Application note

Analyzing lithium-ion battery gases with GC-MS-FTIR

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Introduction

Lithium-ion batteries are extensively used in power, energy storage, and other applications due to their light weight, high energy density and longer service life compared to other battery types. During the recycling or storage of lithium-ion batteries, the membranes of the solid electrolyte interface (SEI) may decompose or become damaged, resulting in gas generation. This can cause the battery to swell, posing safety risks such as thermal runaway, off-gassing, expansion deformation, etc. Understanding the composition of these battery gases is crucial for optimizing electrolyte composition and minimizing these risks.

Gas chromatography mass spectrometry (GC-MS) offers highly efficient separation of complex gaseous samples as well as improved retention times, qualitative mass spectrometry, and the detection of volatile/semi-volatile substances. The addition of Fourier-transform infrared (FTIR) spectroscopy enables the identification of a compound's fingerprint and characteristic absorption bands (to determine its spatial conformation), as well as multi-component analysis for the characterization of mixtures. Combining the high-efficiency separation and quantitative detection of GC-MS with the unique structural identification of FTIR enables a complete analysis of complex gaseous samples.

Combined GC-MS-FTIR leverages the separation of GC together with the improved quantitative and qualitative sensitivity of MS and FTIR. For instance, GC-MS by itself cannot accurately distinguish certain samples such as isomers or homologous compounds due to their similar structures and similar (or even identical) ion fragments. IR spectra, meanwhile, contain a wealth of information on the molecular structure of substances, enabling the identification of these isomeric components. On the other hand, non-IR-active samples, such as diatomic gases, can still be identified with GC-MS.

In this application note, gases produced in a swollen lithium-ion battery are analyzed with a Thermo Scientific™ ISQ™ 7610 GC-MS System along with a Thermo Scientific™ Nicolet™ iS50 FTIR Spectrometer. This approach produces complementary results that supplement and verify the observations made by each method individually. A comprehensive composition of the gas was obtained, highlighting the utility of combined GC-MS-FTIR for the analysis of complex gas mixtures.

Laboratory equipment

The experiments in this application note were performed using a unique combination of Thermo Scientific instrumentation, accessories, and software. These include:

- The Nicolet iS50 FTIR Spectrometer
- The ISQ 7610 GC-MS System
- GC interfacing accessories
- A Thermo Scientific™ TracePLOT™ TG-BOND Alumina GC Column
  - Dimensions: 50 m × 0.32 mm × 5 µm, PN: 26001-6050
- A Thermo Scientific™ TracePLOT™ Particle Trap
  - Dimensions: 2.5 m × 0.32 mm, PN: 60180-860
- Thermo Scientific™ OMNIC™ Software
- Thermo Scientific™ Chromeleon™ 7.3 Software
- Note: Software was activated synchronously without the need for external activation lines

The ISQ 7610 GC-MS System is an easy-to-operate single-quadrupole MS with a highly automated workflow and a wide dynamic linear range, ensuring consistent results across different GC systems. The system features unique Thermo Scientific™ NeverVent™ Technology as well as longer-life detectors and smart software to eliminate unnecessary downtime and maximize sample throughput. Chromeleon 7.3 Data Processing Software was used to quickly set up analytical and data processing methods. The software user interface is simple and easy-to-use, and the report template can be customized according to your specific requirements, facilitating data analysis.

Tandem GC-MS and FTIR system configuration.

Results and discussion

GC-MS of swollen lithium-ion battery gas sample

A full-scan acquisition method in Chromeleon 7.3 Software was used to determine the unknown composition of the lithium-battery gas. This method collects analytical information across the entire mass range while simultaneously validating compounds through spectral library searches. Figure 1 shows a GC-MS total-ion chromatogram (TIC) for the lithium-ion battery gas sample. Peaks on the chromatogram with a relative area ≥0.05% were selected for automatic integration and search against the NIST 2020 spectral library to obtain a qualitative match. Permanent gases, such as nitrogen, oxygen, carbon monoxide, and argon, were detected, as well as gases produced by the lithium battery, such as methane, ethane, ethylene, propane, propylene, acetylene, butane, and isobutane. Additionally, byproducts of lithium battery thermal runaway were also detected (e.g., 1,1-difluoroethylene and monofluoroethylene) along with several isomers of butylene and pentylene (indicated by peaks 15, 16, 17, 20, and 21 in Figure 1).

Butylene and pentylene isomers have similar structures and similar/identical ion fragments, making it practically impossible to distinguish them with GC-MS. Further analysis with FTIR is therefore necessary to assist in this characterization.

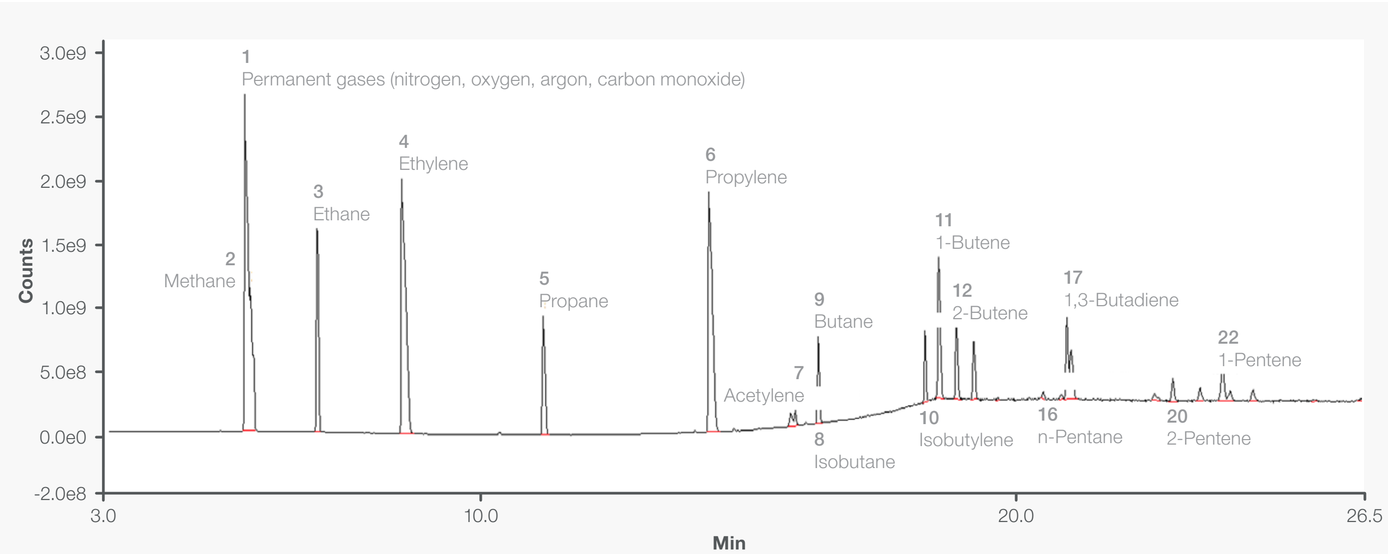
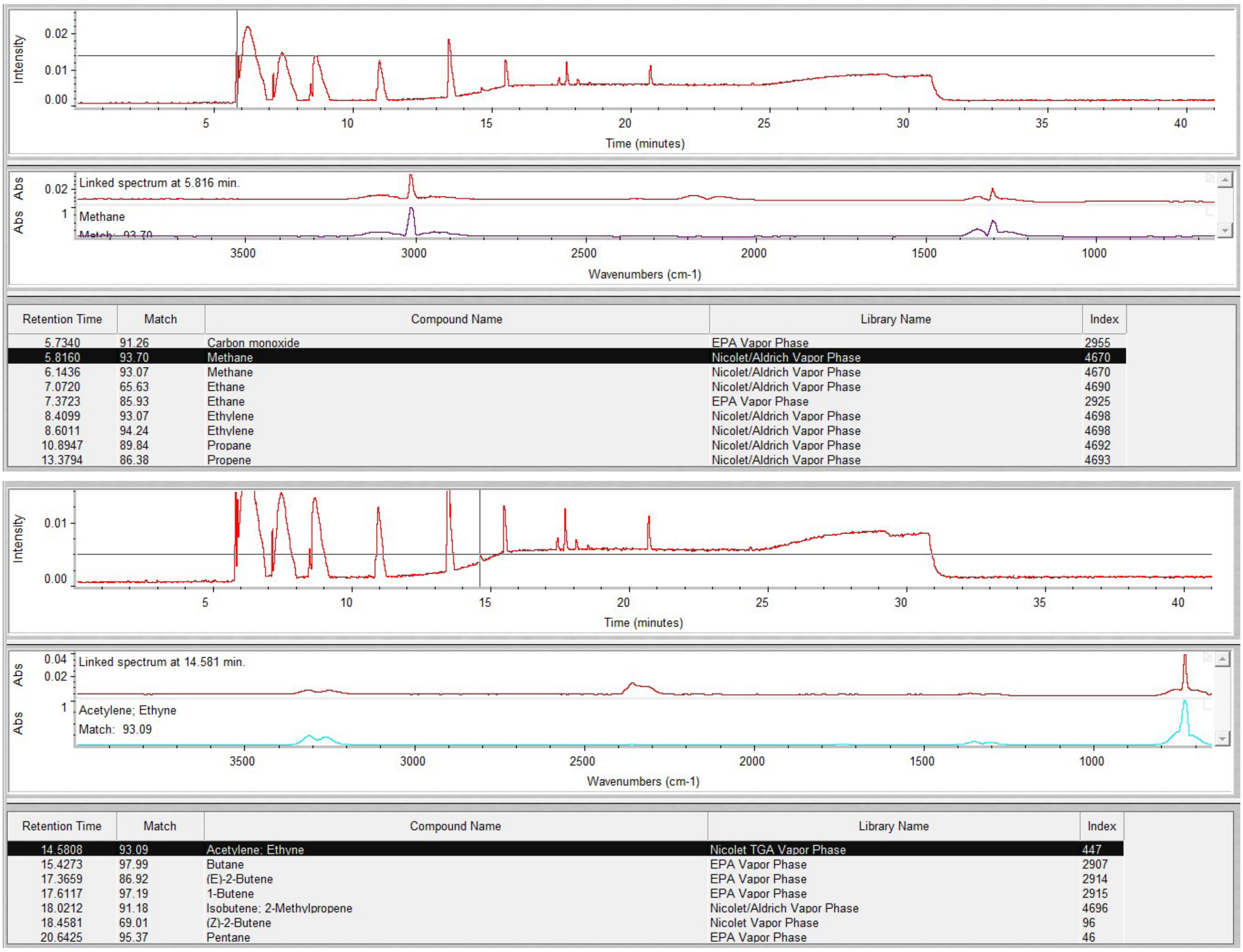


Figure 1. GC-MS total-ion chromatogram (TIC) of the lithium-ion battery gas sample.

FTIR analysis of isomeric compounds

OMNIC Software (part of the FTIR spectrometer) features a unique GC-FTIR data analysis functionality called Mercury GC. This enables one-click, automatic analysis of the complex data obtained through GC-FTIR, making the overall analytical process quick and simple. The calculated, overlaid spectra can be automatically displayed according to retention time, listing each component and trend over time, as well as any other pertinent data (Figure 2). The gas components detected during the entire retention time can be collected and visualized rapidly, making this method faster and more accurate than conventional GC-FTIR data analysis methods.



Retention Time	Match	Compound Name	Library Name	Index
5.7340	91.26	Carbon monoxide	EPA Vapor Phase	2955
5.8160	93.70	Methane	Nicolet/Aldrich Vapor Phase	4670
6.1436	93.07	Methane	Nicolet/Aldrich Vapor Phase	4670
7.0720	65.63	Ethane	Nicolet/Aldrich Vapor Phase	4690
7.3723	85.93	Ethane	EPA Vapor Phase	2925
8.4099	93.07	Ethylene	Nicolet/Aldrich Vapor Phase	4698
8.6011	94.24	Ethylene	Nicolet/Aldrich Vapor Phase	4698
10.8947	89.84	Propane	Nicolet/Aldrich Vapor Phase	4692
13.3794	86.38	Propene	Nicolet/Aldrich Vapor Phase	4693

Retention Time	Match	Compound Name	Library Name	Index
14.5808	93.09	Acetylene; Ethyne	Nicolet TGA Vapor Phase	447
15.4273	97.99	Butane	EPA Vapor Phase	2907
17.3659	86.92	(E)-2-Butene	EPA Vapor Phase	2914
17.6117	97.19	1-Butene	EPA Vapor Phase	2915
18.0212	91.18	Isobutene; 2-Methylpropene	Nicolet/Aldrich Vapor Phase	4696
18.4581	69.01	(Z)-2-Butene	Nicolet Vapor Phase	96
20.6425	95.37	Pentane	EPA Vapor Phase	46

Figure 2. The Mercury GC function in OMNIC Software automatically analyzes the composition of the lithium-battery gas sample for each retention time.

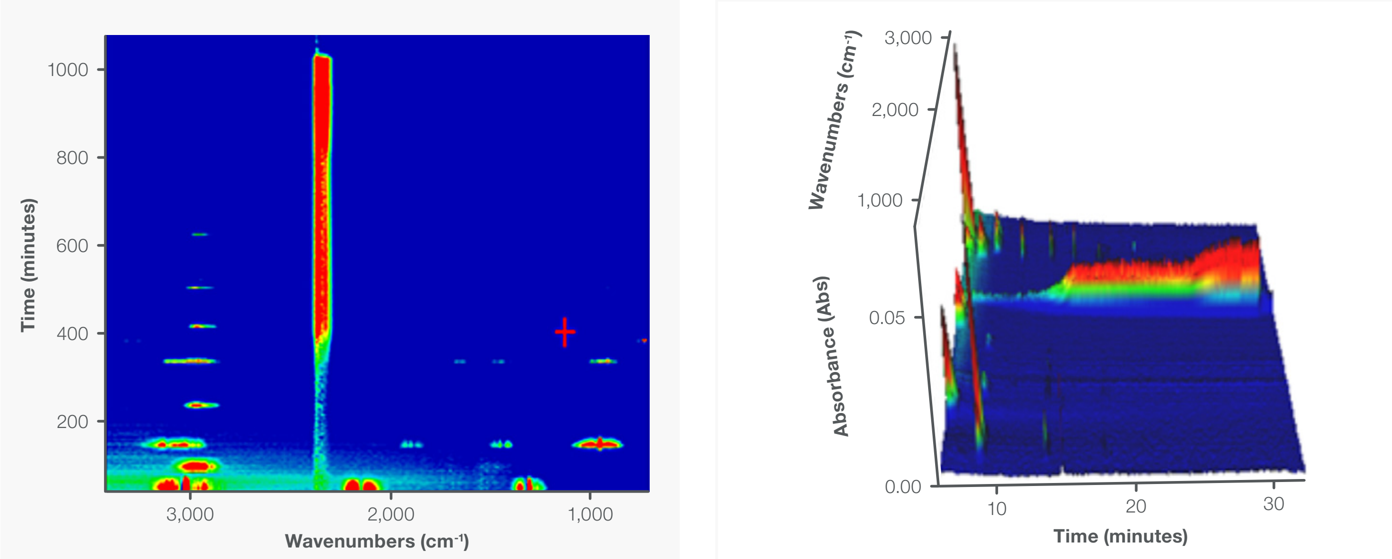


Figure 3. 2D and 3D chemical images of the infrared spectra for various gas components over time.

The Series Composition function of OMNIC Software can produce 2D and 3D chemical images of the infrared spectrograms for the overall gas composition. This allows the evolution of gas components over time to be displayed visually.

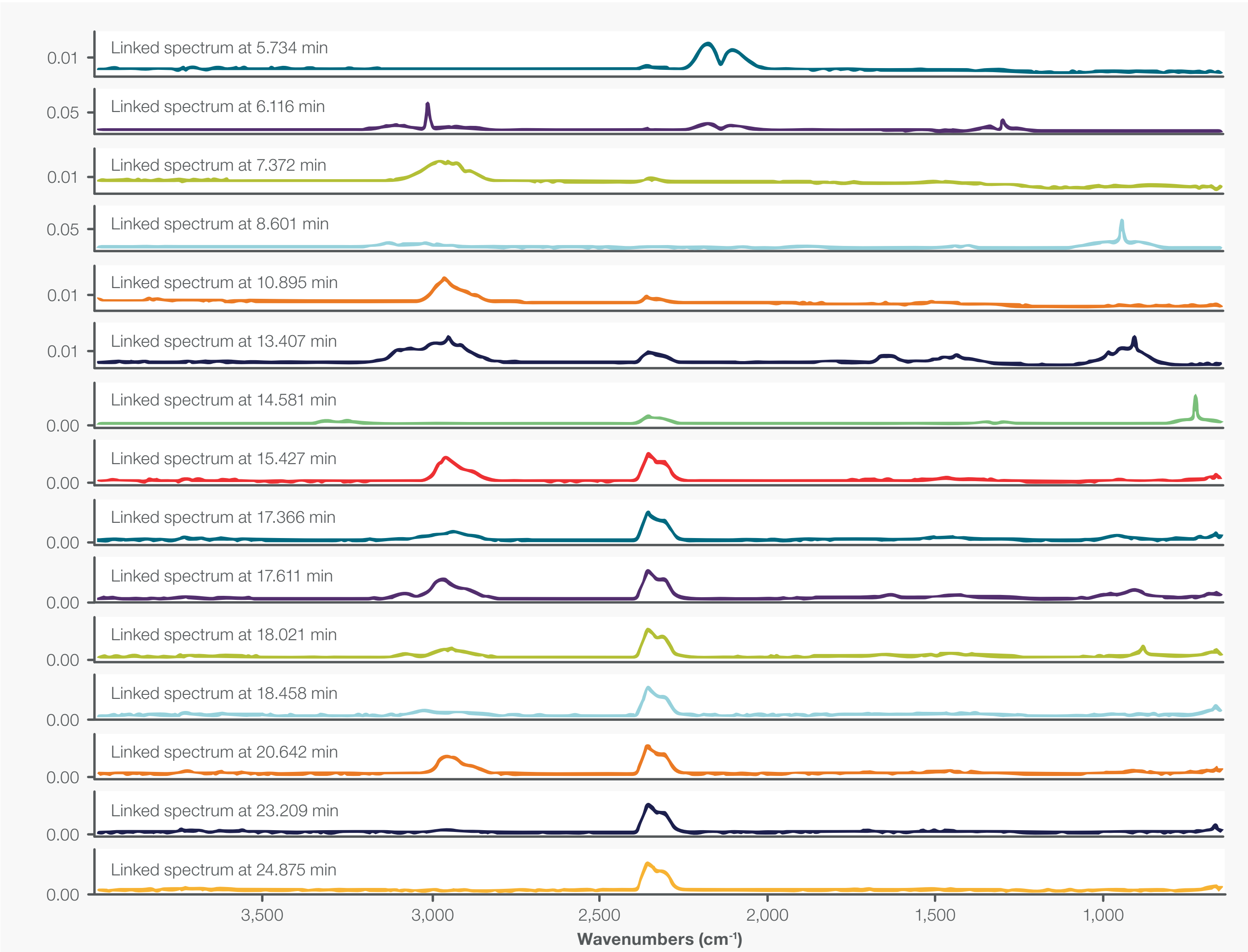


Figure 4. Representative infrared spectra of gas components at different retention times.

The Mercury GC function, along with comparisons to standard spectral libraries, confirmed that the main components of the sample gas were:

- Carbon monoxide
- Carbon dioxide
- Methane
- Ethane
- Ethylene
- Propane
- Propylene
- Acetylene
- Butane
- (E)2-Butene
- 1-Butene
- Isobutene
- (Z)2-Butene
- Pentane
- 1-Pentene

This comprehensive data was able to mutually verify the GC-MS and FTIR results and characterize most of the components in the lithium-battery gas sample (Table 1). The GC-MS data also provided complementary characterization of non-IR active diatomic gases, such as oxygen, argon, and nitrogen, as well as identification of low-concentration components like difluoroethylene. The unique nature of the fingerprint infrared spectrum allowed for further identification of isomers and cis-trans isomeric components (e.g., 1-butene, 2-butene, and isobutylene).

Conclusions and outlook

Lithium-ion battery swelling presents certain safety risks, including thermal runaway, off-gassing, and expansion deformation. Understanding the composition of the battery gas is crucial for optimizing the electrolyte composition and minimizing these risks. Due to the relatively complex composition of lithium-ion battery gases, a multi-modal analysis is necessary for complete characterization. In this application note, GC-MS-FTIR was used to accurately detect and analyze the composition of a gas sample from a swollen lithium-ion battery. This provided a comprehensive dataset of complementary GC-MS and FTIR results, offering more accurate and complete insights than each individual method could provide alone.

No.	Compound name	Qualitative reference ion, m/z	CAS No.	Molecular formula
1	Oxygen	32	7782-44-7	O_2
2	Argon	40	7440-37-1	Ar
3	Nitrogen	14	7727-37-9	N_2
4	Carbon monoxide	12	630-8-0	CO
5	Methane	15, 16	74-82-8	CH_4
6	Ethane	28, 30	74-84-0	C_2H_6
7	Ethylene	26, 27, 28	74-85-1	C_2H_4
8	1,1-Difluoroethylene	45, 64	75-38-7	$C_2H_2F_2$
9	Propane	28, 29, 44	74-98-6	C_3H_8
10	Propylene	39, 41, 42	115-07-1	C_3H_6
11	Monofluoroethylene	45, 46	75-02-5	C_2H_3F
12	Acetylene	26, 27, 28	74-86-2	C_2H_2
13	Isobutane	41, 43	75-28-5	C_4H_{10}
14	Butane	43, 58	106-97-8	C_4H_{10}
15	Isobutylene	41, 56	115-11-7	C_4H_8
16	1-Butene	41, 56	106-98-9	C_4H_8
17	(E)2-Butene	41, 56	107-01-7	C_4H_8
18	(Z)2-Butene	41, 56	107-01-7	C_4H_8
18	n-Pentane	39, 54	109-66-0	C_5H_{12}
19	1,3-Butadiene	39, 54	106-99-0	C_4H_6
20	1-Pentene	42, 55, 70	109-68-2	C_5H_{10}
21	Carbon dioxide	44	124-38-9	CO_2

Table 1. Components found in the swollen lithium-ion battery gas sample.