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Avoid Thermal Runaway by Monitoring Battery Swell Gas and Electrolyte Degradation

Battery safety testing using a valve-free, dual-detector Agilent 8890 GC configured with both an Agilent 5977B GC/MSD and thermal conductivity detector

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Abstract

Lithium hexafluorophosphate is the most used conductor in lithium-ion batteries. Unfortunately, this salt is subject to thermal decomposition and reactive to protic compounds, resulting in reactive species such as hydrofluoric acid.[1] This can lead to further electrolyte decomposition products, swell gas, and potentially thermal runaway. Other recognized mechanisms for battery swell gas generation include intercalation, thermal swelling, and lithium plating.[2] Monitoring aging and failed batteries for changes in the electrolyte composition and the formation of swell gas is critical. Here we present a robust, informative approach to characterize three aspects of battery safety testing.

This application note describes a valve-free instrument configuration for the quality control of battery swell gas and additives in lithium-ion battery electrolyte using an Agilent 5977B gas chromatography/mass selective detector (GC/MSD). In this method, heated headspace injection is adopted for electrolyte analysis. The battery jelly roll swell gas is sampled with a gas-tight syringe. At a split ratio of 10:1, the target compounds in the electrolyte achieved good linearity in a concentration range of 10 to 500 mg/L. This method has excellent reproducibility, and the instrument detection limits (IDL) for all 15 target compounds were below 1.3 mg/L. During the analysis of the actual electrolyte samples, diluted injection can be used to accurately quantify the target compounds and qualitatively identify unknown additives or impurities.

Introduction

Battery gas analysis is widely used in quality control (QC) environments in battery and automotive production facilities to ensure battery cell performance. Such analyses are typically performed by gas chromatography (GC) and micro GC.[3] Additionally, the ability of the QC instrument configuration to identify potential unknowns in the battery gas composition is important to assessing battery quality, which requires incorporation of a GC/MSD into the configuration.

In addition to measuring hydrocarbons in battery swell gas, hydrogen is also monitored for battery performance, as hydrogen evolution often correlates with lithium-ion battery failure. However, hydrogen is not easily detected by mass spectrometry, and so thermal conductivity detection (TCD) is also needed in the QC instrument configuration.

Another key to battery cell performance is the choice of electrolyte. Selecting the right organic electrolyte is key to achieving a higher energy density, a longer cycle life, and greater battery safety. Lithium battery manufacturers also add specific additives to extend battery life. GC/MS is commonly used in studies on lithium battery electrolytes, as it can quantitatively analyze the major components of the organic solvent in the electrolyte. Meanwhile, the strong qualitative capacity of mass spectrometry can also identify and quantify unknown additives and impurities.

This application note describes three analytical methods for determining battery gas hydrocarbon composition, hydrogen, and carbonate and carboxylate solvents and additives in lithium battery electrolyte on a single GC/MSD/TCD system. Known and unknown hydrocarbons found in swell gas are analyzed by GC/MSD, while permanent gases, such as hydrogen, are analyzed by TCD. The electrolyte analysis can be accomplished via direct injection or headspace. We tested both approaches and prefer headspace because the main component of the electrolyte ($LiPF_6$) is unstable and can easily decompose. While both approaches provide good sensitivity, linearity, and reproducibility, headspace does not degrade the inlet or column, which provides a more robust solution.

Experimental

An Agilent 8890 GC configured with dual detectors — a 5977B GC/MSD and TCD — was used for this work. The instrument was equipped with a split/splitless injection port and a CTC PAL3 Series 2 RTC autosampler configured for headspace. The instrument was operated with Agilent MassHunter Workstation software. Three methods were used to comprehensively analyze the battery swell gas, hydrogen, and electrolyte. All methods are detailed in Tables 1 and 2. The swell gas and electrolyte methods use the mass spectrometer, and the hydrogen method relies on the thermal conductivity detector. The mass spectrometer is configured with an Agilent QuickSwap capillary flow module to allow vent-free column changes.

Table 1. Agilent 8890 GC method parameters for battery swell gas, electrolyte, and hydrogen analyses.

	Swell Gas	Electrolyte	Hydrogen
Chromatographic Column	Agilent J&W GS-GasPro column, 60 m × 0.32 mm (p/n 113-4362)	Agilent J&W DB-1701 column, 30 m × 0.250 mm, 0.25 µm (p/n 122-0732)	Agilent J&W CP-Molsieve 5Å column, 10 m × 0.32 mm, 30 µm (p/n CP7535)
Injector	Gas-tight syringe	Headspace	Gas-tight syringe
Injection Volume	100 µL	100 µL	100 µL
Injection Mode	Split, with a split ratio of 10:1	Split, with a split ratio of 10:1	Split, with a split ratio of 10:1
Temperature at the Injection Port	250 °C	250 °C	250 °C
Carrier Gas	Helium, at a constant flow rate of 3.5 mL/min	Helium, at a constant flow rate of 2.6 mL/min	Argon, at a constant flow rate of 10 mL/min
Ramp Program	Hold 40 °C for 5 min, ramp to 100 °C at 5 °C/min, ramp to 200 °C at 10 °C/min, ramp to 250 °C at 15 °C/min, hold 250 °C for 1.333 min	Hold 40 °C for 3 min, ramp to 160 °C at 10 °C/min, hold 160 °C for 2 min	Isothermal 60 °C
Run Time	31.666 min	17 min	30 min
Detection	Mass selective detector (GC/MSD)	Mass selective detector (GC/MSD)	Thermal conductivity detector (TCD); 200 °C, reference gas 30 mL/min, make up gas 5 mL/min

Table 2. Agilent 5977B GC/MSD method parameters for battery swell gas and electrolyte analyses.

	Swell Gas	Electrolyte
Solvent Delay	2 min	2.3 min
Ionization Mode	Electron ionization (EI)	Electron ionization (EI)
Ion Source Temperature	270 °C	270 °C
Quadrupole Temperature	150 °C	150 °C
Interface Temperature	250 °C	250 °C
Detection Mode	Full scan, at 10 to 150 amu	Full scan, at 35 to 450 amu
Gain Factor	0.2	1

The hydrogen method uses an Agilent J&W CP-Molsieve 5Å column. Molsieve columns are moisture sensitive and strongly retain hydrocarbons. Analyzing swell gas samples without using a column isolation setup will allow moisture and hydrocarbons to build up on the column until the chromatography degrades. The column is easy to recondition as necessary by increasing the oven temperature to 300 °C and flushing the column overnight to drive off retained moisture and hydrocarbons.

Standard preparation

Calibration gas can be introduced using a manual gas-tight syringe (through a special adapter that allows the syringe to draw the standard directly from the gas cylinder, e.g. a CJ Tee Syringe Adapter). This approach was used for this application note. A more elaborate approach is outlined by the California Air Resources Board.[4] Agilent does not have standards for all the thermal runaway products we found, but we do provide a universal and NGA combo cylinder (part number 5184-3544) and an RGA checkout sample with argon (part number 5190-0519) that contain many of the compounds we used for quantification. Alternatively, gas supply companies can provide custom mixes based on your battery system. Many of the gas identities can also be confirmed by a NIST library search. Reference chromatographic retention times can also be important in confirming the identity of permanent gases that are difficult to analyze by mass spectrometer. Many of the swell gas and electrolyte samples used in this study were provided as part of the method development process.

Gas sampling of pouch cells

It is important to avoid atmospheric contamination when sampling battery swell gases. Silicon sealant, such as Dow DOWSIL 736 Heat Resistant Sealant, can be used to attach the Agilent PTFE/white silicone septa (part number 5182-0729) to the pouch cell sampling site.[5] A 500 µL Agilent gas-tight syringe flushed with argon was used in this experiment (part number 5190-1523).

Results and discussion

Swell gas analysis

Figure 1A shows the GC/MS analysis of a refinery gas analysis (RGA) standard purchased from a commercial custom gas supplier. The RGA mixture covers the range from C_1 (methane) to C_6 (hexane). This standard also includes carbon monoxide (CO) and carbon dioxide (CO_2). Figure 1B shows the battery gas concentration and quantitation report.

The ability to detect and identify unknowns in lithium battery cell hydrocarbon analysis is a critical attribute of the GC/MS configuration. The J&W GS-GasPro column provides excellent separation of these unknown species from the targeted analytes shown in Figure 1.
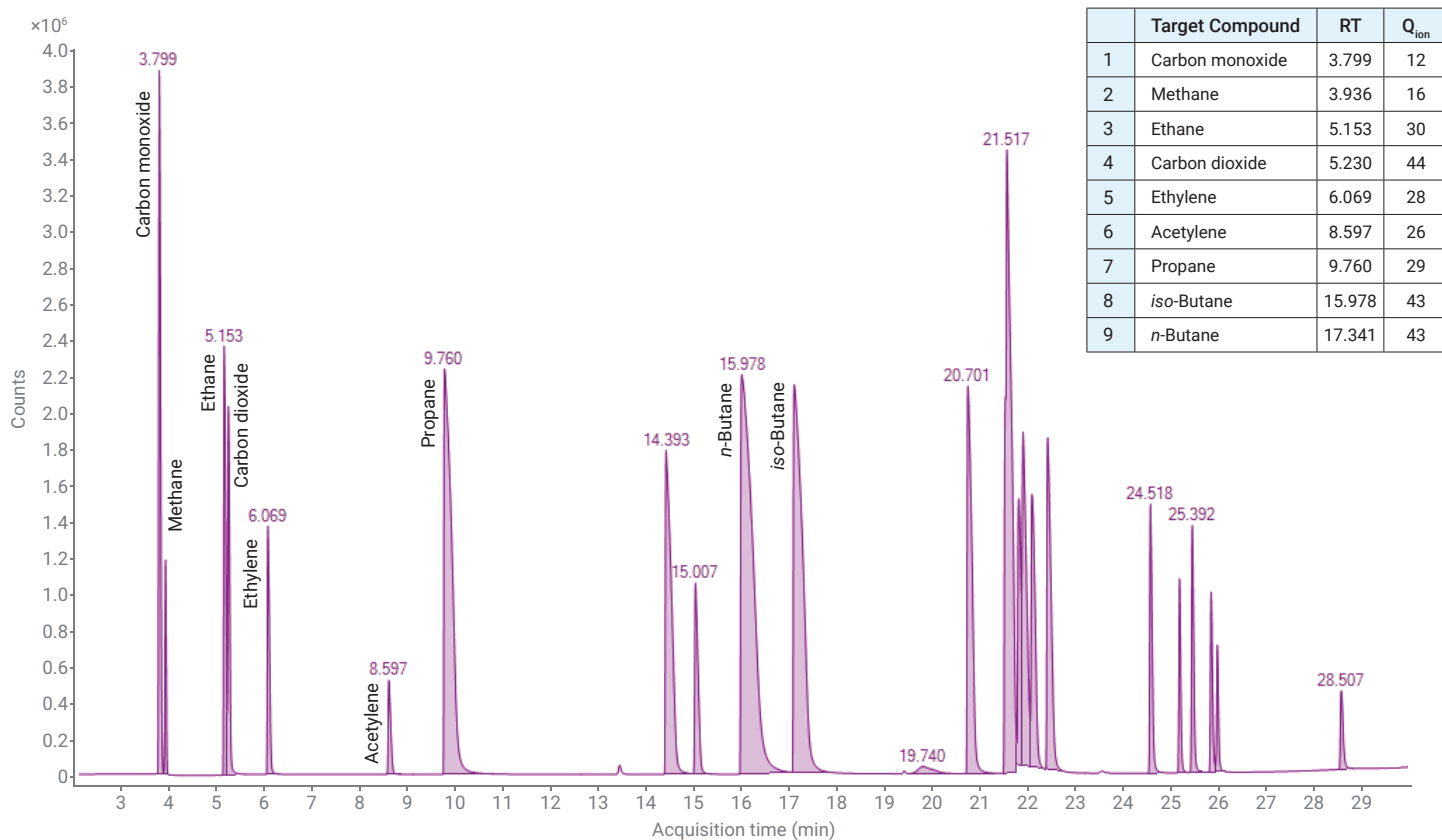
	Target Compound	RT	Q_{ion}
1	Carbon monoxide	3.799	12
2	Methane	3.936	16
3	Ethane	5.153	30
4	Carbon dioxide	5.230	44
5	Ethylene	6.069	28
6	Acetylene	8.597	26
7	Propane	9.760	29
8	iso-Butane	15.978	43
9	n-Butane	17.341	43

Figure 1. Separation of a commercially available refinery gas analysis standard on an Agilent J&W GS-GasPro column.

The chromatograms in Figure 2 indicate regions of unknown hydrocarbons detection in a used battery cell analysis. Unknowns include fluorinated hydrocarbons formed by fluoride salts present in battery electrolyte solution reacting with the presence of short-chain hydrocarbons at elevated battery cell temperatures.
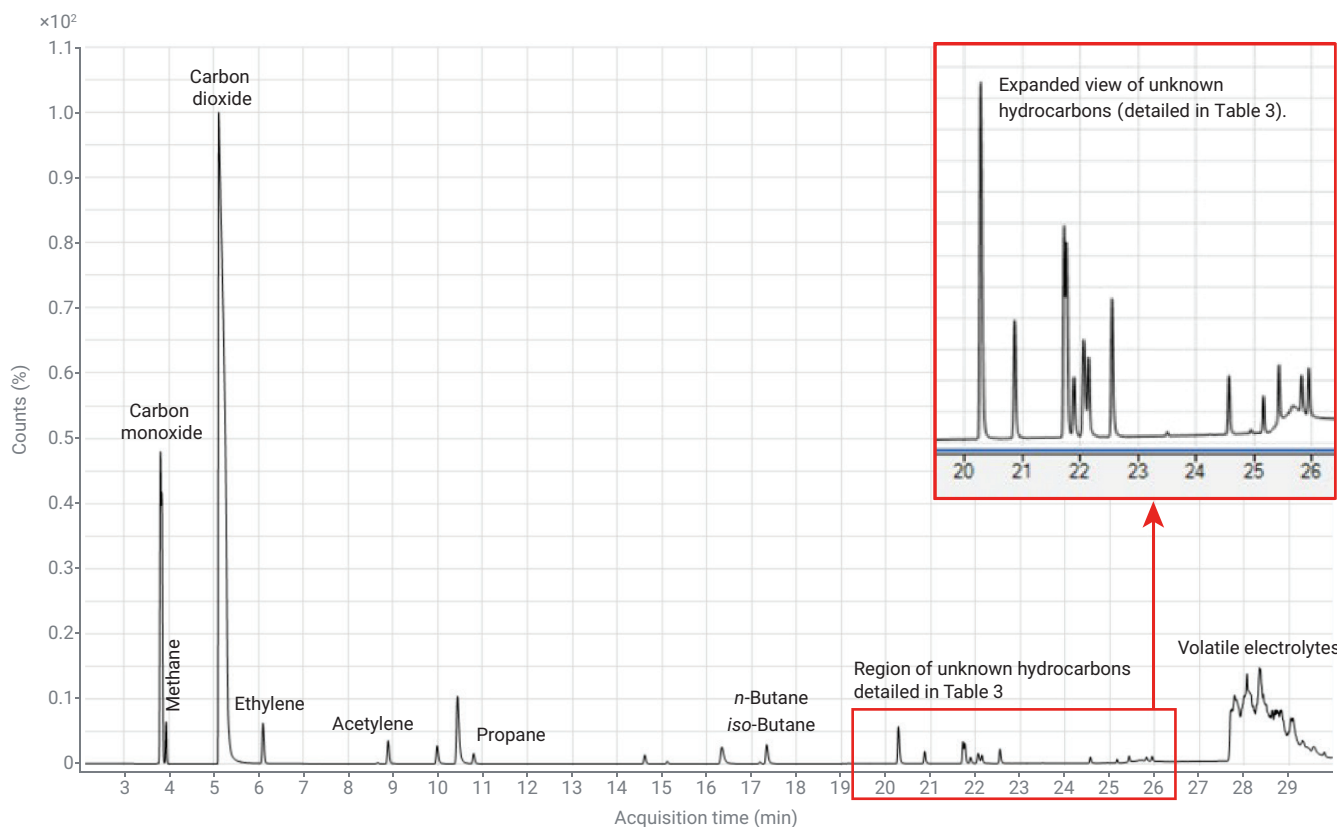

Figure 2. GC/MS separation of known and unknown hydrocarbons in battery swell gas on an Agilent GS-GasPro column with an expanded view of the unknowns, which are detailed in Table 3.

Table 3 shows the swell gas composition identified and measured by Agilent MassHunter Deconvolution Analysis software. The components written in blue demonstrate the improved detection ability of deconvolution analysis.

Table 3. The swell gas composition for the used battery cell analysis shown in Figure 2 identified and measured by Agilent MassHunter Deconvolution Analysis software.

Component RT	Compound Name	Formula	Match Factor	Component Area	Relative Area%	Normalized Area%
3.81	Oxygen	O_2	99.5	1,136,053	2.318	2.88
3.82	Argon	Ar	96.9	130,956	0.267	0.33
3.84	Formaldehyde	CH_2O	98.8	197,145	0.402	0.50
5.10	Formaldehyde	CH_2O	99.4	319,854	0.653	0.81
5.11	Carbon dioxide	CO_2	81.5	39,473,790	80.537	100.00
8.89	Carbonyl sulfide	COS	98.0	517,284	1.055	1.31
9.98	Propane	C_3H_8	64.9	395,985	0.808	1.00
10.43	Phosphorus trifluoride	F_3P	72.5	32,379	0.066	0.08
10.44	Sulfuryl fluoride	SO_2F_2	97.1	2,200,764	4.490	5.58
10.80	Methyl fluoride	CH_3F	99.0	242,697	0.495	0.61
13.45	Propene	C_3H_6	91.0	2,867	0.006	0.01
14.62	Propene	C_3H_6	99.0	214,810	0.438	0.54
15.12	Propadiene	C_3H_4	99.4	55,005	0.112	0.14
16.34	Isobutane	C_4H_{10}	97.7	662,861	1.352	1.68
17.19	Chloromethane	CH_3Cl	95.9	36,789	0.075	0.09
17.34	Butane	C_4H_{10}	93.6	489,256	0.998	1.24
19.16	Ethane, 1,1-difluoro-	$C_2H_4F_2$	89.5	9,191	0.019	0.02
20.28	Ethane, fluoro-	C_2H_5F	98.6	794,252	1.620	2.01
20.87	1-Butene	C_4H_8	97.0	229,340	0.468	0.58
21.72	2-Butene	C_4H_8	90.3	321,338	0.656	0.81
21.76	1,3-Butadiene	C_4H_6	97.4	348,865	0.712	0.88
21.89	Isobutene	C_4H_8	88.7	114,767	0.234	0.29
22.06	Butane, 2-methyl-	C_5H_{12}	96.2	255,678	0.522	0.65
22.14	2-Butene	C_4H_8	92.5	142,972	0.292	0.36
22.54	Pentane	C_5H_{12}	98.1	276,282	0.564	0.70
23.50	Ethyl chloride	C_2H_5Cl	67.9	4,711	0.010	0.01
24.56	2-Methyl-1-butene	C_5H_{10}	94.8	101,157	0.206	0.26
24.95	Propane, 2-fluoro-	C_3H_7F	83.0	6,799	0.014	0.02
25.16	2-Methyl-1-butene	C_5H_{10}	95.3	58,315	0.119	0.15
25.43	2-Methyl-1-butene	C_5H_{10}	95.1	95,415	0.195	0.24
25.82	2-Butene, 2-methyl-	C_5H_{10}	95.5	65,039	0.133	0.16
25.94	*n*-Hexane	C_6H_{14}	96.9	80,629	0.165	0.20
			Total	49,013,246	100.0	

Figure 3A shows these two components coeluting on the GS-GasPro column. Phosphorus trifluoride is a minor component (approximately 1.4% of the larger sulfuryl fluoride at > 5%). Deconvolution easily identifies the coelution and correctly identifies the two swell gas components. Figure 3B provides the extracted ion chromatogram (m/z 69 and 83) view of the two major ions measured in this analysis. Due to the mass separation of these two ions, both the phosphorus trifluoride and sulfuryl fluoride could be accurately measured.

Carbon monoxide (CO) is a critical component of battery cell gas composition. Elution of CO on the GS-GasPro column occurs near the nitrogen (N_2) peak. Figure 4 shows the NIST reference spectra for CO with emphasis on the carbon m/e 12+ fragment.
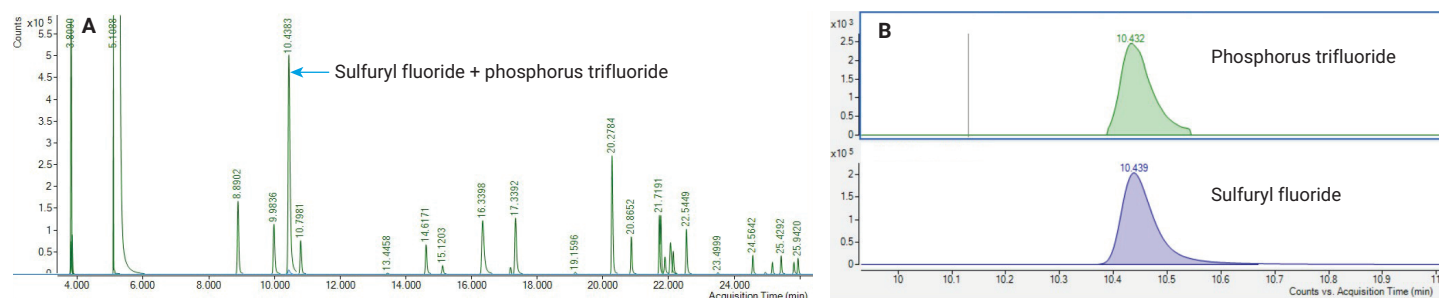

Figure 3. Analysis of coeluting sulfuryl fluoride and phosphorus trifluoride on an Agilent 5977B GC/MSD.
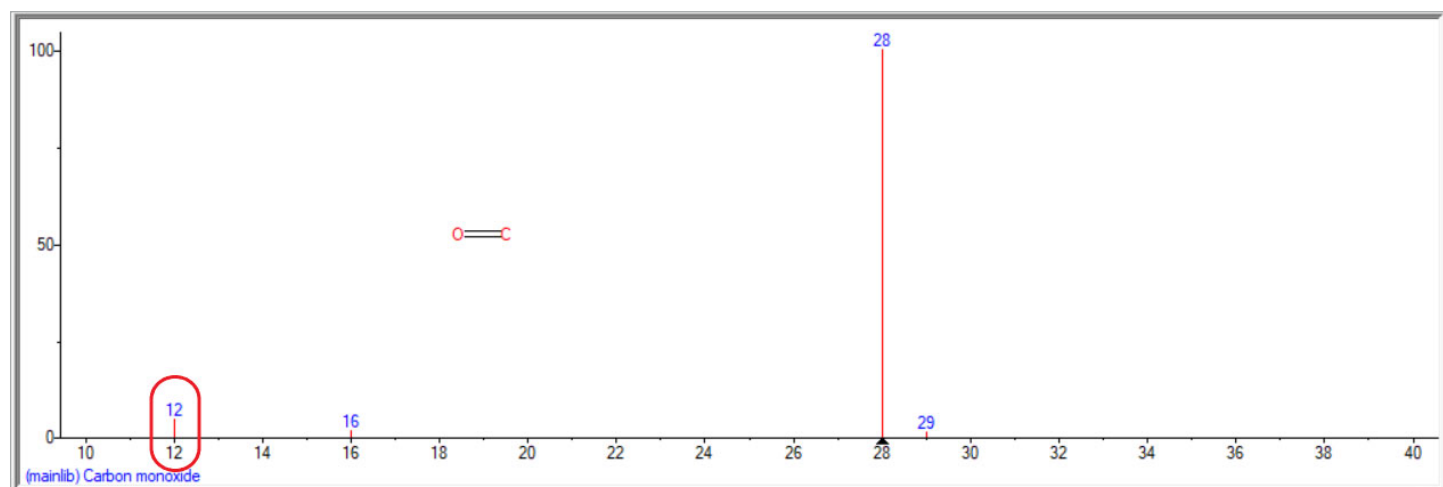

Figure 4. Wiley Registry/NIST Mass Spectral Library spectrum for CO with emphasis on the carbon m/e 12+ fragment.

Figure 5 details the advantage of using the MSD as the detector for CO and methane (CH_4, molecular ion 16^+), as it can easily resolve CO and CH_4 from the N_2 peak due to their unique spectra.
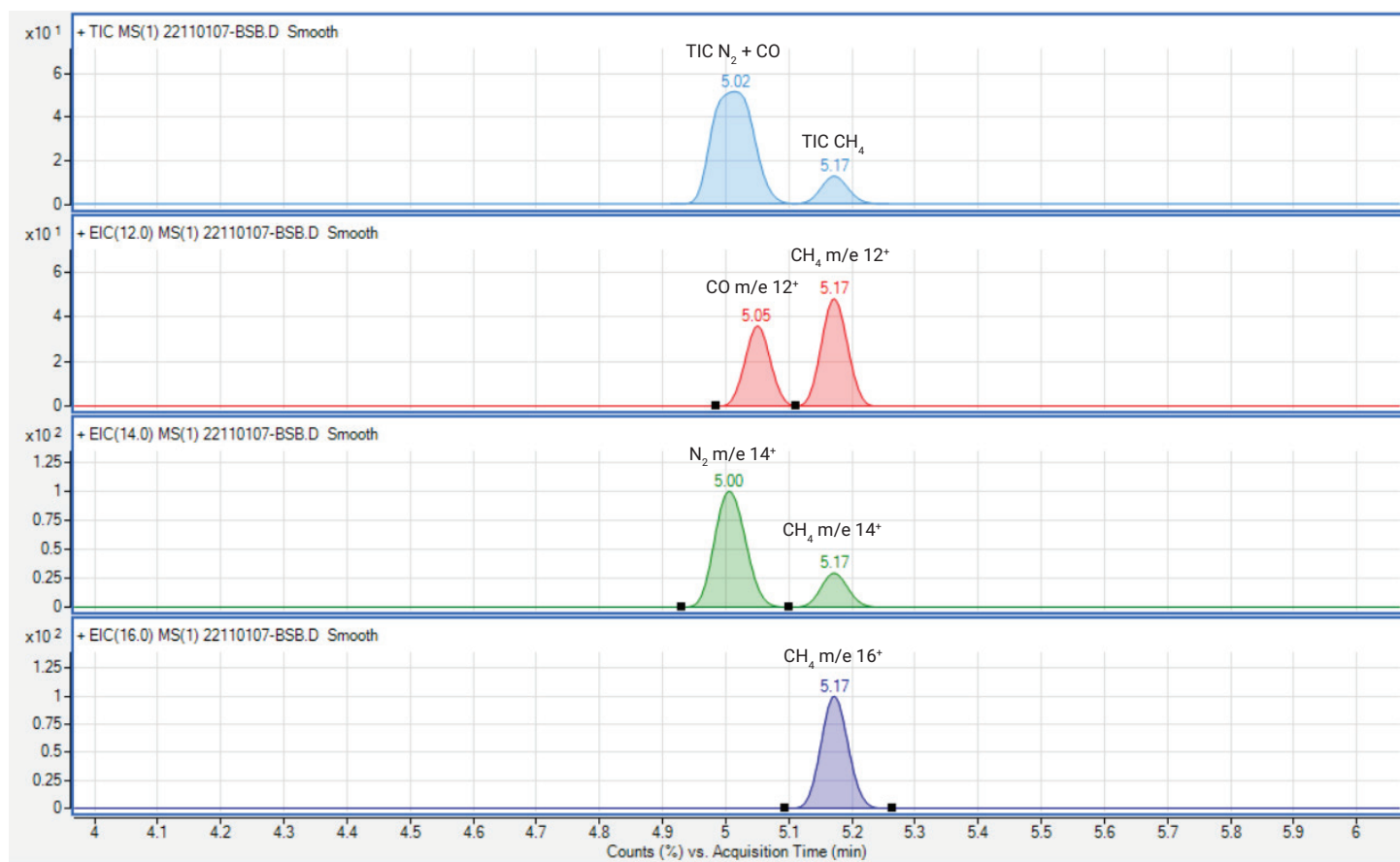

Figure 5. Detection and resolution of nitrogen, methane, and carbon monoxide in battery cell gas on an Agilent 5977B GC/MSD and GS-GasPro column.

Hydrogen analysis

One of the more critical indicators of rechargeable Li battery cell performance/failure is the increasing concentration of hydrogen (H_2) within the cell. It is important that the GC/MS-based configuration can routinely and robustly quantify the amount of H_2 present from 0.1 to 20%. Detection of H_2 is problematic by electron ionization (EI) MS, so TCD detection is included in the configuration to allow detection of a wide concentration range. Argon carrier gas is employed on the purged packed GC inlet to provide sufficient delta of conductivity between H_2 and the carrier gas.[6] A J&W CP-Molsieve 5Å column is used to provide adequate separation of H_2 from N_2 and O_2, as also demonstrated in Agilent publication 5991-4873EN.[7] This publication also addresses how to detect and quantify more retained gases, if needed, using a temperature ramp. Figure 6 shows H_2 reference standards by TCD at 5 and 12% composition.

Figure 7 presents calibration curve results from 0.06 to 5.0% H_2 composition, and the chromatogram in Figure 8 shows H_2 measurement in a used battery cell.
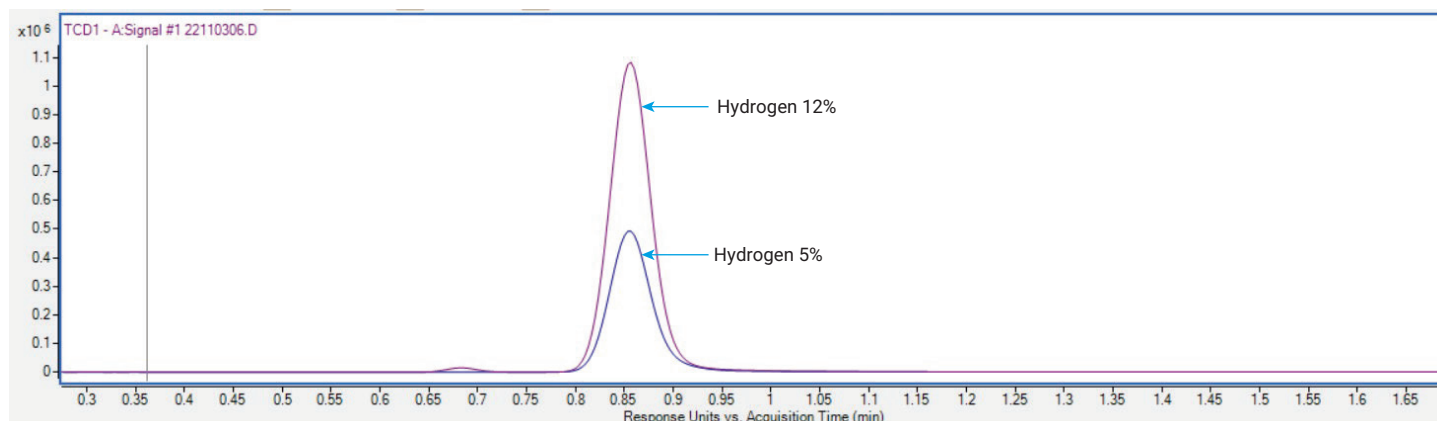

Figure 6. Hydrogen reference standards detected by TCD at 5 and 12% composition on an Agilent 8890 GC.

Batch Table

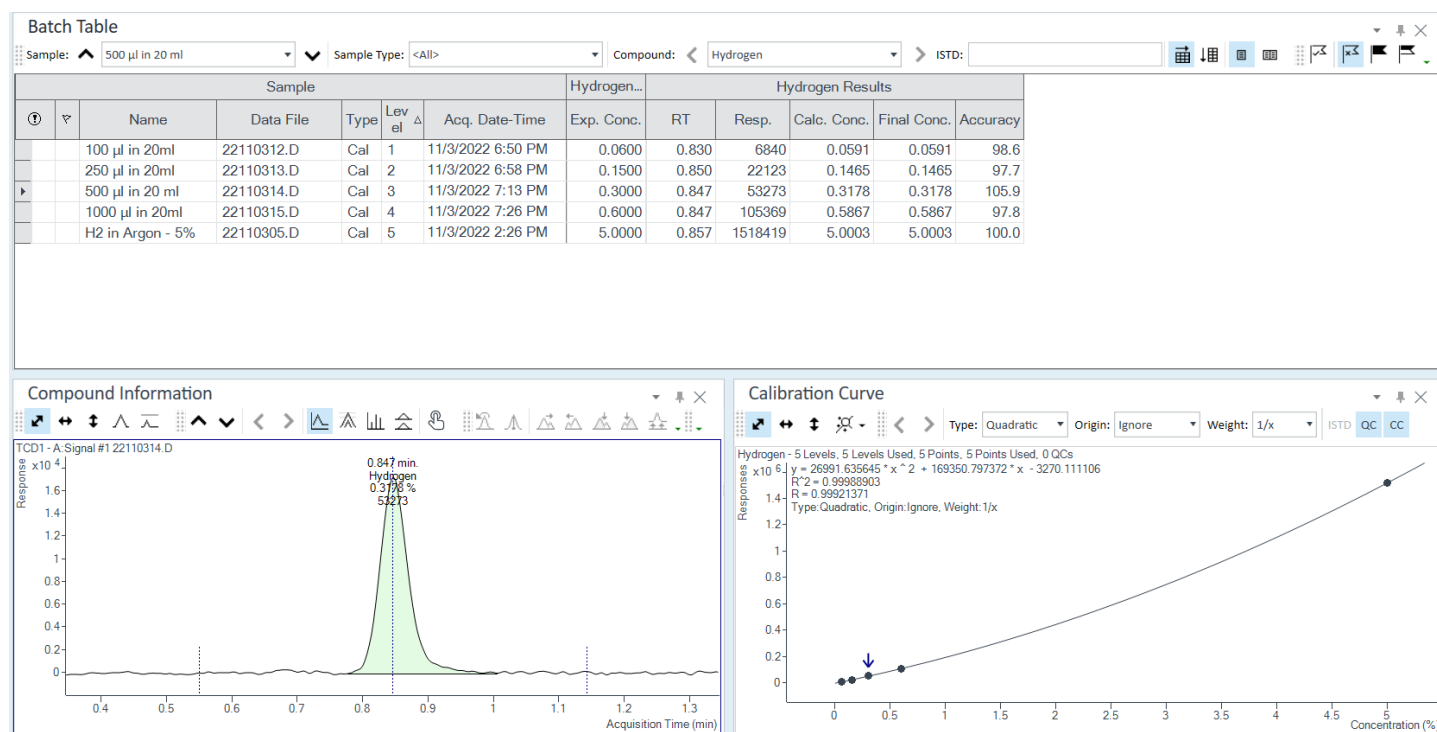|		Sample				Hydrogen...		Hydrogen Results			
⊙	▽	Name	Data File	Type	Level	Acq. Date-Time	Exp. Conc.	RT	Resp.	Calc. Conc.	Final Conc.	Accuracy
		100 µl in 20ml	22110312.D	Cal	1	11/3/2022 6:50 PM	0.0600	0.830	6840	0.0591	0.0591	98.6
		250 µl in 20ml	22110313.D	Cal	2	11/3/2022 6:58 PM	0.1500	0.850	22123	0.1465	0.1465	97.7
▶		500 µl in 20 ml	22110314.D	Cal	3	11/3/2022 7:13 PM	0.3000	0.847	53273	0.3178	0.3178	105.9
		1000 µl in 20ml	22110315.D	Cal	4	11/3/2022 7:26 PM	0.6000	0.847	105369	0.5867	0.5867	97.8
		H2 in Argon - 5%	22110305.D	Cal	5	11/3/2022 2:26 PM	5.0000	0.857	1518419	5.0003	5.0003	100.0

Figure 7. Calibration curve results from 0.06 to 5.0% hydrogen composition on an Agilent 8890 GC with detection by TCD.
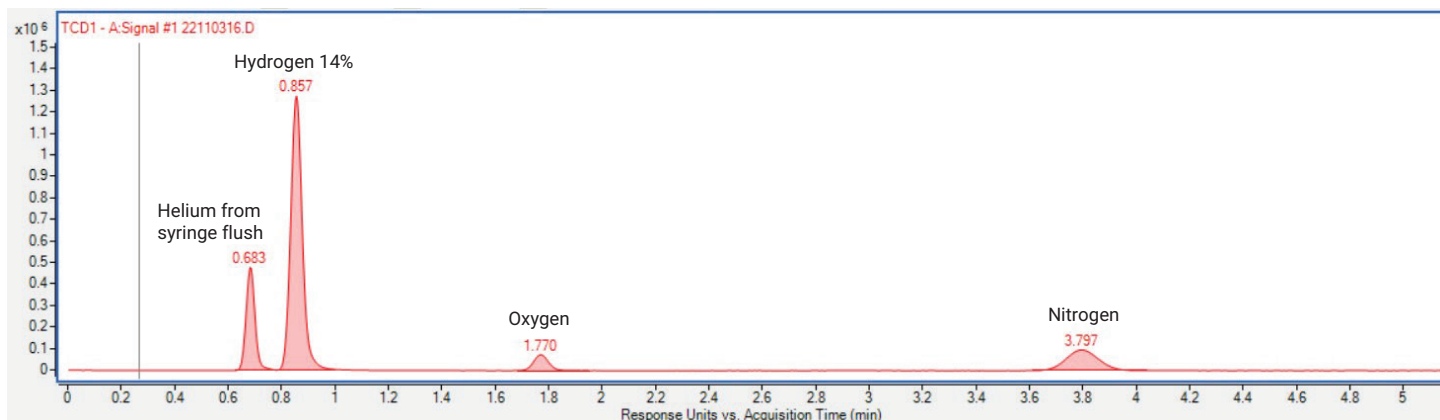
Figure 8. Hydrogen measurement in a used battery cell on an Agilent J&W CP-Molsieve 5Å column. Observed retention time will differ based on method adjustments made for optimal chromatography of swell gas constituents.

Electrolyte analysis

Carbonate mixtures used in lithium battery cell electrolyte solution play a critical role in overall battery performance. The identification of individual components, percent composition and purity measurements, and identification of these mixtures is confirmed on this GC/MS configuration by replacing the GS-GasPro column with a J&W DB-1701 column. The presence of the QuickSwap capillary flow technology module allows for this column change to take place quickly without requiring mass spectrometer venting.

Headspace can be used for both volatile and semivolatile compounds, which is apt for most electrolyte analyses. However, direct liquid injection is also possible for the analysis of electrolytes, if desired. A comparison of heated headspace injection and direct liquid injection is shown in Figures 9 and 10 for a classic carbonate electrolyte mixture and a volatile electrolyte mixture, respectively. As can be seen, these analyses look similar. One notable difference is the detection of ammonium polyphosphate by direct injection, but not by headspace as it is not volatile (Figure 10). While direct injection can detect nonvolatile compounds, it also has disadvantages for electrolyte analysis. Electrolyte samples contain nonvolatile salts like lithium hexafluorophosphate that can degrade and contaminate the GC inlet, leading to more frequent instrument maintenance and downtime. For a more robust electrolyte analysis, headspace sampling is preferred.
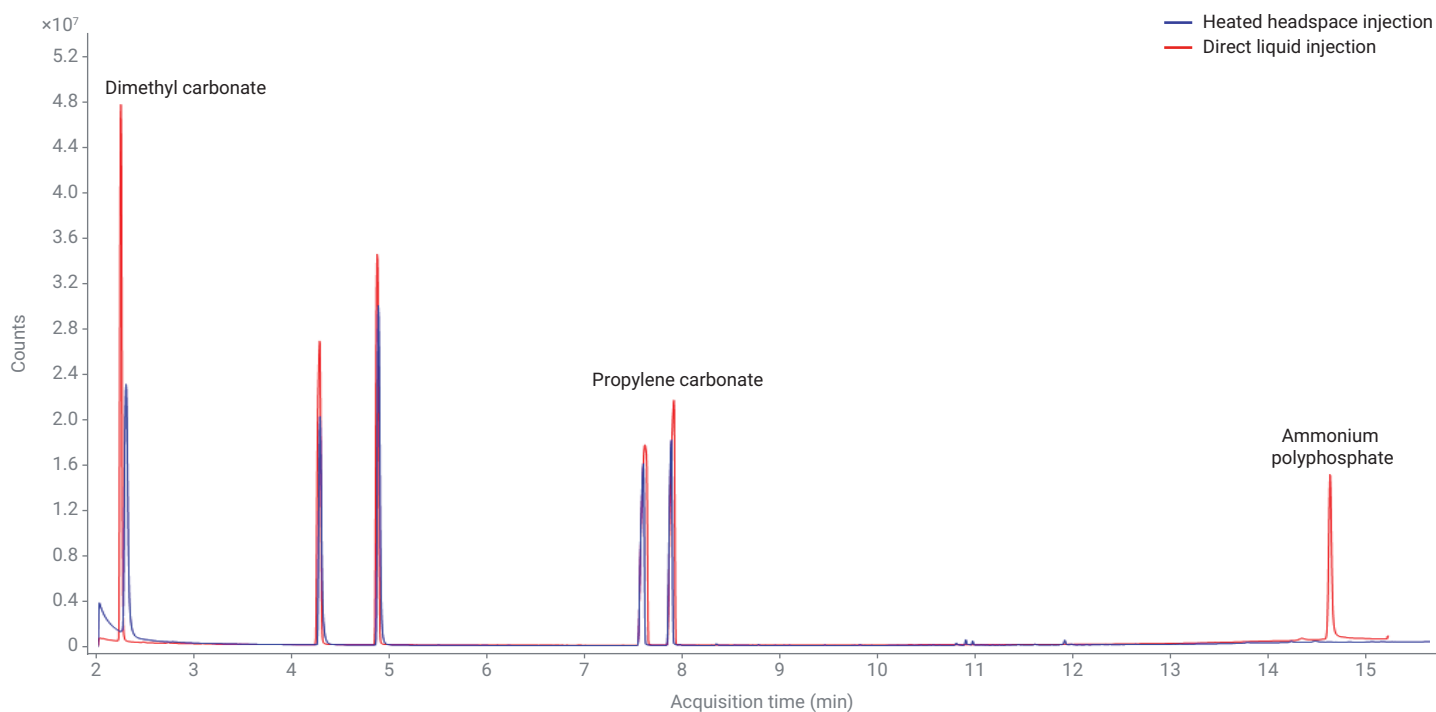
Figure 9. A comparison of heated headspace injection (blue) and direct liquid injection (red) of a classic carbonate electrolyte mixture on an Agilent 8890 GC.
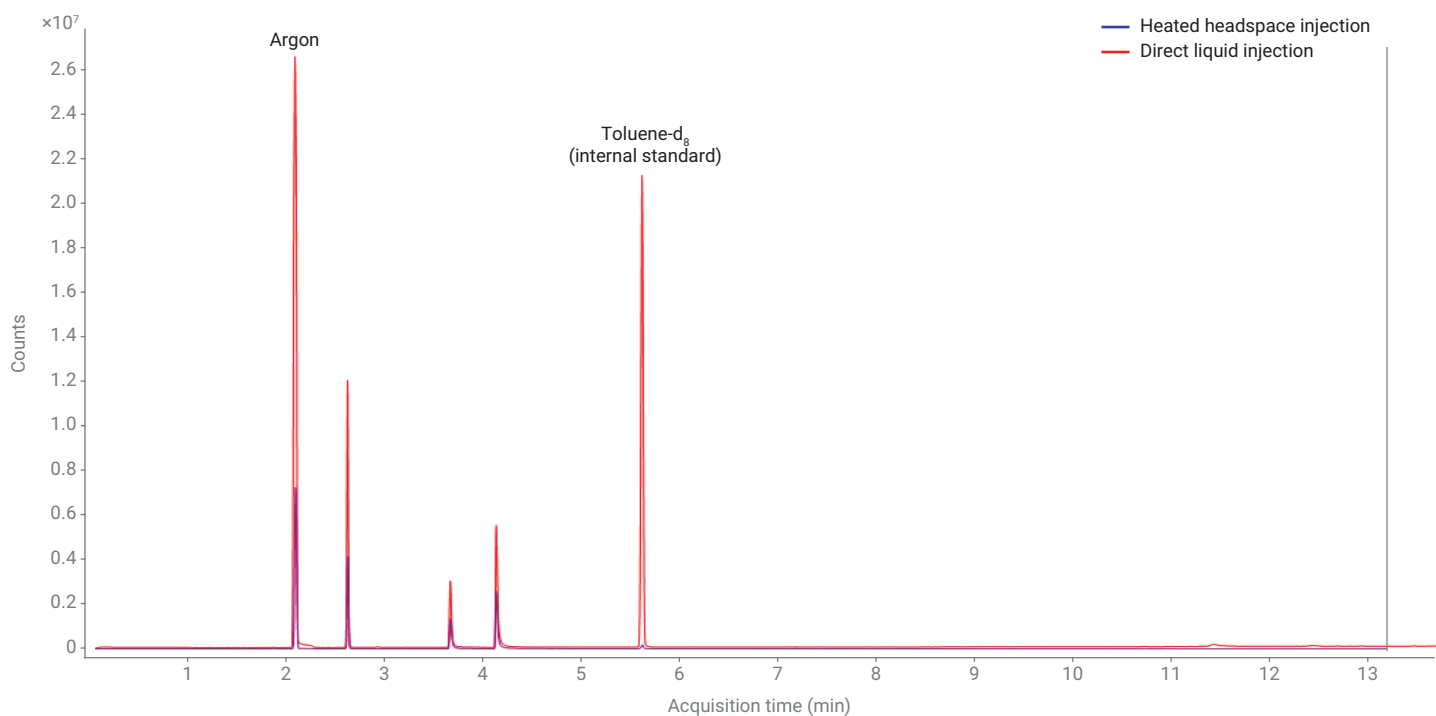

Figure 10. A comparison of heated headspace injection (blue) and direct liquid injection (red) of a volatile electrolyte mixture on an Agilent 8890 GC. The headspace was done at 60 °C. The toluene-d_8 internal standard is more prominent at 80 °C, but the electrolyte starts decomposing.

Conclusion

Using a dual-detector configuration, the Agilent 8890 GC with Agilent 5977B GC/MSD and TCD presents a simple solution for analyzing rechargeable battery cell gas composition without using valves, a valve oven, packed columns, or heated sampling loops. Battery gas composition for critical low-range hydrocarbons as well as CO and CO_2 is determined on an Agilent J&W GS-GasPro column with detection by GC/MS. Hydrogen analysis is achieved on an Agilent J&W CP-Molsieve 5Å column with TCD detection. Also, the detection and identification of unknown hydrocarbons in battery gas composition is demonstrated via deconvolution by Agilent MassHunter Workstation software.

The 8890 GC was also configured with an Agilent QuickSwap capillary flow technology module, which allows for quick column changes without requiring mass spectrometer venting. Installing an Agilent J&W DB-1701 column enabled the addition of electrolyte analysis on this GC/MS/TCD configuration. In total, three methods are successfully set up and run. This provides a comprehensive analysis of battery swell gas, hydrogen, and electrolyte to determine lithium-ion battery quality.

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