

# Quality Control of Lithium-Ion Battery Electrolytes Using LC/MS

Suitable for Agilent  
1260 Infinity III LC



## Author

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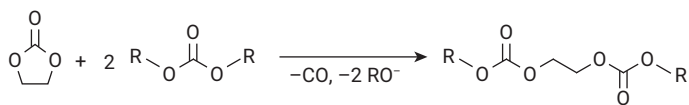
## Abstract

The efficiency and longevity of lithium-ion batteries are largely dependent on the quality of the electrolyte. All electrolyte constituents of most lithium-ion batteries used today are sensitive to degradation caused by reaction with water. This application note presents an HPLC-MS method to separate and quantify frequently used electrolyte solvents and some of their degradation products. Despite strong sample solvent, no peak distortion was noted when using the Agilent 1260 Infinity II Hybrid Multisampler in Feed injection mode. Detection limits lower than 30 ppm are reported for the main constituents, and lower than 5 ppb for the degradation products.

## Introduction

Lithium-ion batteries (LIBs) are ubiquitous in portable consumer electronic devices and electric vehicles. The development of more efficient and lightweight, higher capacity batteries is a vast research field. A key factor for the efficiency of an LIB is the electrolyte and its constituents. Electrolytes consist of a lithium salt, most commonly  $\text{LiPF}_6$ , that is dissolved in organic carbonate solvents.<sup>1</sup> These components are moisture-sensitive, and they will degrade over time at elevated temperatures and high numbers of charge cycles. The determination of main components and degradation products is therefore important to judge the long-term efficiency of an LIB.

Whenever mixtures of ethylene carbonate (EC) and a dialkyl carbonate are present in an electrolyte, they can react to oligomeric carbonates (Figure 1). An electrolyte containing EC, dimethyl carbonate (DMC), and diethyl carbonate (DEC) will, for example, degrade to dimethyl 2,5-dioxahexanedioate (DMDOHC,  $\text{R} = \text{CH}_3$ ) and diethyl 2,5-dioxahexanedioate (DEDOHC,  $\text{R} = \text{C}_2\text{H}_5$ ).



**Figure 1.** Formation of oligomeric carbonates from EC and dialkyl carbonates. Adapted from reference 4.

This application note presents an HPLC-MS method to separate and quantify common electrolyte solvents and their degradation products. Besides EC, DMC, DEC, DMDOHC, and DEDOHC, the separation method includes ethyl methyl carbonate (EMC) and propylene carbonate (PC), which are also common electrolyte solvents. For the determination of elemental impurities in the lithium salt, please see references 2 and 3.

## Experimental

### Instrumentation

The 1260 Infinity II LC consisted of the following modules:

- Agilent 1260 Infinity II Flexible Pump (G7104C)
- Agilent 1260 Infinity II Hybrid Multisampler (G7167C)
- Agilent 1260 Infinity II Multicolumn Thermostat (G7116A)
- Agilent 1260 Infinity II Diode Array Detector WR (G7115A)
- Agilent InfinityLab LC/MSD iQ (G6160A)

### Column

Agilent InfinityLab Poroshell 120 EC-C18,  $2.1 \times 250$  mm,  $4 \mu\text{m}$  (part number 650750-902T)

### Software

Agilent OpenLab CDS, revision 2.6 or later versions

### Solvents

Agilent InfinityLab Acetonitrile (ACN) for LC/MS (part number 5191-5101\*) was used as mobile phase and sample solvent. Fresh ultrapure water was obtained from a Milli-Q Integral system equipped with a  $0.22 \mu\text{m}$  membrane point-of-use cartridge (Millipak). LC/MS grade formic acid was purchased from VWR (Darmstadt, Germany).

### Samples

Reference electrolyte components ethylene carbonate (EC) > 99%, propylene carbonate (PC) 99.7%, dimethyl carbonate (DMC) > 99%, ethyl methyl carbonate (EMC) 99.9%, dimethyl 2,5-dioxahexanedioate (DMDOHC) 98%, diethyl carbonate (DEC) > 99%, diethyl 2,5-dioxahexanedioate (DEDOHC) 98%, and dipropyl carbonate (DPC) 99% were purchased from Merck (Darmstadt, Germany). A battery grade 1 M lithium hexafluorophosphate solution in EC, DMC, and DEC (1:1:1, v:v), also obtained from Merck, was used as an electrolyte sample.

A calibration for all reference electrolytes was created, spanning a range of 10 to 10,000 ppb for EC, PC, DMDOHC, and DEDOHC, and 10 to 100,000 ppm for DEC, DMC, and EMC. DPC was used as internal standard.

For technical reasons, the sample and standards could not be handled in a glove box under inert gas. This limitation, however, proved beneficial to the generation of degradation products, the detection of which was the purpose of this application note.

\* Only available in select countries.

## Method settings

**Table 1.** Chromatographic conditions.

Parameter	Value
Mobile Phase	A) 0.1% Formic acid (FA) in water B) 0.1% FA in acetonitrile
Flow Rate	0.4 mL/min
Gradient	0 min 2% B 2 min 2% B 11 min 60% B 12 min 95% B 14 min 95% B 14.5 min 2% B
Stop Time	20 min
Injection Volume	1 µL
Feed Injection	Feed speed: 20 µL/min Overfeed volume: 3.5 µL Feed solvent (S2): water + 2% ACN + 0.1% FA Inner wash: 150 µL S1 Reconditioning: S2
Needle Wash (S1)	3 s, water/acetonitrile (1:1)
Temperature	40 °C
UV Detection	191/2 nm, no reference 10 Hz data rate
MS Detection	SIM in positive ionization mode

**Table 2.** MSD spray chamber and signal settings.

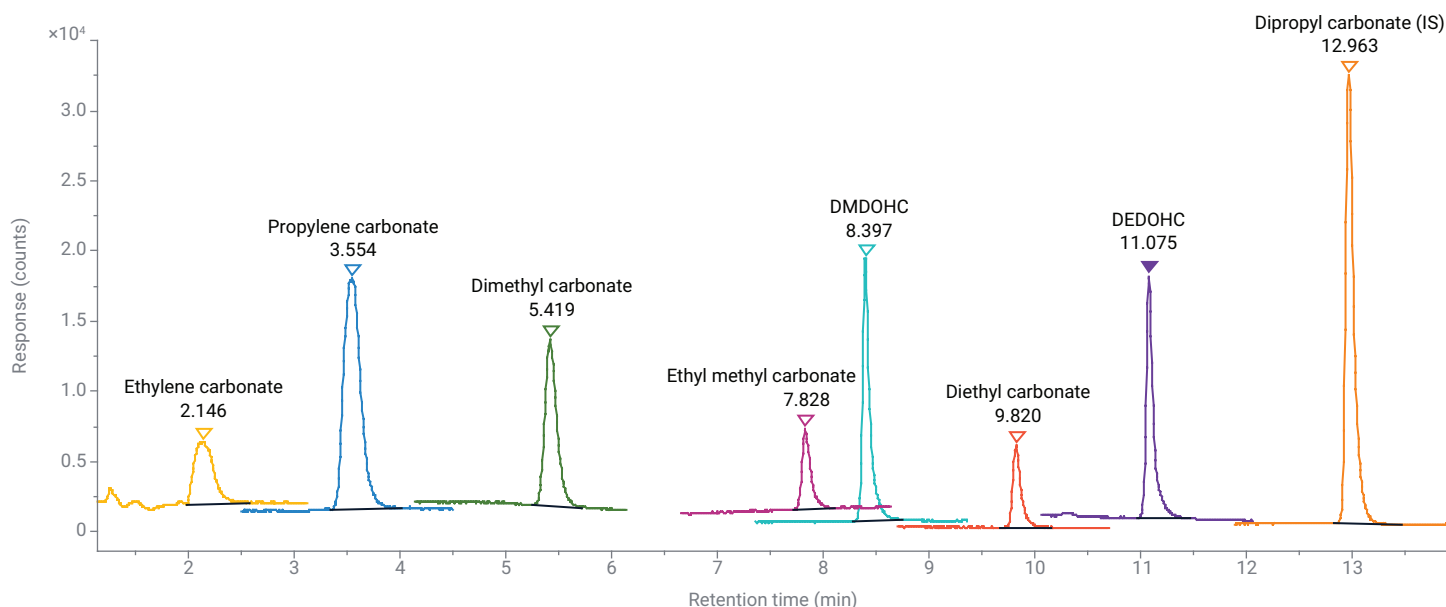
Parameter	Value
Ionization Source	Agilent Electrospray
Nebulizer Pressure	35 psig
Gas Temperature	300 °C
Gas Flow	10.0 L/min
Capillary Voltage	+5,500 V
Targeted Points per Second	3 Hz
SIM signals (m/z)	63 Diethyl carbonate (DEC) 77.1 Ethyl methyl carbonate (EMC) 89 Ethylene carbonate (EC) 91 Dimethyl carbonate (DMC) 103 Propylene carbonate (PC), dimethyl 2,5-dioxahexanedioate (DMDOHC) 117 Diethyl 2,5-dioxahexanedioate (DEDOHC) 147 Dipropyl carbonate (DPC)
Fragmentor Voltage	70 V

## Results and discussion

A separation method for the common electrolyte components EC, DMC, DEC, EMC, and PC was developed, including the determination of the degradation products DMDOHC and DEDOHC (Table 1). The method uses an InfinityLab Poroshell EC-C18 column for superior peak shape and resolution. All compounds were detected by an LC/MSD iQ single quadrupole MSD, operated in SIM mode for high sensitivity and selectivity. Mass-to-charge ratios ( $m/z$ ) for the different analytes were determined in a previous experiment where the MSD was operated in Scan mode (not shown). The best suited  $m/z$  for each compound is listed in Table 2.

Figure 2 shows the separation of a calibration sample, overlaying all SIM traces used to quantify the seven analytes. DPC, a related compound not used in electrolyte solutions, was added as an internal standard. The calibration point shown in the figure contained EC, PC, DMDOHC, and DEDOHC at the 1 ppm level, whereas DMC, DEC, and EMC were present at 1,000 ppm. The internal standard was spiked at 1,000 ppm into every sample and calibrant.

All analytes were separated with high resolution within 14 minutes. The SIM traces are only shown in a window of expected retention time of the compound that is defined in the data analysis method. It is noteworthy that although structurally similar, the different electrolyte components produced signal responses that differed dramatically under the applied conditions. EC, PC, as well as the degradation products DMDOHC and DEDOHC all showed a response approximately 1,000 times higher than DMC, DEC, and EMC. For this reason, a calibration range from 0.01 to 10 ppm was chosen for EC, PC, DMDOHC, and DEDOHC, whereas DMC, DEC, and EMC were calibrated in a range of 10 to 10,000 ppm. Linear calibration curves were constructed with a  $1/x$  weighting and exclusion of the origin. Table 3 summarizes the calibration results and lists the limits of quantitation (LOQ) and detection (LOD) for each compound.



**Figure 2.** Chromatogram overlay (1,000 ppm/1 ppm calibration sample) of all SIM signals used for detection and quantitation of the selected analytes.

**Table 3.** Calibration results of the seven analytes. LOD and LOQ were calculated based on signal height (> 3 and > 10 times the noise level, respectively).

Compound	Linear Range (ppm)	R <sup>2</sup>	LOQ (ppm)	LOD (ppm)
EC	0.01 to 10	0.999	0.147	0.044
PC	0.01 to 10	0.998	0.269	0.081
DMC	10 to 10,000	0.998	52	15
EMC	10 to 10,000	0.999	94	28
DMDOHC	0.01 to 10	0.996	0.011	0.003
DEC	10 to 10,000	0.999	31	9
DEDOHC	0.01 to 10	0.997	0.008	0.002

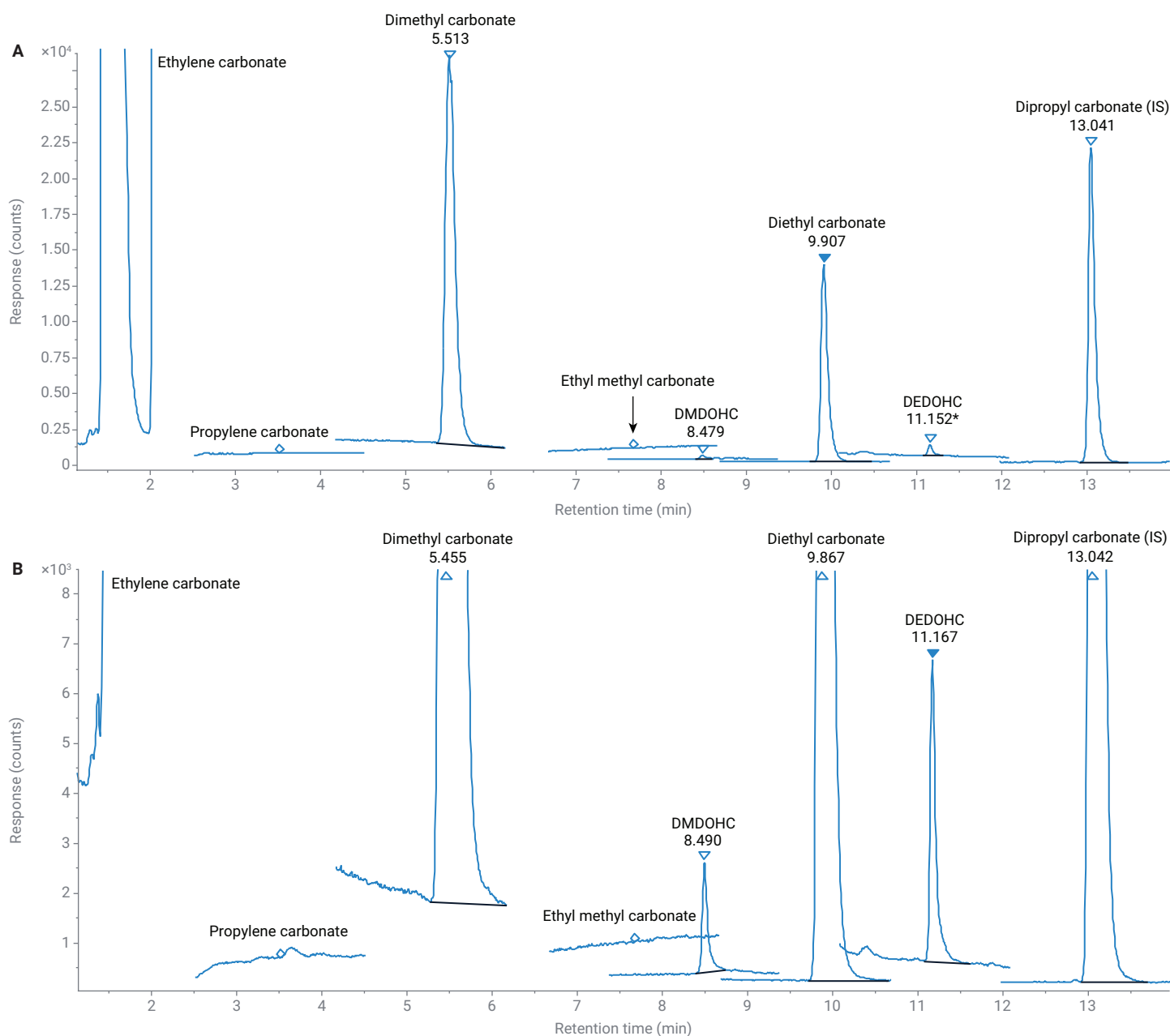
A lithium-ion battery electrolyte solution was analyzed in triplicate. Aliquots of the pure sample were diluted 1:10 and 1:100 with pure ACN and used directly for injection. Samples in strong solvents, such as 100% ACN, can create distorted peaks and poor chromatography when the separation method starts at low solvent strength, e.g., 2% ACN in water. To eliminate this issue, the 1260 Infinity II Hybrid Multisampler was operated in Agilent Feed Injection mode. This operation mode gradually injects the sample into the solvent flow, thereby focusing the analytes at the column head without peak distortion or sample breakthrough.

Figure 3 shows the separation results of a fresh electrolyte sample. The major components EC, DMC, and DEC were detected with high signal response in the 1:100 diluted sample (Figure 3A). DMC and DEC were quantified with  $32.6 \pm 0.6$  and  $40.5 \pm 0.5\%$ , respectively. The EC signal was above the calibration range and could not be quantified. The

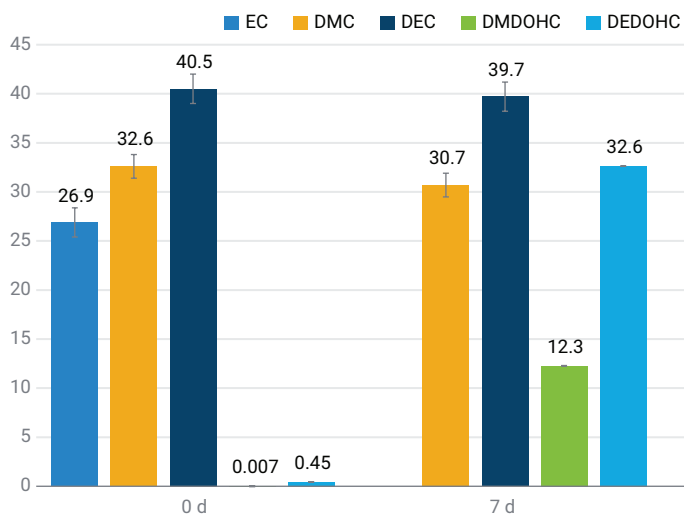
EC percentage in the electrolyte was therefore calculated as the difference between 100% and the sum of DMC and DEC, which amounted to  $26.9 \pm 1.1\%$ . PC and EMC could not be detected in the sample.

The 1:10 dilution already showed small amounts of the degradation products DMDOHC and DEDOHC. This is understandable, as the sample could not be handled in an oxygen- and water-free environment, which caused degradation. The concentration of DMDOHC was below the LOQ, and is therefore reported as 0.007 ppm, equaling half the LOQ. DEDOHC could be quantified at  $0.45 \pm 0.03$  ppm.

The undiluted sample aliquots were stored in closed vials at 40 °C to simulate ageing of the electrolyte solution. After one week, aliquots were taken, diluted 1:10 and 1:100 with ACN, spiked with internal standard, and analyzed. All analytes detected in the fresh sample could be detected in the aged sample as well. DMC and DEC were quantified at slightly lower levels, namely  $30.7 \pm 1.2$  and  $39.7 \pm 1.5\%$ . These numbers indicate that parts of the electrolyte have already degraded. EC was again above the calibration limit; no estimation of the concentration via DMC and DEC was made this time, as those levels had already decreased. The amounts of the impurities DMDOHC and DEDOHC increased during stress storage, and were quantified at  $12.3 \pm 0.04$  and  $32.6 \pm 0.03$  ppm, respectively. Figure 4 illustrates the concentrations of the different electrolyte components and degradation products in a fresh sample and after seven days under stress conditions.



**Figure 3.** Separation of an electrolyte sample, diluted 1:100 (A) and 1:10 (B). The chromatograms show SIM signals and peak labels for all calibrated analytes. The EC signal response was too high to be quantified.



**Figure 4.** Average concentration (N = 3) of electrolyte components before and after storage for seven days under stress conditions. EC, DMC, and DEC amounts are displayed in percent, DMDOHC, and DEDOHC in ppm.

The SIM signals that were used to quantify DMDOHC and DEDOHC ( $m/z$  103 and 117) showed further peaks at different retention times. The monitored mass-to-charge ratios for these analytes do not refer to the intact molecular ion, but to fragments specific to these organic carbonates. The additional peaks present in the stressed sample therefore likely share the same fragments as DMDOHC and DEDOHC. In another analysis of the stressed sample with an LC/MS scan method, the presumed molecular ions of the additional impurities were detected at  $m/z$  239, 253, 281, and 295. These mass-to-charge ratios fit the chemical formula of oligomeric carbonates  $C_2H_6(CH_2)_n(CO_3)_3$  (with  $n = 2, 3, 5, 6$ ) that have been described as typical degradation products of LIB electrolytes.<sup>4</sup> Their formation pathway is the same as for DMDOHC and DEDOHC, which are formed by reaction of EC with two equivalents of DMC or DEC, respectively, in the presence of  $LiPF_6$ . In an electrolyte containing both DMC and DEC, it is to be expected that additional oligo carbonates are formed by mixed reactions of EC, DMC, and DEC. For want of suitable reference compounds, however, none of the postulated oligomeric carbonates could be identified or quantified.

## Conclusion

The method presented in this application note was used to quantify major components as well as degradation products of lithium-ion battery electrolytes. Separation of all analytes was achieved within 14 minutes using an Agilent InfinityLab Poroshell 120 EC-C18 column, which produced excellent peak shape and resolution. Peak distortions caused by the strong sample solvent (pure acetonitrile) were eliminated by operating the Agilent 1260 Infinity II Hybrid Multisampler in Feed injection mode. The use of the Agilent LC/MSD iQ enabled sensitive detection by specifically monitoring SIM signals of the analytes. Detection limits of major components were between 0.04 and 28 ppm, whereas degradation products DMDOHC and DEDOHC could be detected in single-digit ppb amounts. This method can easily be extended to include further degradation products, depending on the availability of reference compounds.

## References

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