Brevis™ GC-2050 Gas Chromatograph

Application News

Analysis of Carbonic Esters and Additives in Lithium Ion Battery Electrolytes

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User Benefits

- Carbonic esters and additives in lithium ion battery electrolytes can be analyzed with high separation and good repeatability by using N_2 as the carrier gas.
- The Brevis GC-2050+FID is the optimum instrument for routine analysis thanks to its space-saving design.

■ Introduction

Diffusion of lithium ion batteries, which are used in electric vehicles (EVs) and power storage systems, has increased in recent years because this type of battery achieves high speed charging/discharging and long battery life. Lithium ion batteries consist of electrodes, separators, and an electrolyte, but among these components, the composition and purity of the carbonic ester and additives in the electrolyte are critical for maintaining the battery quality and performance. These compounds can be analyzed with a gas chromatograph (GC).

The lithium ion battery market has expanded rapidly in recent years, and analysis of the electrolytes used in batteries is indispensable as a key element of quality control. In quality control, it is necessary to analyze as many samples as possible in a limited laboratory space. Under these conditions, one particularly effective option is the Shimadzu Brevis GC-2050, which boasts outstanding analysis performance combined with a space-saving design.

This Application News article introduces an example in which several types of carbonic esters and additives which are frequently used in electrolytes were analyzed with a Brevis GC-2050+FID detector. In this analysis, N_2 was used as the carrier gas.

■ Analysis Conditions

Table 1 shows the analysis conditions. A PTFE syringe (P/N 221-74469) was used.

Table 1 Analysis Conditions

Model	: Brevis GC-2050
Inj. temp.	: 250 °C
Inj. mode	: Split 30:1
Carrier gas	: N_2, constant linear velocity (25 cm/s)
Column	: SH-I-5MS (P/N 221-75940-30) (30 m × 0.25 mm I.D., 0.25 µm)
Column temp.	: 40 °C (3 min) → 10 °C/min → 160 °C (5 min)
Detector	: FID
FID temp.	: 250 °C
Makeup gas	: N_2, 24 mL/min
H2 flow	: 32 mL/min
Air flow	: 200 mL/min

■ Analysis of Standard Sample

As representative compounds used in electrolytes, the 8 types of carbonic ester compounds listed in Table 2 were prepared. These compounds were diluted with dichloromethane, and 8-compound mixed standard samples were prepared for the 6 points of 10 mg/L, 25 mg/L, 50 mg/L, 100 mg/L, 200 mg/L, and 500 mg/L. Calibration curves were prepared and repeatability was confirmed using these standard samples.

Table 2 Types of Carbonic Esters and Additives Used

	Compound name	Abbreviation
1	Dimethyl carbonate	DMC
2	Ethyl methyl carbonate	EMC
3	Vinylene carbonate	VC
4	Diethyl carbonate	DEC
5	Fluoroethylene carbonate	FEC
6	Ethylene carbonate	EC
7	Propylene carbonate	PC
8	1,3-propanesultone	PS

■ Chromatogram Results of 8-Compound Mixed Standard Samples

Fig. 1 shows the total chromatogram for the 100 ppm standard sample.

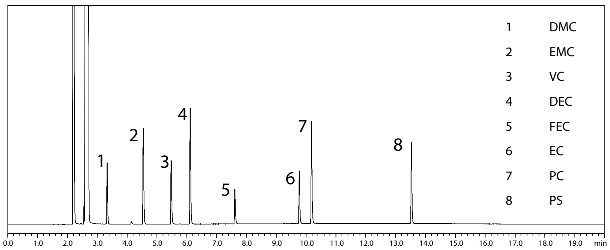
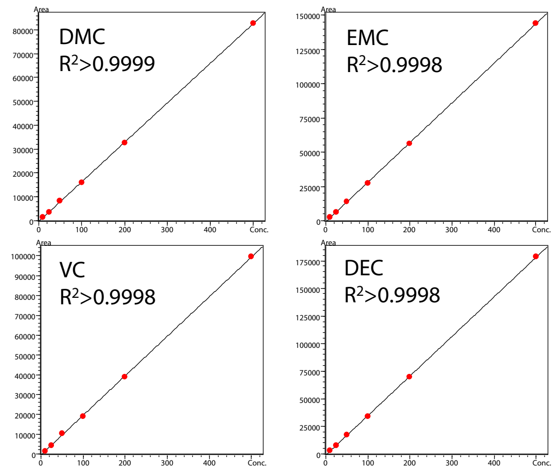


Fig. 1 Chromatogram of Mixed Standard Sample of 8 Compounds (100 ppm)

■ Calibration Curve Results of 8-Compound Mixed Standard Samples

Fig. 2 shows the calibration curve results for the respective compounds. All compounds showed satisfactory linearity, with R^2 = 0.999 or higher. Table 3 shows the peak area repeatability (%RSD) for 5 repeated analyses (n = 5) at 10 mg/L. Good repeatability results were obtained for all compounds.



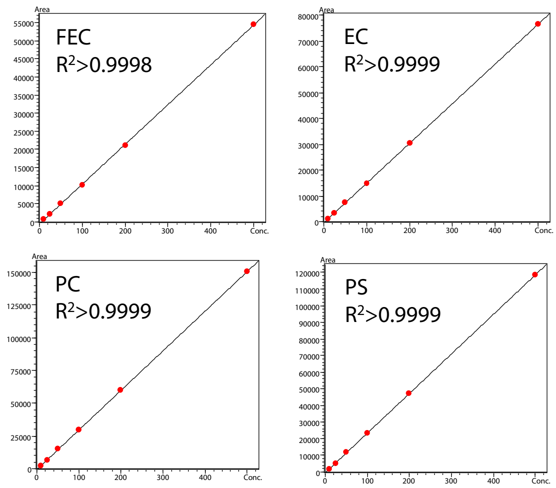


Fig. 2 Calibration Curves of 8 Compounds

Table 3 Peak Area Repeatability (%RSD) in Repeated Analyses (n = 5)

Compound name	%RSD
DMC	1.28
EMC	0.80
VC	1.03
DEC	1.39
FEC	1.73
EC	1.26
PC	1.16
PS	1.10

■ Quantitative Analysis of Electrolyte Samples

Four commercially-available lithium ion battery electrolyte samples with different types of electrolytes and carbonic esters were analyzed. Table 4 shows the types of electrolytes, carbonic esters, and additives contained in each sample.

The samples were analyzed at 1000x dilution with dichloromethane. If the samples are analyzed in the undiluted state, the effect of electrolyte precipitation will be excessive, and it will be necessary to increase number of insert and column maintenance procedures appropriately.

It should be noted that the dispensing work was done in a glovebox to avoid the danger of reaction between moisture in the atmosphere and the Li-based electrolytes.

Fig. 3 shows the chromatograms of the respective samples. Table 5 shows the quantitation values of the carbonic esters and additives prior to dilution with dichloromethane for each sample. The peak top numbers in the chromatograms in Fig. 3 correspond to the numbers in the No. column in Table 5.

Table 4 Types of Actual Samples

	Electrolyte	Carbonic ester/additive
Sample 1	LiFSI	DMC, EMC, EC
Sample 2	LiFSI	DMC, DEC, EC
Sample 3	$LiPF_6$	DMC, EMC, EC
Sample 4	$LiPF_6$	DMC, DEC, EC

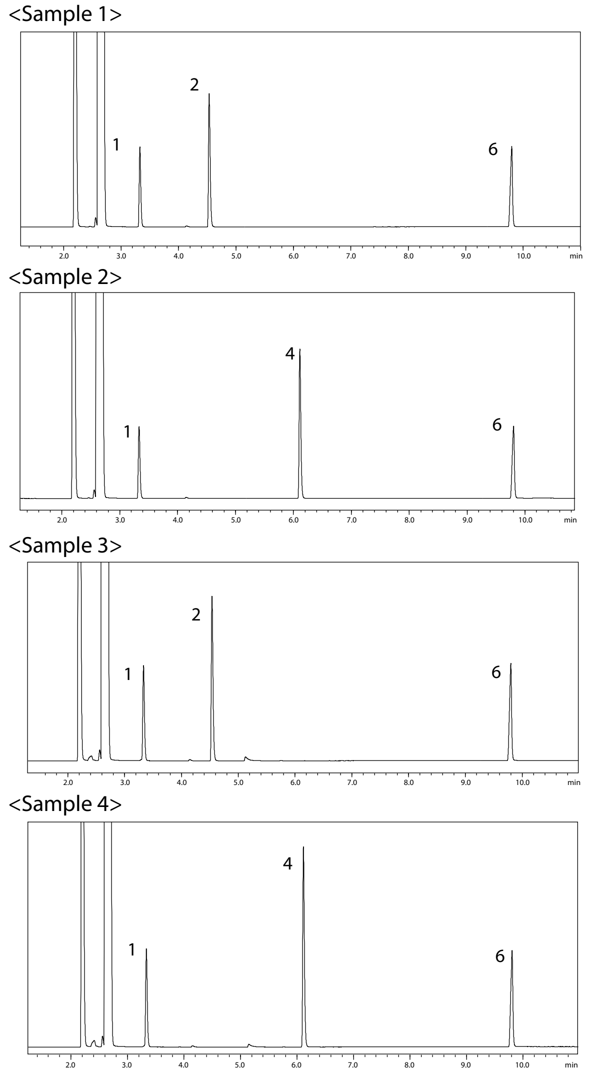


Fig. 3 Chromatograms of 4 Types of Commercial Electrolyte Samples

Table 5 Quantitation Values of 4 Types of Actual Samples (mg/mL)

No.	Compound	Sample 1	Sample 2	Sample 3	Sample 4
1	DMC	278.7	284.1	291.2	301.9
2	EMC	283.5	-	294.9	-
3	VC	-	-	-	-
4	DEC	-	277.6	-	290.3
5	FEC	-	-	-	-
6	EC	402.8	397.0	402.5	414.5
7	PC	-	-	-	-
8	PS	-	-	-	-

■ Conclusion

Chromatograms with excellent separation were obtained for a standard solution of 8 types of carbonic esters and additives which are widely used in the electrolytes of lithium ion batteries. Excellent results were also obtained for the linearity and repeatability of the calibration curves.

The results of this analysis of commercially-available electrolyte samples demonstrated that the Brevis GC-2050 gas chromatograph is an easy-to-use tool for quantitative analyses.

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