Application Note

Energy & Chemicals

Agilent

Trusted Answers

Analysis of Carbonate Esters and Additives in Battery Electrolyte Using Agilent 8860 GC

Authors

Hongtao Shang
Agilent Technologies (Shanghai) Co. Ltd.

Jinqiang Zhang
Agilent Technologies (China) Co. Ltd.

Abstract

This application note presents a reliable, user-friendly, and cost-effective solution to meet the demand for carbonate esters and additives analysis. The solution was developed using the Agilent 8860 GC system with a split-splitless injector and a flame ionization detector (FID). Thirteen carbonate esters and additives can be effectively separated using the Agilent J&W HP-5ms Ultra Inert column, and the entire analysis can be completed in less than 14 minutes. The method exhibited excellent performance, including high linearity (R^2 >0.9995) for the 13 target compounds at concentrations ranging from 10 to 500 mg/L. Repeatability was less than 0.04% for retention time and less than 1.5% for peak area. The method's limit of detection (LOD) and limit of quantification (LOQ) were both below 0.5 and 1.6 mg/L, respectively. Real electrolyte samples were also analyzed, and the components were detected with high peak resolution and repeatability (<1.5%).

Introduction

The global demand for electric vehicles and energy storage systems has increased significantly, leading to a 18.1% compound annual growth rate (CAGR) in the global lithium-ion battery market from 2022 to 2030.[1] Electrolyte is an organic solution inside the battery that serves as an ion carrier, facilitating movement of ions from the cathode to the anode during charging and in reverse during discharge. The composition, proportion, and purity of the solvent and additives in liquid electrolytes play a critical role in the capacity, cycle life, stability, and safety of Li-ion batteries. These facts apply not only during the production stage but throughout the entire life cycle.

Carbonate-based electrolytes, primarily composed of carbonate esters such as dimethyl carbonate (DMC) and ethyl methyl carbonate (EMC), are widely used in lithium-ion cells. However, it has been reported that these solvents are expected to decompose at low potentials, resulting in lower cell performance.[2] Therefore, some additives, such as fluoroethylene carbonate (FEC) and vinylene carbonate (VC), have been investigated and employed in electrolytes to effectively improve the performance of Li-ion batteries.[3,4]

The accurate determination of these compounds is crucial for designing customer Li-ion battery electrolytes and conducting performance improvement research. Agilent has developed a GC/MS method for high-precision quantitative and qualitative analysis of carbonate esters, additives, and their decomposed products.[5] This application aims to develop an easy-to-operate and low-cost analytical solution for commonly used carbonate esters and additives in Li-ion battery electrolytes that can be performed on an 8860 GC equipped with an FID.

Experimental

Chemical, standards, and sample

Single standards (>97%) of 13 compounds (Table 1) and DCM (HPLC grade) were purchased from ANPEL Laboratory Technologies (Shanghai) Inc. Seven samples were collected from customers.

Table 1. Thirteen target carbonate esters and additives.

No.	Target Compounds	Abbreviation	CAS Number
1	Dimethyl carbonate	DMC	616-38-6
2	Fluorobenzene	FB	462-06-6
3	Ethyl propanoate	EP	105-37-3
4	Ethyl methyl carbonate	EMC	623-53-0
5	Diethyl carbonate	DEC	105-58-8
6	*n*-Propyl propionate	PP	106-36-5
7	Vinylene carbonate	VC	872-36-6
8	Fluoroethylene carbonate	FEC	114435-02-8
9	Ethylene carbonate	EC	96-49-1
10	Propylene carbonate	PC	108-32-7
11	Ethylene sulfate	DTD	1072-53-3
12	1,3-Propanesultone	PS	1120-71-4
13	1,4-Dicyanobutane	AND	111-69-3

Standards preparation

For this analysis, the following standards were used:

Stocked standards: Single stocked standards of each compound were prepared with a concentration of 10,000 mg/L in DCM.

Peak identification standards: Standards of each compound with a concentration of 200 mg/L in DCM were prepared by diluting from the stocked standards for retention time (RT) and peak shape determination.

Calibration standards: Standard mixtures containing 13 compounds were prepared using 5 mL volumetric flasks. The concentrations of the standard series were 10, 25, 50, 100, 200, and 500 mg/L in DCM.[4]

MDL standard: A 4.0 mg/L standard mixture was prepared for MDL calculation.

Sample preparation

Samples were diluted 1,000 times with DCM and calculated with an external standard method.

Instrumentation and analytical conditions

The method was developed on an Agilent 8860 GC system with a flame ionization detector (FID). Both standards and samples were injected using an Agilent 7650A automated liquid sampler. For more details on the GC conditions and method parameters, please see Table 2. Data acquisition and processing were performed using Agilent OpenLab CDS, version 2.6.

Table 2. Analytical conditions for the Agilent 8860 GC system.

Agilent 8860 GC System Parameters	
Parameter	**Value**
ALS	Agilent 7650A
Injection Volume	1.0 µL
Inlet Type	Split-splitless injector
Inlet Temperature	250 °C
Liner	Ultra Inert, 4.0 mm id, split with glass wool (p/n 5190-2295)
Carrier Gas	He/N_2
Split Ratio	20:1
GC Column	HP-5ms UI, 30 m × 0.25 mm, 0.25 µm (p/n 19091S-433UI)
Column Flow	Constant flow, 1.2 mL/min
Oven Program	40 °C for 3 min, ramped to 160 °C at 10 °C/min, hold 5 min
FID Temperature	250 °C
FID Air Flow	400 mL/min
FID Fuel Flow	30 mL/min
FID Make Up Flow	30 mL/min
Date Rate	5 Hz

Results and discussion

Target compounds behavior in GC chromatogram

To observe the behavior of the target compounds on the GC chromatogram, a standard mixture with a concentration of 200 mg/L was analyzed using both helium and nitrogen as the carrier gas (see Figure 1). All compounds could elute from the GC column within 14 minutes and achieved baseline separation. It was observed that the retention times of all compounds were earlier with nitrogen as the carrier gas (Figure 1B) compared to helium (Figure 1A).

Calibration curve and linearity

The responses of each compound were evaluated at six concentration levels using the calibration standards prepared in this study. The results obtained using helium as the carrier gas were collected and statistically analyzed. The calibration curves for the 13 compounds are shown in Figure 2. All 13 compounds exhibited strong positive linear correlations between peak area and concentration, with correlation coefficients (R^2) ranging from 0.9996 to 0.9999.

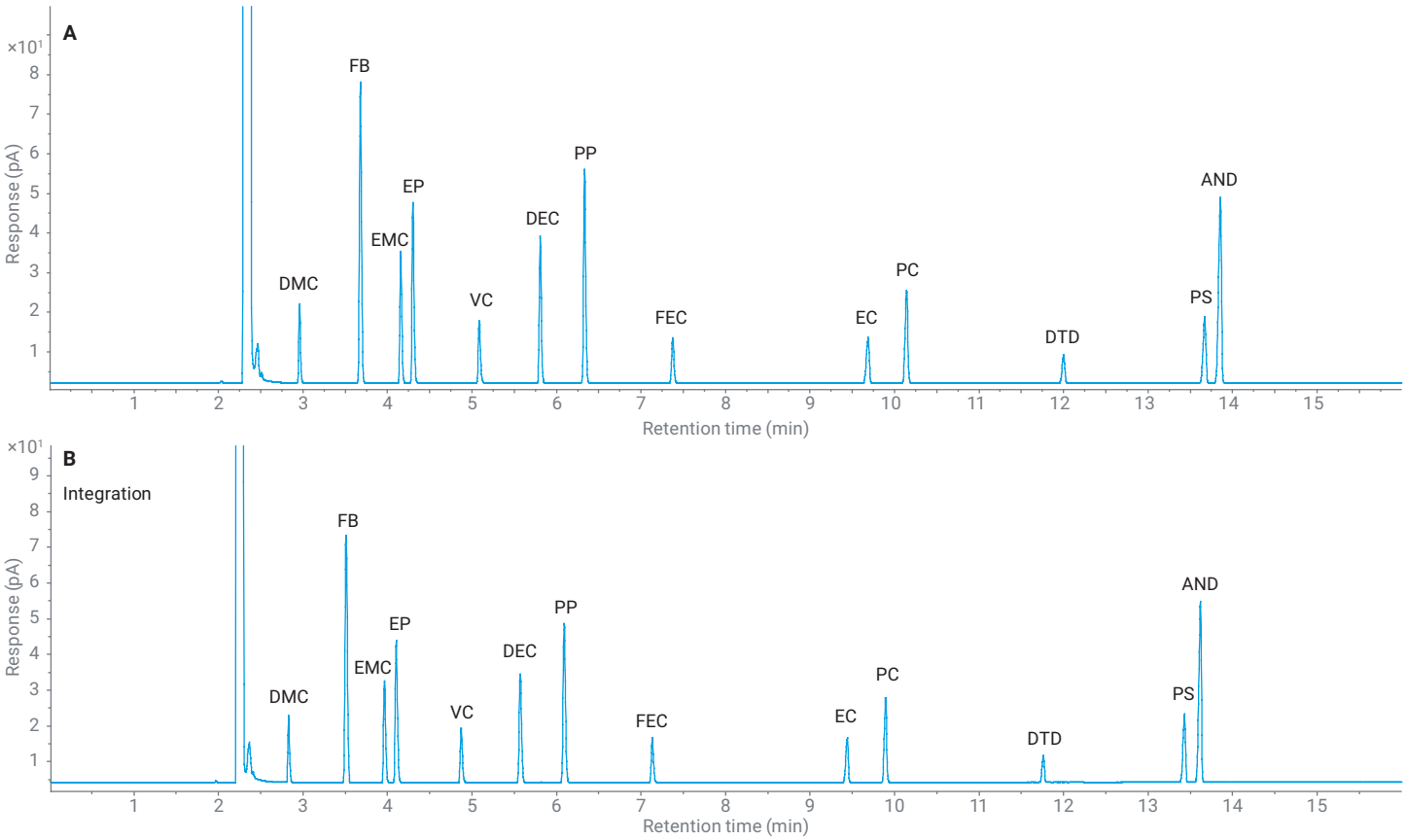
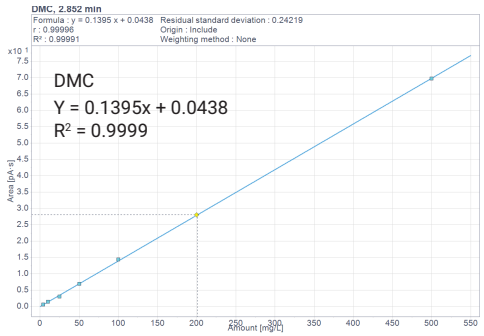
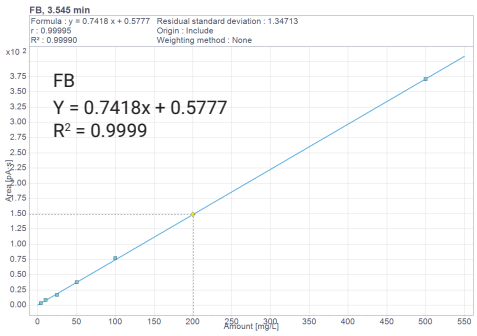
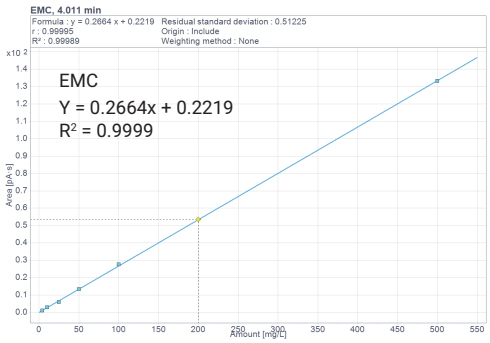
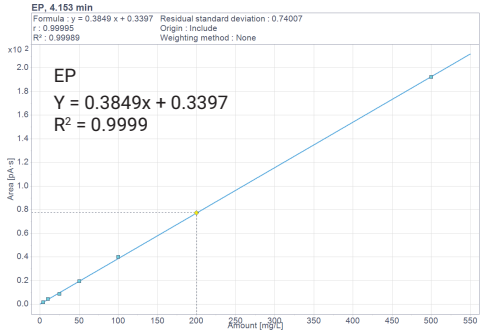


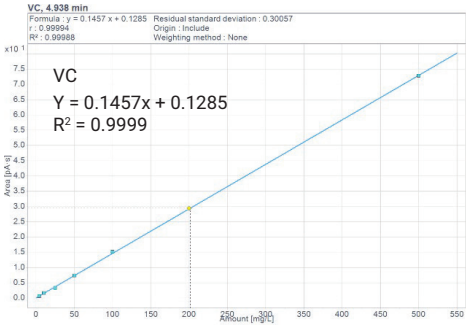
Figure 1. Chromatogram of 13 carbonate esters and additives analyzed with an Agilent 8860 GC with He (A) and N_2 (B).

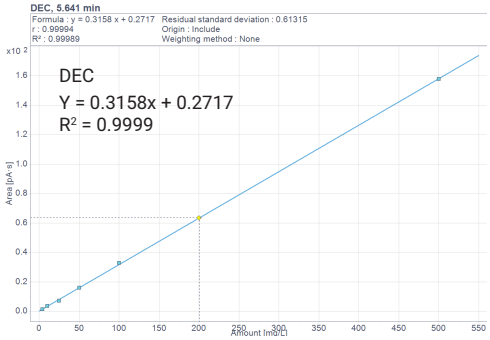

DMC, 2.852 min
Formula : y = 0.1395 x + 0.0438
r : 0.99996
R² : 0.99991
Residual standard deviation : 0.24219
Origin : Include
Weighting method : None
DMC
Y = 0.1395x + 0.0438
R² = 0.9999
Area [pA·s]
Amount [mg/L]

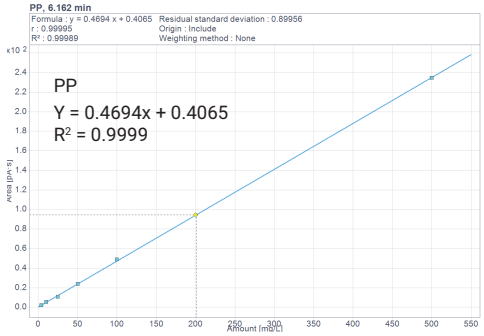

FB, 3.545 min
Formula : y = 0.7418 x + 0.5777
r : 0.99995
R² : 0.99990
Residual standard deviation : 1.34713
Origin : Include
Weighting method : None
FB
Y = 0.7418x + 0.5777
R² = 0.9999
Area [pA·s]
Amount [mg/L]

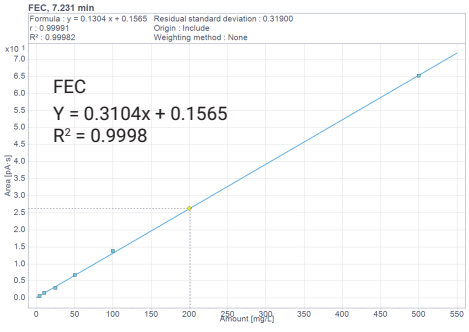

EMC, 4.011 min
Formula : y = 0.2664 x + 0.2219
r : 0.99995
R² : 0.99989
Residual standard deviation : 0.51225
Origin : Include
Weighting method : None
EMC
Y = 0.2664x + 0.2219
R² = 0.9999
Area [pA·s]
Amount [mg/L]

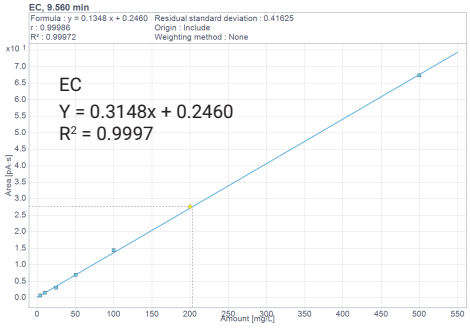

EP, 4.153 min
Formula : y = 0.3849 x + 0.3397
r : 0.99995
R² : 0.99989
Residual standard deviation : 0.74007
Origin : Include
Weighting method : None
EP
Y = 0.3849x + 0.3397
R² = 0.9999
Area [pA·s]
Amount [mg/L]


VC, 4.938 min
Formula : y = 0.1457 x + 0.1285
r : 0.99994
R² : 0.99988
Residual standard deviation : 0.30057
Origin : Include
Weighting method : None
VC
Y = 0.1457x + 0.1285
R² = 0.9999
Area [pA·s]
Amount [mg/L]


DEC, 5.641 min
Formula : y = 0.3158 x + 0.2717
r : 0.99994
R² : 0.99989
Residual standard deviation : 0.61315
Origin : Include
Weighting method : None
DEC
Y = 0.3158x + 0.2717
R² = 0.9999
Area [pA·s]
Amount [mg/L]


PP, 6.162 min
Formula : y = 0.4694 x + 0.4065
r : 0.99995
R² : 0.99989
Residual standard deviation : 0.89956
Origin : Include
Weighting method : None
PP
Y = 0.4694x + 0.4065
R² = 0.9999
Area [pA·s]
Amount [mg/L]


FEC, 7.231 min
Formula : y = 0.1304 x + 0.1565
r : 0.99991
R² : 0.99982
Residual standard deviation : 0.31900
Origin : Include
Weighting method : None
FEC
Y = 0.3104x + 0.1565
R² = 0.9998
Area [pA·s]
Amount [mg/L]


EC, 9.560 min
Formula : y = 0.1348 x + 0.2460
r : 0.99986
R² : 0.99972
Residual standard deviation : 0.41625
Origin : Include
Weighting method : None
EC
Y = 0.3148x + 0.2460
R² = 0.9997
Area [pA·s]
Amount [mg/L]

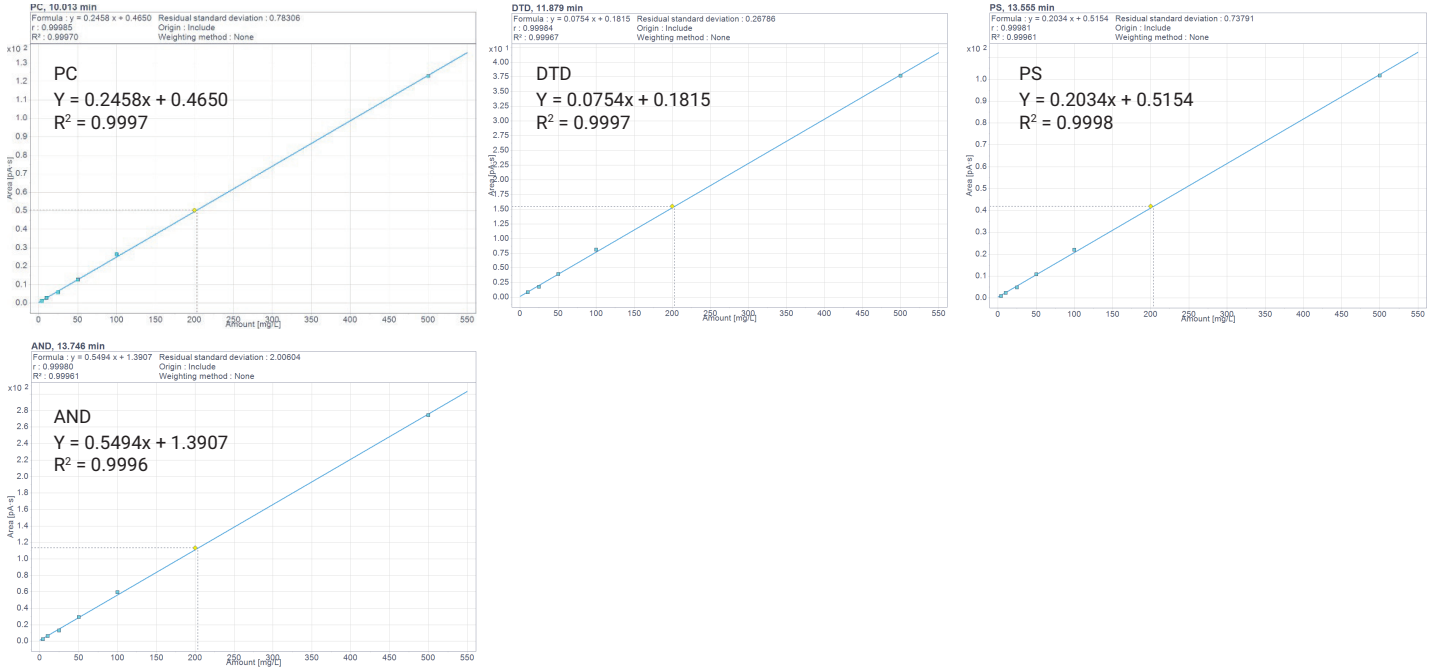


Figure 2. Calibration curves of 13 carbonate esters and additives with He as carrier gas.

Repeatability

Standard mixtures with concentrations of 10, 100, and 500 mg/L were used to evaluate the method repeatability at low, medium, and high concentrations, respectively. Seven injections were performed in parallel for each level, and the results are shown in Table 3. The retention time and peak area repeatability of all 13 compounds were less than 0.04% and 1.5%, respectively.

MDL and LOQ

In this study, the method detection limit (MDL) and LOQ were determined using a signal-to-noise ratio (S/N) of 3:1 and 10:1, respectively. A standard mixture with a concentration of 4 mg/L was used, and each compound was analyzed seven times to determine the S/N ratio. The average S/N ratio, MDL, and LOQ of the 13 compounds were calculated and are presented in Table 4. The MDL and LOQ values for all 13 compounds were found to be less than 0.5 and 1.6 mg/L, respectively.

Table 3. Retention time and area repeatability of 13 carbonate esters and additives.

Repeatability	Concentration mg/L		DMC	FB	EMC	EP	VC	DEC	PP	FEC	EC	PC	DTD	PS	AND
RT	10	Average	2.858	3.549	4.023	4.166	4.951	5.652	6.176	7.237	9.53	9.993	11.858	13.499	13.695
		SD	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.00408	0.001
		RSD	**0.035%**	**0.028%**	**0.025%**	**0.024%**	**0.020%**	**0.018%**	**0.016%**	**0.014%**	**0.010%**	**0.010%**	**0.008%**	**0.030%**	**0.007%**
	100	Average	2.854	3.548	4.015	4.157	4.939	5.643	6.167	7.219	9.516	9.974	11.849	13.513	13.692
		SD	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
		RSD	**0.035%**	**0.028%**	**0.025%**	**0.024%**	**0.020%**	**0.018%**	**0.016%**	**0.014%**	**0.011%**	**0.010%**	**0.008%**	**0.007%**	**0.007%**
	500	Average	2.851	3.546	4.011	4.151	4.938	5.639	6.162	7.231	9.558	10.011	11.878	13.553	13.744
		SD	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.0004779	0.001	0.001	0.001	0.001
		RSD	**0.035%**	**0.028%**	**0.025%**	**0.024%**	**0.020%**	**0.018%**	**0.016%**	**0.014%**	**0.005%**	**0.010%**	**0.008%**	**0.007%**	**0.007%**
Area	10	Average	1.490	8.174	2.998	1.578	1.578	3.488	6.072	1.442	1.550	5.958	0.884	2.374	6.398
		SD	0.007	0.026	0.009	0.011	0.011	0.026	0.013	0.012	0.013	0.02	0.013	0.008	0.034
		RSD	**0.47%**	**0.32%**	**0.30%**	**0.70%**	**0.70%**	**0.75%**	**0.21%**	**0.83%**	**0.84%**	**0.34%**	**1.47%**	**0.34%**	**0.53%**
	100	Average	14.46	74.94	27.47	14.70	14.70	31.98	13.04	13.04	14.03	8.08	8.08	21.76	58.57
		SD	0.028	0.155	0.055	0.041	0.041	0.053	0.033	0.033	0.039	0.03	0.03	0.071	0.172
		RSD	**0.19%**	**0.21%**	**0.20%**	**0.28%**	**0.28%**	**0.17%**	**0.25%**	**0.25%**	**0.28%**	**0.37%**	**0.37%**	**0.33%**	**0.29%**
	500	Average	72.14	367.51	135.06	72.67	72.67	157.41	64.42	64.42	68.42	39.11	39.11	104.69	281.06
		SD	0.355	1.849	0.644	0.369	0.369	0.787	0.369	0.369	0.369	0.241	0.241	0.648	1.705
		RSD	**0.49%**	**0.50%**	**0.48%**	**0.51%**	**0.51%**	**0.50%**	**0.57%**	**0.57%**	**0.54%**	**0.62%**	**0.62%**	**0.62%**	**0.61%**

Table 4. MDL (mg/L) and LOQ (mg/L) of 13 carbonate esters and additives.

MDL and LOQ		DMC	FB	EMC	EP	VC	DEC	PP	FEC	EC	PC	DTD	PS	AND
S/N (seven injections)	1	61.7	239	93.3	130	48.2	99.5	144	41.5	43.2	75.2	25.6	68.0	187
	2	61.4	237	94.3	129	49.3	99.2	143	41.7	42.3	75.8	25.4	67.3	189
	3	62.0	234	93.3	129	48.8	97.1	143	40.4	41.8	73.7	25.6	67.2	186
	4	60.7	234	92.5	128	48.7	98.3	142	40.4	42.1	75.5	25.3	67.2	185
	5	65.3	247	101	139	53.0	107	156	46.4	45.6	82.0	28.1	74.5	206
	6	61.8	236	93.4	129	48.7	99.0	143	41.1	42.1	75.9	25.2	67.3	186
	7	62.3	237	94.2	130	49.1	100	146	41.0	42.4	77.0	25.9	68.1	189
	Average	62.2	238	94.5	131	49.4	100	145	41.8	42.8	76.4	25.9	68.5	190
	SD	1.47	4.41	2.83	3.62	1.62	3.15	4.82	2.09	1.32	2.64	1.01	2.67	7.29
	RSD	2.36	1.86	2.99	2.77	3.29	3.15	3.32	5.01	3.08	3.46	3.9	3.89	3.85
MDL, mg/L (S/N = 3)		0.193	0.050	0.127	0.092	0.243	0.120	0.083	0.287	0.280	0.157	0.464	0.175	0.063
LOQ, mg/L (S/N = 10)		0.643	0.168	0.423	0.306	0.810	0.400	0.275	0.957	0.935	0.523	1.546	0.584	0.211

Analysis of electrolyte samples

Seven samples were obtained from two electrolyte manufacturers with different recipes. The samples were pretreated following the steps described in the Experimental section. Repeatability in real sample analysis was determined by replicating three injections.

The chromatograms of sample 7, performed on the 8860 GC, are shown in Figure 3. Peaks of DMC, EMC, DEC, FEC, EC, DTD, and PS were observed clearly with good peak shapes and resolutions. Analysis results are summarized in Table 5, and differences in the compositions and contents of target compounds were identified with response repeatability lower than 1.5%.

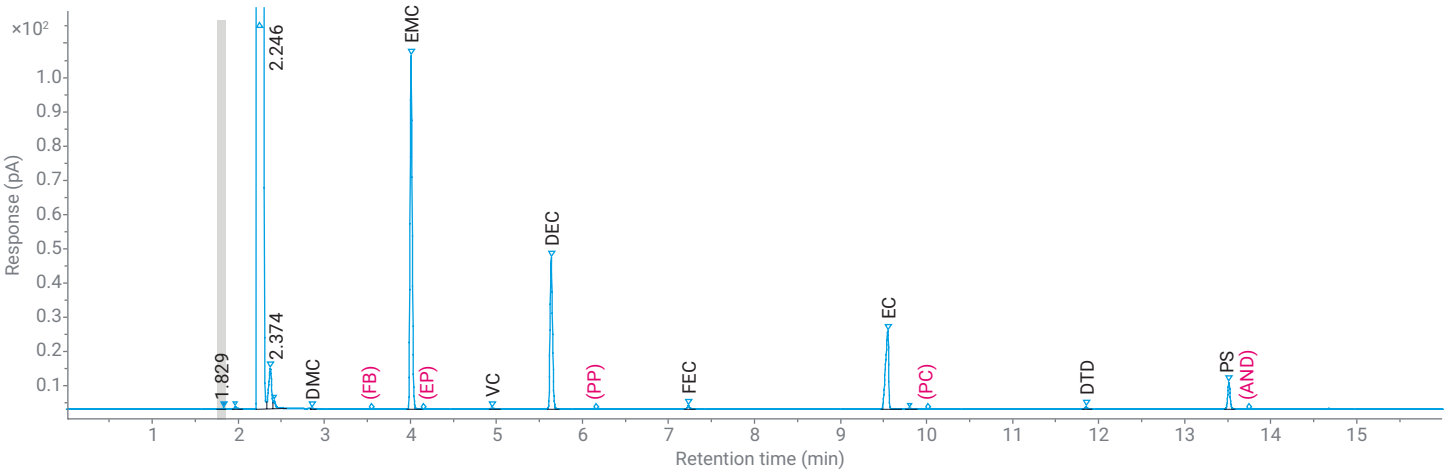


Figure 3. Chromatogram of electrolyte sample 7.

Table 5. Test results of seven electrolyte samples.

Target Compounds	Sample 1		Sample 2		Sample 3		Sample 4		Sample 5		Sample 6		Sample 7	
	Avg conc. (g/L)	RSD	Avg conc. (g/L)	RSD	Avg conc. (g/L)	RSD	Avg conc. (g/L)	RSD	Avg conc. (g/L)	RSD	Avg conc. (g/L)	RSD	Avg conc. (g/L)	RSD
DMC	345	0.45%	3.44	1.12%	3.89	0.29%	–	–	319	0.10%	544	0.55%	3.00	0.29%
FB	–	–	–	–	–	–	–	–	–	–	–	–	–	–
EP	–	–	–	–	–	–	121	0.19%	–	–	–	–	–	–
EMC	250	0.52%	535	0.57%	700	0.49%	3.58	0.13%	372	0.12%	162	0.48%	512	0.56%
DEC	–	–	219	0.52%	57.8	0.37%	–	–	–	–	–	–	209	0.53%
PP	–	–	–	–	–	–	478	0.07%	–	–	–	–	–	–
VC	10.9	1.35%	6.9	0.12%	6.95	0.29%	–	–	40.8	0.97%	–	–	23.6	0.61%
FEC	40.0	0.42%	13.0	0.42%	–	–	95.6	0.10%	–	–	32.9	0.41%	66.5	0.63%
EC	277	0.58%	312	0.48%	316	0.32%	106	0.08%	311	0.03%	272	0.38%	302	0.59%
PC	60.7	0.43%	–	–	–	–	98.7	0.09%	57.0	0.04%	–	–	–	–
DTD	–	–	22.0	0.22%	31.4	0.21%	–	–	17.8	0.08%	–	–	17.8	0.29%
PS	39.2	0.71%	51.0	0.33%	11.1	0.50%	46.4	0.19%	–	–	–	–	12.0	1.12%
AND	–	–	–	–	–	–	16.4	0.16%	–	–	–	–	–	–

Conclusion

This application note describes the development of a method for the analysis of 13 carbonate esters and additives in electrolyte using a GC-FID system (Agilent 8860 GC). All target compounds showed good peak shape and separation on the chromatogram, regardless of whether helium or nitrogen was used as the carrier gas. The method delivered excellent repeatability, linearity, and low MDL, making it suitable for routine analysis of carbonate esters and additives for electrolyte customers.

References

1. Grand View Research. Lithium-Ion Battery Market Size Worth $182.53 Billion by 2030: Grand View Research, Inc. [EB/OL] 2022-07-07. https://www.bloomberg.com/press-releases/2022-06-07/lithium-ion-battery-market-size-worth-182-53-billion-by-2030-grand-view-research-inc
2. Hobold, G. M. *et al.* Moving Beyond 99.9% Coulombic Efficiency for Lithium Anodes in Liquid Electrolytes. *Nat. Energy* **2021**, *6*, 951–960.
3. Markevich, E. *et al.* Improved Performance of Li-Metal Cathodes and Small Amounts of Electrolyte Solutions Containing Fluorinated Carbonates at 30 °C–55 °C. *J. Electrochem. Soc.* **2020**, *167*, 070509.
4. Aurbach, D.; Gamolsky, K. *et al.* On the Use of Vinylene Carbonate (VC) as an Additive to Electrolyte Solutions for Li-Ion Batteries. *Electrochim. Acta.* **2002**, *47*, 1423–1439.
5. Zhiquan, Y.; Shuang, F. Determination of Carbonate Solvents and Additives in Lithium Battery Electrolyte Using the Agilent 5977B GC/MSD, *Agilent Technologies application brief*, publication number 5991-9356EN, **2018**.

www.agilent.com

DE19981573

This information is subject to change without notice.

Printed in the USA, March 8, 2023
5994-5888EN

Agilent

Trusted Answers