Technical note | 002904

Industrial

Automated salt removal and dilution for online analysis of unprocessed lithium battery electrolytes using gas chromatography-mass spectrometry

Authors

Nicholas Warner, Daniel Kutscher

Thermo Fisher Scientific,
Bremen, Germany

Keywords

Li-ion battery, electrolyte degradation, organic carbonates, $LiPF_6$, automated sample prep, TriPlus RSH SMART autosampler, TSQ 9610 triple quadrupole GC-MS

Goal

The goal of this technical note is to highlight a completely automated workflow for the analysis of unprocessed electrolytes commonly used in lithium-ion batteries by means of a Thermo Scientific™ TriPlus™ RSH SMART autosampler. The workflow enables the removal of $LiPF_6$ salt by precipitation and centrifugation, as well as dilution to different levels to cover the analysis of major components, additives, and degradation products.

Introduction

As the world transitions away from fossil fuels as a primary energy source, rapid upscaling in production of lithium batteries is needed, particularly for use in the individual mobility/transportation sector. To meet this demand and consumer expectations, battery producers are under high time constraints to carry out analyses to ensure quality control/assurance for all materials involved in production and to provide insight into processes leading to performance degradation. As the electrolyte is a critical component in battery operation, comprehensive analysis using mass spectrometry can be performed to verify correct composition and presence of potential impurities that affect performance.

While atomic spectroscopy is predominantly used to assess purity in inorganic raw materials, such as lithium salts or ingredients to produce cathode materials, gas chromatography-mass spectrometry (GC-MS) is an ideal analytical technique to characterize electrolyte composition due to the volatile nature of electrolyte components. However, electrolytes cannot be injected directly into a GC-MS system due to the presence of the conducting salt, $LiPF_6$, which damages the separation column and must be removed prior to injection. In addition, depending on the scope of the analysis,

a sample may need to undergo multiple dilution steps. Major components of the electrolyte, such as ethylene- or ethyl methyl carbonate, are present in percent levels, whereas common additives needed for robust operation may be found at part per million (ppm) concentrations or lower. Degradation products produced as the battery ages will be at even lower concentrations. To enable the detection of both major and minor degradation components, multiple injections of the electrolyte using several dilution steps are needed to avoid detector saturation by major components without risking minor components detection.

The workflow presented here can automatically dilute an unprocessed electrolyte sample up to a total dilution factor of 10,000 to produce several extract dilutions to allow both major and minor component analysis. Removal of the conducting salt is facilitated by mixing an aliquot of the electrolyte with dichloromethane followed by centrifugation, which leads to precipitation of the salt. An aliquot of the supernatant can then be injected into the GC or be subsequently diluted into a new vial with dichloromethane if further dilution is needed.

Experimental

A TriPlus RSH SMART autosampler was configured to execute the automated sample preparation workflow and on-line injection into the GC-MS, as illustrated in Figure 1. The detailed configuration with the list of the used tools and consumables is reported in Appendix Table A1.

The workflow consists of two steps, which can be run sequentially. In the first step, $LiPF_6$ is precipitated from the unprocessed electrolyte by addition to dichloromethane (DCM). To ensure quantitative precipitation, the solution is agitated in the vortex mixer station and centrifuged to separate the precipitate from the supernatant. A second step involves an optional dilution of the supernatant to handle highly concentrated analytes. During the individual steps of the workflow (represented in Figures 2 and 3), the tool used by the robotic arm needs to be exchanged to accommodate different syringe sizes. This is accomplished automatically using the automatic tool change station. Here, a total of three individual tools have been used to handle syringe volumes of 1,000 µL (solvent delivery), 25 µL (intermediate solution preparation), and 10 µL (injection into the GC-MS).

If the aim of the analysis is to identify and/or quantify low concentration additives and degradation products, an analysis could be triggered at the end of the first sample processing step (Figure 2), taking care that the injection syringe needle depth in the vial does not result in aspiration of the precipitated salt.

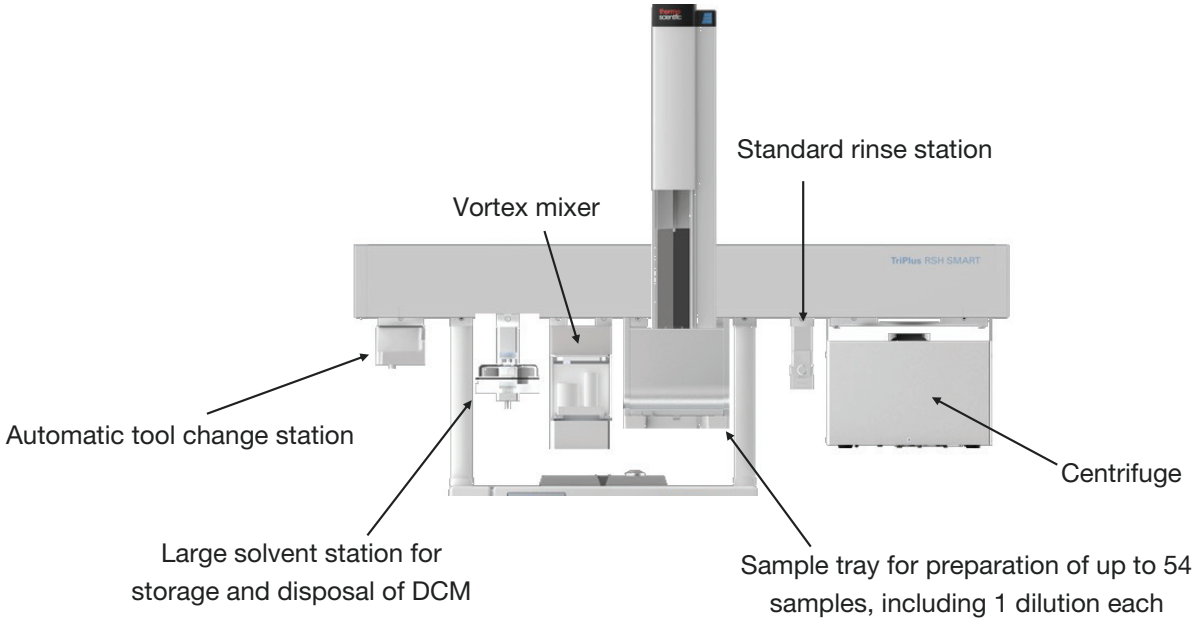

Figure 1. Configuration of the TriPlus RSH SMART autosampler

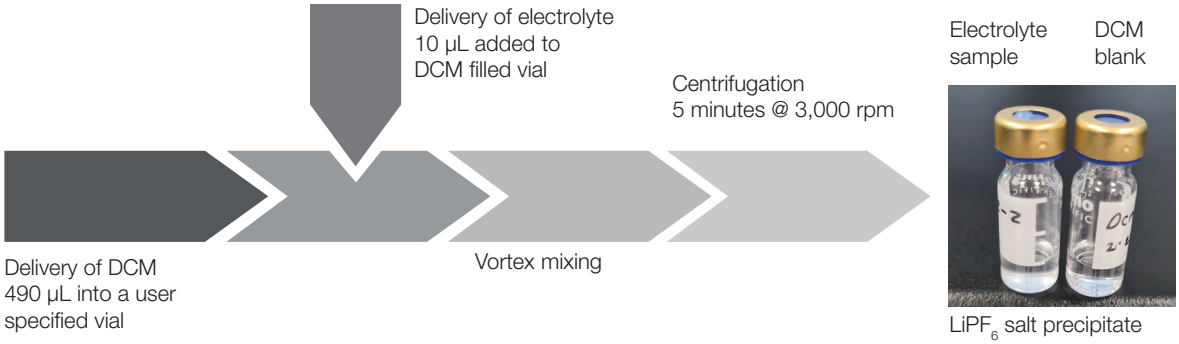

Figure 2. Salt removal process to precipitate $LiPF_6$ from the unprocessed electrolyte (Step 1)

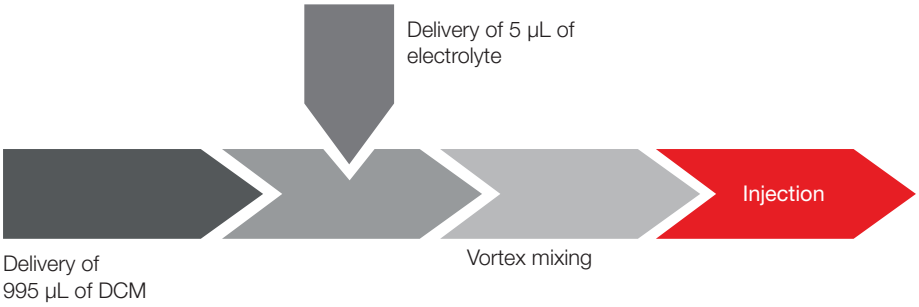

Figure 3. Dilution of the supernatant resulting from Step 1 of the proposed workflow. Different dilution levels can be achieved by modification of the workflow script (Step 2).

In the second step (Figure 3), the supernatant can be further diluted so that abundant compounds, such as the main components of the electrolyte, as well as other potential additives in the ppm concentration range can be analyzed.

When both steps are combined, a total dilution factor of up to 10,000 is achieved with respect to the original electrolyte sample. However, other dilution factors can be obtained after modification of the workflow using Thermo Scientific™ TriPlus™ RSH Sampling Workflow Editor Software. Workflows designed in the Sampling Workflow Editor Software are easily imported into Thermo Scientific™ Chromeleon™ 7.3.2 CDS software, allowing users to control both automation and analysis parameters from a single software solution.

The TriPlus RSH SMART autosampler was mounted on top of a Thermo Scientific™ TRACE™ 1610 gas chromatograph, coupled with a Thermo Scientific™ TSQ™ 9610 triple quadrupole mass spectrometer. Please note that the workflow can also be used in conjunction with other Thermo Scientific GC-MS systems, i.e., the Thermo Scientific™ ISQ™ 7610 single quadrupole GC-MS or the Thermo Scientific™ Orbitrap™ Exploris™ GC high-resolution accurate-mass HRAM GC-MS.

The chromatographic separation method employed in all subsequent experiments was described elsewhere.[1] In this study, the detection was accomplished using full scan acquisition for major component analysis, while selected reaction monitoring was used for minor additive/degradation component analysis on a TSQ 9610 GC-MS/MS system. Ion transitions for the individual components can be found in Appendix Table A2.

Key parameters for the analysis are summarized in Tables 1, 2, and 3.

Table 1. GC injection and column conditions

TRACE 1610 GC parameters	
Injector type	Thermo Scientific™ iConnect™ HeSaver-H_2Safer SSL Inlet
Injection volume (µL)	1
Liner	Thermo Scientific™ LinerGOLD™ Focus 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 (^{0}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 selected reaction monitoring (SRM)

TSQ 9610 triple quadrupole GC-MS parameters	
Transfer line temperature (°C)	280
Ionization source	Advanced EI (AEI)
Ionization mode	EI
Ion source temperature (°C)	260
Electron energy (eV)	70
Full scan range (*m/z*)	35–500
Full scan time (s)	0.2
SRM time (s)	0.3
Minimum baseline peak width (s)	3
Desired peak scans	10

The overall duration of the workflow for the full processing of the sample, including salt removal and dilution, is approximately 18 minutes. Complete overlap with the GC analysis of the previous sample is achieved, helping minimize analysis time and maximize sample throughput. The automation also allows for a completely identical treatment for all samples, avoiding bias that can occur through manual treatment.

Table 3. TriPlus RSH SMART autosampler parameters

TriPlus RSH SMART autosampler parameters	
Step 1	
Electrolyte sample – 25 µL syringe	
Electrolyte sample volume (µL)	10
Electrolyte sample fill speed (µL/s)	3
Electrolyte sample dispense speed (µL/s)	100
Electrolyte sample rinsing cycles	1
Electrolyte sample rinsing volume (µL)	10
Electrolyte sample penetration depth (mm)	31
Syringe post-solvent volume (acetone)	70%
Syringe post-solvent cycles (acetone)	2
Syringe post-solvent volume (DCM, µL)	18
Syringe post-solvent cycles (DCM)	1
Solvent (DCM) – 1,000 µL syringe	
Solvent volume (DCM, µL)	490
Vortexer speed (rpm)	600
Vortexer time (min)	0.17
Centrifugation speed (rpm)	4800
Centrifugation time (min)	5
Step 2 (optional)	
Solvent (DCM) – 1,000 µL syringe	
Solvent volume (DCM, µL)	995
Supernatant – 10 µL syringe	
Supernatant volume (µL)	5
Vortexer speed (rpm)	600
Vortexer time (min)	0.17
Sample injection – 10 µL syringe	
Sample vial penetration depth (mm)	30
Sample fill speed (µL/s)	0.3
Sample dispense speed (µL/s)	20
Sample rinsing cycles	2
Sample rinsing volume (µL)	1
Syringe pre-cleaning volume (acetone)	70%
Syringe pre-cleaning cycles	3
Syringe pre-cleaning volume (DCM, µL)	8
Syringe pre-cleaning cycles (DCM)	2
Syringe post-solvent volume (acetone)	70%
Syringe post-solvent cycles (acetone)	3
Syringe post-solvent volume (DCM)	70%
Syringe post-solvent cycles (DCM)	1
Injection speed (µL/s)	20
Injector penetration depth (mm)	35

Results

To test the ability of the developed workflow to provide repeatable and reliable sample preparation, an electrolyte sample analyzed in a previous study was split into eight identical aliquots, all placed into individual 2 mL glass vials. The conducting salt was removed from each aliquot, followed by an additional dilution prior to analysis. The peak areas obtained for the most abundant compounds, ethyl methyl carbonate and ethylene carbonate, were evaluated. An overlay of all individual chromatograms is shown in Figure 4. The relative standard deviation (RSD) over eight repetitions was found to be below 6%, even without internal standard correction.

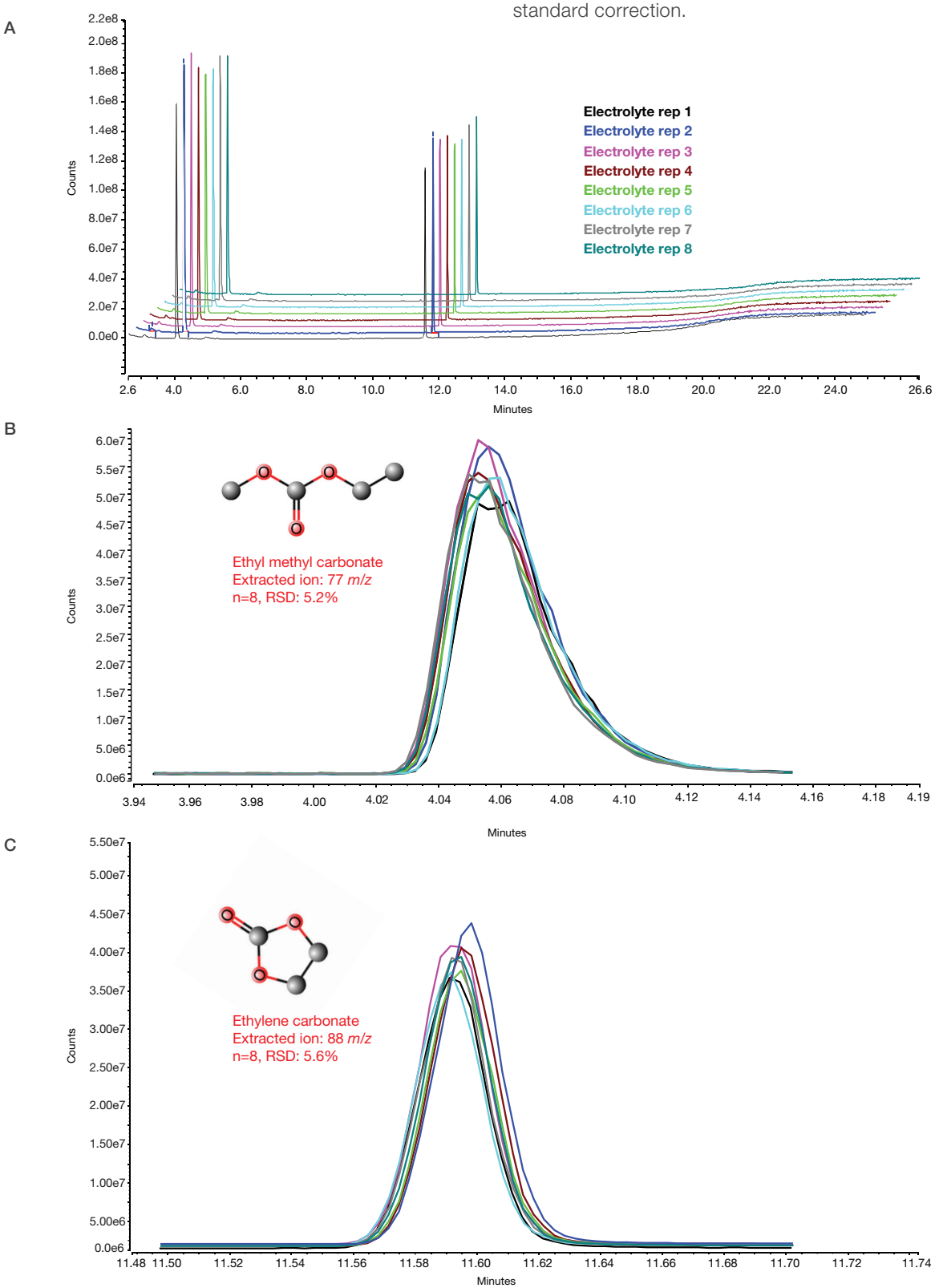

Figure 4. (A) Total ion chromatograms for repeatability performance (n=8) of the automated electrolyte salt removal and subsequent 10,000 dilution for major components; (B) and (C) extracted ion chromatograms, respectively, for ethyl methyl carbonate and ethylene carbonate from eight repetitive injections

To avoid carryover and cross contamination throughout the sample preparation steps, automated washing of each syringe with DCM followed by one sample wash prior to aliquot delivery was programmed. After aliquot delivery, syringes were rinsed three times with acetone followed by a single wash with DCM. No carryover was observed by analyzing a blank sample (clean DCM) immediately after an electrolyte sample, as shown in Figure 5.

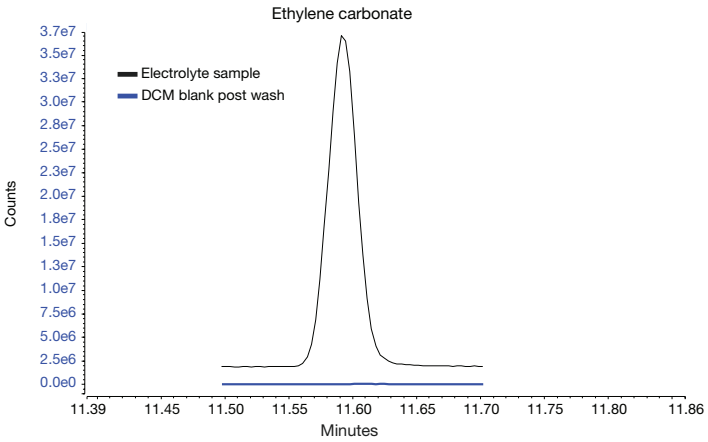

Figure 5. Carryover test by analyzing a blank sample immediately after an electrolyte sample

To test the accuracy of the proposed workflow, the same electrolyte was spiked with known amounts of target compounds, as listed in Table 4 along with the recovery of the spiked concentration. These compounds comprise a selection of common additives and degradation products. Again, individual samples were subjected to salt removal, followed by dilution.

It is noteworthy that the TSQ 9610 system, equipped with a Thermo Scientific™ Advanced Electron Ionization source, provided sufficient sensitivity to also detect several minor components in non-spiked samples, at concentrations of sub µg·L^{-1} in the unprocessed electrolyte. This can be seen in the chromatogram shown in Figure 6.

Table 4. Spike recovery test results obtained with n=3 replicates of an unprocessed electrolyte spiked with 1 µg·L^{-1} of different compounds prior to processing

Compound name	Recovery [%]
Dimethyl carbonate	76.2 ± 4.1
Fluorobenzene	81.5 ± 1.4
Ethylpropionate	81.6 ± 1.1
Diethyl carbonate	69.1 ± 4.5
Vinylene carbonate	80.9 ± 1.1
Fluoroethylene carbonate	75.5 ± 2.2
1,1-Dimethylpropylbenzene	83.2 ± 2.0
Succonitrile	68.0 ± 2.5
2,5-Dioxahexane acid dimethyl ester	61.3 ± 3.7
Phenylcyclohexane	68.9 ± 0.8
1,3-Propanesultone	63.1 ± 2.5
Adiponitrile	43.3. ± 2.0

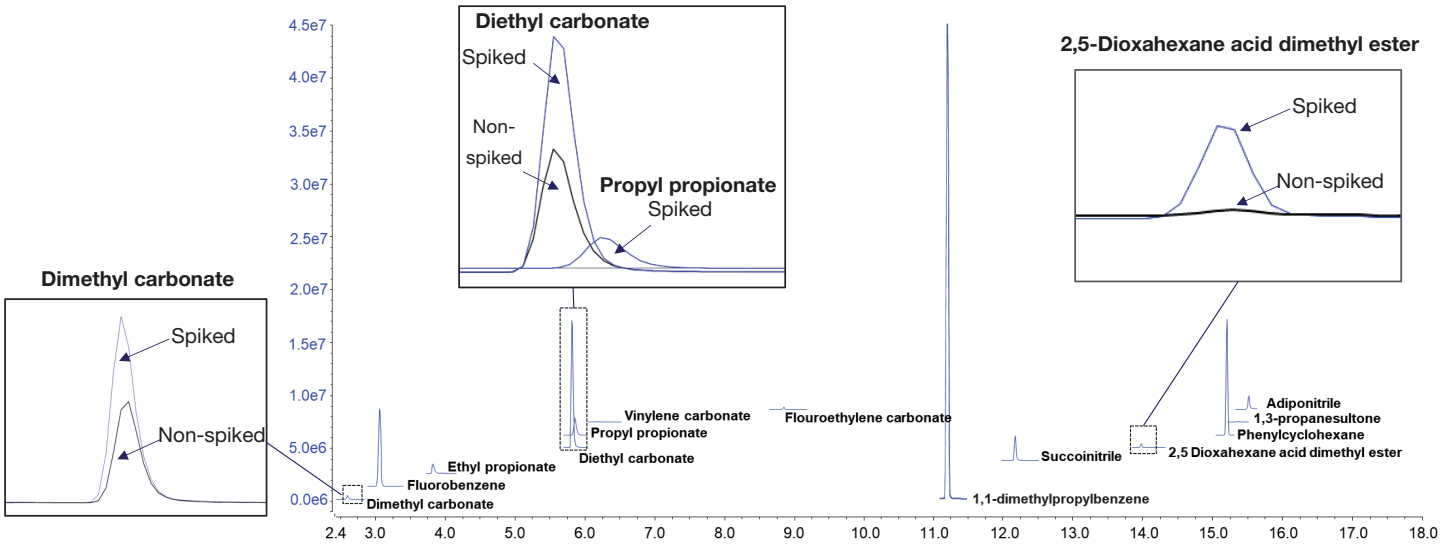

Figure 6. Chromatogram of an electrolyte sample spiked (1 µg·L^{-1}) and unspiked with minor electrolyte components

Results obtained from spiking experiments show acceptable recovery, with excellent precision achieved between individual replicates. While recovery for some of the compounds (i.e., adiponitrile) was found to be lower than expected, recoveries obtained were highly reproducible so that losses can be accounted for correctly. In addition, reduction of electrolyte mass caused by the precipitation of $LiPF_6$ was not corrected for in the calculation of the spike recovery. In a standard electrolyte solution containing 1M $LiPF_6$, the conducting salt accounts for >10% of the electrolyte mass, which would lead to further improvement of the recoveries.

To quantify the recovery, external calibration was used, which could be another contributing factor for the observed recoveries. Using the proposed workflow, exact matrix-matched calibration curves with internal standard addition can be automated, avoiding additional effort required by the lab personnel. This would further improve the quantitative assessment in electrolyte samples, particularly at low concentrations of additives and/or degradation products, and facilitate comparisons between studies containing large number of samples.

Conclusions

The proposed workflow allows the automated processing of lithium battery electrolyte samples for quality control purposes or aging simulation experiments. Samples can be placed directly on the vial tray of the TriPlus RSH SMART autosampler for complete salt removal as well as sample dilution (if required) prior to injection and GC-MS analysis. This not only frees up operator time but also ensures a more reliable process that can be executed automatically and unattended. The capacity of the proposed system allows scheduling up to 54 samples for processing but can be increased with slight modifications to the TriPlus RSH SMART configuration, i.e., a longer rail to allow the addition of more sample trays. The workflow is independent of the GC-MS system used and can be applied in quality control as well as R&D laboratories. Processed samples can also be analyzed subsequently on multiple systems.

Reference

1. Thermo Fisher Scientific Application Note 001124: Comprehensive analysis of electrolyte solutions for lithium-ion batteries using gas chromatography-mass spectrometry

Appendix

Table A1. TriPlus RSH SMART autosampler, tools/modules, and consumables description and part numbers

TriPlus RSH SMART autosampler configuration*	Part number
TriPlus RSH SMART Advanced configuration for liquid injection, regular rail length	1R77010-2003
Automatic Tool Change Station	1R77010-1019
Liquid syringe tool for 57 mm syringe needle (0.5–100 µL syringe volume)	1R77010-1007
Liquid syringe tool for 57 mm syringe needle (250–1,000 µL syringe volume)	1R77010-1009
Solvent Station with 3 x 100 mL bottles	1R77010-1031
Centrifuge	1R77010-1193
Vortexer	1R77010-1033
Consumables	
10 µL Fixed Needle Gas-Tight SMART Syringe 23s Gauge 57 mm Length	365D0311SM
25 µL Fixed Needle Gas-Tight SMART Syringe 26s Gauge 57 mm Length	365F2461SM
1,000 µL Fixed Needle Gas-Tight Syringe 22 Gauge 57 mm Length	365K2811SM
Cap, Blue magnetic screw (9 mm) with silicone/PTFE seal	6PMSC9ST1
Vial, 2 mL clear screw glass (9 mm short thread), 100/pack	6ASV9-1P
Vial, 0.3 mL clear screw glass with fixed insert (9 mm short thread), 100/pack	6PSV9-03FIVP
Software	
TriPlus RSH Sampling Workflow Editor Software	1R77010-1200

*Configuration for 54 sample capacity

Table A2. Retention time (RT), parent mass, product mass, and collision energy for selected ion monitoring transitions of targeted electrolyte components

Name	RT (min)	Mass (*m/z*)	Product mass (*m/z*)	Collision energy (eV)
Dimethyl carbonate	2.62	59	15.1	10
Dimethyl carbonate	2.62	90	31.1	5
Dimethyl carbonate	2.62	90	45	10
Fluorobenzene	3.07	96.1	50.1	20
Fluorobenzene	3.07	96.1	70	15
Ethyl propionate	3.88	74.1	56.1	5
Ethyl propionate	3.88	102.1	56.1	10
Ethyl propionate	3.88	102.1	74.1	5
Diethyl carbonate	5.86	91	45	20
Diethyl carbonate	5.86	91	63	5
Propyl propionate	5.89	57	29.1	5
Propyl propionate	5.89	75	29.1	10
Propyl propionate	5.89	75	57.1	5
Vinylene carbonate	6.2	58	30.1	5
Vinylene carbonate	6.2	58	41.1	10
Vinylene carbonate	6.2	58	29.1	10
Fluoroethylene carbonate	8.83	62	29.1	5
Fluoroethylene carbonate	8.83	62	31.1	10
Fluoroethylene carbonate	8.83	106	29.1	10
Fluoroethylene carbonate	8.83	62	41	10
1,1-Dimethylpropylbenzene	11.26	119.1	65.1	25
1,1-Dimethylpropylbenzene	11.26	119.1	91.1	10
Succonitrile	12.15	79	28.1	15
Succonitrile	12.15	79	51.1	30
Succonitrile	12.15	79	52	10
2,5-Dioxahexane acid dimethyl ester	14.02	91	47.1	5
2,5-Dioxahexane acid dimethyl ester	14.02	91	59	5
Phenylcyclohexane	15.2	160.1	104.1	10
Phenylcyclohexane	15.2	160.1	117.1	15
1,3-Propanesultone	15.36	122	28	10
1,3-Propanesultone	15.36	122	57.1	5
Adiponitrile	15.51	68	39.1	15
Adiponitrile	15.51	68	41.1	5