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Comprehensive analysis of electrolyte solutions for lithium-ion batteries using gas chromatography-mass spectrometry

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Goal
The goal of this application note is to demonstrate the Thermo Scientific™ ISQ™ 7610 Single Quadrupole GC-MS capabilities for accurate quantitation and characterization of lithium battery electrolyte components.

Introduction
The development of the lithium-ion battery (LIB) over the past three decades has led to groundbreaking advancements in energy storage. This comes at an opportune time as the world's current and ever-growing energy demands have reached a critical point. Traditional petroleum-based energy sources (i.e., oil, natural gas) are dwindling, while strict mandates have been initiated by governments to reduce petroleum-based carbon emissions under the Paris Agreement by 2030. In addition, recent geopolitical factors have made access to traditional energy sources in Europe highly volatile and unstable, further driving the need for new sources of energy. While renewable energy sources (i.e., solar, hydro, wind) could be a viable alternative, storage of energy is a limiting factor for larger scale use.

The biggest impact of LIBs can be seen in the transport sector with their implementation in electric vehicles. However, the longevity of LIB operation is a crucial factor to become a suitable energy replacement to petroleum in motor vehicles. The durability of LIBs is attributed to the thermodynamics of the battery electrolyte. The most common electrolyte used in LIBs is lithium hexfluorophosphate ($LiPF_6$) salt mixed with organic carbonate solvents (i.e., dimethyl carbonate, ethyl methyl carbonate, diethyl carbonate).

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Upon the first cycling of the LIB, reduction of the electrolyte at the anode surface produces a conductive film known as the solid electrolyte interface (SEI), where current (i.e., Li$^+$) can pass through while simultaneously preventing further reduction of the electrolyte. However, the LiPF$_6$ is thermodynamically unstable at elevated operating temperatures (>60 °C) causing the organic carbonate solvents to be further reduced. As a result, a thicker and more resistive SEI is formed, limiting current flow and LIB charging capacity. In addition, thermal dissociation of the LiPF$_6$ to PF$_5$ causes deterioration of the SEI through side reactions, resulting in continued electrolyte degradation as it comes in contact again with the anode surface.[1]

The addition of electrolyte additives can help reduce electrolyte degradation in LIB batteries. These chemicals are preferentially reduced at higher potentials, helping prevent further electrolyte degradation under such operating conditions. Differences in additive functional groups will alter the properties of the SEI. Thus, knowledge of electrolyte composition and byproducts formed during battery operation is key for future development of more efficient, stable, and high performing LIBs.

In this application note, an analytical method for the compositional analysis of LIB electrolytes is demonstrated. Extraction and analysis of LIB electrolytes for 16 different electrolyte solvent, additive, and degradation compounds were performed using the Thermo Scientific™ TRACE™ 1610 gas chromatograph coupled to the Thermo Scientific™ ISQ™ 7610 single quadrupole GC-MS system. High linearity was observed over an extended calibration range with trace level detection possible at µg·L^{-1} levels. Quantification, confirmation, and identification were achieved using full scan together with selected ion monitoring (SIM) acquisition for accurate determination of LIB electrolyte composition.

Experimental

Standard and sample preparation

Individual standard stock solutions of different organic carbonate solvents (Sigma-Aldrich, USA), electrolyte additives (Sigma-Aldrich, USA) and dioxahexane acid dimethyl ester (abcr chemicals, Germany) were weighed and diluted in dichloromethane (Honeywell, USA) to a concentration of 10 g·L^{-1}. A secondary stock solution containing all analytes was prepared in dichloromethane at a concentration of 500 mg·L^{-1} followed by serial dilution to produce a 7-point calibration curve (0.1, 1.0, 10, 25, 50, 100, 200 mg·L^{-1}).

For sample preparation, 20 µL aliquots of LIB electrolyte material were diluted with 1 mL of dichloromethane. Sample dilutions were centrifuged for 5 min at 8,500 rpm using a Thermo Scientific™ Sorvall™ ST 8R centrifuge (P/N 75007203) for removal of the LiPF$_6$ salt to avoid detrimental effects to the

GC column. The supernatant was then diluted by factors of 10, 100, and 1,000 (total sample dilution of 500, 5,000, and 50,000, respectively) for analysis by GC-MS using external calibration.

Instrument and method setup

Analysis was carried out using the ISQ 7610 GC-MS. Automatic sample injection was performed using a Thermo Scientific™ TriPlus™ RSH autosampler with chromatographic separation obtained using a TRACE 1610 GC equipped with a Thermo Scientific™ TraceGOLD™ TG-35MS 30 m × 0.25 mm i.d. × 0.25 µm film capillary column (P/N 26094-1420). Sample analysis was performed in full scan and selected ion monitoring (SIM) acquisition modes. Additional instrument parameters are displayed in Table 1 and Table 2.

Table 1. GC injection and column conditions

Trace 1610 GC system parameters	
Injection volume (µL)	1
Liner	Thermo Scientific™ LinerGold™ Precision liner (P/N 453A1255-UI)
Injection mode	Split
Split ratio	1:20
Injector temperature (°C)	250
Carrier gas, (mL·min^{-1})	He, 1.0 (constant flow)
Oven temperature program	
Initial temperature (°C)	35
Hold time (min)	3
Temperature 1 (°C)	160
Rate (°C·min-1)	10
Hold time (min)	0
Temperature 2 (°C)	200
Rate (°C·min^{-1})	20
Hold time (min)	5
Total run time (min)	23

Table 2. Mass spectrometer conditions for using simultaneous full scan and timed acquisition (t-SIM)

ISQ single quadrupole GC-MS parameters	
Transfer line (°C)	280
Thermo Scientific™ Exactabrite™ ion source (°C)	260
Ionization mode	EI
Electron energy (eV)	70
Full scan range (*m/z*)	35–500
Full scan time (s)	0.2
SIM time (s)	0.6
Minimum baseline peak width (s)	6
Desired peak scans	10

Results and discussion

Chromatography

Using the TraceGOLD TG-35MS capillary column, separation of targeted analytes was achieved within 16 minutes (Figure 1, Table 3). Potential interferences due to coelution between diethyl carbonate and propyl propionate are avoided using mass spectrometric detection, where selective mass separation is achieved. This eliminates the need for an extended oven temperature program for chromatographic separation, providing faster and more efficient analyses.
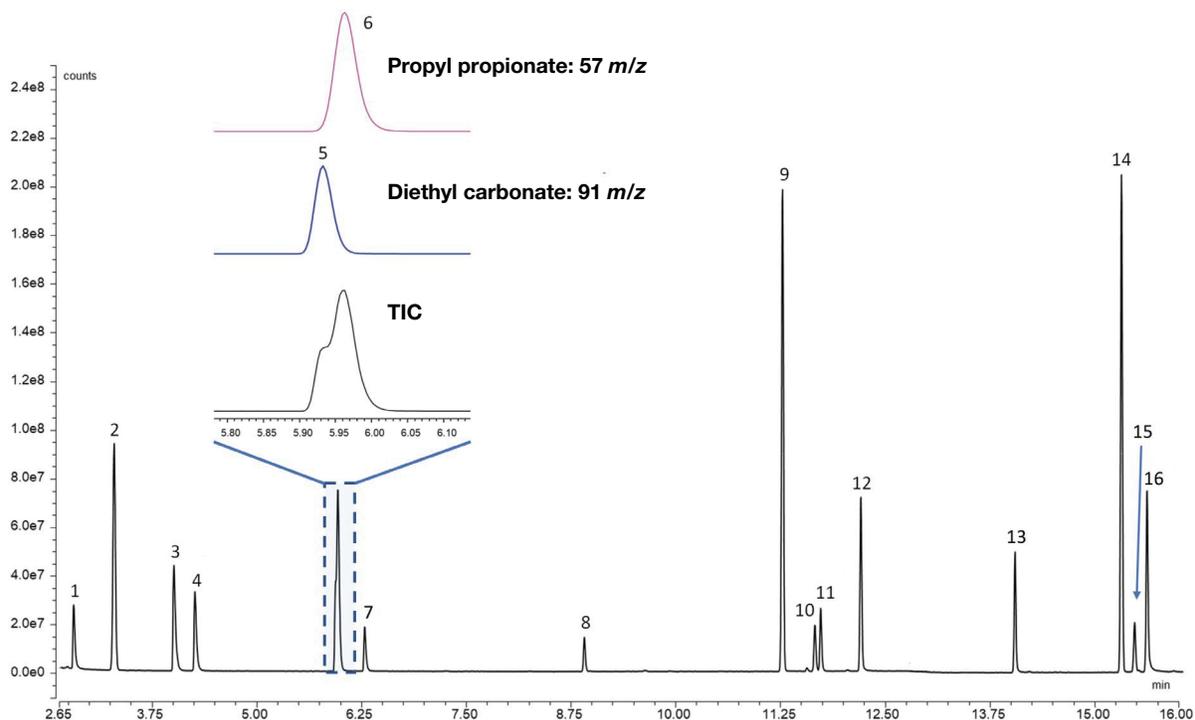

Figure 1. Full scan acquisition of 10 mg·L⁻¹ standard of LIB electrolyte solvent, additive, and degradation compounds. A full list of all compounds is given in Table 3.

Table 3. Compound retention time, acquisition ions, and calibration correlation coefficients acquired in full scan (0.1–200 mg·L⁻¹) and t-SIM (0.1–100 mg·L⁻¹) acquisition modes

Compound	Electrolyte component	Retention time (min)	SIM ions (m/z)[a]	Full scan (0.1–200 mg·L⁻¹) r²	SIM (0.1–100 mg·L⁻¹) r²
1. Dimethyl carbonate	Solvent	2.80	**45**, 51, 90	0.9993	0.9997
2. Fluorobenzene	Co-solvent	3.29	**96**, 70, 95	0.9958	0.9992
3. Ethyl propionate	Additive/co-solvent	4.00	**57**, 102, 74	0.9952	0.9990
4. Ethyl methyl carbonate	Solvent	4.26	**77**, 45, 59	0.9998	0.9998
5. Diethyl carbonate	Solvent	5.94	**91**, 45, 63	0.9962	0.9962
6. Propyl propionate	Additive/co-solvent	5.97	**57**, 87, 75	0.9906	0.9991
7. Vinylene carbonate	Additive	6.28	**86**, 44, 58	0.9997	0.9990
8. Flouroethylene carbonate	Additive	8.92	**62**, 44, 106	0.9326	0.9992
9. 1,1–dimethylpropylbenzene	Additive	11.29	**119**, 91, 148	0.9825	0.9992
10. Ethyl carbonate	Solvent	11.67	**88**, 102, 43	0.9998	0.9982
11. Propyl carbonate	Solvent	11.75	**57**, 43, 87	0.9969	0.9988
12. Succoinitrile	Additive	12.22	**53**, 79, 80	0.9969	0.9993
13. 2,5 Dioxaheznedioc acid dimethyl ester	Degradation product	14.04	**59**, 91, 102	0.9986	0.9936
14. Phenylcyclohexane	Additive	15.28	**160**, 104, 117	0.9961	0.9993
15. 1,3-propanesultone	Additive	15.43	**58**, 57, 122	0.9996	0.9983
16. Adiponitrile	Additive/co-solvent	15.58	**68**, 54, 55	0.9922	0.9985

[a]Bold text represents the quantification ion

Linearity

Calibration analysis showed all compounds, with exception of fluoroethylene carbonate, displayed linear correlation from 0.1 to 200 mg·L[1] with full scan acquisition (Table 3), demonstrating the high dynamic linear range of the new Thermo Scientific™ XLXR™ electron multiplier detector. In SIM acquisition mode, correlation coefficients for all compounds improved, including fluoroethylene, with all compounds displaying linear response between 0.1 and 100 mg·L^{-1}.

Sensitivity

Analytical variation observed in replicate analysis (n=10) of the lowest calibration standard was used to determine instrument detection (IDL: 3 × standard deviation) andquantification (IQL: 10 × standard deviation) limits (Table 4). Detection and quantification limits were compound dependent, with IDLand IQL of 0.021 and 0.07 mg·L^{-1} or lower for all compounds, respectively.

Table 4. Instrument detection (IDL) and quantification (IQL) limits for electrolyte solvents and additives. Relative standard deviation (% RSD) based on replicate injection (n = 10) of 0.1 mg·L^{-1} standard.

Compounds	IDL	IQL	%RSD
Dimethyl carbonate	0.010	0.035	2.6
Fluorobenzene	0.006	0.019	2.5
Ethyl propionate	0.004	0.015	2.0
Ethyl methyl carbonate	0.006	0.020	2.5
Diethyl carbonate	0.007	0.023	2.8
Propyl propionate	0.011	0.037	2.4
Vinylene carbonate	0.006	0.021	3.2
Fluoroethylene carbonate	0.015	0.049	6.3
1,1-Dimethylpropylbenzene	0.004	0.014	1.9
Ethylene carbonate	0.005	0.017	2.2
Propyl carbonate	0.021	0.070	2.0
Succononitrile	0.010	0.034	5.0
Dioxahexane acid dimethyl ester	0.007	0.023	4.6
Phenylcyclohexane	0.003	0.011	2.2
1,3-propanesultone	0.004	0.014	1.9
Adiponitrile	0.003	0.009	1.8

Electrolyte composition and unknown determination

Full scan acquisition of both new and cycled LIB electrolytes showed differences in their composition (Figure 2).
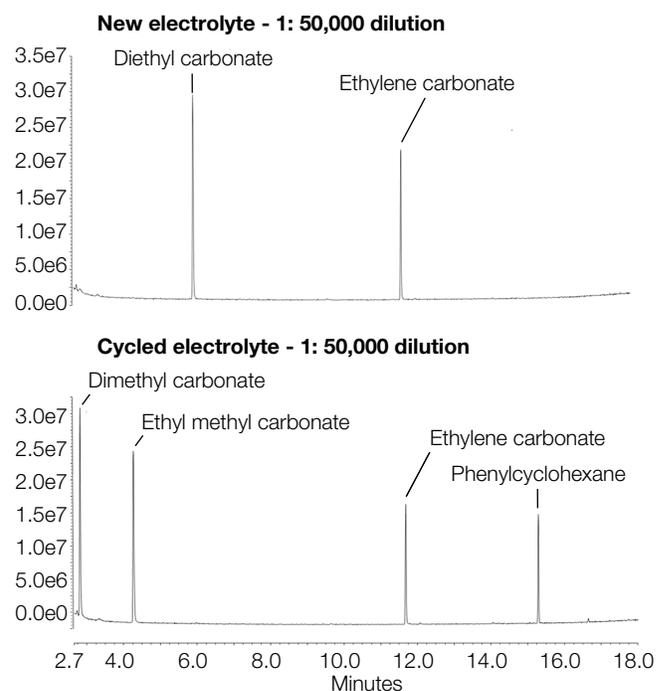

Figure 2. Full scan acquisition of new and cycled electrolyte solutions at 1:50,000 dilution

Such differences are not unexpected as composition will differ depending on their source of production. Analysis of three new electrolyte solutions showed similar composition between electrolyte samples 1 and 2 (i.e., diethyl carbonate and ethylene carbonate dominated), but differed in that observed in electrolyte 3 (i.e., ethyl methyl carbonate and ethylene carbonate dominated) (Table 5). Composition analysis of cycled electrolytes showed dimethyl carbonate, ethyl methyl carbonate, ethylene carbonate, and phenylcyclohexane were dominate components.

In addition to the electrolyte solvent and additive compounds detected in cycled electrolytes, several other minor peaks were observed close to the chromatographic baseline. NIST spectral library search of the full scan acquisition identified one of these peaks as biphenyl, a common additive in LIBs for its flame retardant properties[1] (Figure 3). To confirm these findings, a 1:5,000 dilution of the cycled electrolyte was analyzed. Not only was biphenyl confirmed to be present but also dioxahexane acid dimethyl ester, a known degradation product of LIB electrolytes[2] (Figure 4.)

An additional peak was identified as 1,4-meracapto-2,3-butanediol prior by the NIST search library. However, the low probability score (24.6%) indicates further investigation using a standard to confirm spectra and retention time is needed

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Table 5. Composition analysis (mg·L⁻¹) of LIB electrolyte solutions at 1:5000 dilution

Compound[a]	Electrolyte 1 (new)	Electrolyte 2 (new)	Electrolyte 3 (new)	Electrolyte 4 (cycled)	Electrolyte 5 (cycled)
Dimethyl carbonate	0.08	0.10	0.04	64.0	71.9
Ethyl propionate	ND	ND	ND	0.01[b*]	0.02
Ethyl methyl carbonate	ND	0.06	102	43.9	46.9
Diethyl carbonate	77.8	114	ND	0.25	0.31
Vinylene carbonate	ND	ND	ND	0.01[b*]	ND
Ethylene carbonate	89.2	129	128	63.4	59.9
Dioxahexane acid dimethyl ester	ND	ND	ND	0.21	0.30
Phenylcyclohexane	ND	ND	ND	4.25	4.25

[a]Compounds reported if both confirmation ion ratios passed

[b]Detected in 1:500 dilution of electrolyte sample
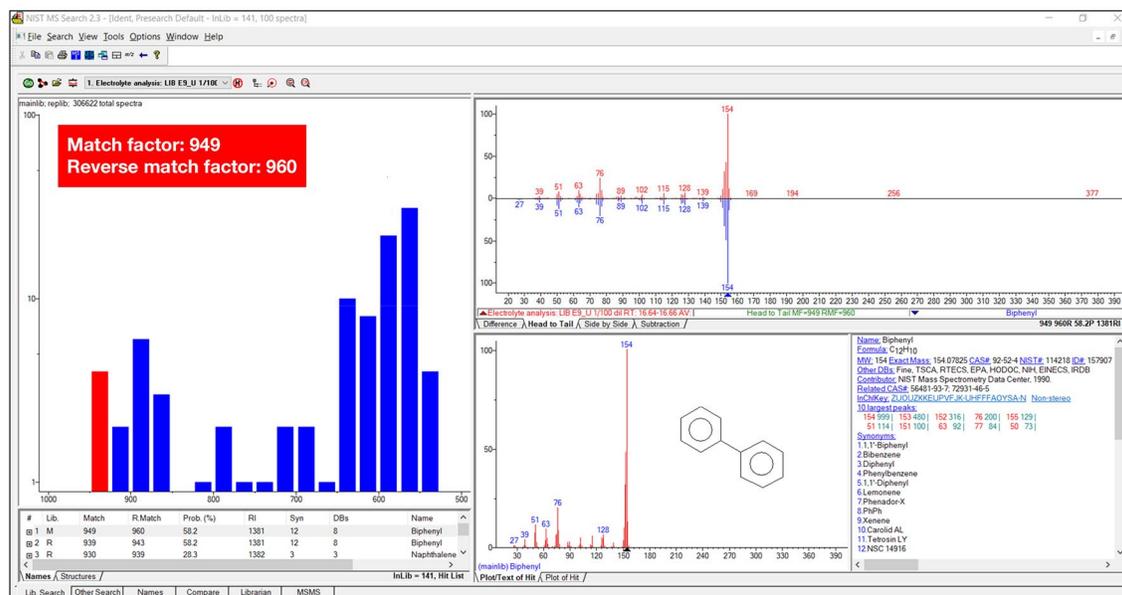
*Above IDL but below IQL

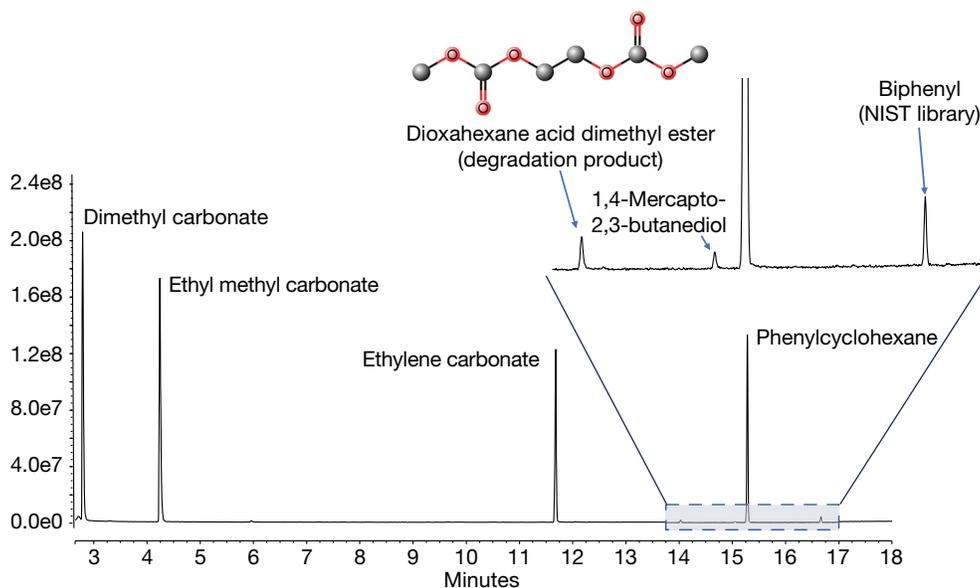Figure 3. NIST library identification of unknown peak as biphenyl

Figure 4. Full scan acquisition of cycled LIB electrolyte at 1:5,000 dilution

Additive confirmation with SIM analysis

Complete composition analysis of LIB electrolytes is challenging due to the wide concentration range of the different components. The organic carbonate solvents (i.e., dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, ethylene carbonate) are present at high concentrations (vol%) and require high dilution ratios to be analyzed by MS. Meanwhile, electrolyte additives or products of side reactions may be present at much lower concentrations and risk avoiding detection with high dilution ratios. Analysis using SIM acquisition can aid detection by reducing overall signal noise encountered in full scan analysis through selective ion acquisition for targeted analytes present at low concentrations. An example of this can be seen in the full scan and SIM acquisition of vinylene carbonate in cycled electrolyte sample diluted 1:500 (Figure 5). In full scan, the quantification ion for vinylene carbonate was not detected. However, the quantification ion and both confirmation ions for vinylene carbonate were detected using SIM acquisition. Moreover, ion ratios for both confirmation ions were within the expected ion ratio criteria (± 20%) based on the standard fragmentation, confirming the presence of vinylene carbonate. Ethylene propionate was also detected in both cycled electrolytes using SIM analysis (Table 5). Traces of fluorobenzene were also observed in several electrolyte samples with confirmation ratios passing criteria but were below IDL. Results from the compositional analysis of analyzed LIB electrolytes are reported in Table 5.
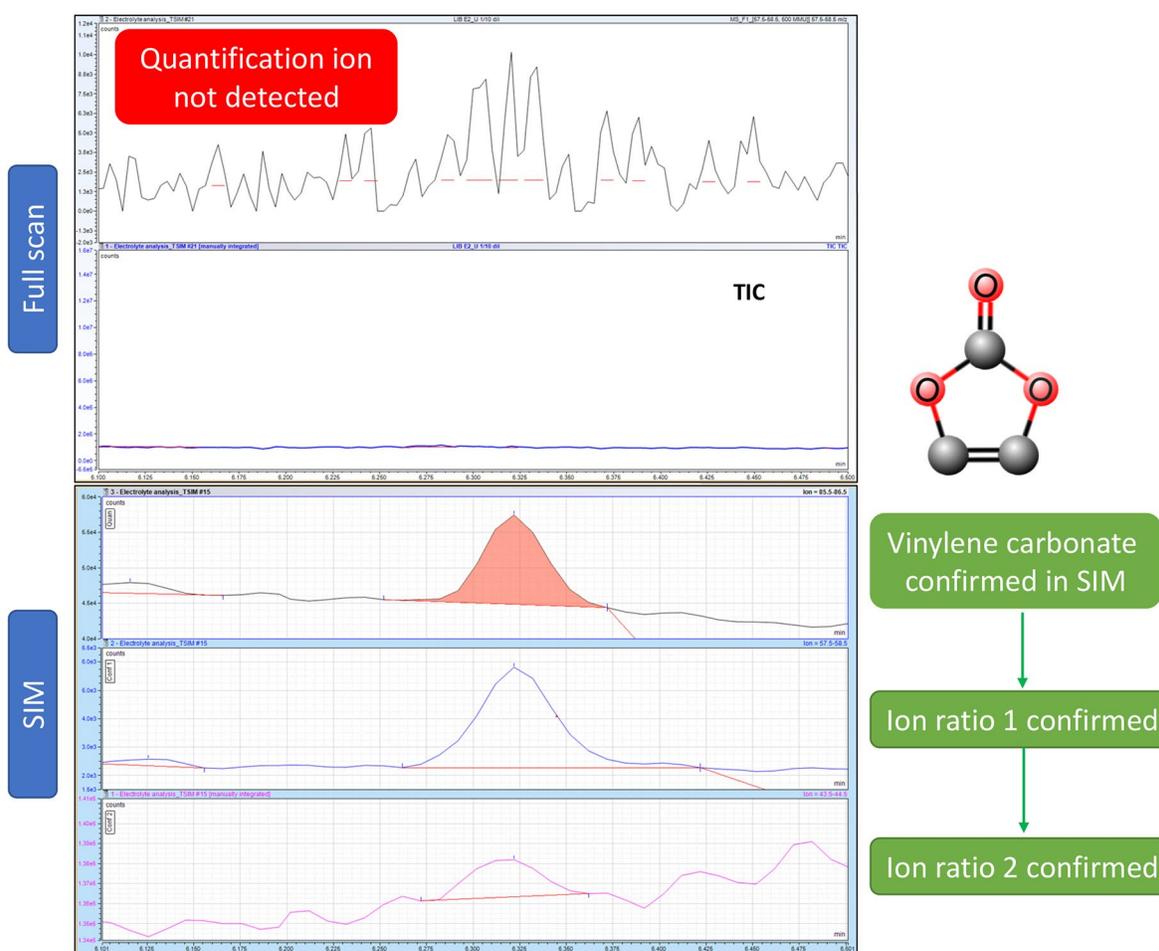

Figure 5. Full scan and SIM acquisition of vinylene carbonate in cycled LIB electrolyte at 1:500 dilution

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Conclusion

This application demonstrates the ISQ 7610 MS equipped with the new XLXR detector provides a high linear dynamic range for quantification of LIB electrolyte components over varying concentration ranges.

- Efficient separation of various electrolyte components was achieved within 16 min.

- Full scan analysis provided characterization of unknown additives present in electrolyte samples while t-SIM acquisition provided confirmation of electrolyte additives not achievable with full scan acquisition.

- Linear dynamic range of over 4 orders of magnitude was achieved using the XLXR detector.

- Detection of LIB electrolyte components were achievable at $\mu g \cdot L^{-1}$ levels with IDLs ranging from 0.003 to 0.021 $\mu g \cdot L^{-1}$.

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