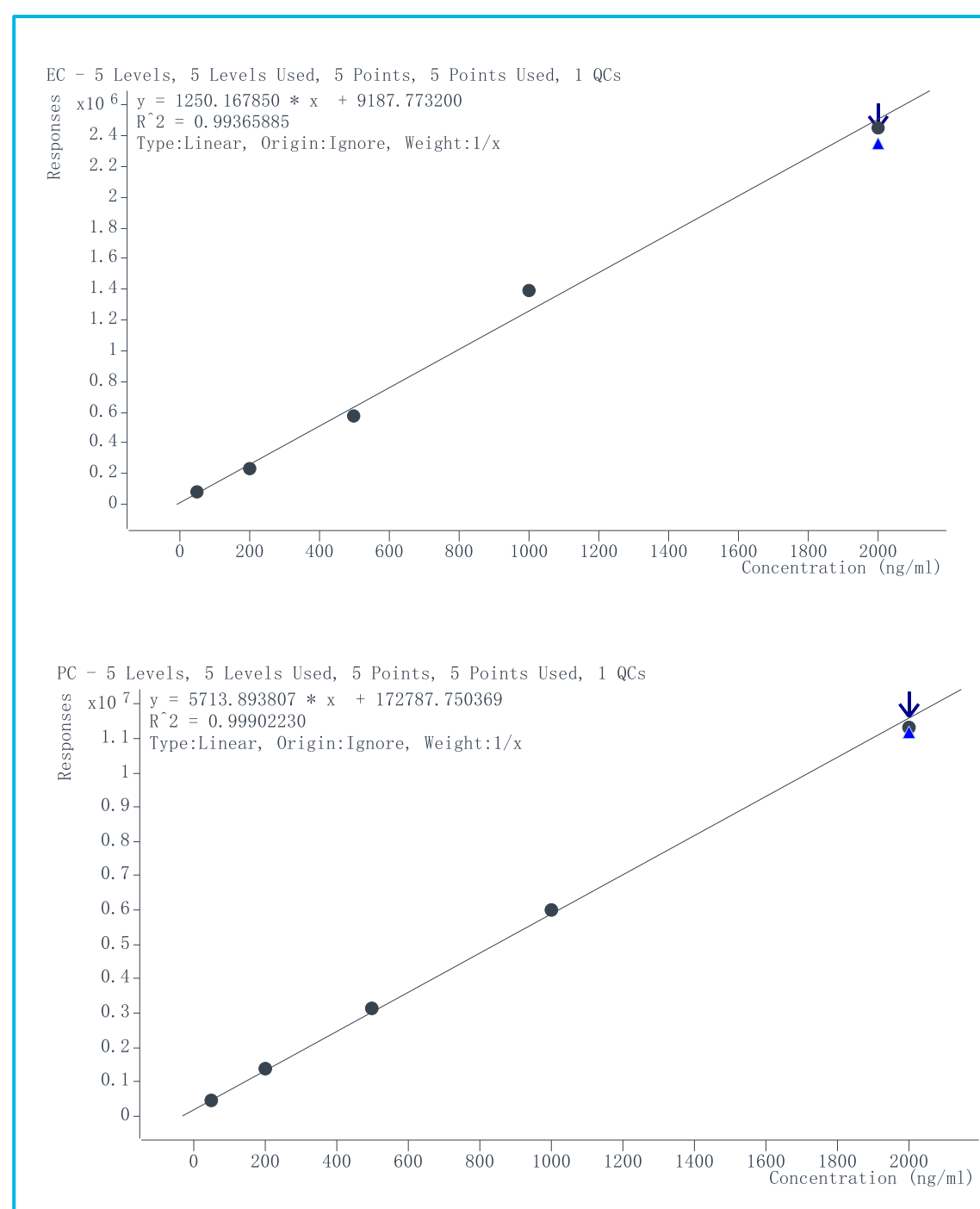


Figure 5. The standard curve of the concentration of EC and PC between 50 and 2000 ng/mL

Quantitative EC and PC analyses were performed on three battery electrolyte samples by using this experimental method. Samples were tested after dilution with acetonitrile. The results are shown in Table 2. The concentration of EC in all three samples was 2-5 times higher than that of PC. This data can provide a reliable basis for optimizing the organic solvent ratio of the battery electrolyte and improving battery performance.

Quantitative results of EC and PC in battery electrolyte samples, $\mu\text{g/mL}$

Sample No.	EC	PC
1	2.0×10^5	1.1×10^5
2	2.5×10^5	5.0×10^4
3	2.6×10^5	5.0×10^4

Conclusion

Using liquid chromatography quadrupole time-of-flight high resolution mass spectrometry to analyze the organic solvent components of carbonate in lithium batteries, we successfully identified four main organic solvents: EC, PC, DMC, and EMC.

We established a method for the quantitative analysis of EC and PC in lithium battery electrolytes using LC/Q-TOF.