

Determination of Carbonate Solvents and Additives in Lithium Battery Electrolyte Using the Agilent 5977B GC/MSD

Authors

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Abstract

This application note describes a method for determining carbonate solvents and additives in lithium battery electrolyte using the Agilent 5977B single quadrupole gas chromatography/mass selective detector (GC/MSD). In this method, direct liquid injection is adopted. At a split ratio of 20:1, the target compounds achieved good linearity in a concentration range of 10–500 mg/L. This method has excellent reproducibility, and the instrument detection limits (IDL) for all of the 15 target compounds analyzed were below 1.3 mg/L. During the analysis of the actual electrolyte samples, diluted injection can be used to accurately quantify the target compounds and qualitatively identify unknown additives or impurities.

Introduction

Lithium battery electrolyte is the carrier of ion transport in a lithium battery, which is generally composed of lithium salt and organic solvent. In the electrolyte, the commonly used lithium salt is LiPF_6 , and the solvent is a binary, ternary, or multinary system composed of a mixture of cyclic carbonates and chain carbonates. Selecting the right organic electrolyte is the key to achieving a higher energy density, a longer cycle life, and greater battery safety. Lithium battery manufacturers also add specific additives to extend battery life. Therefore, studies on the composition of lithium battery electrolyte play an important role in the development of new lithium batteries.

GC/MS analysis is commonly used in the studies on lithium battery electrolyte, and can accurately and quantitatively analyze the major components of the organic solvent in the electrolyte. Meanwhile, the strong qualitative capacity of mass spectrometry can also qualitatively identify and analyze unknown additives and impurities.

This application note describes the method for determining carbonate and carboxylate solvents and additives in lithium battery electrolyte using the 5977B GC/MSD. In regard to the fact that LiPF_6 , the main component of the electrolyte, is unstable and can easily decompose, diluted injection was adopted, which ensured good sensitivity, linearity, and reproducibility.

Experiment

Reagents and samples

Standards of carbonate solvent and additives, and electrolyte samples (A and B) were provided by the customer (see Table 1 for information about the compounds). Dichloromethane was an analytical reagent which was purchased from Guangzhou Chemical Reagent Factory.

Instrumentation

In this experiment, an Agilent 7890B GC and 5977B GC/MSD were used, which were equipped with a split/splitless injection port and Agilent 7693A automatic liquid sampler.

Preparation of standard solutions

Dichloromethane was used to prepare the standards into 10, 50, 100, 250, and 500 mg/L mixed standard solutions for GC/MS analysis. External standards were used to quantitatively analyze the electrolyte samples.

Sample preparation

The electrolyte samples were diluted 1,000 times with dichloromethane and directly injected for analysis.

GC conditions

Chromatographic column:	Agilent J&W DB-1701 capillary column, 30 m × 0.25 mm, 0.25 μm
Injection volume:	1.0 μL
Injection mode:	Split, with a split ratio of 20:1
Temperature at the injection port:	250 °C
Carrier gas:	Helium, at a constant flow rate of 1.0 mL/min
Ramp program:	The temperature was kept at 40 °C for 3.0 min, and was then increased to 160 °C at a rate of 10 °C/min, which was kept for 2 min

MS conditions

Solvent delay:	2.3 min
Ionization mode:	EI
Ion source temperature:	280 °C
Quadrupole temperature:	150 °C
Interface temperature:	250 °C
Detection mode:	Full scan, at 35–450 amu
Electron multiplier voltage (EMV):	1,137 V
Gain factor:	1
Quantitation method:	External standard quantitation, and the qualitative and quantitative ions of each compound are shown in Table 1

Results and discussion

Result of separation

Due to the relatively poor polarity of the analyte, the DB-1701 chromatographic column was used to analyze the mixed standard solution of carbonate solvent and additives. As shown in Figure 1, the 15 target compounds in the 250 mg/L mixed standard solution eluted within 17 min, and baseline separation was achieved. Detailed information about the target compounds is provided in Table 1.

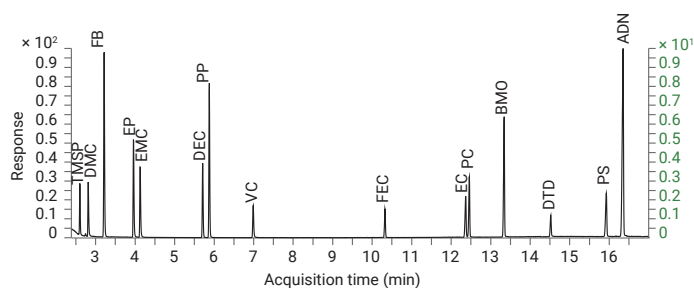


Figure 1. The full-scan total ion chromatogram of a mixed standard solution of 15 target compounds at a concentration of 250 mg/L.

Table 1. Retention time and characteristic ion information of the 15 target compounds.

Compound	Abbreviation	Retention Time (min)	Quantitative Ion (m/z)	Qualitative Ion 1 (m/z)	Qualitative Ion 2 (m/z)
Tris (trimethylsilyl)phosphate	TMSP	2.60	147	73	131
Dimethyl carbonate	DMC	2.81	45	59	44
Fluorobenzene	FB	3.22	96	70	50
Ethyl propionate	EP	3.96	57	102	75
Ethyl methyl carbonate	EMC	4.13	45	59	77
Diethyl carbonate	DEC	5.71	45	63	91
Propyl propionate	PP	5.88	57	75	87
Vinylene carbonate	VC	6.99	86	42	58
Fluoroethylene carbonate	FEC	10.34	62	106	58
Ethylene carbonate	EC	12.37	43	88	44
Propylene carbonate	PC	12.48	57	43	87
Butadiene monoxide	BMO	13.35	39	42	69
Ethylene sulfate	DTD	14.53	48	124	65
1,3-Propanesultone	PS	15.95	58	57	64
Adiponitrile	ADN	16.38	41	68	54

Precision and instrument detection limit

The mixed standard solution with a concentration of 10 mg/L was consecutively injected and analyzed eight times, and the results are shown in Table 2. For all of the 15 compounds, the RSD of peak area was less than 5%, showing excellent reproducibility. Based on this result, it was calculated that at a split ratio of 20:1, the instrument detection limit (IDL) was lower than 1.3 mg/L, which indicates that the method has good sensitivity.

Table 2. Results of precision and instrument detection limit of the 15 target compounds (n = 8).

Compound	Abbreviation	RSD (%)	IDL (mg/L)
Tris (trimethylsilyl)phosphate	TMSP	3.7	1.1
Dimethyl carbonate	DMC	1.8	0.6
Fluorobenzene	FB	2.2	0.7
Ethyl propionate	EP	1.4	0.4
Ethyl methyl carbonate	EMC	1.4	0.4
Diethyl carbonate	DEC	2.8	0.8
Propyl propionate	PP	3.1	0.9
Vinylene carbonate	VC	4.4	1.3
Fluoroethylene carbonate	FEC	4.3	1.3
Ethylene carbonate	EC	4.3	1.3
Propylene carbonate	PC	4.2	1.3
Butadiene monoxide	BMO	3.0	0.9
Ethylene sulfate	DTD	4.5	1.4
1,3-Propanesultone	PS	4.1	1.2
Adiponitrile	ADN	2.6	0.8

Calibration curve

Mixed standard solutions with concentrations of 10, 50, 100, 250, and 500 mg/L were prepared and analyzed, based on which a five-point calibration curve was created. The results are shown in Figure 3. The 15 target compounds that had been analyzed achieved outstanding linearity in a concentration range of 10–500 mg/L, and the correlation coefficient R^2 of each compound was higher than 0.997.

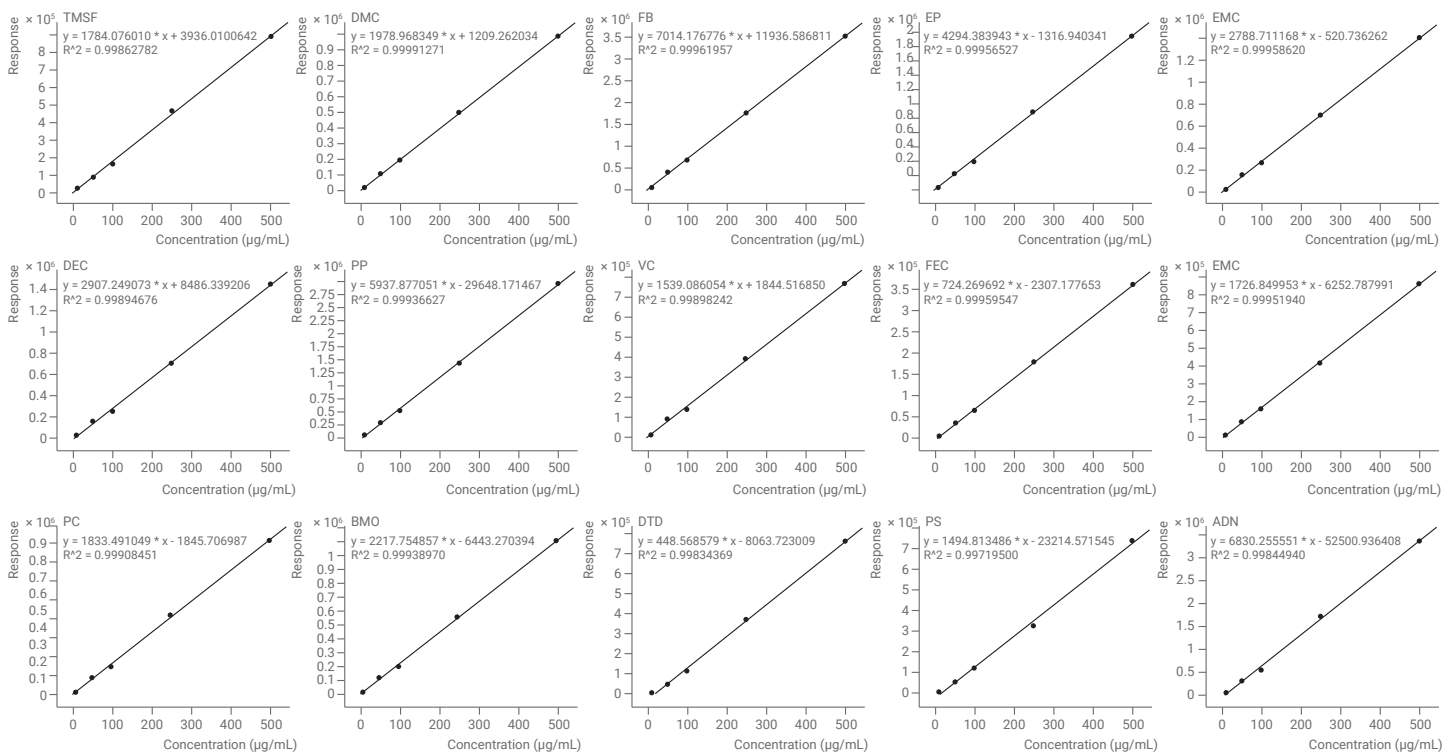


Figure 2. Calibration curve of 15 target compounds in a concentration range of 10-500 mg/L.

Electrolyte sample analysis results

Electrolyte sample A was diluted 1,000 times with dichloromethane, and analyzed with an injection volume of 1 µL based on the above conditions. Data was collected in full-scan mode, and the total ion chromatogram is shown in Figure 3. External standard quantitation was used to quantify the target compounds, and the results are shown in Table 3.

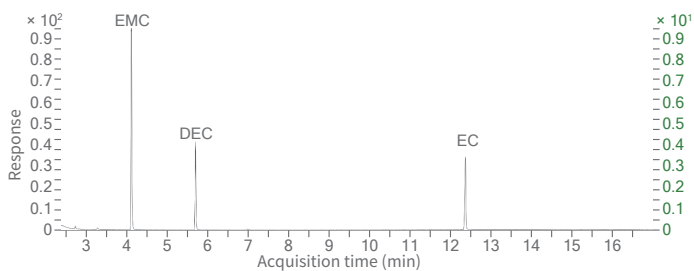


Figure 3. Total ion chromatogram of electrolyte sample A.

Table 3. Quantitative analysis results of electrolyte sample A.

Compound	Abbreviation	Retention Time (min)	Quantitative Ion (m/z)	Concentration (g/L)
Ethyl methyl carbonate	EMC	4.13	45	455
Diethyl carbonate	DEC	5.71	43	276
Ethylene carbonate	EC	12.37	45	192

The detection mode used in this application note is the full-scan acquisition mode of mass spectrometry, which can not only perform accurate quantitative analysis but also obtain complete sample information for qualitative analysis of unknown additives or impurities. Figure 4 indicates the qualitative analysis results of electrolyte sample B, which contains carbonate solvents DMC, EMC, and EC, and additives VC, FEC, and PS. In addition, an unknown peak emerged at 16.56 min in the chromatogram, which was subject to deconvolution and library searching. The results showed that the sample also contained 1-propene-1,3-sultone (PST).

Conclusion

In this application note, a method for analyzing carbonate solvents and additives in lithium battery electrolyte was developed with an Agilent 7890 GC and Agilent 5977B GC/MSD. The method is easy to use, and can achieve great separation, a wide linear range, and excellent reproducibility and sensitivity for various components in the electrolyte, making it very suitable for qualitative and quantitative analysis of organic solvents, additives, and impurities in lithium battery electrolyte.

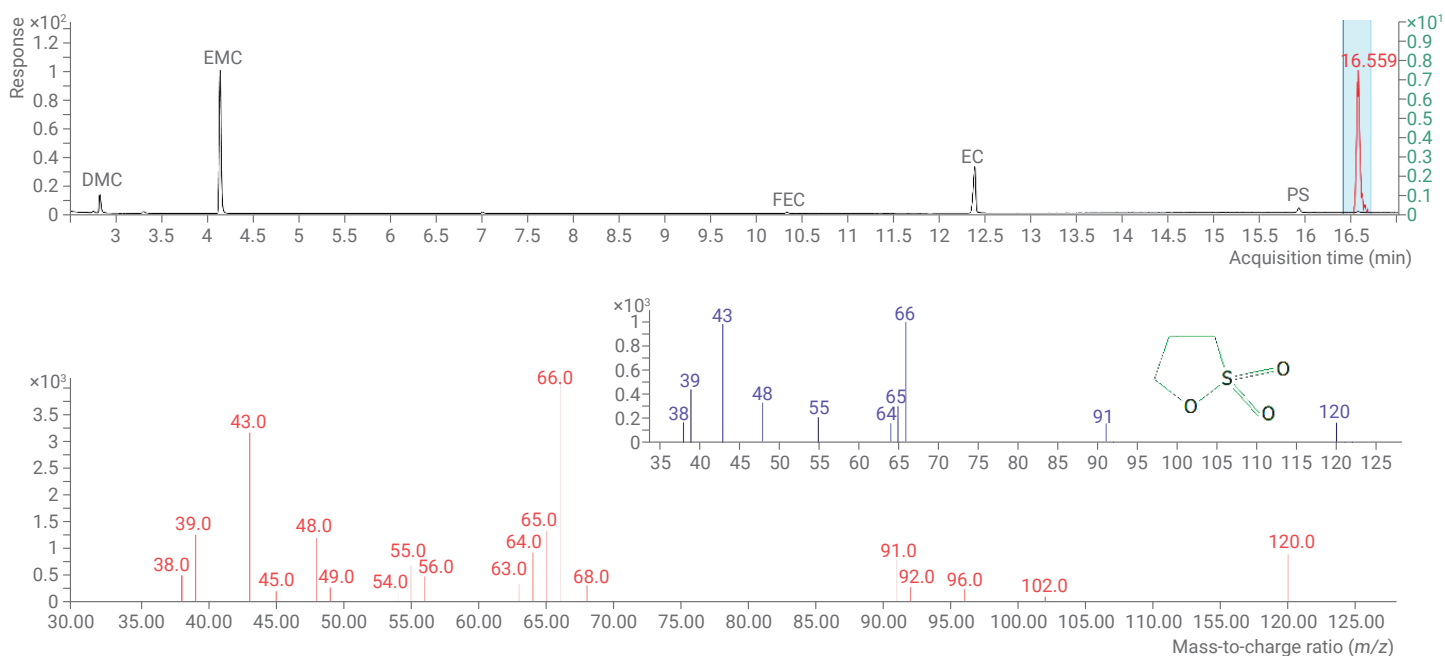


Figure 4. Qualitative analysis results of electrolyte sample B.

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