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Industrial

Rapid determination of residual *N*-methyl-2-pyrrolidone (NMP) in lithium battery electrodes by headspace gas chromatography

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Keywords

Headspace gas chromatography (HS-GC), lithium battery, residual solvent, *N*-methyl-2-pyrrolidone (NMP), flame ionization detector, FID, TRACE 1600 Series GC, TriPlus 500 HS

Goal

The aim of this application note is to demonstrate the performance of a simple and robust method for the determination of residual *N*-methyl-2-pyrrolidone in electrode sheets using gas chromatography coupled to static headspace sampling.

Introduction

Lithium-ion batteries have been integrated into a wide range of consumer products due to their small size, utility, and affordability.[1] Because of their high energy density, they also offer a suitable solution for the currently growing number of electric vehicles.
A lithium-ion battery consists primarily of the electrodes (anode and cathode), an electrolyte, and a separator. The cathode is mainly composed of active material (often binary or ternary alloys containing nickel, cobalt, and manganese) and a conductive skeleton. In the manufacturing process, *N*-methyl-2-pyrrolidone (NMP) is used to dissolve the cathode binder, polyvinylidene fluoride (PVDF), allowing for uniform coating of both sides of the collector. PVDF is a fluoropolymer characterized by high thermal stability and excellent chemical resistance, which makes it suitable to the specific chemical environment of Li-ion cells. Thus, it is mainly used as a positive binder and separator coating in lithium batteries.

After the battery electrode coating is completed, NMP needs to be removed to avoid residual amounts of it leading to the deterioration of the battery cycle performance and safety. Therefore, effective monitoring of residual NMP content in the electrode skeleton is key to ensure battery quality and electrode performance. To date, the standard procedure for extracting residual NMP from electrode sheets involves using a large quantity of a different and more volatile organic solvent in an ultrasonic bath. This is a time-consuming procedure that produces a considerable amount of organic waste.

An alternative, more convenient method for the determination of residual NMP on lithium battery electrodes was developed by using headspace sampling coupled to gas chromatography with flame ionization detection (FID). The headspace sampling technique allows for the extraction of NMP from the solid matrix in a fast and simple way by heating the sample in a closed vial, thus eliminating time-consuming sample preparation and organic solvent consumption. This method meets the sample throughput and productivity requirements of contract testing laboratories offering this service. A few microliters of water are added to the sample to keep consistency with the external standards preparation. The addition of such a low amount of water combined with the total vaporization technique[2] allows for quick, safe, and easy sample preparation in compliance with the ever-growing Green Chemistry concept.[3]

Figure 1. Li-ion battery electrodes

Experimental

Instrumentation

In all experiments, a Thermo Scientific™ TRACE™ 1610 Series GC equipped with a Thermo Scientific™ iConnect™ Split/Splitless (SSL) injector and a Thermo Scientific™ iConnect™ Flame Ionization Detector (FID) was coupled to a Thermo Scientific™ TriPlus™ 500 Headspace autosampler. Chromatographic separation was achieved on a Thermo Scientific™ TraceGOLD™ TG-WaxMS capillary column, 30 m × 0.32 mm × 0.25 µm (P/N 26088-1430).

The TraceGOLD column provides superior inertness and low column bleed for increased run-to-run and batch-to-batch reproducibility. For this application, nitrogen represents a viable and cost-effective alternative to helium as carrier gas, as it can easily be produced in the lab with high purity using a nitrogen generator. GC-FID and HS autosampler method parameters are reported in Table 1.

Table 1. GC-FID and HS autosampler experimental parameters

TRACE 1610 GC parameters	
Inlet module and mode	SSL, split
Split ratio	20:1
Septum purge mode, flow (mL/min)	Constant, 5
Carrier gas, carrier mode, flow (mL/min)	N_2, constant flow, 2.0
Oven temperature program	
Temperature 1 (°C)	50
Hold time (min)	2
Temperature 2 (°C)	200
Rate (°C/min)	15
Hold time (min)	5
FID	
Temperature (°C)	250
Air flow (mL/min)	350
H_2 flow (mL/min)	35
N_2 flow (mL/min)	40
Acquisition rate (Hz)	10

TriPlus 500 HS parameters	
Incubation temperature (°C)	180
Incubation time (min)	20
Vial shaking	Medium
Vial pressurization mode	Pressure
Vial pressure (kPa) (auxiliary gas nitrogen)	100
Vial pressure equilibration time (min)	0.5
Loop size (mL)	1
Loop/sample path temperature (°C)	200
Loop filling pressure (kPa)	62
Loop equilibration time (min)	0.5
Needle purge flow level	2
Injection mode	Standard
Injection time (min)	0.5

Data acquisition, processing, and reporting

Data was acquired using the Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software, version 7.3. This single platform integrates instrument control, method development functionality, quantitation-focused workflows, reporting, and storage in compliance with Title 21 CFR part 11, ensuring effective data management, ease of use, data integrity, and traceability.[4] Chromeleon CDS also offers the option to scale up the entire data handling from a single workstation to an enterprise environment.

Standard and sample preparation

Standard preparation

N-methyl-2-pyrrolidone (GC headspace grade, P/N 15552413) was purchased from Fisher Scientific. A bulk solution at 10,000 µg/mL was prepared by diluting 1 g (±0.001 g) of NMP pure standard in a 100 mL volumetric flask with HPLC-MS grade water (Fisher Scientific P/N W-0112-17). Stock solutions were obtained diluting the bulk solution in HPLC-MS grade water as reported in Table 2.

Table 2. NMP stock solution preparation

Stock solution	Concentration (µg/mL)	Bulk solution (µL)	Diluent (water, µL)
1	50	50	9,950
2	250	250	9,750
3	500	500	9,500
4	1,000	1,000	9,000
5	2,500	2,500	7,500
6	5,000	5,000	5,000

Sample preparation

Samples for analysis were obtained by cutting the lithium battery electrode sheets into small pieces (ca. 5 mm × 5 mm) and accurately weighing 0.5 g (±0.05 g) of sample into a 20 mL crimp cap headspace vial (P/N 20-HSV). 10 µL of HPLC-MS grade water were added prior to vial capping (using a magnetic crimp cap P/N 6PMSC18-ST2) to maintain consistency with the spiked matrix-matched standards.

Matrix-matched calibration curve preparation

A calibration curve was obtained by accurately weighing 0.5 g (±0.05 g) of electrode sheet pieces, which previously tested negative for NMP residues, in 20 mL crimp cap headspace vials. The vials were then spiked with 10 µL of the stock solutions reported in Table 2 to obtain six calibration levels ranging from 1 to 100 µg/g. Vials were immediately capped after spiking.

Sample preparation for recovery assessment

Recovery was assessed by accurately weighing 0.5 g (±0.05 g) of electrode sheet pieces, which previously tested negative for NMP residues, in 20 mL crimp cap HS vials. The vials were then spiked with 10 µL of the stock solutions at 50, 500, and 5,000 µg/mL to obtain a final concentration of 1, 10, and 100 µg/g, respectively. Each concentration level was prepared in duplicate.

Sample preparation for repeatability assessment

Repeatability was assessed by accurately weighing 0.5 g (±0.05 g) of electrode sheet pieces, which previously tested negative for NMP residues, in 20 mL crimp cap HS vials (n=6). The vials were then spiked with 10 µL of the stock solution at 500 µg/mL to obtain a final concentration of 10 µg/g.

Results and discussion

Chromatography

Headspace sampling is a clean technique that allows for NMP extraction, eliminating the complexity of the matrix in the injected sample and thus ensuring a cleaner chromatogram. An example of a chromatogram obtained for a Li-battery electrode sample tested negative for NMP is reported in Figure 2. The high inertness and low bleed of the TraceGOLD TG-WaxMS capillary column ensured low baseline noise.

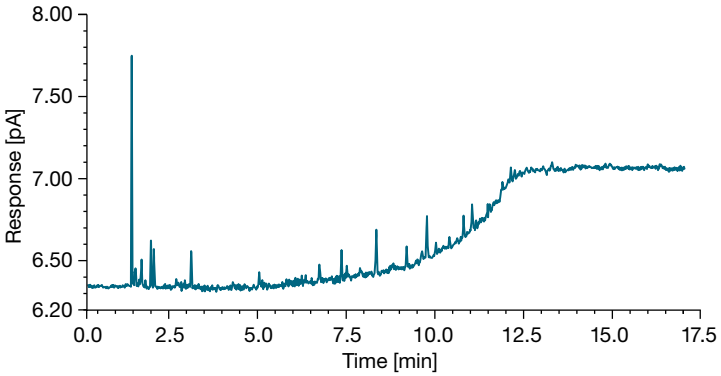


Figure 2. Example of a chromatogram obtained for a lithium battery electrode sample that tested negative for NMP. The headspace sampling technique allowed for cleaner baseline irrespective of the matrix complexity.

Linearity

Linearity was evaluated by injecting six matrix-matched calibration levels ranging from 1 to 100 µg/g. The calibration curve was plotted using the external standard method and the linear fit. The calculated coefficient of determination (R^2) was 0.9996 with %RSD of average response factors of 2.6%, confirming the excellent linearity (Figure 3). The extrapolated detection limit of NMP considering a S/N=3 is 0.05 µg/g.

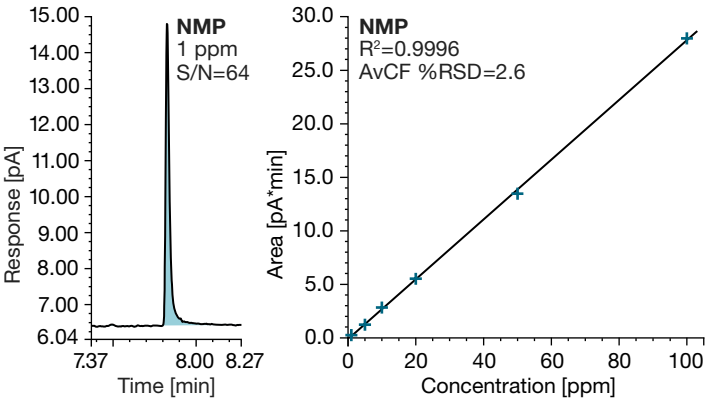


Figure 3. Matrix-matched calibration curves ranging from 1 to 100 µg/g. R^2 and AvCF %RSD are annotated.

Recovery

To assess the measurement accuracy (%) and recovery (%), n=6 samples spiked with NMP at low (1 µg/g), medium (10 µg/g), and high (100 µg/g) concentrations were injected. The average recoveries for the spiked matrix samples ranged from 98 to 115% with calculated amounts within 15% of the spiked concentrations (Table 3).

Table 3. Calculated amounts (µg/g) and recoveries (%) for n=6 samples spiked at low (1 µg/g), medium (10 µg/g) and high (100 µg/g) concentrations

Injection number	Theoretical amount (µg/g)	Calculated amount (µg/g)	Calculated recovery (%)
1	1.0	1.15	115
2	1.0	1.10	110
3	10.0	9.79	98
4	10.0	10.68	107
5	100.0	104.99	105
6	100.0	101.80	102

Carryover

NMP is a polar solvent with a high boiling point that can generate a carryover effect in the presence of active sites or cold spots along the sample path from the headspace autosampler to the gas chromatographic column. The TriPlus 500 HS removes this possible effect thanks to a direct connection of the analytical column to the valve manifold, removing the typical long external transfer line and by-passing the injector. The shorter sample path ensures uniform heating with no cold spots while maximizing inertness towards critical compounds. The inertness of the sample path, efficient heating, and continuous purging of the pneumatic circuit of the TriPlus 500 HS autosampler minimize the risk of high boiling point compound residuals, thus preventing carryover. To demonstrate the absence of carryover, an empty vial was analyzed after the highest calibration point. No NMP could be detected when analyzing a blank after the highest calibration point (Figure 4).

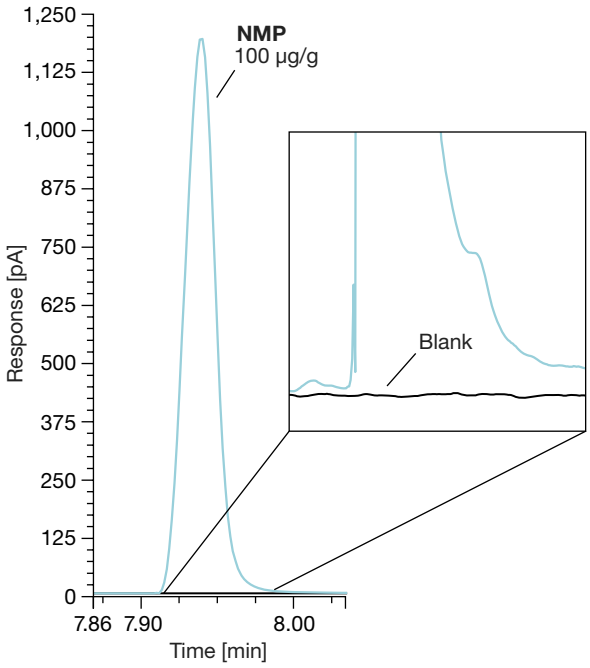
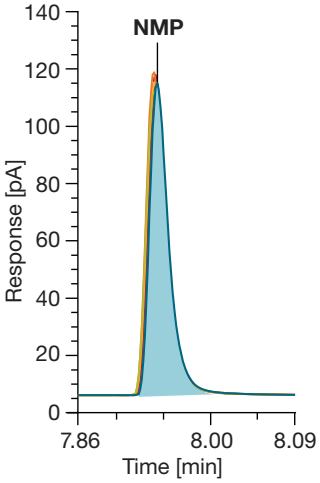


Figure 4. Overlaid chromatogram of the highest calibration point (blue trace, 100 µg/g) and an empty vial run immediately after (black trace). The inset shows the zoomed-in baseline of the empty vial where no NMP could be detected.

Repeatability

Instrument repeatability was assessed by injecting six individual samples, each spiked at 10 µg/g. Again, the highly efficient pneumatic control of the TRACE 1610 GC and the sample path inertness of the TriPlus 500 HS with the direct connection to the GC column ensured reliable and reproducible sample transfer, with an absolute peak area %RSD of 1.02. Overlaid chromatograms for n=6 injections of samples spiked with NMP at 10 µg/g, as well as absolute peak area and calculated %RSD, are reported in Figure 5.



Injection number	Absolute peak area [pA*min]
1	2.615
2	2.633
3	2.592
4	2.576
5	2.622
6	2.567
Std deviation	0.03
Average	2.60
%RSD	**1.02**

Figure 5. Overlaid chromatograms for n=6 injections of samples spiked with NMP at 10 µg/g (left) as well as absolute peak area and calculated %RSDs (right)

Conclusion

The results obtained in these experiments demonstrate that the TRACE 1600 Series GC in combination with flame ionization detection and the TriPlus 500 headspace autosampler is a reliable analytical tool for determination of residual NMP in Li-ion battery electrodes, with no time-consuming sample preparation required. The use of nitrogen as a carrier gas offers an efficient chromatographic process with reduced costs of operation.

- Headspace sampling allowed for the extraction of NMP from the solid matrix in a fast, simple, and safe way, removing time-consuming sample preparation and solvent waste.
- The direct column connection to the valve manifold with a short sample path ensured efficient analyte extraction and transfer resulting in excellent linearity (R^2=0.9996, AvCF %RSD=2.6) and % recovery between 98 and 115 with the calculated amount falling within 15% of the expected values.
- The highly efficient pneumatic control of the TRACE 1610 GC and the sample path inertness of the TriPlus 500 HS ensured reliable and reproducible analyte transfer to the column, offering outstanding repeatability and precision for everyday analysis of residual NMP, with absolute peak area %RSDs (n=6) of 1.02 in n=6 samples spiked 10 µg/g.
- Efficient purging of the pneumatic circuit of the TriPlus 500 HS and uniform heating of the sample path prevents the risk of carryover of high boilers. No NMP could be detected when analyzing a blank after the highest standard.
- Chromeleon CDS (compliant with the FDA Title 21 CFR part 11 requirements) ensures data integrity, traceability, and effective data management, allowing for easy and fast data processing, quantitation, and reporting.

References

1. Liu, Y.; Zhang, R.; Wang, J.; Wang, Y. Current and future lithium-ion battery manufacturing, *iScience* 23 April **2021**, *24*(4), 102332. https://www.sciencedirect.com/science/article/pii/S258900422100300X
2. Kolb, B.; Ettre, l. Static headspace-gas chromatography Theory and Practice, Second Edition Wiley, **2006**.
3. Unites States Environmental Protection Agency, Green Chemistry. https://www.epa.gov/greenchemistry#:~:text=Green%20chemistry%20is%20the%20design,innovation%20and%20a%20strengthened%20economy
4. Thermo Fisher Scientific, Chromeleon CDS Enterprise—Compliance, Connectivity, Confidence, BR72617-EN0718S. https://assets.thermofisher.com/TFS-Assets/CMD/brochures/br-72617-chromeleon-cds-enterprise-br72617-en.pdf

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