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

An analysis approach using the Agilent 8697 headspace sampler with the Agilent 8860 GC system and flame ionization detector

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Abstract

Accurately measuring N-methyl-2-pyrrolidone (NMP) residue is crucial for ensuring appropriate control of electrode quality in lithium-ion battery manufacturing. This necessitates the extraction of residual NMP from battery electrodes for subsequent gas chromatography (GC) analysis. Two common extraction approaches include liquid extraction (LE) of NMP from electrodes and heated extraction through a headspace sampler. This application note describes an NMP analysis method using headspace-based extraction and GC analysis with a flame ionization detector (FID). Residual NMP analysis was then conducted on real electrode samples to compare the results between headspace sampling (HS) and LE techniques.

Introduction

NMP is a solvent frequently used in the slurry formulation of lithium-ion battery cathodes.[1] Its primary function is to dissolve a polymer binder such as polyvinylidene fluoride, which binds the lithium ions and conductive additives. Once the slurry is applied to aluminum foils, the NMP should be eliminated by drying the coated current collector at a higher temperature. In some anode manufacturing processes, NMP is also added to minimize cracking issues during electrode baking. Monitoring residual NMP in both types of electrodes (primarily cathodes) is crucial to ensure that the residue levels are low enough to avoid affecting the battery's performance.[2]

Liquid extraction is one of the sample preparation methods for analyzing residual NMP in electrodes. Solvents such as ethyl acetate and ethanol are used for NMP extraction in the ultrasound-assisted extraction process. In this process, NMP and other active materials in the electrode are extracted into the solvent, and a subsequent filtration is necessary to remove graphite and other particles prior to injection for GC analysis. Compared with liquid extraction, heating the electrodes in a sealed vial under a temperature close to NMP's boiling point and analyzing the NMP that evaporates into the vial headspace is a less labor-intensive sample preparation approach. In recent years, the lithium-ion battery industry began to apply the HS technique to residual NMP analysis for electrodes due to its cleaner gas sample, lack of solvent usage, and more automated sample preparation.

This application note demonstrates an NMP extraction method using the Agilent 8697 headspace sampler. The performance of the 8697 headspace sampler, coupled with the Agilent 8860 GC system and an FID detector for residual NMP analysis, is assessed. The quantitation results obtained from the headspace and liquid extraction methods are also compared and application scenarios where the headspace approach would be most effective are described.

Experimental

Chemicals and electrode samples

The NMP standard (> 99%) was provided by an industry laboratory, while ethanol was procured from ANPEL Laboratory Technologies (Shanghai) Inc. De-ionized water was obtained from the laboratory. Four electrode samples were collected from different electrode suppliers.

Blank electrodes, calibration standard, and real sample preparation

Cathodes and anodes (0.5 g) were cut from the electrode foils and baked at 200 °C for at least three hours to get the blank electrodes. Among the four types of electrode samples, cathode type 2 was baked for seven hours to get a clean baseline in the NMP retention time (RT) window.

NMP calibration standards were prepared in water across eight concentration levels: 200, 500, 1,000, 2,000, 5,000, 10,000, 20,000, and 50,000 µg/mL. Calibration standards of different levels (10 µL) were spiked to blank electrodes for matrix-based linearity assessment. The blank anode samples and cathode type 1 were spiked from calibration level 1 to level 6 to check linearity. Cathode type 2 was spiked from calibration level 1 to level 8 to check dynamic range. The different calibration range was determined by the real residual NMP quantity in the corresponding electrodes. The 10 µL NMP calibration standards were spiked on 0.5 g blank electrodes. The corresponding NMP mass concentrations (µg/g) for each blank electrode are shown in Table 1.

Table 1. NMP mass spiked on blank electrodes and the corresponding NMP mass concentration.

Calibration Level Number	Liquid Standard Concentration Spiked on Electrode (µg/mL)	NMP Mass Spiked on 0.5 g Electrodes (µg)	NMP Mass Concentration on Blank Electrodes (µg/g)
1	200	2	4
2	500	5	10
3	1,000	10	20
4	2,000	20	40
5	5,000	50	100
6	10,000	100	200
7	20,000	200	400
8	50,000	500	1,000

For the precision assessment of NMP analysis, calibration standards of levels 1, 3, and 6 were spiked onto 0.5 g blank electrodes, with six replica samples analyzed for each concentration level. The 0.5 g blank electrodes must be cut into small pieces for easy placement into the headspace vial. The specific shape does not affect the analysis results.

The 0.5 g electrodes were cut from cathode and anode foils and sealed into 20 mL headspace vials for real sample analysis.

Instrumentation and consumables

The 8860 GC system, configured with a split/splitless inlet and FID, was applied for NMP analysis.

The instrument parameters and consumables used are shown in Table 2.

Table 2. Analytical conditions and consumables used for the Agilent 8697 headspace sampler and the Agilent 8860 GC system.

Agilent 8860 GC System	
Inlet Temperature	220 °C
Liner	Deactivated quartz liner, splitless, 2 mm id (part number 5181-8818)
Carrier Gas	N_2
Column Flow	Constant flow mode, 1.0 mL/min
Split Ratio	20:1
Oven Program	60 °C (2 minutes), 25 °C /min to 250 °C (3 minutes)
Column	Agilent J&W DB-WAX Ultra Inert column, 30 m × 0.25 mm, 0.25 μm (part number 122-7032UI)
FID	250 °C
Air	400 mL/min
H_2	30 mL/min
N_2	25 mL/min
Agilent 8697 XL Headspace Sampler	
Loop Size	1 mL
Vial Pressurization Gas	N_2
HS Oven Temperature	190 °C
HS Loop Temperature	190 °C
HS Transfer Line Temperature	190 °C
Vial Equilibration Time	20 min
Vials Size	20 mL, PTFE/silicone septa (part number 8010-0413)
Vial Shaking	Level 2, 25 shakes/min with acceleration of 90 cm/s^2
Vial Fill Mode	Default
Vial Fill Pressure	15 psi
Loop Fill Mode	Custom
Loop Ramp Rate	20 psi/min
Loop Final Pressure	10 psi
Loop Equilibration Time	0.1 min
Carrier Control Mode	GC carrier control
Vent After Extraction	On
Post Injection Purge	150 mL/min, 3 min

Results and discussion

Optimization of headspace vial incubation temperature and time

The optimization of incubation temperature and equilibration time was executed using the HS method development function. The method development function is integrated on the headspace method development page in Agilent OpenLab CDS. For temperature method development, the incubation time was set at 20 minutes and the HS oven temperature was initially set at 170 °C, then increased by increments of 10 °C until it reached a maximum of 210 °C. The response of the extracted NMP on anodes and cathodes was plotted against the incubation temperature, as illustrated in Figure 1. The final incubation temperature was selected at 190 °C to achieve high NMP response for both anodes and cathodes.
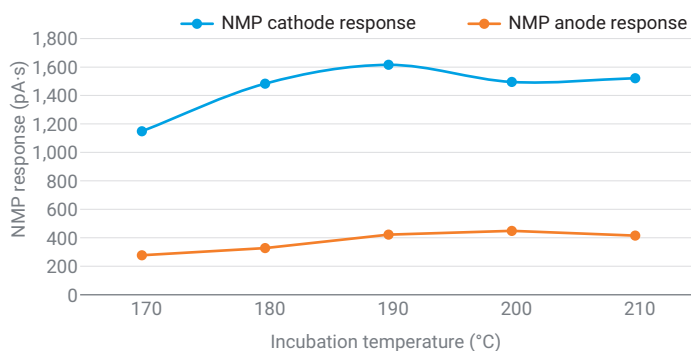

Figure 1. NMP response under different incubation temperatures.

In optimizing the equilibration time, the headspace oven was set at 190 °C, and the vial incubation time began at 15 minutes, increasing in 5-minute increments up to a maximum of 30 minutes. Figure 2 illustrates the response of NMP as it changes with equilibration time. This plot did not show a clear trend of extracted NMP amounts changing with the equilibration time, especially for cathodes. This was probably due to suboptimal homogeneity in the electrode structure, which impacted the real NMP quantity on each test sample. However, comparing the average NMP response of cathode and anode samples under each incubation time and balancing the extraction time used, an equilibration time of 20 minutes was selected for the following analysis.
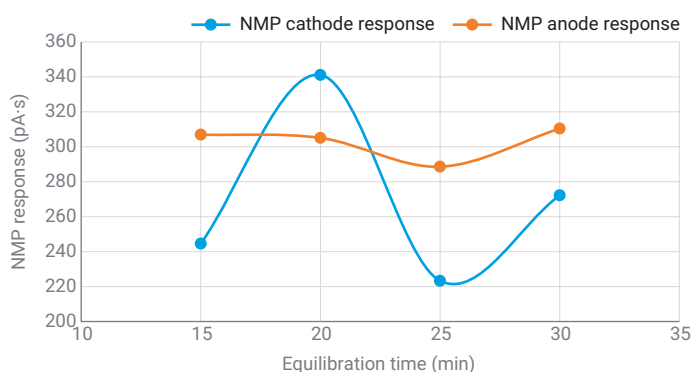

Figure 2. NMP response under different equilibration times.

Dynamic range and repeatability of NMP analysis in the headspace approach

Evaluations for method linearity and repeatability were conducted on blank electrodes spiked with NMP calibration standards, as described in the "Experimental" section. Four types of electrode samples were tested. The matrix-matched calibration curve based on two anode samples showed linear response across the calibration range with an average correlation coefficient R^2 greater than 0.999 (Figures 3A and 3B). The linearity results based on two types of cathodes were quite different. Cathode type 1 had a matrix-matched linearity with R^2 at 0.9989 (Figure 3C). Cathode type 2 did not produce a linear response across the calibration range, and a quadratic curve was established accordingly, as shown in Figure 3D. The linearity performance difference on the two types of cathodes probably resulted from differences in electrode composition and structure, for which there was not detailed information provided from the suppliers. The electrode coating of cathode type 2 was visibly thicker than that of cathode type 1. And the residual NMP level of cathode type 2 was several times that measured for cathode type 1. Our assumption is the pore structure and the thickness of coating on cathode type 2 makes it more difficult for NMP to evaporate and leave the electrode surface during the drying process, so more residual NMP can be detected.

The observed linear or nonlinear results showed the response of NMP had a positive correlation with its concentration in electrodes. The linearity test was repeated on different foils of the four types of cathode and anode samples. The same results were reproduced. Based on this, the residual NMP on anodes can be measured quite accurately using the pre-established matrix-matched linearity curve. In the actual manufacturing process control, the amount of residual NMP on anodes can even be measured with acceptable accuracy by using the single-point calibration method. When monitoring the residual NMP on cathodes, a matrix-matched dynamic range test should be run first to determine whether it is linear so that a single-point calibration method can be applied in the process control. For cathodes with a composition and structure like cathode type 1, the single-point calibration can be used. For cathodes that perform more like cathode type 2, multilevel calibration can give more accurate quantitation than single-level calibration.
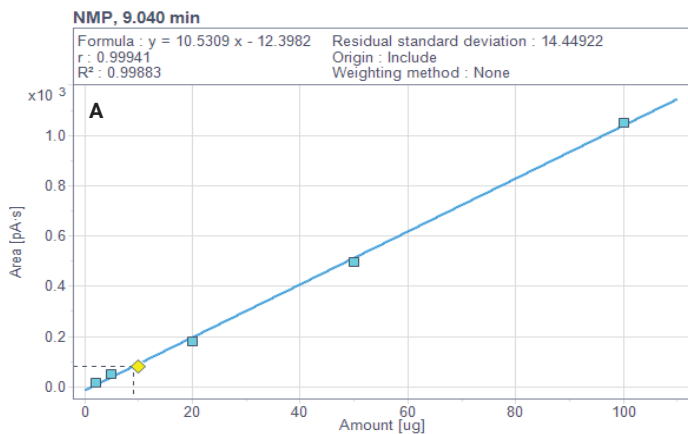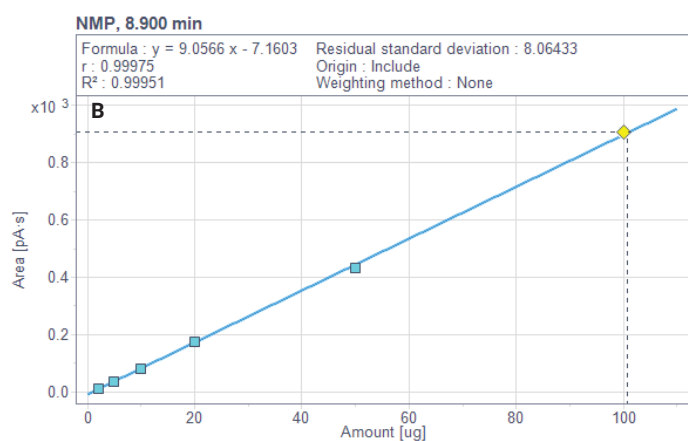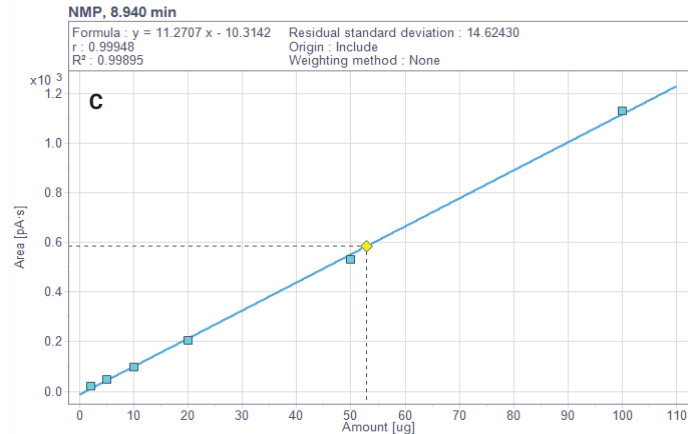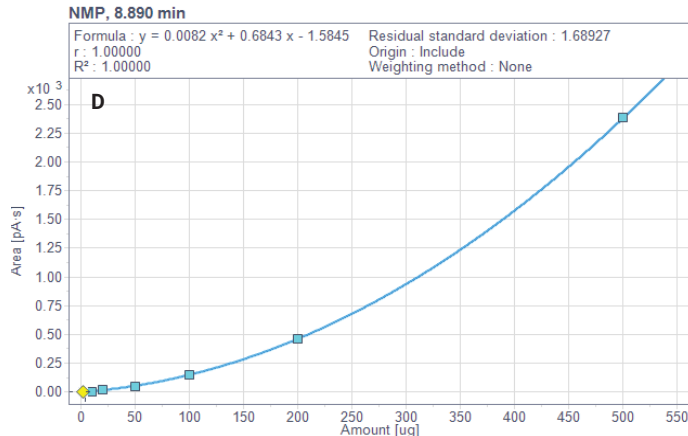
Figure 3. Matrix-matched calibration curve on different types of electrodes. (A) linear, anode type 1; (B) linear, anode type 2; (C) linear, cathode type 1; (D) quadratic, cathode type 2.

The response repeatability of NMP extracted was assessed by analyzing blank electrodes spiked with NMP at three concentration levels. Six replicas were run for each level. The area %RSD on the spiked cathode type 1 and anode type 1 are shown in Table 3. The area precision values on the anode and cathode samples at a low spiking level of 4 µg/g were 2.16 and 3.81%, respectively. For the other two spiking levels, the NMP response precision was less than 1.5%.

Table 3. NMP response precision on the spiked electrodes.

Electrodes	Anode Type 1 (n = 6)			Cathode Type 1 (n = 6)		
NMP Mass Concentration on Electrodes (µg/g)	4	20	200	4	20	200
RT %RSD	0.02	0.01	0.01	0.01	0.01	0.01
Area %RSD	2.16	1.45	0.68	3.81	0.98	0.99

The carryover performance

The system carryover was evaluated by running a blank vial after analyzing a spiked 0.5 g blank cathode (spiked with 10 µL of 10,000 µg/mL NMP). There was no peak identified among the NMP RT window in the blank run. The chromatogram in Figure 4 demonstrates the carryover result using the described sample and test conditions.

Method detection limit and quantification limit

The method detection limit (MDL) and limit of quantification (LOQ) were calculated for the anode samples using the signal-to-noise ratios (S/N) of 3:1 and 10:1 (see Table 4). Three blank anode samples were spiked at a final concentration of 0.2 µg/g, and the average S/N of the NMP peak was 24:1. The MDL and LOQ for anodes were determined to be below 0.03 and 0.1 µg/g, respectively. Considering the different NMP adsorption abilities of the

cathodes from different manufacturers, and the fact that typical residual NMP concentration in the cathodes is at least in the tens of ppms level, which can be easily detected by the HS technique, the MDL and LOQ for cathode samples in the HS method were not measured separately. In Figure 5, the chromatogram of the spiked blank cathode at a 4 µg/g concentration level shows the HS method's excellent ability to detect trace levels of NMP in cathodes.

Table 4. MDL and LOQ (µg/g) of NMP on anodes with a spiked concentration of 0.2 µg/g.

MDL and LOQ (µg/g)	S/N	MDL (S/N = 3:1)	LOQ (S/N = 10:1)
Spiked Blank Anode 1	22.9	0.026	0.087
Spiked Blank Anode 2	26.1	0.023	0.077
Spiked Blank Anode 3	24.9	0.024	0.080
Average	24.6	0.025	0.081

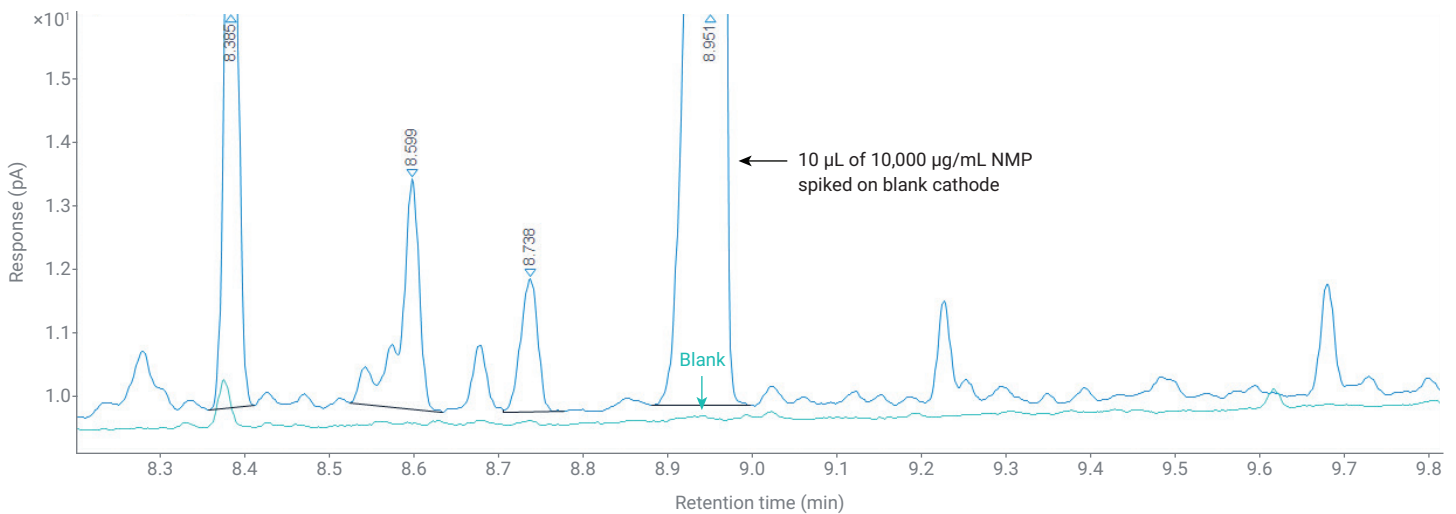**Figure 4.** Chromatograms showing 10 µL of 10,000 µg/mL NMP on 0.5 g blank cathode sample (corresponding to NMP mass concentration of 200 µg/g) and the following blank run.
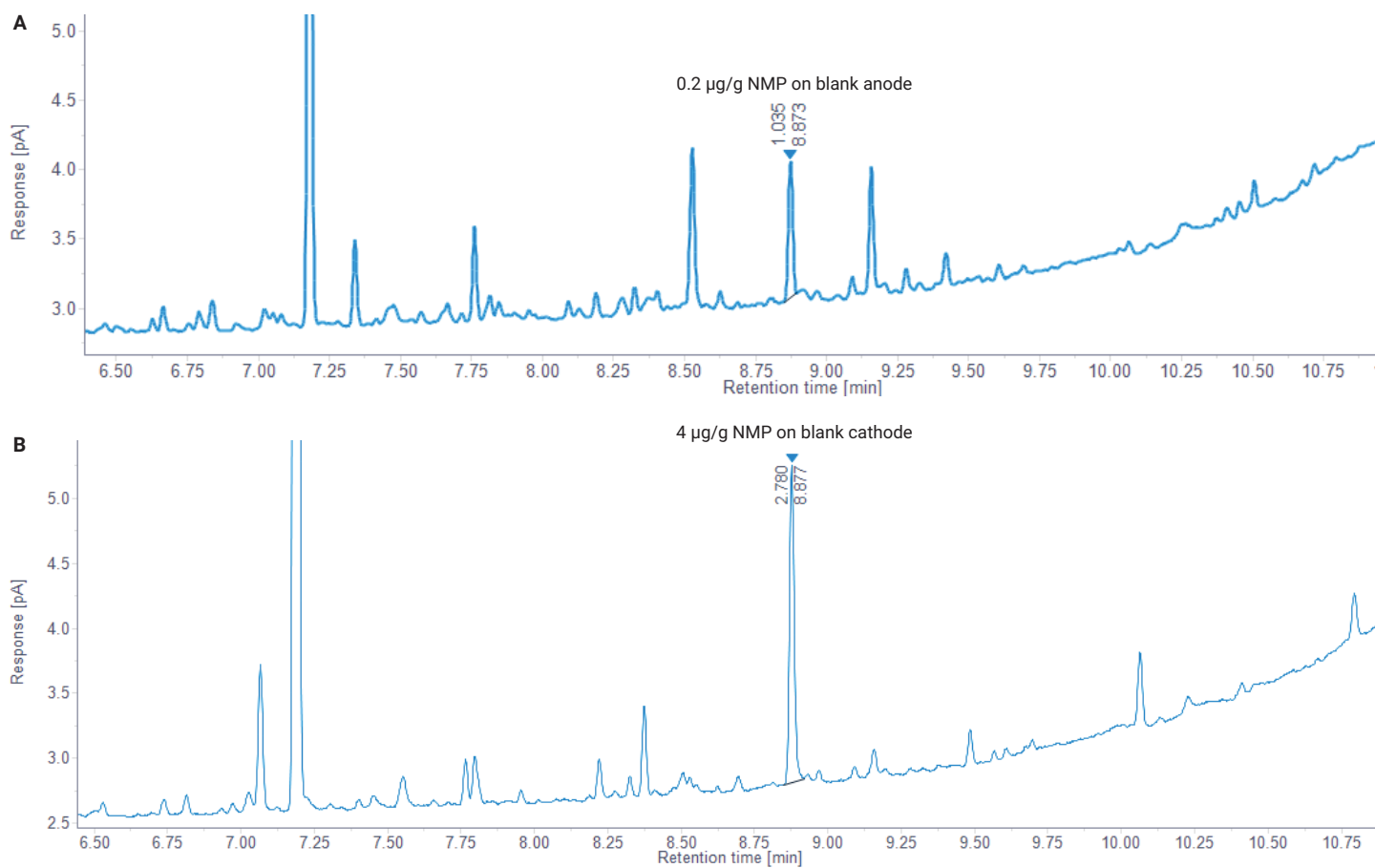
Figure 5. Chromatograms of the blank anode spiked at 0.2 µg/g NMP (A) and the blank cathode spiked at 4 µg/g NMP (B).

NMP analysis of electrode samples

Residual NMP analysis was performed on four types of samples, including two cathode and two anode samples. These electrodes were real-world samples produced from established production lines of different manufacturers. Each sample was cut and weighed to 0.5 g and then placed into headspace vials. The matrix-matched calibration curve (quadratic type) based on eight calibration levels was used to quantify cathode type 2 samples because the real residual NMP exceeded the upper limit of six calibration levels. The remaining samples were quantified using a matrix-matched linear calibration curve of six levels. In addition to the HS analysis, these samples were measured using the liquid extraction analysis method, as outlined in a separate application note.[3] The chromatograms of anode type 2 and cathode type 2 samples from two extraction methods are shown in Figures 6 and 7. The test results are summarized in Table 5. The calculated concentration ratios from the two analysis methods revealed that the NMP test results for anode samples were very similar between the two methods. The residual NMP in cathode type 1 detected by the HS method was 77% of that measured by LE method. The NMP level in cathode type 2 detected by the HS method was 65% of that detected with the LE method. The LE method produced a higher recovery of NMP from the electrodes, which can give a more accurate reflection of the residual NMP level in electrode samples. The results accuracy of the HS method was not as good as that of LE method for some types of cathodes. However, the HS method can still effectively monitor the NMP amount change if the residual NMP concentration increases or decreases compared to the history levels.
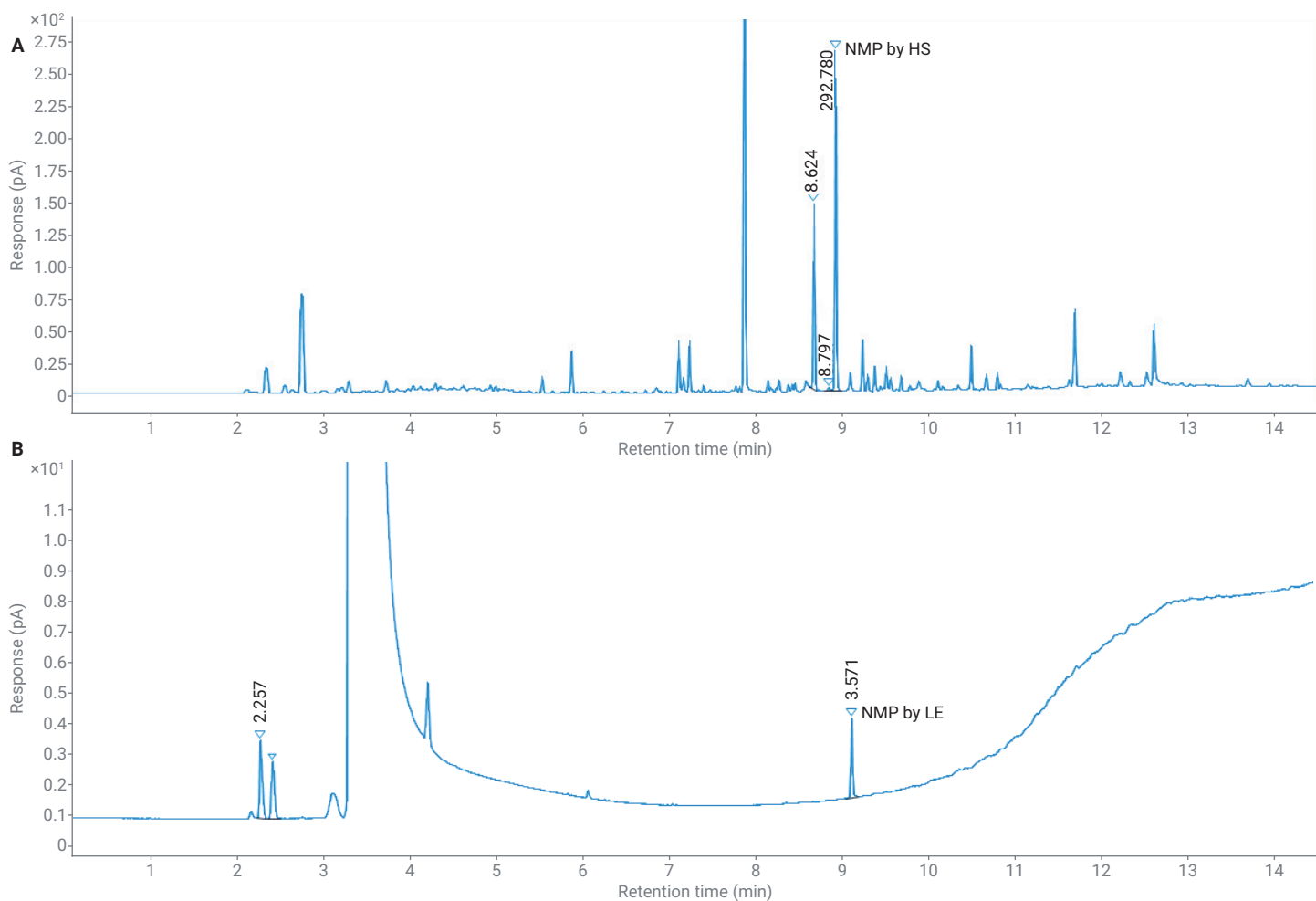

Figure 6. Chromatograms of NMP in anode type 2 samples: (A) headspace-based approach, (B) liquid extraction-based approach.
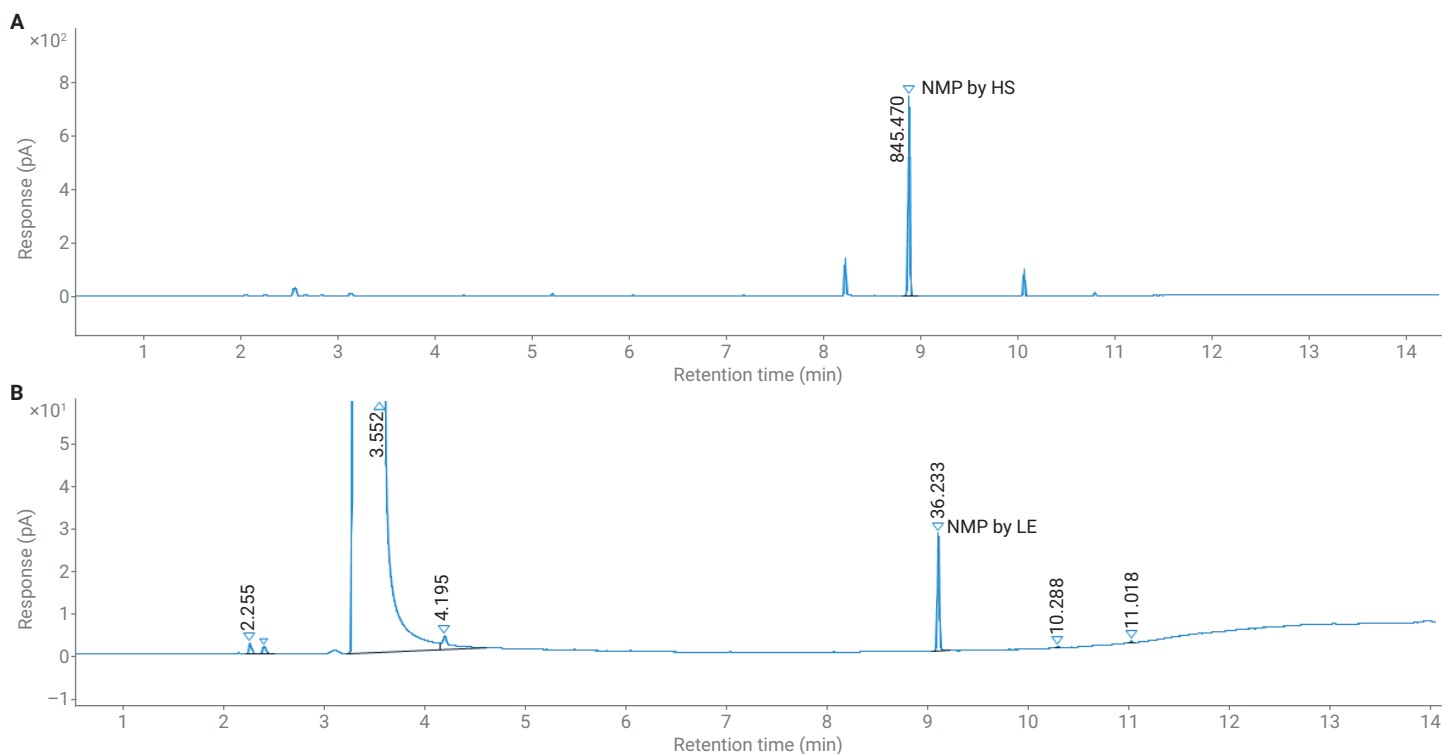
Figure 7. Chromatograms of NMP in cathode type 2 samples: (A) headspace-based approach, (B) liquid extraction-based approach.

Table 5. Residual NMP analysis of electrode samples using HS and LE approaches.

		Cathode		Anode	
		Type 1	Type 2	Type 1	Type 2
NMP Mass Concentration Measured (µg/g)	HS	105.6	475.9	137.8	66.7
	LE	136.8	721.9	155.2	72.3
Concentration Ratio Measured by HS and LE Methods (%)		77.2	65.9	88.8	92.3

In an established manufacturing process, a practical, reliable, and easy-to-operate analytical method is necessary. The headspace-based analytical method offers a straightforward sample preparation process: cutting, weighing, and sealing the electrodes for the subsequent GC analysis. It eliminates the need for solvent usage, ultrasonic extraction, and filtration operations during sample pretreatment. Its simplicity of operation, combined with its stable/precise quantification capability, makes the HS technique very suitable for process control on a stable electrode manufacturing line. By comparison, the LE method is recommended for residual NMP determination during the manufacturing process development stage.

Headspace analysis is more susceptible to variation in the matrix effects from different cathode and anode materials. If a significant deviation in NMP concentration is detected by an HS analysis, laboratories should use the LE method to calibrate HS analysis results for new materials, or when precise results are required. This is easily achieved on the same GC system by using a transfer line interface accessory (XLSI) weldment to allow both liquid and headspace sample introduction on the same GC inlet.

Conclusion

In this study, a method for analyzing residual NMP in electrodes was developed using the Agilent 8697 headspace sampler coupled with the Agilent 8860 GC system and FID. The method's investigation assessed the system's performance in terms of matrix-matched calibration, quantitation precision, detection limit, and system carryover. The HS approach demonstrated an excellent detection limit and quantitation precision for targeted NMP analysis. In the carryover test, no NMP was detected in the blank run immediately after analyzing a blank cathode spiked with 100 µg NMP. The comparison between HS and LE analytical methods showed that HS could accurately quantify NMP in anode samples. The recovery rate of NMP from cathodes using the HS technique was approximately 65 to 78% of that achieved by the LE-based method. Given its operational simplicity and quantitation precision, HS is suitable for the process control of an established electrodes manufacturing route, while LE is recommended for the development of manufacturing processes and troubleshooting electrode quality issues.

References

1. Liu, Y.; Zhang, R.; Wang, J.; Wang, Y. Current and Future Lithium-Ion Battery Manufacturing. *iScience* **2021**, *24*, 102332. DOI: 10.1016/j.isci.2021.102332.

2. Zhang X., Han G., *et al.* Effect of NMP Addition on Battery Performance in Negative Electrodes, *Henan Chemical Industry* **2021**, *38*, 23−25.

3. Shang H. T.; Zhang, J.; Jiang, F. Analysis of N-Methyl-2-Pyrrolidone (NMP) in Battery Electrodes, *Agilent Technologies application note*, publication number xxxx-xxxx, **2024**.

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