Application Note

Lithium-Ion Battery Testing

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Quantitative Analysis of NMP in Lithium-Ion Battery Anode and Cathode Electrodes

Using the Agilent 8697 headspace sampler and 5977B GC/MSD

Authors

Seonghoon Kang and Byeongho Kim
Agilent Technologies, Inc.
Seoul, Korea

Abstract

N-methyl-2-pyrrolidinone (NMP) is a solvent used in large quantities for surface deposition in the manufacture of batteries, semiconductors, and so on. Due to its toxicity, the U.S. Environmental Protection Agency announced a usage restriction regulation on NMP in January 2017. In April 2018, NMP was added to the Registration, Evaluation, Authorization, and Restriction of Chemicals (REACH) restricted list. If the relevant substances are manufactured or used at a concentration of 0.3% or higher, the company must have appropriate risk management measures and operating conditions in place to protect workers from exposure.

In this application note, we established the analytical conditions for NMP in lithium-ion battery electrodes using the Agilent 8697 headspace sampler and 5977B GC/MSD, which enables fast and easy analysis of solid matrices for NMP monitoring, and determined the calibration linearity (R^2), repeatability (%RSD), and limit of detection (LOD). The results showed that NMP had a calibration linearity R^2 of 0.999 or greater in the calibration range of 50 to 2000 µg. To test repeatability, low (50 µg), medium (200 µg), and high (2000 µg) concentrations of the standards were analyzed four times with RSDs of 4.2, 3.7, and 2.9%, respectively, and the limit of detection (LOD) of NMP was calculated to be 6.33 µg from the results of the replicate analyses at the low concentration (50 µg).

Introduction

As interest in the use of alternative energy increases due to the depletion of fossil fuels and environmental issues, the energy storage system (ESS) industry, which can store the energy produced, is attracting attention. The lithium-ion battery stands out in the alternative energy industry for being lightweight, having a high energy density, and lacking memory effect. These advantages have led to a rapid increase in lithium-ion battery usage across various areas in society. Electrodes are one of the four major components of lithium-ion batteries. They consist of an anode, which determines the battery's capacity and average voltage, and a cathode, which stores and releases lithium ions and allows current to flow. NMP, used as a solvent in the manufacturing process of lithium-ion battery anodes, is widely used in the semiconductor and battery industries due to its high selectivity, low corrosion, and low viscosity. In particular, NMP solvent is used in large quantities as a binder and separator coating that serves as an adhesive for conductive materials in the lithium-ion battery process. After the coating of lithium-ion battery electrodes is completed, residual NMP is removed to prevent degradation of battery cycle performance and safety. Recovery methods such as absorption, cooling condensation and concentration are used to remove NMP. However, since this recovery method cannot recover 100% of the solvent used, effective monitoring of residual NMP levels is a key monitoring issue to ensure electrode performance and battery quality. NMP residues are monitored by gas chromatography (GC), which requires time-consuming and expensive sample preparation. A headspace sampler offers the advantage of time and money savings by analyzing solid samples directly without sample preparation. A headspace sampler is an instrument that can extract NMPs from solid matrices quickly and easily by heating the sample in a sealed vial, resulting in high efficiency with little sample preparation time and low solvent volumes.

The reasons for using mass-spec for this analysis are as follows.

1. This is to separate the target compound from various interference that may appear in actual sample analysis.
2. Although the concentration currently being managed is high, it was determined that a small amount of analysis may be needed in the future.

In this application note, we established analytical conditions for NMPs in the electrodes of lithium-ion batteries using an 8697 headspace sampler and 5977B GC/MSD, and determined the calibration linearity (R^2), repeatability (%RSD), and LOD.

Experiment

Reagents and standards

The NMP (ultrahigh-purity grade, 99.7%) standard solution used in this experiment was purchased from Chemaral, Inc. The calibration standards were diluted with methanol to prepare six points of calibration standards from 50 to 2000 µg/µL. The three electrode samples used for quantitative analysis (samples 1, 2, and 3) were provided by the customer and, without any preparation, were placed in a 20 mL headspace vial to be used for quantitative analysis.

Equipment and conditions

For the quantitative analysis of NMP, an Agilent 8697 headspace sampler and 5977B GC/MSD were used with an Agilent J&W DB-624 Ultra Inert (UI) column, which is widely used for volatile organic compound analysis. The instrument conditions are shown in Tables 1, 2, and 3.

Table 1. Agilent 8697 headspace sampler operating conditions.

Parameter	Value
Oven Temperature	180 °C
Loop Temperature	190 °C
Transfer Line Temperature	200 °C
Vial Equilibration Time	20 min
Injection Time	0.5 min

Table 2. GC operating conditions.

Parameter	Value
Inlet	230 °C
Injection Mode	Split injection, split ratio 50:1
Column	Agilent J&W DB-624 UI (30 m × 0.25 mm × 1.4 µm)
Gas Flow in the Column	1.5 mL/min (constant flow, He)
Oven	50 °C (hold for 2 min) 15 °C/min to 200 °C (hold for 5 min)

Table 3. Single quadrupole MS operating conditions.

Parameter	Value
Ion Source	Electron ionization
Electronic Energy	70 eV
Ion Source Temperature	230 °C
Quadrupole Temperature	150 °C
Detector Settings	Use gain factor (gain factor 2)
Acquisition Mode	Selected ion monitoring (*m/z* 99, 98)

Results and discussion

NMP chromatograms with 8697 headspace sampler and 5977B GC/MSD

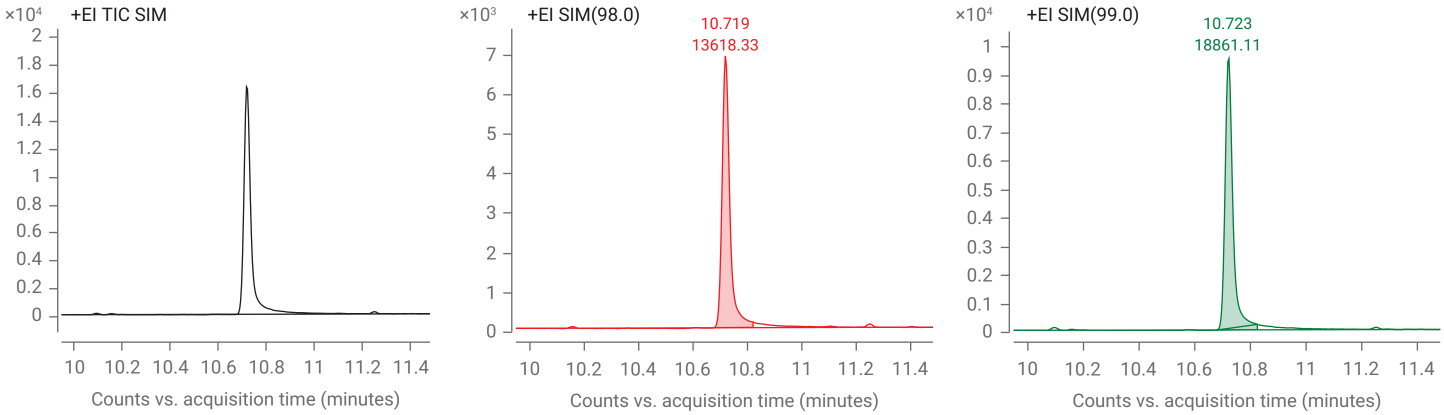

Figure 1. Analytical chromatograms (TIC/SIM) of NMP using the Agilent 8697 headspace sampler and 5977B GC/MSD.

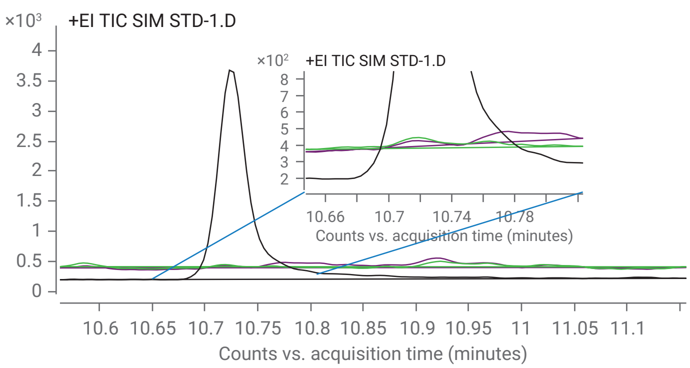

Figure 2. NMP and blank chromatograms.

The chromatogram of the analyte, NMP, is shown in Figure 1. Using the specified analysis conditions, we confirmed good peak shapes and no interference from other interfering components. NMP is a polar solvent with a high boiling point. If there are active sites or cold spots in the path from the headspace sampler to the column, they can adsorb and interfere with the next analysis. The headspace sampler and GC inlet materials can minimize the effects of this cross contamination. Blank chromatograms before and after the standard (STD) analysis are shown in Figure 2.

Calibration curve

The calibration curve was created with a total of six points in the concentration range of 50 to 2000 µg. The linearity R^2 value of the NMP calibration curve using the 8697 headspace sampler and 5977B GC/MSD was determined to be 0.9999. The NMP calibration curve and chromatograms for each level are shown in Figure 3 below.

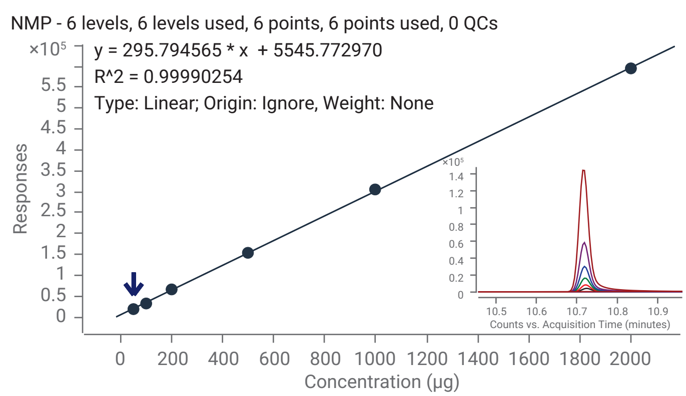

Figure 3. NMP calibration curve and overlapping chromatograms for each level using the Agilent 8697 headspace sampler and 5977B GC/MSD.

Repeatability and limit of detection

The repeatability (%RSD) for NMP was calculated using Agilent MassHunter Quantitative Analysis software with measurements from four replicate analyses of low (50 µg), medium (200 µg), and high (2000 µg) concentrations of the standards, resulting in RSDs of 4.2, 3.7, and 2.9% for low, medium, and high concentrations, respectively. The LOD was calculated to be 6.33 µg from four replicate analyses of 50 µg standards.

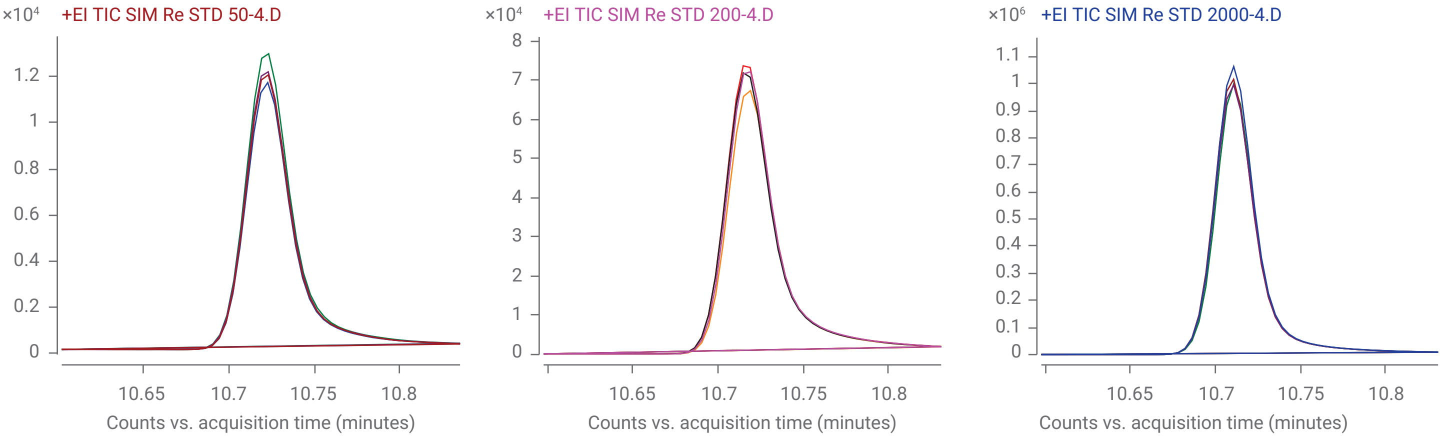

Figure 4. Overlapping repeatability chromatograms for each level (left to right: 50, 200, and 2000 µg concentrations).

Table 4. Repeatability and LOD calculation table for NMP.

NMP	Standard (STD) Concentration (µg)				%RSD	LOQ	LOD
	STD-1	STD-2	STD-3	STD-4			
Low Concentration (50 µg)	52.70	47.64	50.30	49.37	4.2	21.09	6.33
Medium Concentration (200 µg)	189.67	201.49	201.64	207.20	3.7	-	-
High Concentration (2000 µg)	1945.36	2079.49	1968.53	2006.63	2.9	-	-

Sample quantitation

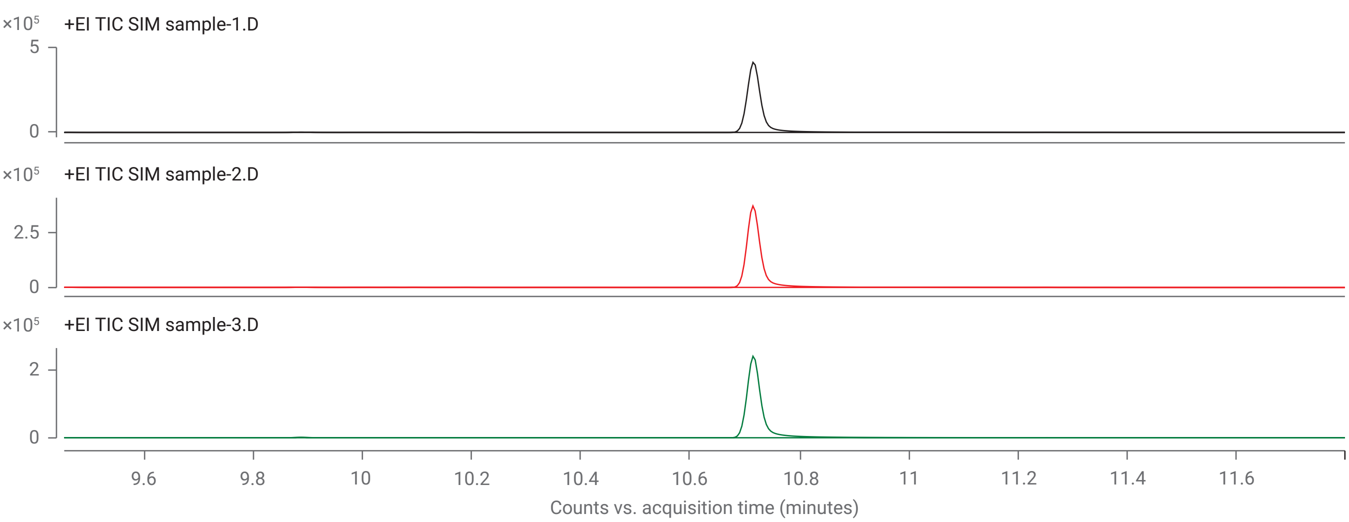

Figure 5. Chromatograms of samples with NMP.

The chromatograms of samples with NMP in the electrode of a lithium-ion battery are shown in Figure 4. The 0.1 g electrode samples were provided by the customer and placed in a 20 mL headspace vial for analysis. The instrumental concentrations of NMP analyzed on the electrodes of the lithium-ion battery were found to be 1384.42 µg in sample 1, 1245.58 µg in sample 2, and 822.13 µg in sample 3. The RT (minutes), area, instrumental concentration, and calculated sample concentration for each sample are shown in Table 5.

Table 5. Quantitative analysis results of NMP.

	Quantification in electrolyte sample			
	RT (Minutes)	Area	Instrument Concentration (µg)	Sample Concentration (µg/g)
Sample 1	10.715	424371	1384.42	138.44
Sample 1	10.715	382268	1245.58	124.66
Sample 1	10.715	253862	822.13	82.21

Conclusion

- In this application note, the Agilent 8697 headspace sampler and 5977B GC/MSD were used to establish conditions for the quantitative analysis of NMP in lithium-ion battery electrodes.
- The conditions established resulted in good peak shapes and no interference from other interfering components, and cross contamination testing with blanks confirmed no cross contamination between standards.
- The linearity R^2 of the NMP calibration curve was 0.999 or greater, the repeatability (%RSD) for low, medium, and high concentrations was 4.2, 3.7, and 2.9%, respectively, and the LOD was 6.33 µg.
- With this application note, it is expected that a quick and easy preparation method using the 8697 headspace sampler will enable rapid and accurate monitoring of NMPs in the lithium-ion battery industry.

References

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2. Na. S, M., Park. H, G., Kim. S. W., Cho. H. H., and Park. K. j., (2020), Research Trends of Cathode Materials for Next Generation Lithium-Ion Battery, *KIC News*, 23 (1)

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Agilent Technologies, Inc. Headquarters
5301 Stevens Creek Blvd
Santa Clara, CA 95051
United States
Tel: +800-227-9770 (Directory)
Fax: +1 866 497 1134
Email: cag_sales-na@agilent.com

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