Application Note

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Analysis of N-Methyl-2-Pyrrolidone (NMP) in Battery Electrodes

Using the Agilent 8860 GC with ultrasound-assisted extraction

Authors

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Abstract

This application note describes a robust, cost-effective, and efficient method for analyzing N-methyl-2-pyrrolidone (NMP) residue in electrodes while achieving reliable results with an error rate below 2.5%. The sample pretreatment involved the application of ultrasound-assisted extraction using 10 mL of ethanol as the extraction solvent for a duration of 15 minutes. Extraction efficiency was more than 90% for the samples before being calendered and 60% after being calendered. The samples were then analyzed using the Agilent 8860 GC system with a split/splitless injector and a flame ionization detector (FID) after being filtered by a 0.45 µm polytetrafluoroethylene (PTFE) filter. The elution of NMP occurred on an Agilent J&W DB-WAX column within approximately 8 minutes, resulting in a peak symmetry of approximately 1.07. The solution exhibited excellent linearity (R^2 = 0.9998) across a concentration range of 0.5 to 100 mg/L in the extracts. Intersample and intrasample repeatability of NMP were both less than 0.01% for retention time and 2.0% for peak area. The method's limit of detection (MDL) and limit of quantification (LOQ) were both below 0.10 and 0.30 µg/mL in the extracts. NMP was detected both in cathode and anode samples with high sensitivity and repeatability of less than 5.5%.

Introduction

Slurry casting is a widely used method in electrode fabrication, with steps including slurry mixture preparation, coating, drying, calendering, slitting, and vacuum drying.[1] A binder, active materials, and conductive additives are homogenized in a solvent to form the slurry. NMP is a commonly used solvent in cathode slurry preparation, thanks to its high flash point, low vapor pressure, excellent chemical and thermal stability, and great miscibility with the polymer binder polyvinylidene fluoride. In the drying stage, NMP is eliminated from the coating with a strictly controlled heating process to form a homogeneous microporous layer that ensures diffusion of lithium ions in the electrolyte.[2]

Electrode drying is a time-consuming and complex process including aggregation; film consolidation; film shrinkage; and pore emptying, segregation, and bonding.[2] During the pore-emptying stage, the remaining solvent is inclined to retreat into the smallest pores due to surface tension, which poses a challenge for solvent elimination, as less solvent is able to diffuse to the surface.[2,3] A mathematical model at the continuum level demonstrated that it typically takes approximately half of the drying time to eliminate the final 10% of solvent.[4] Because of its significantly higher boiling point (202 °C) and low vapor pressure, an NMP-based electrode necessitates a lengthier drying period compared to an aqueous electrode, thereby enhancing the probability of NMP persisting in the electrode. The presence of NMP can enhance the adhesion, flexibility, and electrochemical performance of the electrode coating. However, if there is an excessive amount of NMP residual (> 1.0%) in the cathode, it can negatively impact the discharge specific capacity, charge and discharge characteristics, cell cycle capacity, and charge transfer impedance of the cathode.[5,6] To improve the flexibility of the anode coating and prevent film cracking, certain manufacturers incorporate NMP into an aqueous slurry. However, the remaining NMP can lead to the degradation of the solid electrolyte interphase layer formed on the anode surface.[7] Also, the European Commission restricted NMP in April 2018 due to its hazardous properties.[8]

Therefore, accurate identification of NMP residue in cathode coatings is crucial, not just for verifying electrode performance but also for ensuring compliance during sales. This application note assesses NMP performance on an 8860 GC system equipped with an FID after extraction using ultrasound-assisted pretreatment, aiming to provide a user-friendly and cost-effective analytical solution.

Experimental

Chemicals, materials, and electrode samples

The NMP standard (> 99%) was sourced from an industry laboratory, while ethanol, methanol, ethyl acetate, dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) (HPLC grade) were procured from ANPEL Laboratory Technologies (Shanghai) Inc. Deionized water was obtained from the laboratory.

Additionally, 5 mL disposable syringes, 15 mL centrifuge tubes, and 0.45 µm PTFE hydrophilic syringe filters were purchased from ANPEL Laboratory Technologies (Shanghai) Inc.

Five electrode samples were collected. The sample blank matrix was prepared by heating the cathode at 120 °C for 24 hours.

Standards preparation

In this study, the term "spiked standard" refers to a standard that is spiked into a centrifuge tube for extraction, while "final concentration" denotes the standard concentration in the GC vial after extraction. The standards prepared for this study were as follows:

1. **Stocked standards**: NMP was prepared at a concentration of 100,000 mg/L in ethanol.
2. **Peak identification standards**: Based on published literature, DMF and DMSO are considered potential alternatives to NMP.[9–11] Therefore, the behavior (retention time and resolution compared to NMP) of these two compounds on the 8860 GC system was also evaluated in this study. Singles and mixtures of DMF, DMSO, and NMP at a concentration of 500 mg/L in ethanol were prepared by diluting from the stocked standards for retention time and peak shape determination.
3. **Spiked calibration standards**: These standards were prepared using 5 mL volumetric flasks, with concentrations of the standard series set at 500, 1,000, 5,000, 10,000, 20,000, 50,000, and 100,000 mg/L in ethanol.
4. **MDL standard**: A 500 mg/L spiked standard mixture was used for the MDL and LOQ test. A 10 µL aliquot of the spiked standard was pretreated and analyzed for MDL calculation, resulting in a final concentration of 0.5 mg/L in the GC vial.

Sample preparation

Samples, cut from the electrode sheet to dimensions of approximately 0.5 × 2.0 cm and weighed to approximately 0.8 g (the sample weight may vary depending on the amount of sample collected for testing), were placed at the bottom of a 15 mL centrifuge tube. Subsequently, 10 mL of ethanol was added to the tube, and the contents were vigorously shaken to eliminate any bubbles between the solvent and the sample surface. An ultrasound extraction was then carried out for 15 minutes in a Kunshan Shumei ultrasonic bath (KQ2200E). Approximately 3 mL of the extract was drawn using a 5 mL syringe, and roughly 1 mL of the extract was filtered into a GC vial using a 0.45 µm PTFE hydrophilic syringe filter. Alternatively, particles can be removed from the extracts using a centrifuge.

Instrumentation and analytical conditions

The method was developed on an 8860 GC system with an FID. Both standards and samples were injected using an Agilent 7650A automatic liquid sampler. For more details on the GC conditions and method parameters, please see Table 1. Data acquisition and processing were performed using Agilent OpenLab CDS, version 2.6.

Table 1. Analytical conditions for the Agilent 8860 GC system.

Agilent 8860 GC System Parameters	
Parameter	**Value**
Automatic Liquid Sampler	Agilent 7650A
Injection Volume	1.0 µL
Inlet Type	Split/splitless injector
Inlet Temperature	250 °C
Liner	Agilent Ultra Inert, ID 4.0 mm, split with glass wool (p/n 5190-2295)
Carrier Gas	N_2
Split Ratio	20:1
GC Column	Agilent J&W DB-WAX, 30 m × 0.25 mm, 0.25 µm (p/n 122-7032UI)
Column Flow	Constant flow, 2.0 mL/min
Oven Program	60 °C for 2 min, ramp to 250 °C at 20 °C/min, hold 3 min
FID Temperature	250 °C
FID Air Flow	400 mL/min
FID Fuel Flow	30 mL/min
FID Make Up Flow	30 mL/min
Data Rate	5 Hz

Results and discussion

Extraction agent selection

As an extraction agent, the solvent should possess a high capability to extract NMP from the sample, be cost-effective, and pose minimal risk to operators and the environment. In this application, four polar solvents (water, methanol, ethanol, and ethyl acetate) were chosen to assess their ability to extract NMP from the samples. Three samples were prepared and analyzed in parallel for each solvent, and the NMP response (peak area against sample weight) is depicted in Figure 1.

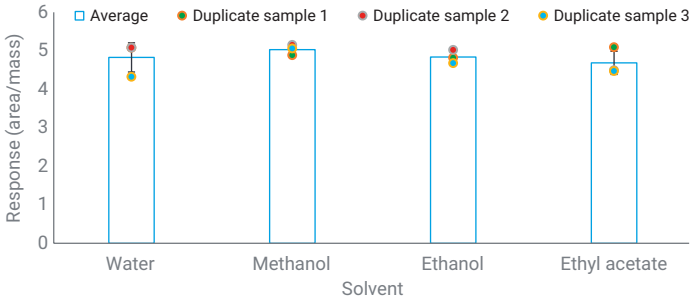

Figure 1. Solvent capability to extract NMP from cathode samples.

The results show slight variations in NMP response among the four solvents. Water and ethanol emerge as preferred options, considering low cost and low toxicity. However, water's larger vapor volume compared to ethanol necessitates injecting a smaller volume for analysis, which may result in low response for some samples. Additionally, water's high surface tension may lead to the formation of a liquid film at the neck of the GC vial, and water vapor can easily condense in the upper part of the vial. Therefore, ethanol was chosen as the extracting agent for this application.

NMP behavior in GC chromatogram

As DMF and DMSO were suggested as possible NMP substitutes in some publications, these two compounds were also considered in this study to assess their behavior on the GC chromatogram. A standard mixture with a concentration of 500 mg/L in ethanol was analyzed using nitrogen as the carrier gas (see Figure 2). All compounds could elute from the GC column within 10 minutes and achieved baseline separation with narrow peak width (w_h = 0.021 to 0.022) and peak symmetry (1.01 to 1.07).

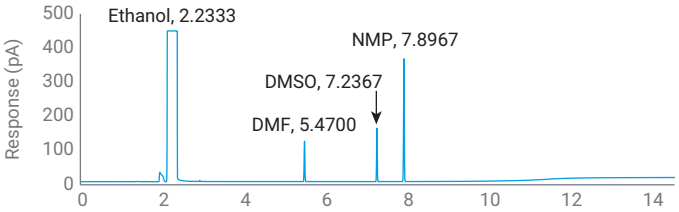

Figure 2. Chromatogram of NMP, DMF, and DMSP analyzed with an Agilent 8860 GC.

Sample extraction efficiency

The accurate determination of NMP requires a high extraction efficiency from the sample. Two types of cathode samples were obtained (Figure 3): one uncalendered (Figure 3A) after the solvent recovery step, and the other calendered (Figure 3B). The uncalendered cathode exhibits a loose coating that is prone to peeling off compared to the calendered cathode.

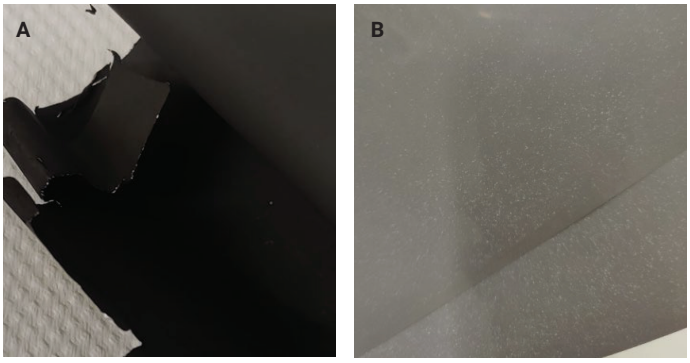

Figure 3. Cathode samples; (A) uncalendered, (B) calendered.

The test procedure is as follows: approximately 0.8 g of each sample was weighed and pretreated following the steps detailed in the "Sample preparation" section. The solvent was refreshed every 10 minutes, and the filtered extract was then transferred to a GC vial. Subsequently, the coating was scraped off from the cathode after six cycles, repositioned in the centrifuge, and vortexed for an additional 30 minutes to continue the extraction process. The extract efficiency results from the two cathode samples are presented in Figure 4.

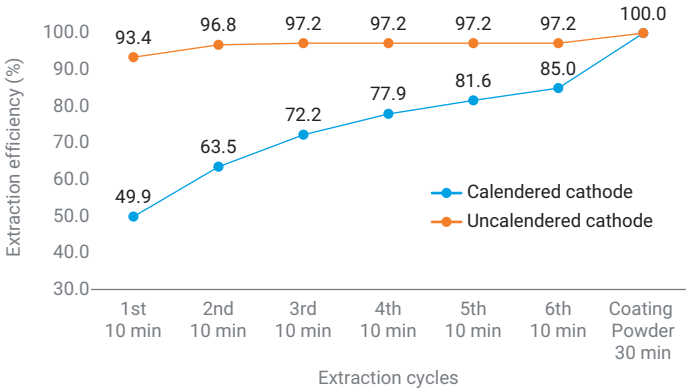

Figure 4. Extraction efficiency of ethanol to NMP from uncalendered and calendered cathode samples.

The findings reveal that over 90% of NMP could be extracted from the uncalendered samples within 10 minutes. In this study, the extraction time was prolonged to 15 minutes, considering both extraction efficiency and the daily workload demands. Conversely, even with an extended extraction time of one hour for the calendered samples, the extraction efficiency remained significantly lower. For such samples, pressurized fluid extraction may be a more suitable option.

Calibration curve and linearity

The calibration curve was established by spiking standards onto a blank electrode matrix, posing a challenge in finding a suitable blank electrode. While the anode may appear to be a logical choice due to water being the solvent in the anode slurry preparation, research indicates that small amounts of NMP may be introduced into the slurry to enhance the adhesion and flexibility of the anode coating.[5,6] In addition, the microstructure of the anode coating is distinct compared to that of the cathode, and careful consideration is essential when selecting the anode as a blank matrix.

This study investigated the NMP residues in uncalendered cathode and anode samples after baking at 120 °C for 4, 6, and 24 hours. The findings (Table 2) indicated that even after 24 hours of baking, the NMP peak remained detectable with a signal-to-noise ratio (S/N) of 17. However, the NMP peak of the cathode on the chromatogram was sufficiently small, with an S/N of less than 3. Therefore, the uncalendered cathode baked for 24 hours was chosen as the blank matrix for establishing the calibration curve in this study.

Table 2. NMP residue and S/N of samples after baking at 120 °C for different durations.

Baking Duration (hours)	Cathode		Anode	
	Peak Area	S/N	Peak Area	S/N
4	0.16	12.48	0.74	51.63
6	0.09	5.433	0.42	26.50
24	0.04	2.524	0.32	17.17

The calibration curve was established by spiking 10 µL of the spiked calibration standards onto the 0.80 g sample blank matrix in a 15 mL centrifuge tube, followed by pretreatment as part of the sample preparation process. The final concentrations of the calibration standards in GC vials were 0.5, 1.0, 5.0, 10, 20, 50, and 100 mg/L. The calibration curve was constructed based on the response of NMP to the final concentration of the relevant standards. The calibration curves for NMP, ranging from 0.5 to 20 mg/L and 0.5 to 100 mg/L, are shown in Figure 5. NMP demonstrated strong positive linear correlations between peak area and concentration, with correlation coefficients (R^2) of 0.9998 and 0.9999 for concentrations ranging from 0.5 to 100 mg/L and 0.5 to 20 mg/L, respectively. It is highly recommended to choose an appropriate calibration curve based on the characteristics of the actual sample, as discussed in the "Repeatability and accuracy" section.

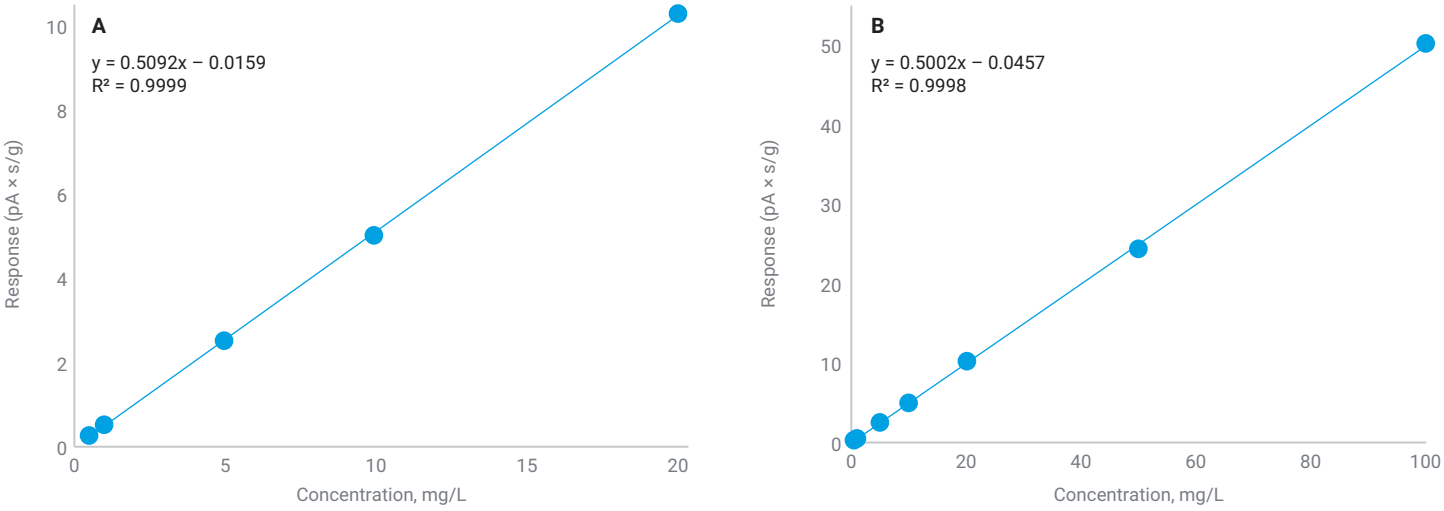

Figure 5. Calibration curves of NMP in ethanol with concentrations ranging from 0.5 to 20 mg/L (A) and 0.5 to 100 mg/L (B).

A series of standards with concentrations of 0.5, 1.0, 5.0, 10, 20, 50, and 100 mg/L were prepared and directly injected to investigate the recovery of sample pretreatment. The peak area ratio of spiked standards after pretreatment compared to that of direct injection ranged from 96 to 106% (Table 3), indicating that the matrix bias introduced by blank samples could be disregarded when establishing the calibration curve.

Table 3. The recovery of sample pretreatment.

Concentration (mg/L)	Area of Standards Injected Directly	Area of Spiked Standards After Pretreatment	Area Ratio of Spiked/Direct Injection (%)
0.5	0.2634	0.268529	101.9
1.0	0.5084	0.488557	96.1
5.0	2.5076	2.509573	100.1
10.0	4.8618	4.967535	102.2
20.0	9.654	10.21553	105.8
50.0	24.4818	24.35551	99.5
100.0	48.6216	50.20945	103.3

Repeatability and accuracy

Spiked standard mixtures with concentrations of 500, 1,000, 10,000, and 50,000 mg/L (final concentrations is 0.5, 1.0, 10, and 50 mg/L) were used to evaluate the method repeatability at low, medium, and high concentrations, respectively. Six parallel samples were prepared for each concentration level, with five injections performed in parallel for each sample. The results are presented in Table 4, showing repeatability percentages of less than 2.0% for all injections.

Table 4. Repeatability verification of the method for NMP across various concentrations.

Repeatability	0.5 mg/L (%)	1.0 mg/L (%)	10 mg/L (%)	50 mg/L(%)
Parallel 1	1.65	0.85	0.36	0.60
Parallel 2	1.64	0.85	0.36	0.60
Parallel 3	1.23	1.11	0.68	0.21
Parallel 4	1.43	0.88	0.84	0.25
Parallel 5	0.45	0.58	0.00	0.11
Parallel 6	1.90	1.09	0.51	0.32
RSD of Samples in Parallel	1.80	1.39	0.77	0.74

A set of samples with final concentrations of 0.5, 1.0, 2.5, 8.0, 10, 50, and 60 mg/L in the GC vial, following standard sample pretreatment, were individually prepared along with calibration standards for testing method accuracy. The measured concentrations were then calculated using different methods to evaluate the error introduced by varying calibration curves. In the first method, all concentrations were determined using a calibration curve covering the range from 0.5 to 100 mg/L. Conversely, the second method involved using distinct calibration curves for different samples: concentrations below 20 mg/L were calculated using a curve ranging from 0.5 to 20 mg/L, while concentrations of 50 and 60 mg/L were determined using a curve spanning 0.5 to 100 mg/L. The results (Figure 6) revealed a significant improvement in accuracy when employing the second method, reducing the error from approximately 13% to less than 3%. Therefore, having a calibration curve with a suitable concentration range is crucial for enhancing accuracy when analyzing real samples.

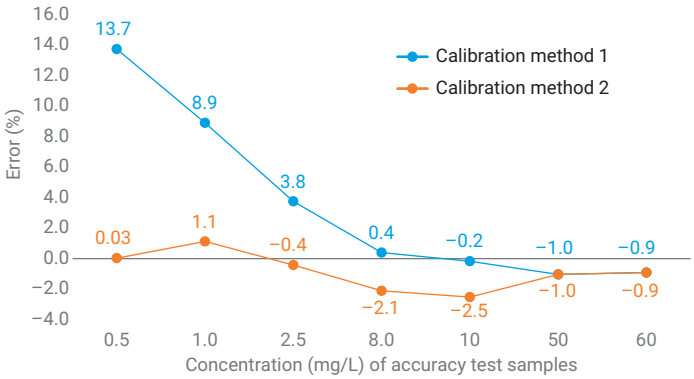

Figure 6. Accuracy of NMP calculated with different calibration curves.

MDL and LOQ

In this research, the MDL and LOQ were established using S/Ns of 3:1 and 10:1, respectively. Five parallel standard mixtures with a final concentration of 0.5 mg/L were prepared, and each mixture underwent five parallel injections to determine the S/N. The average S/N, MDL, and LOQ for NMP were computed and are detailed in Table 5. The MDL and LOQ were determined to be below 0.10 and 0.30 mg/L, respectively.

Table 5. MDL (mg/L) and LOQ (mg/L) of NMP with a final concentration of 0.5 mg/L.

MDL and LOQ (mg/L)	S/N	MDL (S/N = 3)	LOQ (S/N = 10)
Parallel 1	17.73	0.085	0.282
Parallel 2	17.06	0.088	0.293
Parallel 3	18.01	0.083	0.278
Parallel 4	17.53	0.086	0.285
Parallel 5	18.43	0.081	0.271
Average	17.75	0.085	0.282

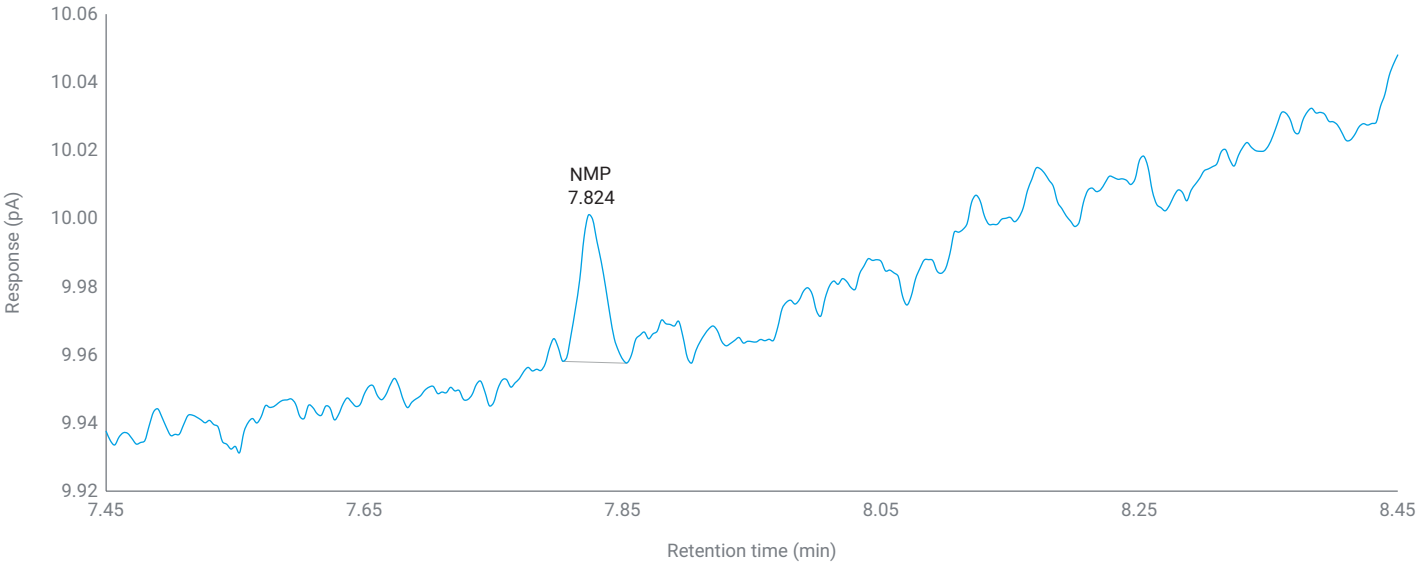

Figure 7. Performance of NMP with a concentration of 0.10 mg/L on the chromatogram.

Analysis of electrode samples

Five samples were collected comprising two uncalendered cathode samples, two uncalendered anode samples, and one calendered cathode sample. All samples underwent pretreatment as outlined in the "Experimental" section, with three parallel samples processed, except for the calendered cathode sample and one uncalendered anode sample due to limited sample availability. Repeatability in the real sample analysis was assessed by replicating three injections. The chromatograms of one uncalendered cathode and one anode sample are depicted in Figure 8, showing clear detection of NMP with well-defined peak shapes, resolutions, and baselines.

The analysis results are summarized in Table 6, revealing the presence of NMP not only in cathode samples but also in anode samples. Moreover, the NMP concentrations varied significantly among the different samples, possibly influenced by manufacturing techniques and coating thickness. It is important to note that the calendered cathode sample was only extracted for 15 minutes, which may not accurately reflect its true concentration.

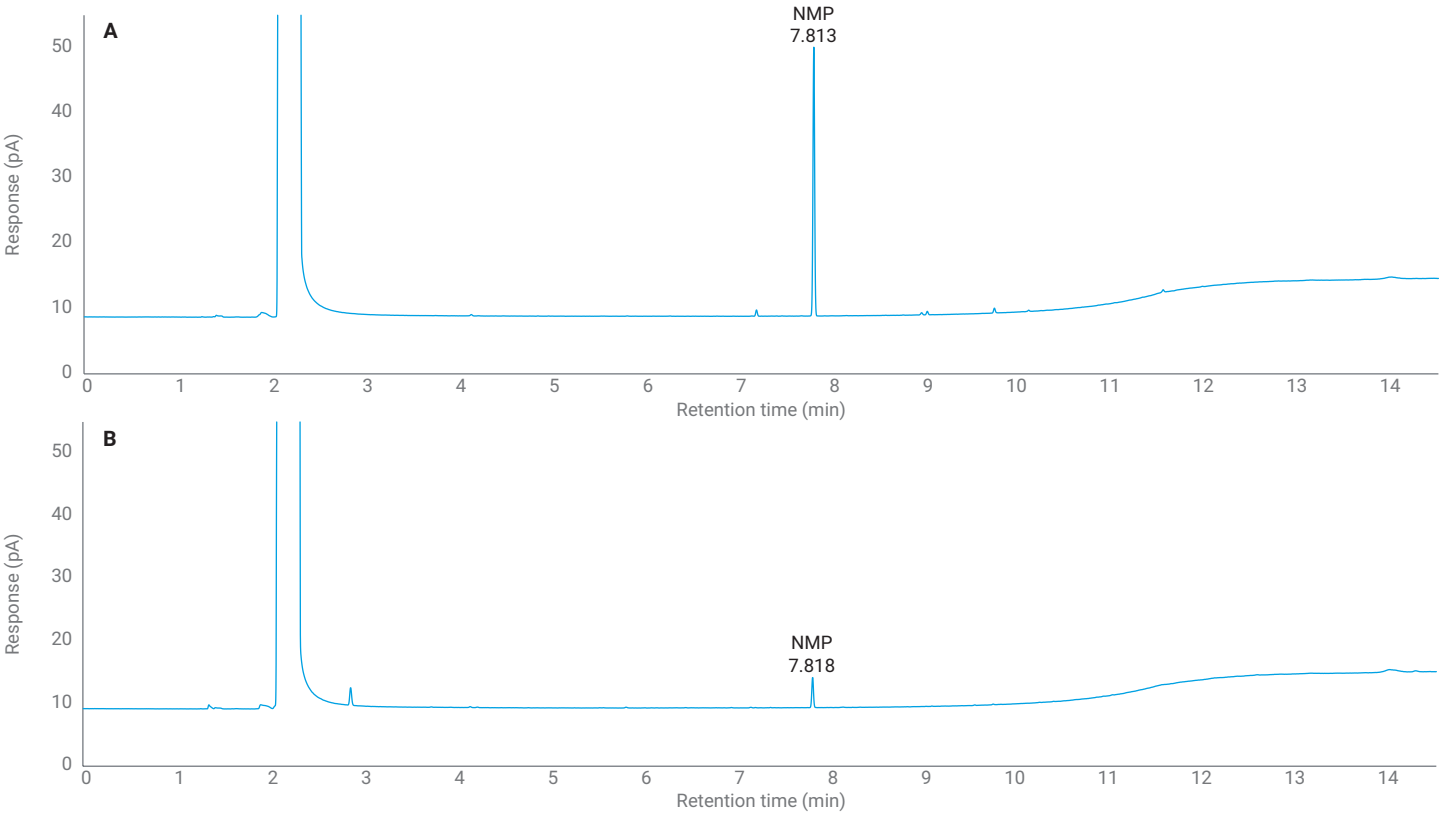

Figure 8. Chromatograms of NMP in real samples: (A) cathode (uncalendered 2), (B) anode (uncalendered 1).

Table 6. Test results of seven electrolyte samples.

NMP in Sample (µg/g)	Cathode			Anode	
	Uncalendered 1	Uncalendered 2	Calendered 3*	Uncalendered 1	Uncalendered 2*
Parallel 1	138.8	1,145	36.56	164.2	81.41
Parallel 2	134.6	1,147	37.15	151.6	86.60
Parallel 3	135.4	1,170	–	149.9	–
Average	136.3	1,154	36.85	155.2	84.00
RSD	1.62%	1.20%	–	5.03%	–

* Sample was not large enough for three parallel tests.

Conclusion

This application note outlines the establishment of a method for analyzing NMP in cathode and anode samples using the Agilent 8860 GC system with a split/splitless injector and FID. NMP exhibited well-defined peak shapes and effective separation on the chromatogram across various real samples. The method exhibited exceptional repeatability, linearity, and a low MDL, making it well suited to the routine analysis of NMP in the battery industry.

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