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Application News

Residual NMP and Solvent Analysis in Lithium-ion Battery Cathode

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User Benefits

- Analyze residual NMP and similar solvent structures in the cathode of lithium-ion batteries.
- Optimize drying conditions in the cathode manufacturing process and quantify the amount of residual solvents for quality control.
- Minimize equipment footprint by combining Brevis GC-2050 and GCMS-QP2050.

■ Introduction

Lithium-ion batteries (LiB) consist of cathode and anode, electrolyte, separator, etc. The electrodes are formed by coating a slurry of active material, conductive additives, binders, etc., mixed in an organic solvent, on a metal film (current collector) and then dried. N-Methyl-2-pyrrolidone (NMP) is known as an organic solvent used in solvent-based slurries, and especially for quality control of the cathode, the residual amount of NMP in the cathode is examined during the drying process.

In this application, a simple analysis method for residual NMP in the cathode of lithium-ion battery NCM (nickel-cobalt-manganese ternary material) using GC-FID with headspace method is introduced. In addition, results of qualitative analysis of other solvents remaining in the NCM cathode using GC-MS and comparison of residual solvent amounts in five different cathodes with different drying processes are also presented.

■ Residual NMP analysis in cathode

Figure 1 shows the new compact model GC, the Brevis GC-2050, used for this measurement. Table 1 shows the Instrument configuration and analysis conditions used in this measurement. The analysis column used was a 624 column, which is a medium-polarity column of the cyano-propyl-phenyl type designed to separate polar solvents like NMP and its similar components.

Fig. 1 Compact model GC Brevis™ GC-2050 (Left), and Headspace sampler HS-20NX (Right)

The headspace method maintains a vial containing the sample at a constant temperature to measure the gas in the vapor phase or gas-solid equilibrium state. Even for samples containing solid samples or compounds with low volatility, GC measurements can be performed simply by sealing a certain amount of sample in a vial.

By setting the headspace vial at relatively high temperature, the experiment examined the amount of NMP in the NCM cathode under the assumption that most of the remaining NMP in the cathode is in the vapor phase inside the vial.

Table 1 Analysis of NMP in the cathode
Instrument configuration and analysis conditions

GC		
Model	:	Brevis GC-2050
Detector	:	FID (Flame Ionization Detector)
Column	:	SH-I-624Sil MS (0.32 mm I.D.×30m, d.f.= 1.8 µm) P/N：227-36077-01
Column Temp.	:	100˚C – 5˚C /min – 180˚C (3 min)
Injection Mode	:	Split 20
Carrier Gas	:	Linear velocity 30 cm/sec (He)
Detector Temp.	:	250˚C
FID H_2 Flow Rate	:	32 mL/min
FID Make up Flow Rate	:	24 mL/min (N_2)
FID Air Flow Rate	:	200 mL/min
HS		
Model	:	HS-20 NX USTL (Ultra Short Transfer Line)
Oven Temp.	:	180˚C
Sample Line Temp.	:	200˚C
Transfer Line Temp.	:	200˚C
Vial Equilibrating Time	:	30 min
Vial Pressurizing Time	:	1.0 min
Vial Pressure	:	65 kPa (N_2)
Loading Time	:	0.5 min
Load Equilib. time	:	0.1 min
Needle Flush Time	:	1.0 min

■ Sample preparation and Result

Prepared NMP acetone solutions of 10, 100, and 1000ppm as standard solutions, and injected 2 µL each into 20 mL headspace vials. Conducted measurements five times in a row, and the relative standard deviations and calibration curves obtained are shown in Table 2 and Figure 2. The density of NMP was calculated as 1.03 g/cm^3.

Table 2 Result of standard solution

STD ppm	NMP ng	Area (n=5)	Area RSD%
10	20.6	311	3.18
100	206	3485	1.19
1000	2060	38003	1.94

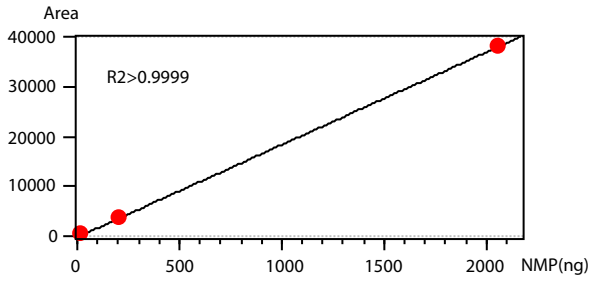


Fig. 2 Calibration curve of NMP

Following this, the cathode sheet was cut into 10 mm squares, with the electrode surface facing upwards for easier solvent evaporation, and sealed in 20 mL headspace vials. The obtained chromatograms and an expanded view of the NMP elution position are shown in Figure 3. It was found that trace amounts of residual NMP were detected.

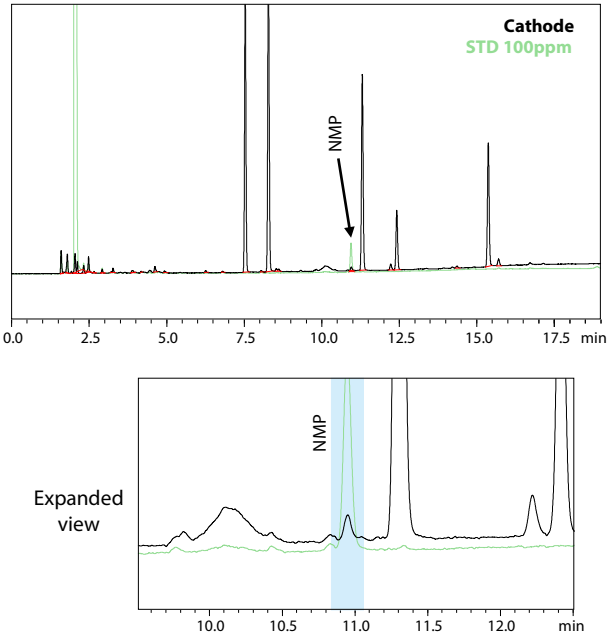


Fig. 3 Chromatogram of cathode
and enlarged view of NMP elution position

Considering the differences in residual amounts depending on the cutting location, three cut samples were measured, and using the calibration curve shown in Figure 2 for quantification, the NMP detected from the cathode was found to be an average of 33.5 ng. Comparing this to the mass of the sealed cathode, a residual amount of 2.76 ppm (w/w) was calculated (Table 3).

Table 3 Quantification of residual NMP

No.	Cathode sheet mg	Detected NMP ng	Residual NMP ppm(w/w)
1	11.30	32.30	3.12
2	12.51	34.40	2.75
3	12.79	30.85	2.41
	Average	33.5	2.76

■ Residual solvent Analysis in cathode

When examining the chromatogram in Figure 3, it is evident that residual solvents other than NMP are present. In cases where unknown residual solvents or peaks detected vary by product, qualitative analysis of compounds by mass spectrometry is useful in quality control during the cathode manufacturing process. The compact model GCMS-QP2050 (Figure 4) is a user-friendly gas chromatograph mass spectrometer that is easy to maintain and can be retrofitted to existing GC systems. Table 4 shows the device configuration and analysis conditions used for qualitative analysis of residual solvents in NCM cathode. Here, we use the expandable Nexis™ GC-2030 in the front GC, but the qualitative results do not change depending on the GC model.

Similar to the analysis of NMP, the cathode sheet is cut into 10 mm squares, sealed in a 20 mL headspace vial, and the obtained TIC chromatogram is shown in Figure 6. Five main components (A to E) can be identified, and spectral searches using the NIST library revealed compounds similar to NMP as candidate compounds for each peak (Table 5).

Fig. 4 Gas chromatograph Nexis™ GC-2030
and Mass Spectrometer GCMS-QP2050
and Headspace sampler HS-20NX(Trap model)

Table 4 Analysis of residual solvent in the cathode
Instrument configuration and analysis conditions

GC		
Model	:	Nexis GC-2030
Column	:	SH-I-624Sil MS (0.32 mm I.D.×60m, d.f.= 1.8 µm) P/N：221-75963-60
Column Temp.	:	100˚C – 5˚C/min – 180˚C (15 min)
Injection Mode	:	Split 20
Carrier Gas	:	Linear velocity 40 cm/sec (He)
MS		
Model	:	GCMS-QP2050 (TMP exhaust: 255 L/sec)
Ion Source Temp.	:	200˚C
Interface Temp.	:	200˚C
Acquisition Mode	:	Scan
Event Time	:	0.3 sec
m/z Range	:	35 – 500
HS		
Model	:	HS-20 NX (Trap model)
Mode	:	Loop mode
Oven Temp.	:	180 ˚C
Sample Line Temp.	:	200 ˚C
Transfer Line Temp.	:	200 ˚C
Vial Equilibrating Time	:	30 min
Vial Pressurizing Time	:	1.0 min
Vial Pressure	:	65 kPa (N_2)
Loading Time	:	0.5 min
Load Equilib. time	:	0.1 min
Needle Flush Time	:	1.0 min

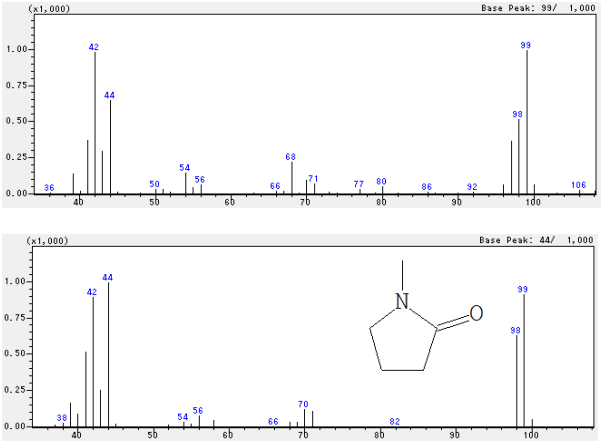


Fig. 5 MS spectrum at retention time 13.9 min (top)
and the MS spectrum of the hit NMP by library search (bottom)

Based on the MS chromatogram of m/z 99 zoomed in on Figure 6 and the MS spectrum in Figure 5, it is considered that NMP elutes around 13.9 minutes. The separation characteristics of the 624 column suggest that NMP and similar compounds to NMP are well separated.

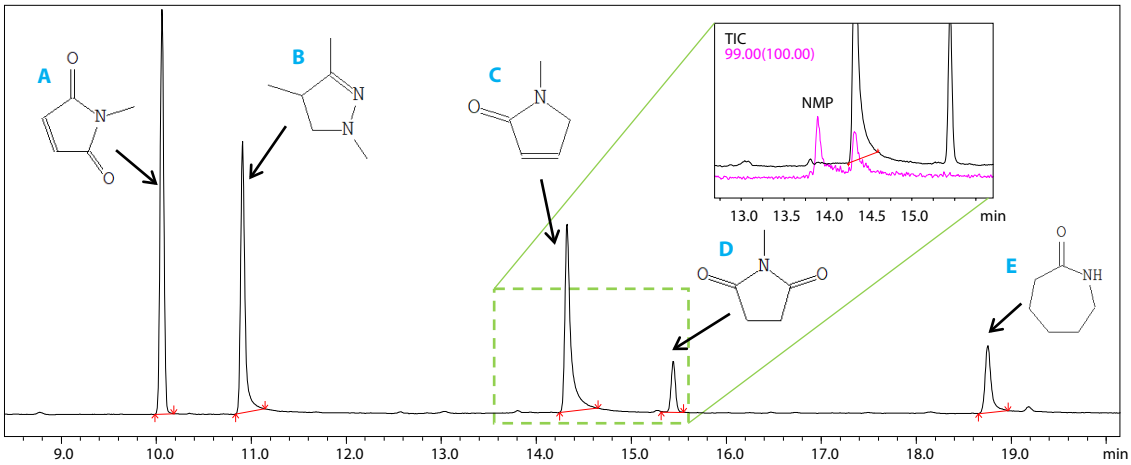
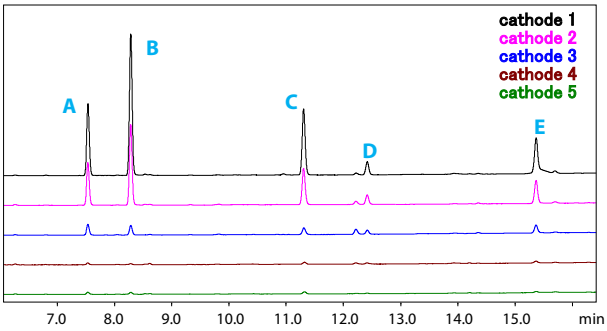


Fig. 6 TIC chromatogram in headspace-GC-MS, along with candidate compounds from library search for major peaks.
Top right: Expanded view of NMP elution position and the *m/z* 99 MS chromatogram.



Cathode No.	Drying process ˚C	Time min
1	80	10
2	80	30
3	80	60
4	120	30
5	80 + Vacuum(120)	30 + One night

Fig. 7 Comparison of chromatograms and drying conditions for five different NCM cathodes with different drying processes

■ Comparison of residual solvents with cathodes drying processes

Residual solvent levels were compared for five different NCM cathodes with varying drying processes using the instrument method in Table 1 with headspace GC-FID. The chromatogram comparisons obtained are shown in Figure 7, and the comparison of the area values of major organic solvents A to E is shown in Figure 8. It was confirmed that the amount of residual organic solvents remaining in the cathode varies depending on the drying conditions.

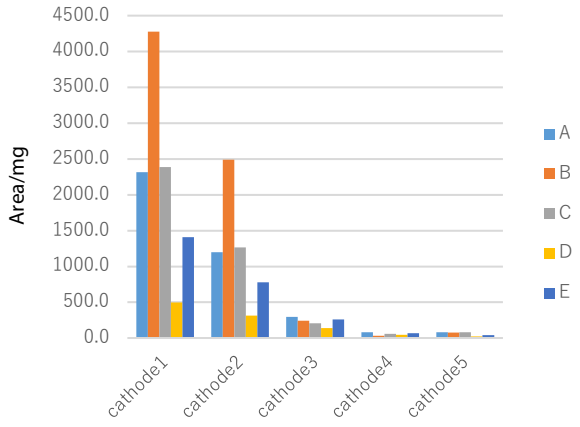


Fig.8 Comparison of residual solvent levels from five different NCM cathodes with different drying processes (n=3 average)

Table 5 Similarity search results

	Candidate compounds	CAS No.	similarity
A	N-Methylmaleimide	930 - 88 - 1	97
B	1,3,4-Trimethyl-2-pyrazoline	14044 - 41 - 8	84
C	3-Pyrrolin-2-one, 1-methyl-	13950 - 21 - 5	91
D	2,5-Pyrrolidinedione, 1-methyl-	1121 - 07 - 9	94
E	Caprolactam	105 - 60 - 2	80

■ Summary

By using headspace GC-FID, it is possible to easily analyze residual NMP in the cathode and quantify residual solvents without the need for preprocessing. Additionally, with headspace GC-MS, qualitative analysis of residual organic solvents can also be performed.

Using compact models such as Brevis GC-2050 or GCMS-QP2050 allows for minimization of experimental space and detailed analysis of solvent analysis for each drying process. This can be applied to quality control and research and development in the cathode manufacturing process.

<Acknowledgment>
We would like to express our sincere gratitude to Dainen material Co., Ltd. for their significant cooperation in providing cathodes and analyzing experimental results for the development of this application.

<Related Applications>

1. Analysis of battery electrolytes and N-methyl-2-pyrrolidone (NMP) via headspace GC-FID- Application News No.05-SCA-180-049-EN
2. Analysis of Carbonic Esters and Additives in Lithium Ion Battery Electrolytes- Application News No.01-00708-EN

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