Application Note

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The Analysis of Swelling Gas in Lithium-Ion Batteries with an Agilent 990 Micro GC

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Abstract

This application note describes the analysis of lithium-ion-battery swelling gas using an Agilent 990 Micro GC. Three channels were recommended for permanent gas and hydrocarbons analysis in battery gassing. C_6/C_{6+} hydrocarbons were analyzed as one combined peak on a backflush-to-detector aluminum oxide channel. If a detailed hydrocarbons profile is needed, an Agilent CP-Sil 5 CB channel can replace the Agilent CP-Al_2O_3/KCl channel for the analysis of hydrocarbons heavier than propane.

Introduction

Lithium-ion batteries (LIBs) have widely been applied in electronic devices due to their high energy densities, flexible design, light weight, and long lifespan compared to other types of batteries. Gas generation (also called gassing, the volume swelling of a battery) is a common phenomenon of Li-ion performance degradation. This is usually caused by electrolyte degradation during the lifespan of Li-ion batteries. Knowing the composition of swelling gas is critical to optimizing the electrolyte composition. The key constituents in swelling gas are some permanent gases and light hydrocarbons. Gas chromatography is usually used for LIBs swelling gas analysis. However, some small-size LIBs can only generate several milliliters of swelling gases during their service. This gas volume is not adequate for the effective purge of the sample-load flow path in the gas sampling valve of conventional GCs, and so the quantitation accuracy is impacted. For these types of samples, the 990 Micro GC, equipped with a manual injection accessory, can be a good choice because of its sensitive µ-TCD detection and compact design, requiring only 5 to 10 mL of sample for effective sample flow path purging.

Experimental

A 990 Micro GC was configured with three channels for LIBs swelling gas analysis. The gas sample was injected through the Micro GC manual injection accessory, which was installed on the left side of the 990 system via a specially designed bracket. The bulged part of the Li-ion battery was perforated by a 10 mL gas-tight syringe and the gases were drawn into the barrel. The gases were then injected into the Micro GC injector at a constant dispensing speed of 10 to 20 mL/min via the manual injection port.

A 10 m backflush CP-Molsieve 5Å channel was used for hydrogen, methane, and carbon monoxide analysis. The 10 m backflush CP-PoraPLOT U channel was for C_2 hydrocarbons and CO_2 analysis. The 10 m backflush to detector CP-Al_2O_3/KCl channel was for analysis of the individual C_3 to C_5 hydrocarbons and combined C_6/C_{6+} compounds. For detailed hydrocarbons profile analysis, a 6 m CP-Sil 5 CB channel was used. The analytical parameters are shown in Table 1.

The calibration sample was purchased from Air liquid Inc. Its composition is shown in Table 2. A gas bag was filled with calibration standard to use the same sample introduction for both samples as well as for the calibration gas. A lithium-ion battery containing swelling gas was provided by a local brand vendor. The size of the battery was 6 cm (W) × 8 cm (L) × 0.6 cm (H).

Table 1. Channel configuration and analytical parameters of the Agilent 990 Micro GC.

Agilent 990 Micro GC Analytical Parameters					
Channel No.	Channel Type	Column Temperature (°C)	Column Pressure (KPa)	BF Time (s)	Carrier Gas
1	10 m, CP-Molsieve 5Å, BF	90	150	5.2	He
2	10 m, CP-PoraPLOT U, BF	90	150	8	He
3	10 m, CP-Al_2O_3 / KCL, BF2D	100	300	4.5	He
4	6 m, CP-Sil 5 CB, str	100	150	NA	He

Table 2. Calibration gas composition.

Compound No.	Compound Name	Concentration (mol/mol)
1	Hydrogen	12.9%
2	Nitrogen	63.5%
3	Methane	5.06%
4	Carbon monoxide	1.01%
5	Carbon dioxide	3.01%
6	Ethane	4.06%
7	Ethylene	2.02%
8	Acetylene	1.04%
9	Propane	2.01%
10	Isobutane	0.495%
11	n-Butane	0.504%
12	Isopentane	0.101%
13	n-Pentane	0.102%
14	n-Hexane	0.0502%

Results and discussion

Figures 1A, 1B, and 1C show chromatograms of the calibration standard on three analytical channels. H_2, CO, and CH_4 were resolved on the CP-Molsieve 5Å channel. Helium was used as carrier gas because hydrogen concentration in the calibration standard and real sample were at the percent level. If a more sensitive detection is needed for low concentration H_2, argon can be used as the carrier gas. CO_2, ethylene, ethane, and acetylene were analyzed on the CP-PoraPlot U channel. The C_3 to C_5 components were separated on the aluminum oxide channel. The hydrocarbons heavier than *n*-hexane were backflushed and eluted as a combined peak on the CP-Al_2O_3/KCl channel. All three channels were of the backflush type.

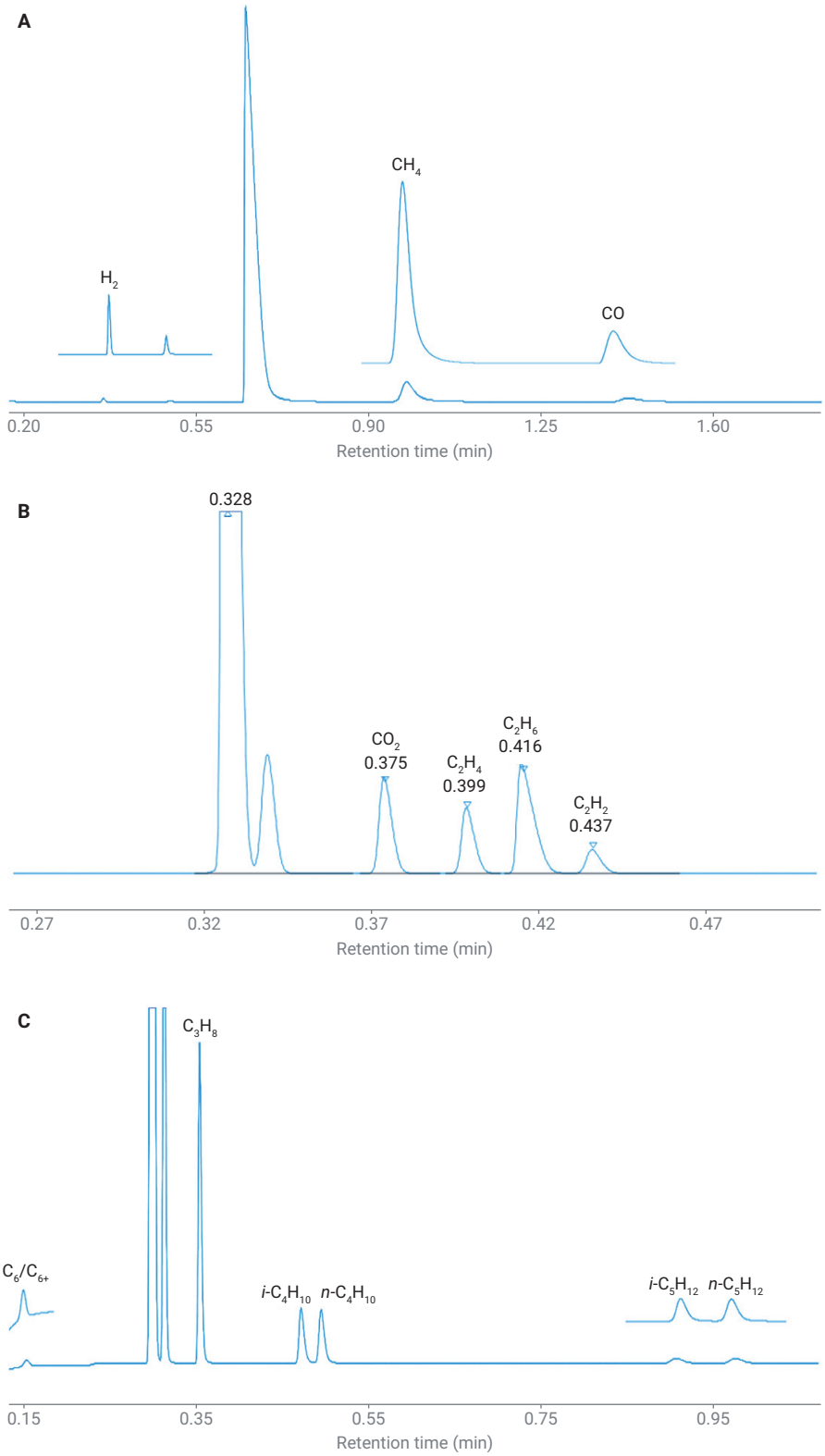

Figure 1. Calibration standard on the Agilent CP-Molsieve 5Å, CP-PoraPLOT U, and CP-Al_2O_3/KCl analytical channels.

The analysis repeatability of manual injection was evaluated by 10 consecutive syringe injections of calibration standard. The area and retention time (RT) repeatability are shown in Table 3. The area response of each target component in the first injection was similar to the responses achieved in subsequent injections, which meant that the 10 mL sample could effectively purge the internal volume from the syringe injection port to the outlet of sample loop on channel injectors in each run.

A real swelling gas sample from a Li-ion battery of a local brand was analyzed. A 10 mL amount of swelling gas was drawn from the gassing chamber and injected. The identified peaks were marked in the chromatograms (Figures 2A, 2B, and 2C). Some unknown peaks could be observed eluting after propane on the CP-Al_2O_3/KCl channel. These peaks could not be identified because of the lack of calibration standards. All identified components were quantitated according to Equation 1 using their response factors calculated from the calibration standard. The bundled peak of C_6/C_{6+} was quantitated by the response factor of *n*-hexane. The measured concentration of the identified components are shown in Table 3.

$$V_{ri} = A_{ri}/F_i \qquad \textbf{Equation 1.}$$

$$F_i = V_i/A_i$$

V_{ri} Calculated volume concentration of component i in the real sample (mol/mol)

A_{ri} Area response of component i in the real sample

F_i Response factor of component i in the calibration sample

V_i Nominal volume concentration of component i in the calibration sample (mol/mol)

A_i Area response of component i in the calibration sample

Table 3. Area and RT repeatability of 10 syringe injections of calibration standard.

Compound	RT (min)	RT RSD%	Area (mv*s)	Area RSD%	Concentration of Compounds Identified in Swelling Gas (mol/mol)
H_2	0.356	0.009	0.57	2.68	12.86%
CH_4	0.978	0.007	19.29	0.12	46.47%
CO	1.434	0.008	4.55	0.25	1.65%
CO_2	0.375	0.02	20.37	0.37	2.94%
C_2H_4	0.4	0.015	14.02	0.37	0.31%
C_2H_6	0.414	0.012	29.94	0.33	6.74%
C_2H_2	0.437	0.011	5.93	0.37	2.35%
C_3H_8	0.354	0.009	8.23	0.36	0.086%
i-C_4	0.471	0.013	2.34	0.39	NA
n-C_4	0.494	0.013	2.51	0.48	NA
i-C_5	0.901	0.023	0.53	1.58	NA
n-C_5	0.969	0.024	0.56	2.43	NA
C_6/C_{6+}	0.156	0.017	0.33	0.70	1.79%

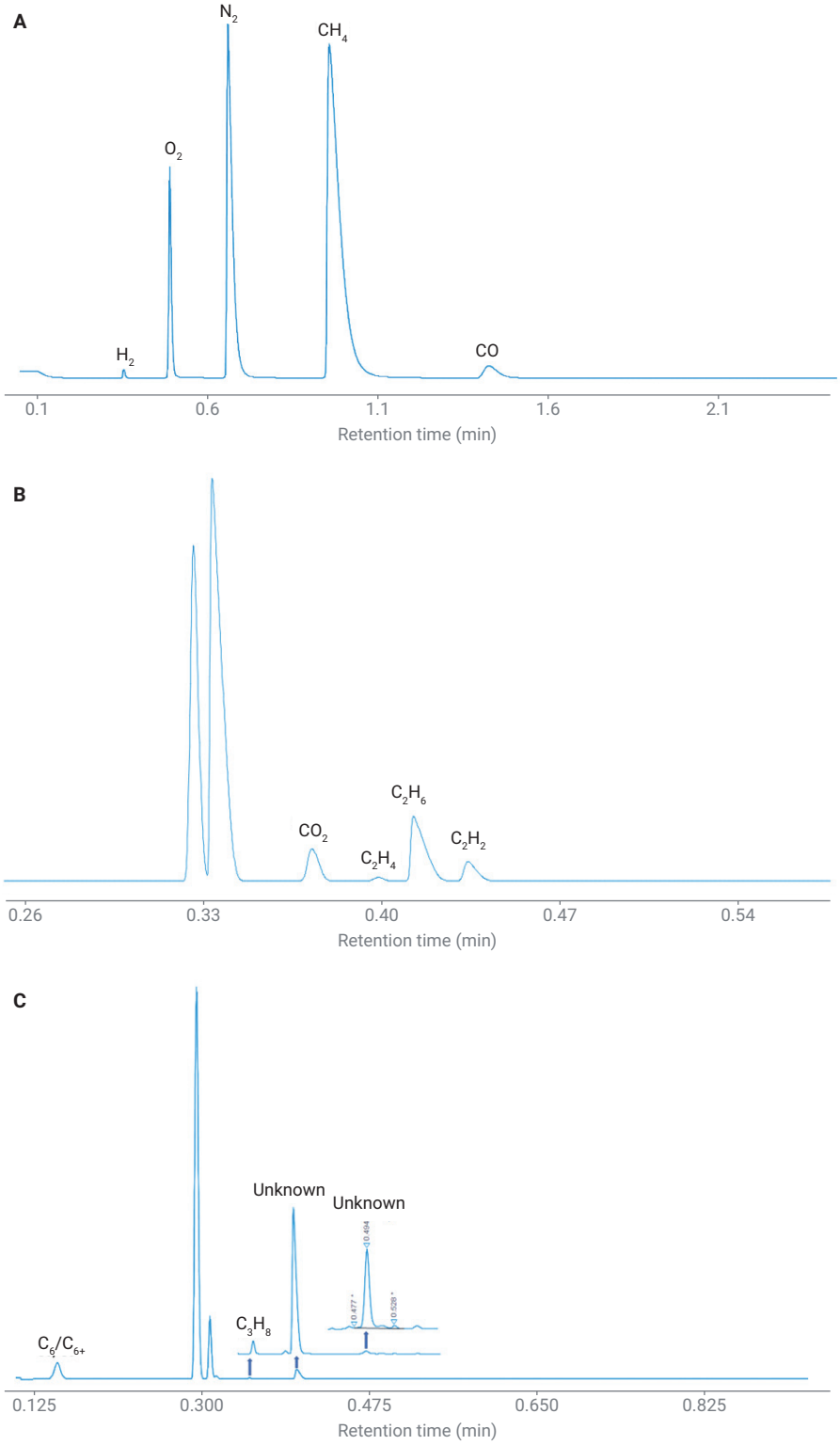

Figure 2. Chromatograms of swelling gas on the analytical channels.

In this work, the heavy hydrocarbons (≥*n*-hexane) were analyzed as a combined C_6/C_{6+} peak. Sometimes, the fingerprint information of the heavy hydrocarbons is needed. To meet such an analysis requirement, a 6 m CP-Sil 5 CB straight channel is recommended for separation. As shown in Figure 3, the hydrocarbons from propane to *n*-hexane in the calibration standard can be resolved on the CP-Sil 5 CB column. Our previous work showed *n*-octane eluted before 150 seconds on this type of channel.[1,2] This channel can give the separation of heavier hydrocarbons up to *n*-nonane. The chromatogram of the real swelling gas on the CP-Sil 5 CB channel is shown in Figure 4. In this figure, propane was marked as 5cb-C3 at 0.225 minutes. There were four peaks eluting between the time window of *n*-butane (0.268 minutes) and *n*-hexane (0.501 minutes). Three components eluted after *n*-C_6 (0.501 minutes). The good resolution on the 6 m CP-Sil 5 CB channel made the identification of unknown peaks easy if calibration standards were available.

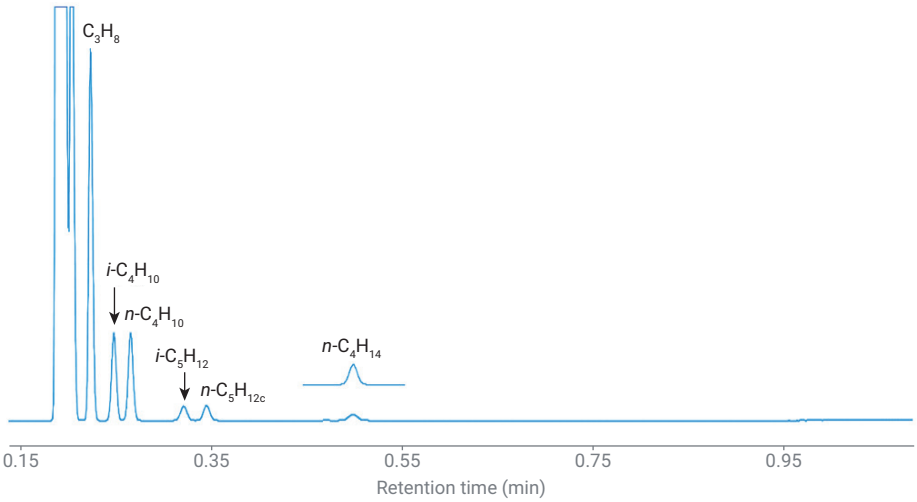

Figure 3. Chromatogram of C_3 to C_6 on the 6 m Agilent CP-Sil 5 CB channel.

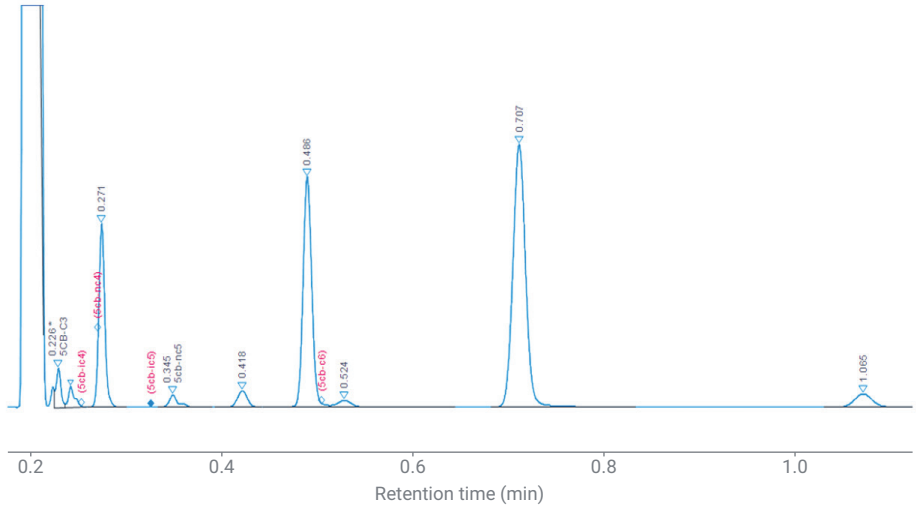

Figure 4. Chromatogram of swelling gas sample on the 6 m Agilent CP-Sil 5 CB channel.

Conclusion

In this work, a 990 Micro GC configured with a manual injection accessory and three analytical channels was used for analysis of low-volume swelling gas in lithium-ion batteries. The syringe injection was a good and reliable way of sampling low-volume gas samples. Permanent gases were analyzed on a CP-Molsieve 5Å channel, and CO_2 and C_2 hydrocarbons were separated on a CP-PoraPLOT U channel. The C_3 to C_5 hydrocarbons were analyzed on a BF2D Al_2O_3 channel with combined information on C_6/C_{6+} achieved simultaneously. A straight CP-Sil 5 CB channel can replace an aluminum oxide channel for detailed hydrocarbons profile analysis if needed. The cycle time of a single run was less than 150 seconds. The area repeatability was good, with response RSD% ranging from 0.1 to 3%. The test results show that the Agilent 990 Micro GC is a good choice for fast, low-volume, fuel-cell gas analysis.

References

1. Van Loon, R.; Amarasinghe, S.; Ahmed, K. Fuel Cell Development and Testing Using an Agilent Micro GC. *Agilent Technologies application note*, publication number 5991-3364EN, **2011**.
2. Fast Analysis of Natural Gas Using the Agilent 990 Micro GC Natural Gas Analyzer. *Agilent Technologies application note*, publication number 5994-1040EN, **2019**.

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