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Multiplatform Approach for Lithium-Ion Battery Electrolyte Compositional Analysis

Decoding volatile, organic, and elemental composition of unknown electrolyte sample

Authors

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Abstract

Electrolytes in lithium-ion batteries (LIBs) play an important role during the charging and discharging life cycle. Lithium salts, organic solvents, and additives are typical components of an LIB electrolyte. In this application note, compositional analysis of three unknown electrolyte solutions was performed using complementary instrumentation. Agilent gas chromatography/triple quadrupole mass spectrometry (GC/TQ), liquid chromatography/quadrupole time-of-flight mass spectrometry (LC/Q-TOF/MS), and inductively coupled plasma mass spectrometry (ICP-MS) instruments were used for profiling electrolyte components. Split mode injections using GC/MS revealed highly abundant volatile components in the electrolyte sample, while splitless mode detected 27 other trace-level volatile components. The LC/Q-TOF data complemented the study by providing information on various organic components among the three electrolyte samples. The Agilent ICP-MS not only offered the quantitative results for target elements but also provided valuable insight on the semiquantitative report for "all-element" in unknown samples by use of the QuickScan function. Results from various platforms confirmed the benefit of having a multidisciplinary analysis that allows users to carry out electrolyte analysis with a holistic approach.

Introduction

Over recent decades, lithium-ion batteries (LIB) have revolutionized the field of portable electronics, the automotive industry, and renewable energy storage for a dynamic range of applications. The main components of a LIB, including the cathode, anode, electrolytes, separator, and collector, work together to manage the electrochemical reactions that occur during the charging and discharging of battery cells.[1,2] The liquid electrolyte (LE) is one of the common electrolytes used for commercial LIBs since it is cheaper and easier to manufacture than other electrolytes. LE is a complex mixture containing organic solvents, lithium electrolytic salt, and additives that play an important role in ionic conductivity and stability, cycle life, safety, and overcharge protection for the LIB. LE composition changes over repeated charge cycles and thus aging can affect the overall cell performance.[2] Also, many researchers are interested in investigating the recipe of commercial LE through reverse engineering technologies.[3] Many complimentary analytical techniques are required to establish a complete profile of various components effectively due to the matrix complexity of LEs ranging from organic to inorganic substances. Having a suitable analytical methodology to elucidate the complete profiling of electrolytes to monitor compositional changes over time and to perform reverse engineering of electrolytes could be beneficial to battery manufacturers. In this application note, multiple Agilent instruments including gas chromatography/triple quadrupole mass spectrometry (GC/TQ), liquid chromatography/quadrupole time-of-flight mass spectrometry (LC/Q-TOF MS), and inductively coupled plasma mass spectrometry (ICP-MS) instruments were used to perform compositional analysis for three unknown LE samples.

Experimental

Sample preparation

Three different LE samples were obtained from a local commercial LIB manufacturer. No special sample preparation was implemented for LE samples except solvent dilution to avoid by-reactions or by-products bringing uncertainties to the composition analysis.

For the identification of high abundant volatile components present in electrolytes using GC/MS, samples were diluted with dichloromethane (DCM, GC grade, Merck, New Jersey, USA) 1,000x and were analyzed in split mode. As for the trace level volatile organic additives analysis, the electrolyte samples were directly injected into GC/MS with splitless mode without dilution.

For LC/Q-TOF analysis, 10 µL of each LE sample was evaporated to dryness and reconstituted with 100 µL methanol, maintaining a dilution factor of 10x.

Lithium electrolytic salt poses challenges for ICP-MS analysis due to the significant solvent carbon effect and salt effect. Li salts, such as $LiPF_6$, $LiBF_4$, and $LiClO_4$ are typically used for the manufacture of LIB electrolytes.[3,5] To minimize the matrix effect due to electrolytic salts, the sample was diluted prior to ICP-MS analysis by using high-purity battery-grade dimethyl carbonate (DMC, ≥99% purity on trace metals basis, Sigma-Aldrich) which is a common solvent used for LIB manufacturers.

GC/TQ instrumentation

An Agilent 8890 GC coupled with an Agilent 7010 triple quadrupole GC/MS (GC/TQ) with the high-efficiency source (HES) was used for the volatile component analysis. The GC/TQ was operated in Scan Mode to acquire the full mass spectrum for the organic volatile compound information from all the three unknown LE samples. The GC/TQ operating parameters are listed in Table 1.

Table 1. Agilent 7010 GC/TQ instrument parameters.

Parameter	Value
Column	Agilent J&W DB-1701, 30.0 m × 0.25 mm, 0.25 µm (part number 122-0732)
Injection Volume	1.0 µL
Inlet Temperature	250 °C
Injection Modes	Split (with split ratio of 100:1) and Splitless
Carrier Gas	He, constant flow, 1.0 mL/min
Oven Program	Initial: 40 °C, hold for 3.0 min. Ramp 1: 10 °C/min to 160 °C, hold for 2 min Ramp 2: 20 °C/min to 240 °C, hold for 9 min
Acquisition Mode	Scan, m/z 15 to 450 amu
Ion Source Temperature	280 °C
Quadrupole Temperature	150 °C
Transfer Line Temperature	250 °C
Solvent Delay	− 2.3 min (Split injection) − 5.5 min (Splitless injection)

LC/MS instrumentation

An Agilent 1290 Infinity II LC coupled with an Agilent 6545XT AdvanceBio LC/Q-TOF was employed to analyze organic components and additives in the LE samples. Table 2 summarizes instrument conditions for LC/Q-TOF instrumentation.

Table 2. Instrument conditions for the Agilent 1290 Infinity II LC and the Agilent 6545XT Q-TOF.

Parameter	Value
Column	Agilent ZORBAX RRHD Eclipse Plus C18, 2.1 × 150 mm, 1.8 μm (part number 959759-902)
Mobile Phase A	5 mM ammonium formate in water
Mobile Phase B	100% methanol
Gradient	Time (min) Percentage mobile phase (%B) 0 5 10 95 15 95 15.5 5 20 5
Column Temperature	40 °C
Flow Rate	0.3 mL/min
Injection Volume	2 μL
Source	ESI AJS
Acquisition Mode	MS
Polarity	Positive
Gas Temperature	250 °C
Drying Gas	8 mL/min
Nebulizer	35 psi
Sheath Gas Temperature	300 °C
Sheath Gas Flow	10 mL/min
Capillary Voltage	3,500 V
Nozzle Voltage	0 V
Reference Mass	121.0509 and 922.0098
Mass Range	50 to 1,000 m/z
Acquisition Rate	4 spectra/second

ICP-MS instrumentation

Organic sample analysis can be performed routinely on Agilent ICP-MS systems with a few changes to the instrument configuration and settings. By applying the same conditions and parameters reported in the previous application for LIB solvents[4], an Agilent 7900 ICP-MS equipped with organic solvent sample introduction kit (part number G3280-60580) and platinum-tipped interface cones was used for this work. Other added instrument features were, a MicroMist nebulizer, a quartz torch with 1.5 mm id injector, an I-AS integrated autosampler probe (0.15 mm id), solvent-resistant uptake, and drain tubing. The optional fifth gas line for the addition of O_2/Ar (20/80 mix) to the plasma was fitted with the ICP-MS to prevent the deposition of undissociated carbon (soot) on the interface cones. The instrument operating parameters are given in Table 3.

Table 3. ICP-MS operating parameters.

Cell Mode	No Gas	He	HEHe	H$_2$
RF Power (W)	1,600			
Sampling Depth (mm)	9			
Nebulizer Gas Flow (L/min)	0.55			
Ar/O$_2$ Option Gas (%)	20			
Ext 1 (V)	0			
Ext 2 (V)	−250			
Omega Bias (V)	−110			
Omega Lens (V)	11.1			
ORS Gas (mL/min)	–	3.5	8.5	5
Energy Discrimination (V)	5		7	3

Results and discussion

Analysis of volatile organics by GC/TQ

GC/TQ is a powerful technique for the identification of organic volatile compounds. Battery electrolyte is a mixture composed of high-purity organic solvents, electrolyte lithium salt, and many additives, where organic solvents are normally the main component. The GC/TQ TIC of all three diluted electrolyte samples using split mode is shown in Figure 1.

The acquired GC/TQ data files were processed using the MassHunter Unknowns Analysis program with deconvolution of the data first to extract the compounds followed by library matching according to the Wiley 12/NIST 20 library. The split mode results confirmed DMC as the main component in all three electrolyte samples with consistent RT and high match factors obtained from the NIST library.

Splitless injections of the three LE samples were also performed to identify the trace volatile components in addition to the main component (Figure 2). The Unknowns Analysis uses the power of chromatogram deconvolution to pull out all trace compounds followed by a library search. The Unknowns Analysis displays comprehensive information of each volatile compound including RT, name, CAS#, match factor, formula, and more (Figure 3).
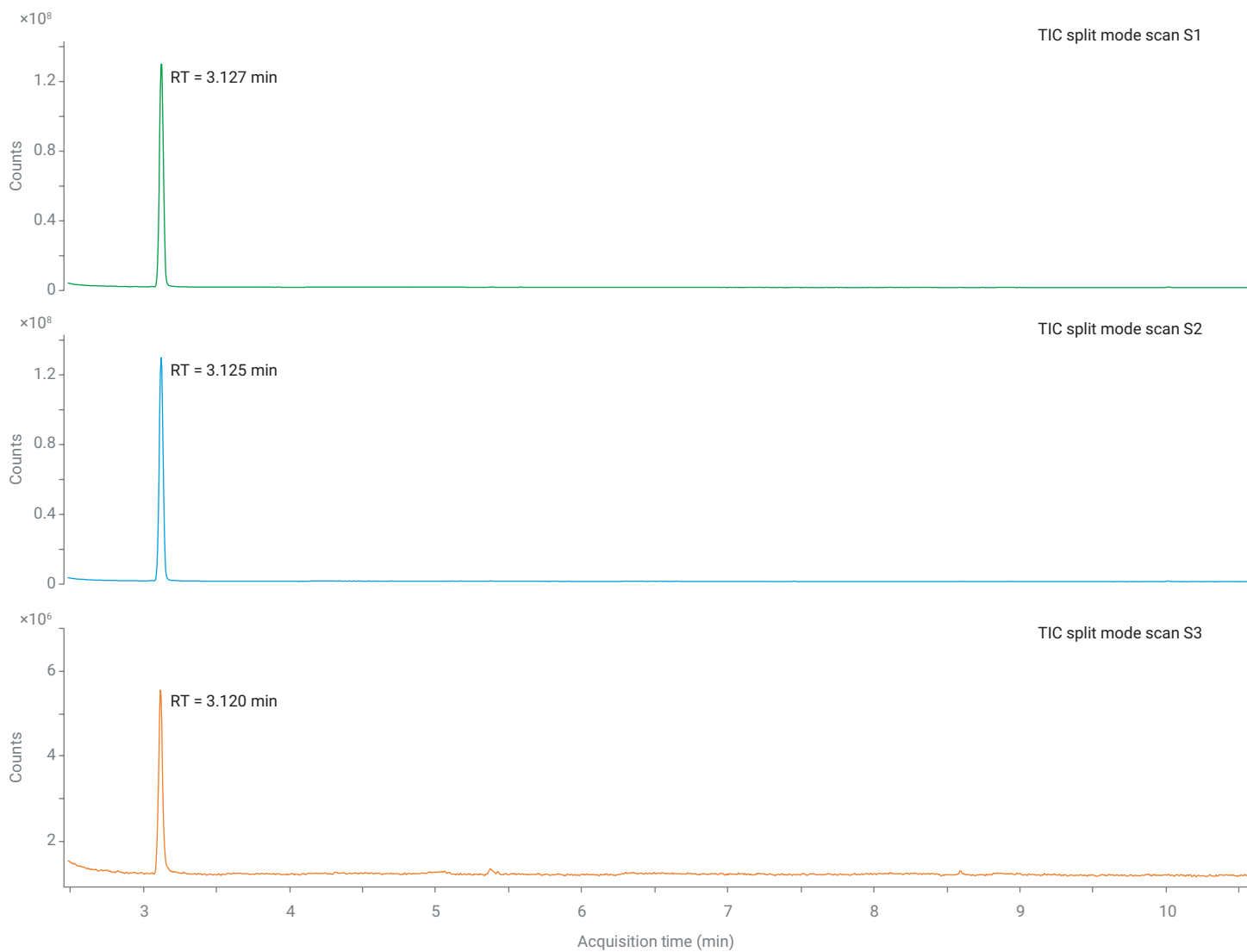
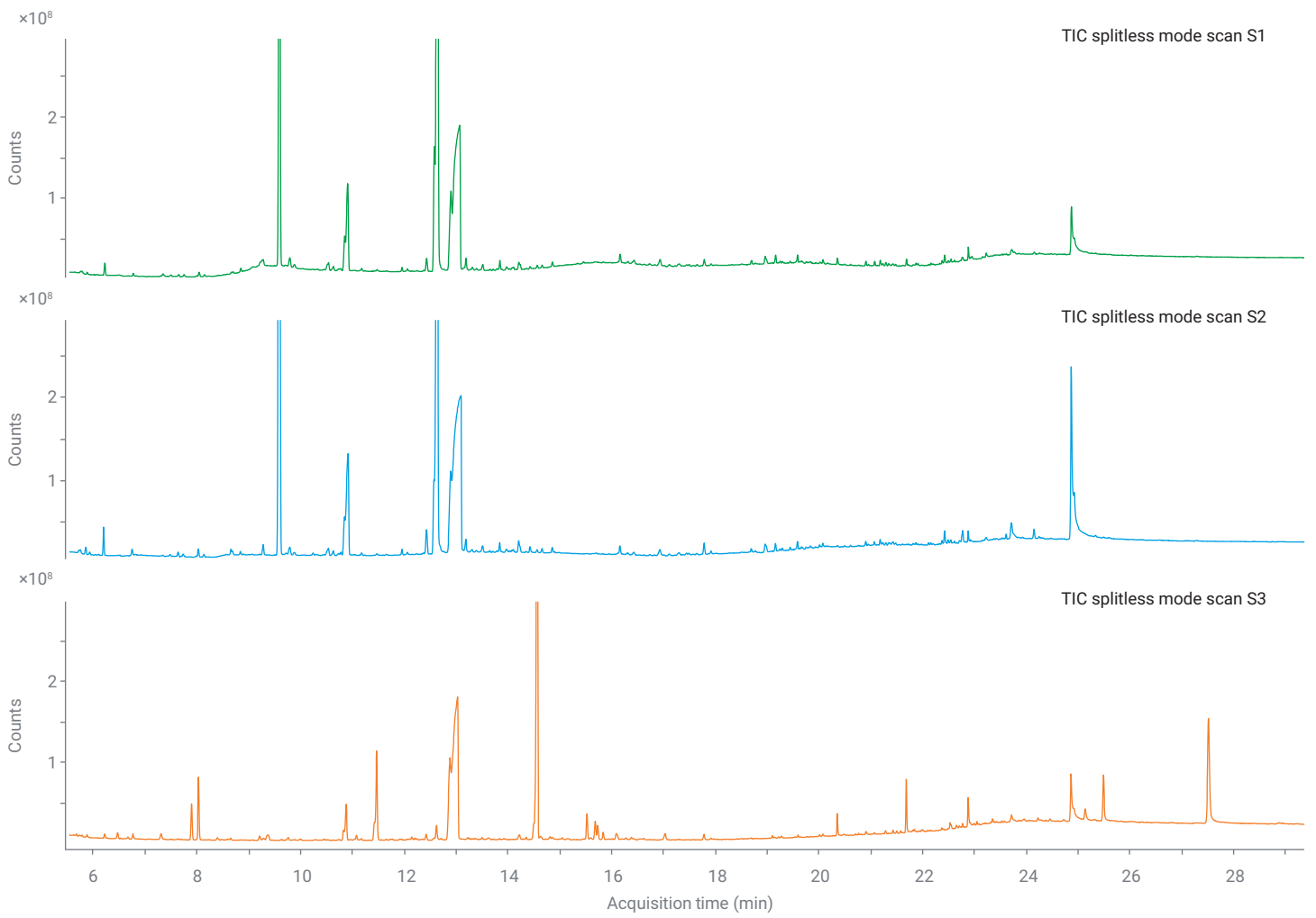**Figure 1.** GC/TQ TIC of three electrolyte samples (S1, S2, and S3) with 1,000x dilution using split mode.

Figure 2. GC/TQ scan of three electrolyte samples (S1, S2, and S3) with splitless mode injection.

Figure 3. MassHunter unknowns analysis for electrolyte sample 3.

In the three LE samples, 28 volatile compounds were identified (combined in both split and splitless modes), all with a minimum match factor of 60. Among these, eight targets were found to be in common across all three LE samples, which are compounds usually used in the formulation of commercial LIB electrolytes.[3] DMC, diethyl carbonate (DEC), toluene, diphenyl sulfide, trimethyl phosphate, hexadecane, 1,3-dioxolan-2-one (EC), and N-methyl-2-pyrrolidone (NMP) are the common eight components. A compound identification summary from three samples is illustrated in Figure 4.

The summary of GC/TQ results for the 8 common components across the three LE samples is presented in Table 3. Consistent RT and high match factor (> 90%) were obtained for the identical compounds from different LE samples, demonstrating the superior power of Agilent GC/TQ with the MassHunter Unknowns Analysis tool for tentative unknown compound identification.
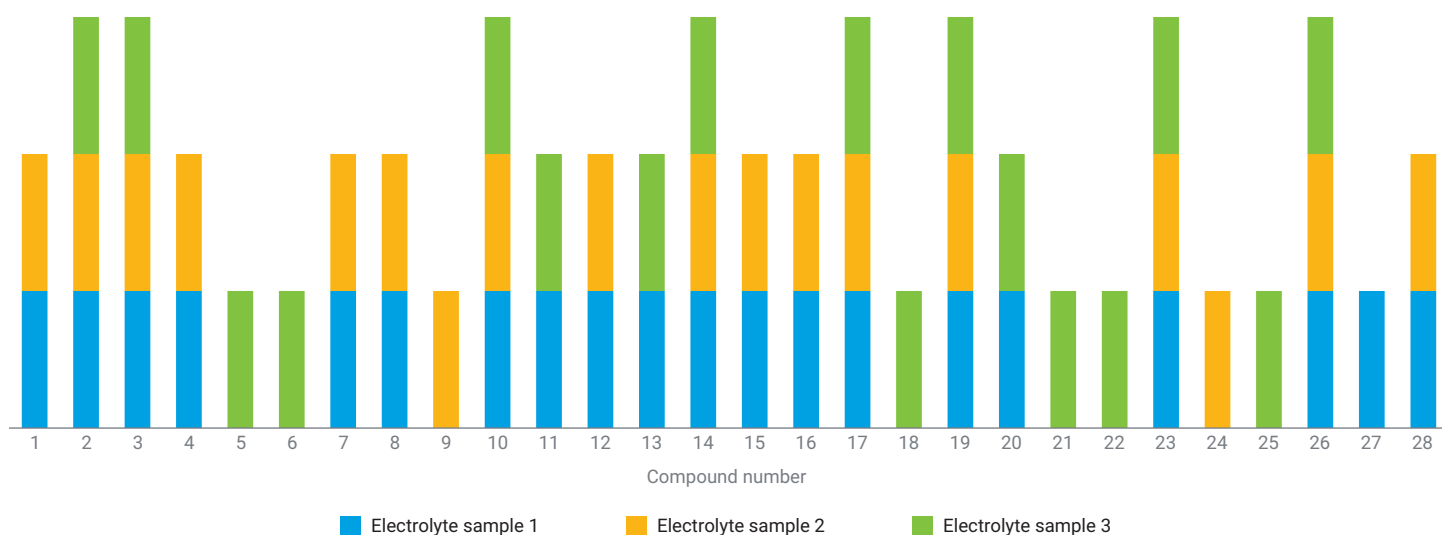
Figure 4. Summary of 28 identified compounds across three electrolyte samples. The number of identified targets from electrolyte samples 1, 2, and 3 are 20, 18, and 17, respectively.

Table 4. RT and match factor for eight common compounds identified in three electrolytes.

Compound Number	Compound Name	RT (min)			Match Factor		
		Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3
2	Diethyl carbonate (DEC)	6.538	6.515	6.533	90.4	91.3	90.5
3	Toluene	5.789	5.754	5.785	94.5	92.0	94.0
10	Diphenyl sulfide	19.393	19.392	19.392	75.4	80.4	79.6
14	Trimethyl phosphate	10.640	10.635	10.630	94.3	94.9	88.5
17	Hexadecane	17.933	17.931	17.931	90.2	97.2	90.7
19	Dimethyl carbonate (DMC)	3.127	3.125	3.120	94.4	94.3	93.8
23	1,3-Dioxolan-2-one (EC)	13.069	12.899	12.883	92.8	95.4	95.5
26	N-methyl-2-pyrrolidone (NMP)	12.580	12.634	12.620	97.1	95.8	97.0

Nonvolatile organic analysis by LC/Q-TOF

Accurate mass analysis using LC/Q-TOF is superior in identifying trace amounts of organic components or high-boiling-point substances that are not compatible with GC/MS. Electrolyte samples were analyzed with LC/Q-TOF by following a nontargeted approach for a statistical assessment. The chromatographic gradient method allowed the separation of polar and nonpolar nonvolatile compounds with excellent precision, mass accuracy, and dynamic range delivered by the high resolution Q-TOF instrument (Figure 5). The acquired data files were then processed using MassHunter Explorer, which combines advanced data extraction with statistical analysis and identification procedures. The first steps of the guided workflow allowed the extraction of all features with easy visualization of the data followed by a filter step to remove unwanted variations (principal component analysis (PCA) plot, Figure 6). Then, the statistical analysis tools helped to reduce the dimensionality of the data to focus on compounds that are significantly different or common between the three electrolyte samples. A filter based on variability (Coefficient of variation less than 25% between the three groups) was applied to the initial data before applying some of the statistical techniques. A fold change analysis (All against Blank with fold change > 300, Figure 6) was carried out and the results were presented as a hierarchical cluster analysis (HCA) plot (Figure 7). The HCA plot groups the components into various clusters based on the similarity between the three LE samples. A unique feature Venn diagram was then generated to identify unique and common organic components among the three electrolyte samples (Figure 7). The last step of the guided workflow using LC/Q-TOF data consisted of the identification step, where compounds of interest can be searched against a database. A partial list of detected potential targets from LE sample 3 is shown in Table 5.
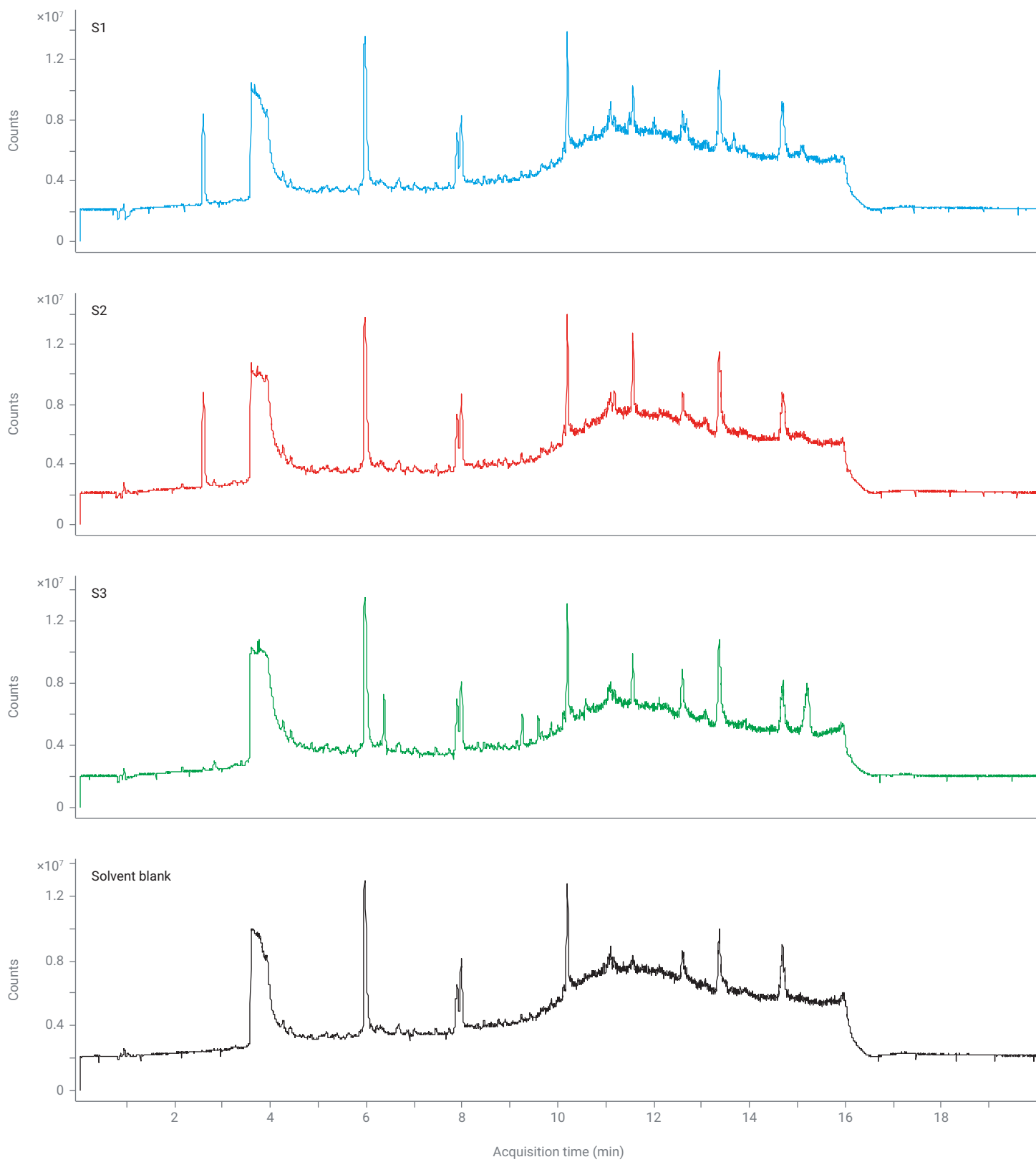
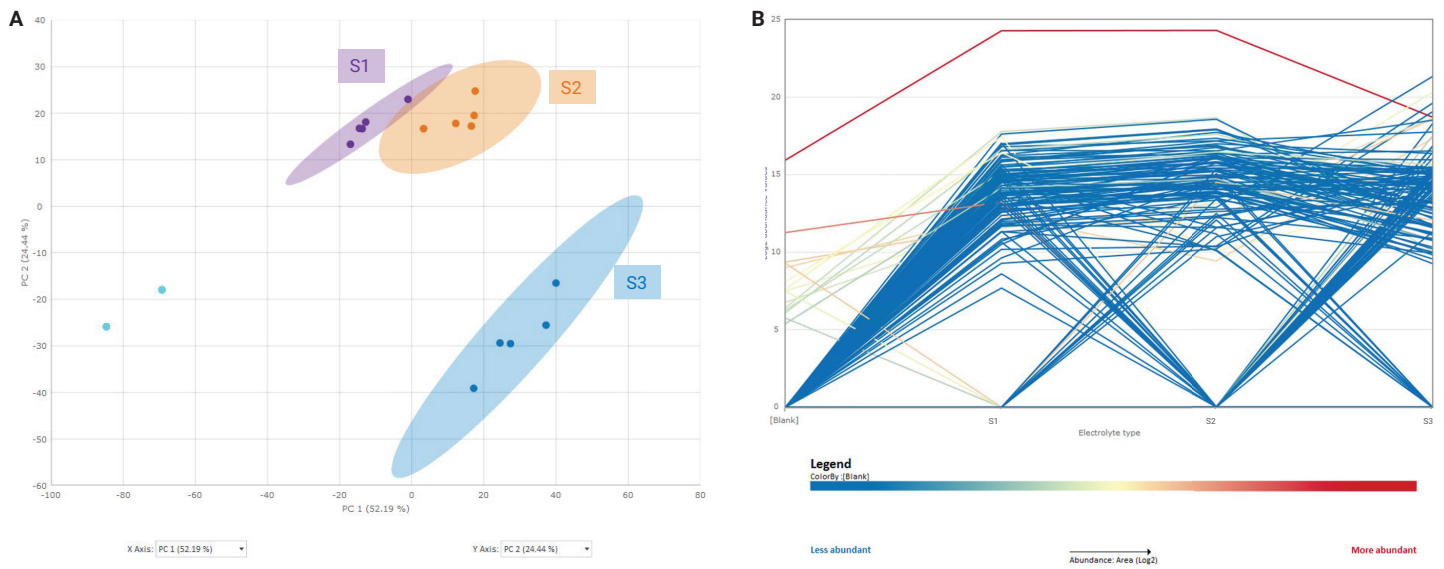**Figure 5.** Overlay of all three LC/Q-TOF TIC data together with methanol blank.

Figure 6. PCA plot (A) and fold change analysis (B) data for all three electrolyte samples.
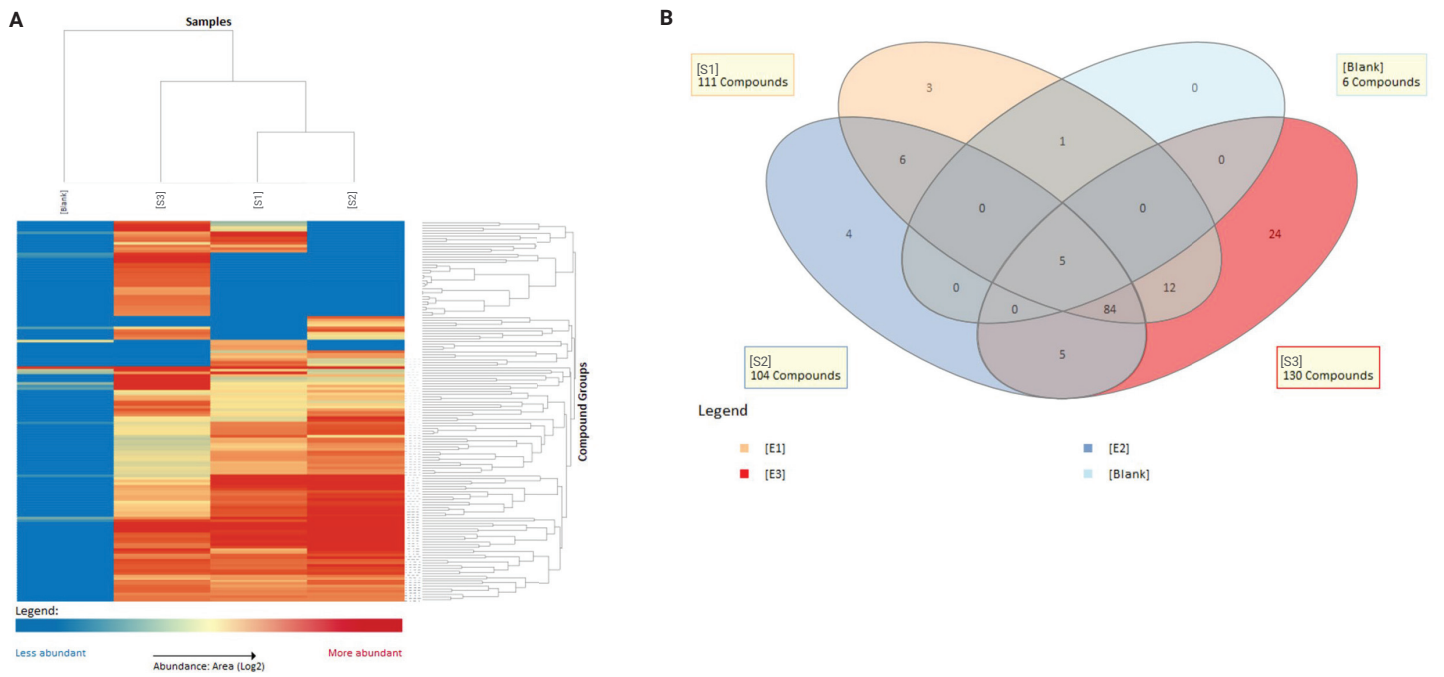

Figure 7. HCA plot (A) and unique feature Venn diagram (B) of all three electrolyte samples.

Table 5. Partial list of potential components in electrolyte sample 3 from LC/Q-TOF analysis.

Precursor *m/z*	Charge State	Retention Time (min)	Ion Species
103.0748	1	4.35	$(M+H)^+$
326.1802	1	5.22	$(M+H)^+$
180.1271	1	5.65	$(M+H)^+$
518.316	1	6.02	$(M+H)^+$
532.295	1	6.09	$(M+Na)^+$
562.3423	1	6.21	$(M+H)^+$
576.3214	1	6.28	$(M+H)^+$
606.3679	1	6.37	$(M+H)^+$
620.3475	1	6.44	$(M+H)^+$
503.311	2	7.163	$(M+2H)^{+2}$
547.3374	2	7.326	$(M+2H)^{+2}$
569.3503	2	7.399	$(M+2H)^{+2}$
591.3634	2	7.47	$(M+2H)^{+2}$
635.3893	2	7.60	$(M+2H)^{+2}$
129.0907	1	7.93	$(M+H)^+$
129.0909	1	8.31	$(M+H)^+$
161.1165	1	9.14	$(M+H)^+$
125.0957	1	9.15	$(M+H)^+$
139.1115	1	9.59	$(M+H)^+$
680.3624	1	10.95	$(M+H)^+$
115.1116	1	11.00	$(M+H)^+$
700.3311	1	11.23	$(M+H)^+$
764.7111	1	15.20	$(M+H)^+$
465.3332	1	15.21	$(M+K)^+$

Elemental profiling and quantitation by ICP-MS

Agilent ICP-MS systems have a robust, solid-state, 27 MHz variable frequency impedance-matching RF generator that can easily cope with the demands of organic solvent analysis and provide elemental profiling. Since DMC was identified as the main solvent based on GC/MS data, the same was chosen to dilute the electrolyte sample before ICP-MS analysis. The Agilent ICP-MS MassHunter QuickScan function enables automatic acquiring of full mass range, "all-element" data for an unknown sample in helium cell mode, giving users an ultimate view of the elemental profile in the sample. In this study, QuickScan data were acquired for all three samples with 100x dilution. The data were processed using Agilent IntelliQuant software and displayed in a periodic table heat map view, as shown in Figure 8. The elements with a darker color like Li, P, B, S, Cl,
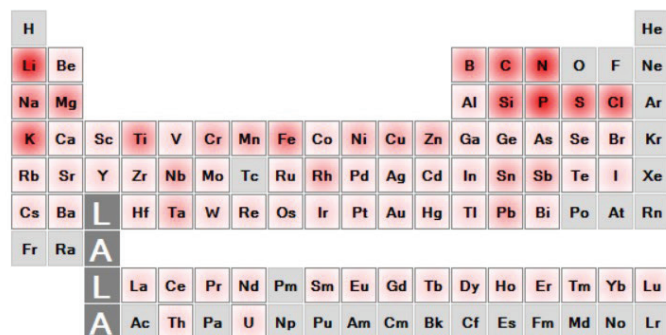
etc. indicate the relatively higher concentration presented in measured samples. Other unexpected elements were also observed as impurities, including Na, K, Mg, Cr, Fe, Co, Zn, Ni, etc. Thus, a further study using FullQuant based on matrix-matched external calibration (DMC solvent based) was carried out to quantify these suspicious elements in the samples. The analytical results for the selected 21 elements were summarized in Table 6, which aligned with the rapid assessment by IntelliQuant in the first place, demonstrating the high sensitivity and selectivity of Agilent ICP-MS system for elemental analysis in unknown samples. The result also indicated that lithium salts, $LiPF_6$, $LiBF_4$, and $LiClO_4$, are highly presented in the three electrolyte samples, which helps reverse engineering decode the formulation of lithium salts in an electrolyte mixture.

Table 6. ICP-MS Quantitative results for selected elements in three electrolytes.
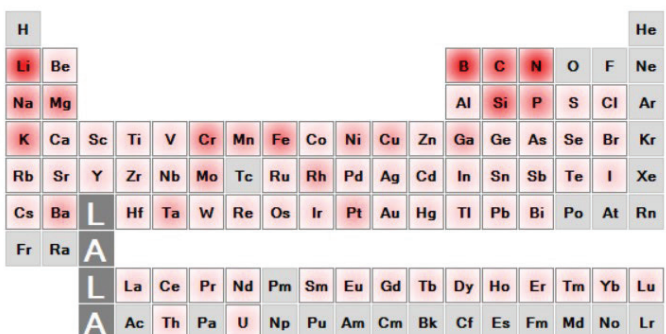
Element	Mass	Cell Gas	Measured Concentration in 100x Diluted Samples (ppb)		
			Electrolyte Sample 1	Electrolyte Sample 2	Electrolyte Sample 3
B	10	No Gas	97.64	502.87	37.34
Na	23	No Gas	46.10	42.23	47.64
Mg	24	H_2	18.44	16.81	12.64
Al	27	No Gas	1.05	1.11	0.82
P	31	HEHe	484.04	237.75	209.27
K	39	H_2	58.79	50.26	52.43
Ca	40	H_2	2.18	1.67	1.10
Ti	47	He	10.16	3.57	2.49
V	51	He	0.41	0.53	0.38
Cr	52	HEHe	24.00	39.67	28.70
Mn	55	He	0.28	0.31	0.26
Fe	56	H_2	4.76	3.85	6.12
Ni	60	He	3.08	1.45	0.35
Cu	63	He	2.15	2.60	2.71
Zn	66	He	27.11	11.56	23.30
Mo	95	He	0.95	5.21	2.35
Ag	107	He	0.54	0.98	0.11
Cd	111	He	0.30	0.37	0.43
Sn	118	He	0.41	0.23	0.20
Ba	137	He	1.12	2.97	2.57
Pb	208*	He	0.44	0.26	0.22

* Pb was measured as the sum of the three most abundant isotopes, 206, 207, and 208.
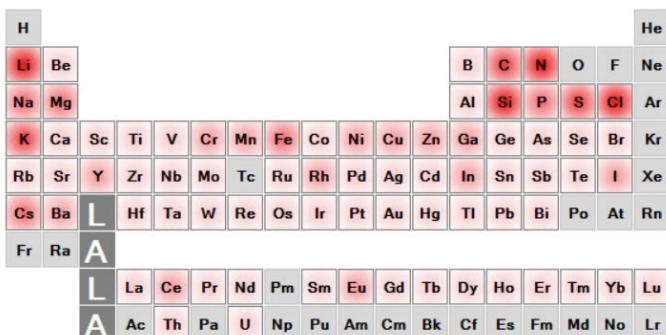
S1

S2

S3

Figure 8. IntelliQuant periodic table heat map for three electrolyte samples.

Conclusion

This work demonstrated a successful application of various Agilent complimentary instrumentation to decode an unknown electrolyte solution composition for the identification of both organic, volatile, and inorganic constituents. Main volatile solvents and trace level additives were successfully identified using an Agilent 8890 GC coupled with the Agilent 7010 GC/TQ with the HES. The nontargeted approach by Agilent LC/Q-TOF coupled with Agilent MassHunter Explorer data analysis software provided valuable statistical insight into nonvolatile constituents and helped to perform statistical analysis between three electrolyte solutions. An Agilent 7900 ICP-MS configured with solvent introduction parts was applied for inorganic Quantitative Analysis to identify the main lithium electrolytic salt used as well as elemental impurities in the electrolyte solution. The smart combination of Agilent hardware and software offers a promising tool to uncover analytical challenges associated with the reverse engineering of electrolyte solution recipes. This approach helps LIB manufacturers implement routine quality control analysis and close monitoring of electrolyte degradation studies over battery aging.

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