



Mass spectrometry

Identification of lithium-ion battery degradation products using GC Orbitrap mass spectrometry

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Keywords

Lithium-ion battery, electrolyte degradation products, Orbitrap Exploris GC, Orbitrap technology, high resolution accurate mass, mass accuracy, gas chromatography, research

Goal

To demonstrate the identification of characteristic carbonate substructures and electrolyte solvent degradation in lithium-ion batteries using the Thermo Scientific™ Orbitrap Exploris™ GC mass spectrometer.

Introduction

From consumer electronics to electric vehicles, the growing demand for better-performing, safer, and less costly batteries has led researchers to focus on improving several aspects of lithium-ion battery technology. The experiments shown in this study by Münster Electrochemical Energy Technology (MEET) aim to investigate electrolyte aging, a major factor affecting lithium-ion battery life. Using gas chromatography coupled to high-resolution accurate-mass mass spectrometry (GC-HRAM-MS), MEET's Analytics and Environment division gains the flexibility and data quality to have a deeper understanding of their samples. This in turn provides detailed insight into the complex reaction mechanisms involved in electrolyte aging. Ultimately these discoveries will enable the research team to identify additives to curtail, halt, or even tailor electrolyte aging.

Of the basic components of a lithium-ion battery, the electrolyte provides a conductive medium for lithium ions to move between electrodes. It consists of conducting salts, which are highly fluorinated, and various solvents. Lithium hexafluorophosphate (LiPF₆)-based electrolytes dissolved in mixtures of aprotic organic carbonate solvents are commonly used. As the electrolyte degrades, several decomposition complex products are formed, such as carbonate oligomers, fluorophosphates, and organofluorophosphates. Using a variety of analytical approaches, researchers at MEET's Analytics and Environment division identify and quantify these compounds as they are generated during aging.

There are significant challenges associated with this research. To begin, the degradation mechanisms and the resulting degradation products are often unknown and not described in published literature. Thus, there are no reference materials available, and research published to date has used low-resolution gas chromatography–mass spectrometry techniques (GC-MS),¹⁻³ nuclear magnetic resonance (NMR),⁴ and other techniques to identify compounds. Often these approaches do not provide sufficient structural information or sensitivity to detect and identify all compounds of interest. Another challenge is the complexity of the sample matrices studied, which are rich in highly fluorinated compounds and concentrated solvents. Matrix effects can lead to interferences, reduce sensitivity, and increase instrument maintenance requirements. Instrument sensitivity is a significant benefit as it allows a high split or dilution to be applied to protect the system from high concentration components, while allowing detection of the trace levels of decomposition species of interest in electrolyte aging.

In this study the identification of known carbonate dimers using GC-HRAM-MS is shown as part of a targeted analysis in an aged electrolyte matrix. Subsequently, the identification of unknown related carbonates identified from similar retention and fragmentation profiles is investigated and confirmed using both electron ionization (EI) and positive chemical ionization (PCI) with GC Orbitrap mass spectrometry.

Experimental

Sample and standard preparation

The pure aged electrolyte was collected by centrifugation of the separator and negative electrode of the battery after cell formation. For precipitation of the GC-harmful LiPF₆ conducting salt, the electrolyte was diluted in dichloromethane (1/100; v/v) and stored at 3 °C overnight. The supernatant was taken for analysis.

Instrument and method setup

Automatic sample injection was performed using a Thermo Scientific™ TriPlus™ RSH autosampler, and chromatographic separation was performed using a Thermo Scientific™ TRACE™ 1310 GC system fitted with a Thermo Scientific™ TraceGOLD™ TG-5SiIMS 30 m × 0.25 mm i.d. × 0.25 μm film capillary column with a 5 m integrated guard ([P/N 26096-1425](#)). Finally, a Thermo Scientific Orbitrap Exploris GC-MS was used for accurate mass measurements in full-scan mode at 60,000 mass resolution (FWHM at *m/z* 200). Data processing was performed using Thermo Scientific™ FreeStyle™ software. Additional details of instrument parameters are displayed in Tables 1–3.

Table 1. GC and injector conditions

TRACE 1310 GC system parameters			
Injection volume	1.0 μL		
Liner	Thermo Scientific™ LinerGOLD™ Split/splitless with quartz wool (P/N 453A2265)		
Inlet	250 °C		
Carrier gas, flow	He, 1.16 mL/min		
Inlet module and mode	SSL, Split		
Split ratio	100 (EI), 10 (PCI)		
Purge flow	2 mL/min		
Column	TraceGOLD TG-5SiIMS 30 m × 0.25 mm i.d. × 0.25 μm film (P/N 26096-1425)		
Oven temperature program	Rate (°C/min)	Target temperature (°C)	Hold time (min)
Initial	-	40	1.0
Ramp 1	3.0	60	0
Ramp 2	30.0	260	2.0
Run time	16.3	-	-

Table 2. Orbitrap Exploris GC-MS parameters (EI)

Orbitrap Exploris GC mass spectrometer parameters	
Transfer line	250 °C
Ionization type	EI
Ion source	200 °C
Electron energy	70 eV
Acquisition modes	Full-scan
Mass range	35–500 Da
Resolving power	60,000 (FWHM at m/z 200)

Table 3. Orbitrap Exploris GC-MS parameters (PCI)

Orbitrap Exploris GC mass spectrometer parameters	
Transfer line	250 °C
Ionization type	PCI
Ion source	300 °C
CI reagent gas	Ammonia (3.5 purity)
CI gas flow rate	2.5 mL/min
Acquisition modes	Full-scan
Mass range	50–500 Da
Resolving power	60,000 (FWHM at m/z 200)

Results and discussion

The objective of the experiments was to identify carbonate substructures by detection of known species, followed by screening for lower abundance related compounds by inspection of similar accurate mass fragmentation and chromatographic features. The presence of carbonate substructures is indicative of electrolyte solvent degradation, and information on elemental composition provides information about the possible mechanisms.

Targeted carbonate substructures

Figure 1 shows the EI extracted ion chromatogram of dimethyl, ethyl methyl, and diethyl carbonate structures containing dimers in the aged electrolyte. The marker fragments for methyl carbonate mainly correspond to m/z 103.0389 ($C_4H_7O_3$), m/z 77.0233 ($C_2H_5O_3$) and for ethyl carbonate m/z 63.0076 (CH_3O_3). The accurate mass fragmentation patterns observed in the full scan data in Figure 2 provides reliable confirmation of which substructure is present. When determining these compounds in unknown samples, these accurate mass ions provide the selectivity to extract against a complex chemical background and certainty in the detection. The mass accuracy of the ions in the spectra in Figure 2 are all <2 ppm even at these relatively low masses (<105 Da).

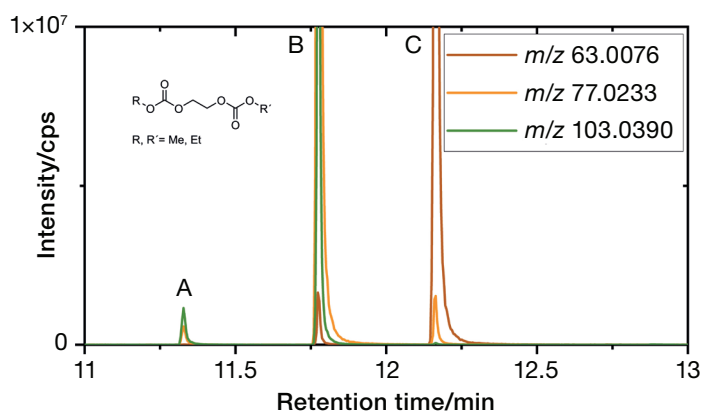


Figure 1. Overlaid EI extracted ion chromatogram of m/z 103.0389 ($C_4H_7O_3$), m/z 77.0233 ($C_2H_5O_3$), and m/z 63.0076 (CH_3O_3). Peaks labeled (A) dimethyl carbonate, (B) ethyl methyl carbonate, and (C) diethyl carbonate. For ethyl methyl species both m/z 103.0389 and m/z 63.0076 are detectable.

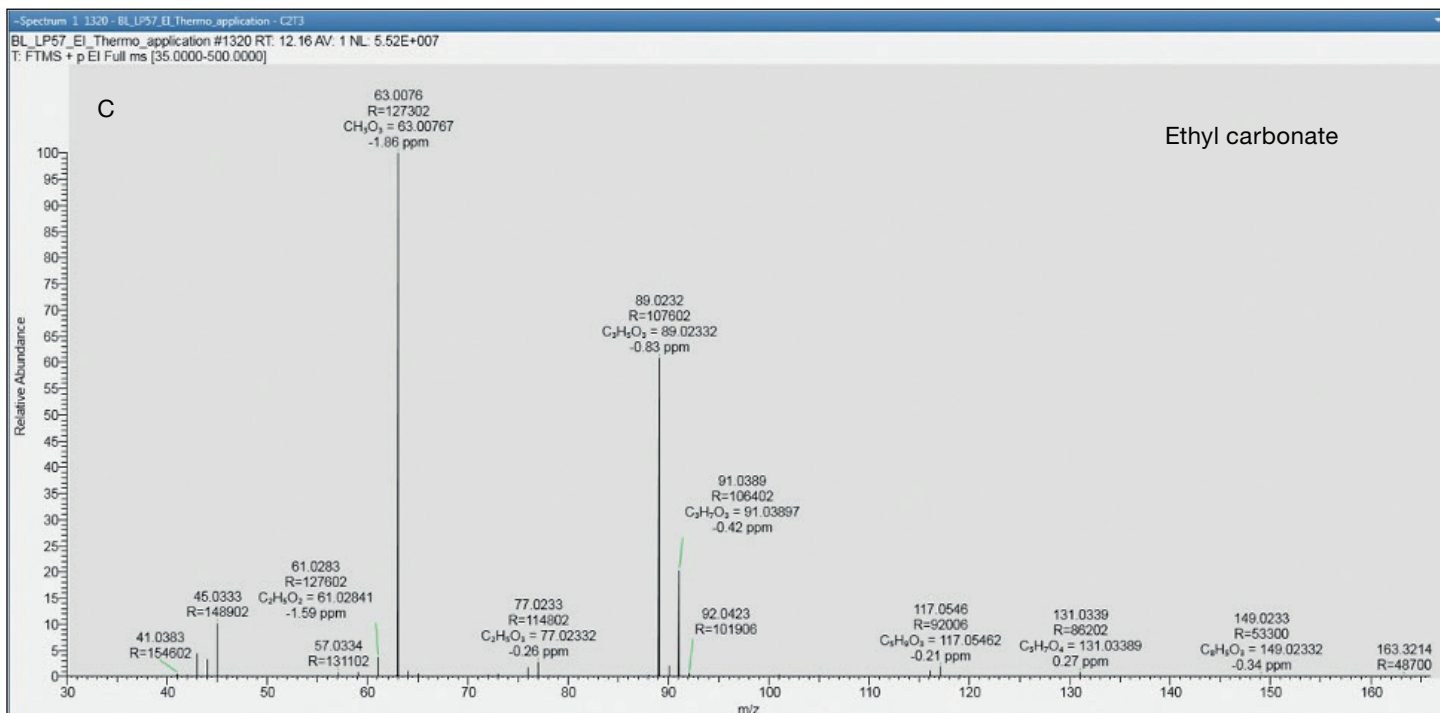
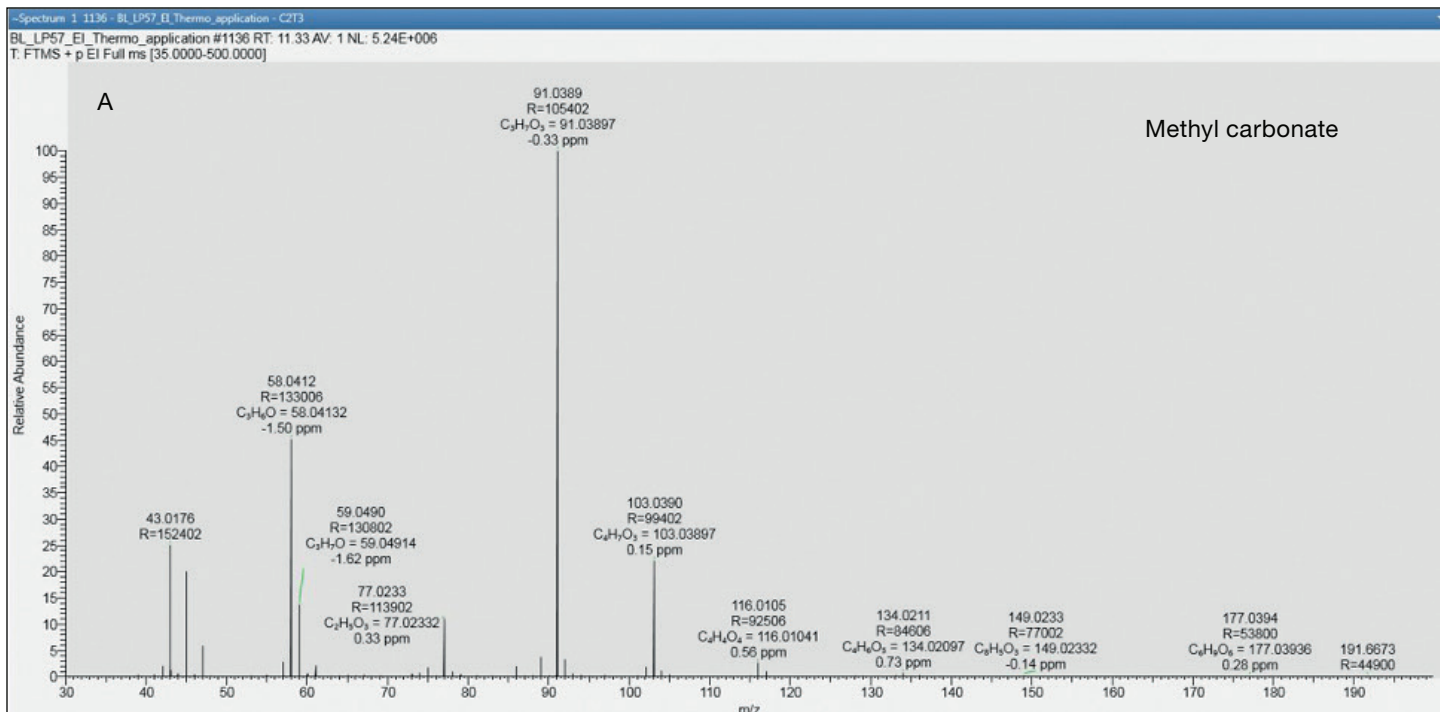


Figure 2. Full scan accurate mass spectra of dimer peaks at 11.3 and 12.2 minutes, peaks A and C. Upper spectrum shows characteristic fragmentation for methyl carbonate (m/z 103.0390), and lower spectrum for ethyl carbonate (m/z 63.0076).

Identification of unknown carbonate substructures

The extraction of the accurate mass ions in the targeted analysis of methyl and ethyl carbonate revealed the presence of peaks later in the chromatogram at 13.9, 14.1, and 14.4 minutes (Figure 3) with similar fragmentation and elution patterns. This similarity led to the suspicion that these were structurally related to the known compounds and therefore of interest in the context of electrolyte degradation. As such, it was important that the peaks could be identified with a high degree of certainty. With no certified standards, the accurate mass information provided a pathway to proposing an identify based on their elemental formula.

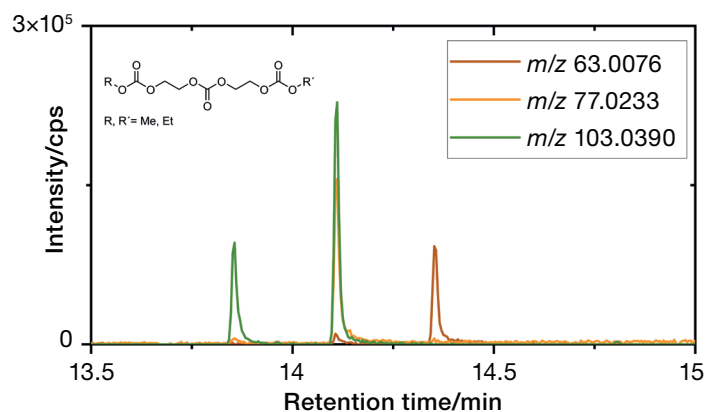


Figure 3. Overlaid EI extracted ion chromatogram of m/z 103.0389 ($C_4H_7O_3$), m/z 77.0233 ($C_2H_5O_3$), and m/z 63.0076 (CH_3O_3). The chromatographic pattern at 13.9, 14.1, and 14.4 minutes is similar to the known carbonate dimers, and therefore the peaks are interesting to this study of electrolyte degradation.

Due to strong fragmentation behavior of organic carbonates with electron ionization, molecular ion information was not obtained by this analysis. Furthermore, carbonate dimers and trimers also fragment when methane is used as a chemical ionization reagent gas. Therefore, soft PCI with ammonia was performed as it was critical to identify the molecular ion of the peaks through a chemical ionization acquisition. The Orbitrap Exploris GC is capable of switching from EI to PCI without breaking the system vacuum, enabling a change within minutes. This provides a quick

route to identification of the molecular ion by inspection of the spectrum of known adducts. Positive chemical ionization data was acquired using ammonia as the reagent gas to generate $[M+H]^+$ and $[M+NH_4]^+$ ions in the spectrum. The mass adducts identify which is the molecular ion in the spectrum to then propose an accurate elemental composition. The better the mass accuracy, the lower the number of possible elemental compositions that need to be evaluated.

The zoomed spectrum of the peak at 13.9 minutes is shown in Figure 4 (upper) showing the $[M+H]^+$ and $[M+NH_4]^+$ ions at m/z 267.07106 and m/z 284.09761, respectively. The proposed elemental composition corresponds to $C_9H_{15}O_9$ when using the elements C 1-50, H 1-50, O 1-20, P 0-10, and F 0-10. The importance of good mass accuracy is demonstrated in Figure 5 where <1 ppm mass accuracy suggests only two possible elemental compositions. Whereas, with poor mass accuracy at 5 or 10 ppm there are up to 11 formulae that would fit. This means it takes longer to work through each suggested composition, and the certainty in the result is not as high as with the sub 1 ppm mass accuracy provided by Orbitrap-based mass spectrometry. The two suggested elemental compositions can be quickly reviewed with the correct answer— $C_9H_{15}O_9$ fitting with -0.51 ppm and the alternative $C_{10}H_{18}O_3FP_2$ with -0.18 ppm. The latter can be excluded because the ratio of P, O, and F does not fit for PF_6 originating species and the previously observed EI fragment ions cannot be matched with these elements.

Ethyl and methyl carbonate structures have three possible termination species; the peaks at 14.1 and 14.4 minutes align with these to show a trimer and therefore agree with the pattern observed in literature known dimers.² For peaks at 14.1 and 14.4 minutes, both $[M+H]^+$ and $[M+NH_4]^+$ ions are observed as seen in Figure 4 with excellent mass accuracy to support elemental proposals of $C_{10}H_{17}O_9$ and to $C_{11}H_{19}O_9$, respectively. This information can either be applied as a targeted screen of future samples or used to support further understanding of the mechanisms of electrolyte degradation.

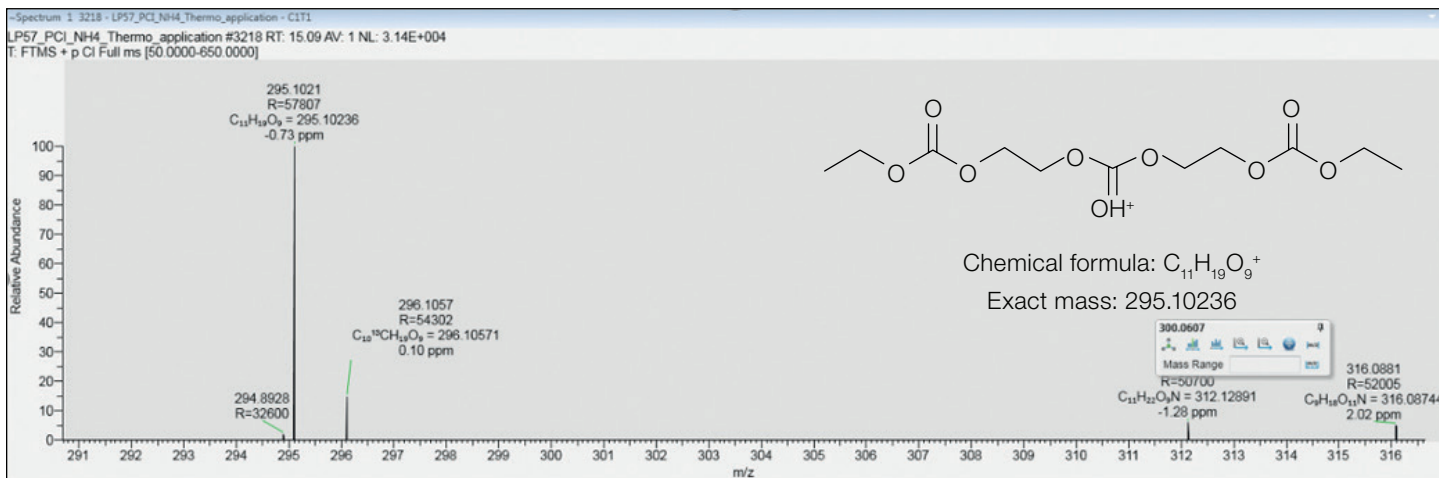
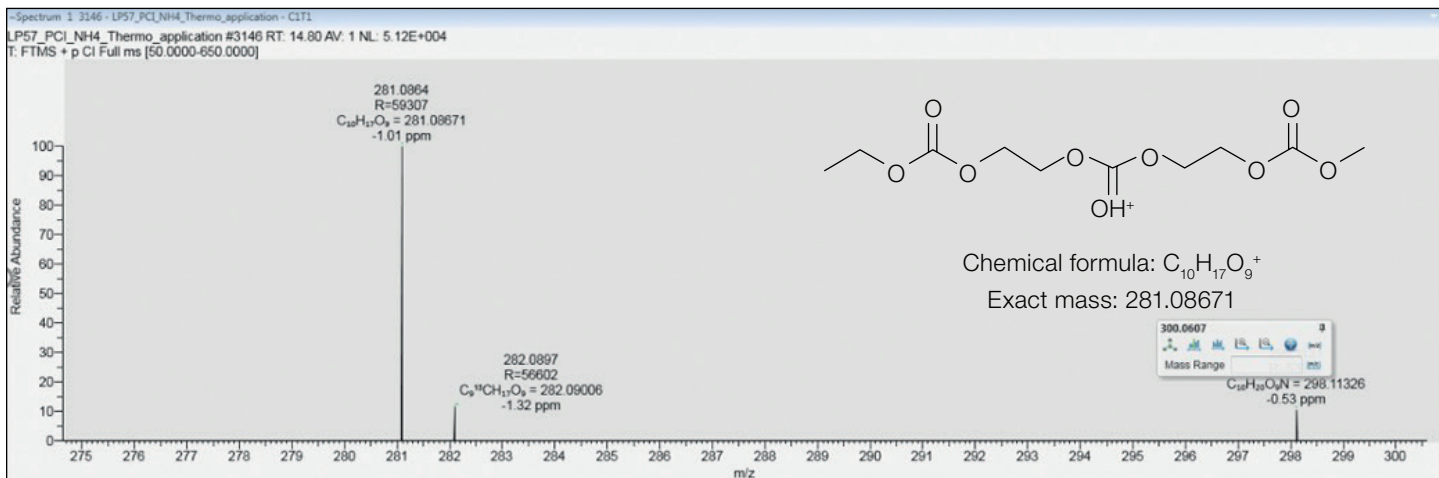
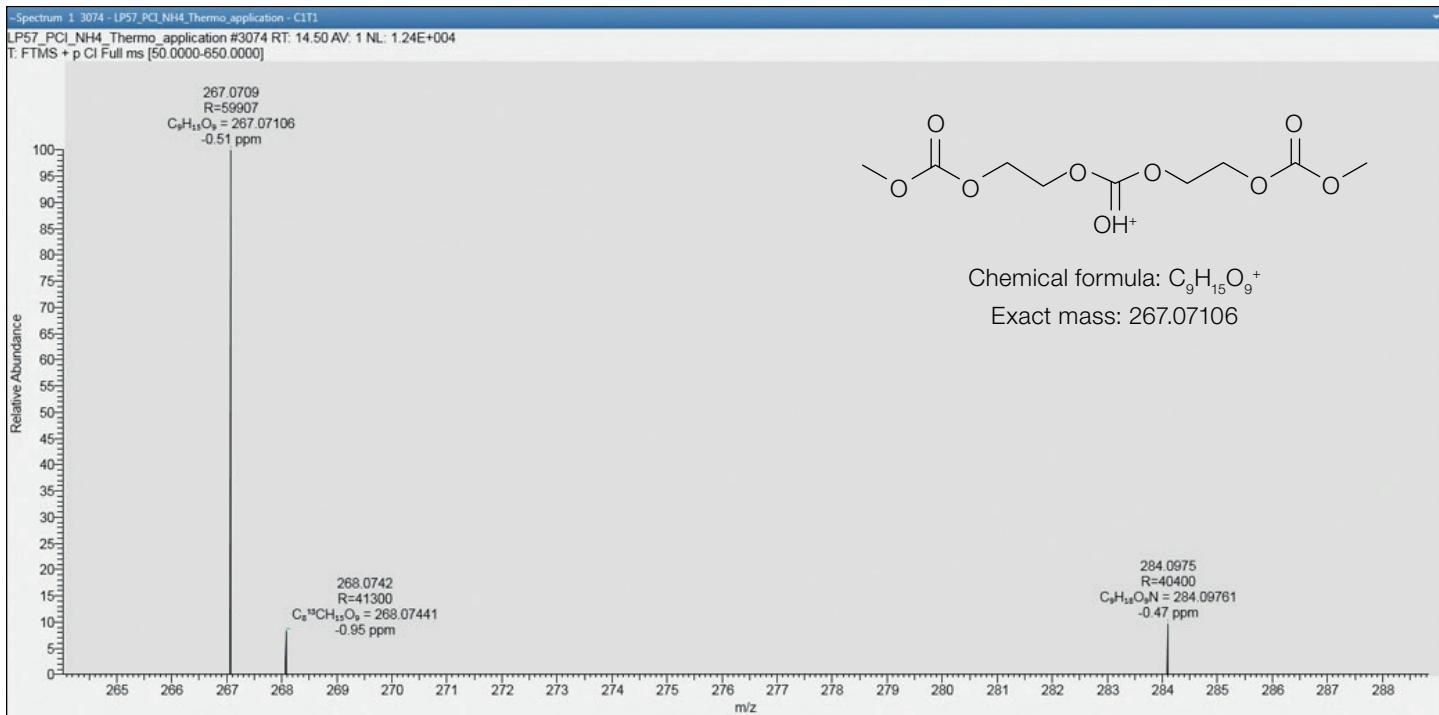


Figure 4. Zoomed positive chemical ionization spectra of peaks at 13.9 (upper), 14.1 (middle,) and 14.4 (lower) minutes. $[M+H]^+$ and $[M+NH_4]^+$ ions are labeled with theoretical accurate mass, proposed elemental formula, and ppm mass accuracy. The R value corresponds to the mass resolution of the ion.

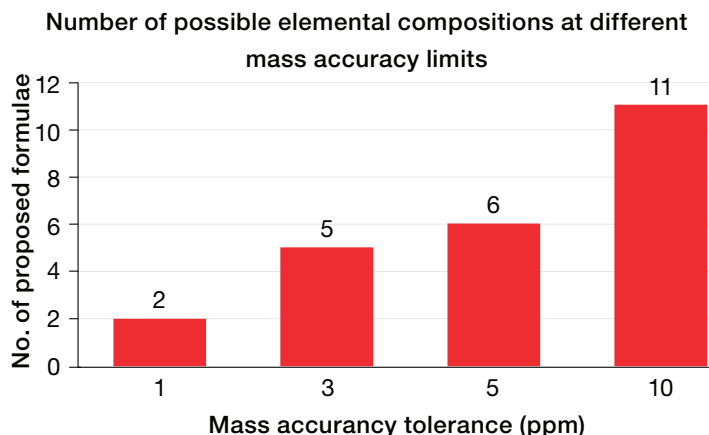


Figure 5. Bar chart showing the number of possible elemental compositions with increasing mass accuracy. The expected sub 1 ppm mass accuracy of the GC Orbitrap system shows only two possible formulae, meaning that identification can be achieved in a shorter time and with a higher degree of confidence.

Conclusions

The results of this study demonstrate that the benchtop Orbitrap Exploris GC mass spectrometer provides a powerful tool for the detailed characterization of lithium-ion battery electrolytes.

- Target compounds, ethyl carbonate and methyl carbonate, could be accurately determined against a complex chemical background through identification of unique fragmentation profiles including m/z 103.0389 ($C_4H_7O_3$), m/z 77.0233 ($C_2H_5O_3$), and m/z 63.0076 (CH_3O_3). The mass resolving power of 60,000 enabled chromatographic peaks to be extracted with narrow windows, providing clear detection of target compounds from background chemical interferences.

- GC unknown trimer peaks exhibiting similar elution profiles to known compounds could be identified through EI and PCI data acquisitions that provided information on the elemental composition of mass adduct ions in the spectra. The ability to change between EI and CI without breaking system vacuum enables a convenient route to obtain this important structural information.
- Good mass accuracy ensured that the correct elemental composition $C_9H_{15}O_9$, $C_{10}H_{17}O_9$, and $C_{11}H_{19}O_9$ could be proposed for unknowns without an extensive workload and that proposals could be made with a high degree of certainty. This information can then be used as part of a targeted screening analysis or to understand electrolyte aging mechanisms.

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