Application Note

Materials Testing & Research

Purity Analysis of N-Methyl Pyrrolidone (NMP) Using an Agilent 8850 GC

Author

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Abstract

This application note describes a method for the analysis of N-methyl pyrrolidone (NMP). Commercial and customer samples were analyzed on the small-footprint Agilent 8850 GC using an Agilent J&W DB-23 capillary column to assess solvent purity of NMP. The J&W DB-23 separation revealed additional minor impurities when compared to other column chemistries, providing critical data for characterizing production or batch trends. Precision statistics for 10 replicates of each sample ranged from 0.5 to 4% RSD in NMP solvent area using the 8850 GC with an Agilent 7650A automatic liquid sampler (ALS), and calculated purities were within ± 0.22% of sample certification.

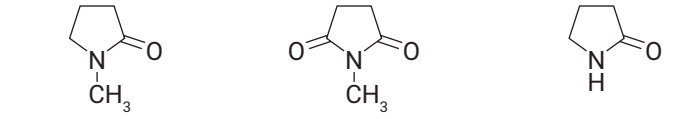
Introduction

Analysis of organic solvents to determine purity is a ubiquitous laboratory task that is well suited for gas chromatography (GC). Purity testing is an important part of process monitoring and provides key quality metrics for both feedstocks and products, as well as insights into process conditions by monitoring intermediate streams. The highly used solvent NMP is critical in many industries, including semiconductors, coatings and adhesives, and pharmaceuticals. The role of NMP in the manufacturing process of lithium-ion batteries (LiB) is of particular interest.

Within the LiB market, NMP is analyzed at both gross and residual levels. NMP as a bulk solvent must be screened for impurities that may affect performance in the battery electrodes. High-purity NMP is employed in creating the slurry applied to the LiB electrodes.[1] NMP dissolves the polymer binder to apply the slurry to the aluminum foils, resulting in a functional LiB cathode. Once that application is complete, the residual NMP is removed, usually by drying the product. Two quantitation approaches to determine residual NMP on electrodes have been evaluated in recent publications.[2,3] To complement the detection of low-level NMP, this work will address the purity of NMP as a starting material.

NMP is a highly polar, aprotic solvent with a relatively high boiling point of more than 200 °C. The pure solvent has an alkaline pH of approximately 10, and has a low vapor pressure and high flash point, which lend to its success in manufacturing environments. These characteristics also make NMP more challenging than volatile solvents when performing routine solvent purity analysis on GC systems. Solvents with lower volatility and higher viscosity require more frequent maintenance of both the GC inlet and the autosampler to manage carryover and repeatability quality checks.

The two most common impurities associated with NMP are N-methyl succinimide (NMS) and 2-pyrrolidinone (2PYR), shown in Figure 1. As there are similarities in both structure and properties among the three compounds, a robust purity analysis using an 8850 GC can be achieved by combining appropriate column selection, GC oven temperature control, and inlet pressure control. While this would be more simply executed if all compounds were present at the same level, the expectation of a solvent purity method is that it can perform well for both the highest and lowest concentration in the mixture.



N-Methyl pyrrolidinone
CAS number 872-50-4

N-Methyl succinimide
CAS number 1121-07-9

2-Pyrrolidinone
CAS number 616-45-5

Figure 1. Structures and Chemical Abstracts Service (CAS) numbers of N-methyl pyrrolidinone (NMP), N-methyl succinimide (NMS), and 2-pyrrolidinone (2PYR).

Experimental

All data were generated on an 8850 GC with a split/splitless (S/SL) inlet and flame ionization detector (FID). Samples were introduced to the GC inlet using a 7650 ALS. Agilent OpenLab CDS software, version 2.7, was used for data acquisition and analysis. The GC flow path is shown in Figure 2, and the method conditions are provided in Table 1. NMP samples were sourced from both a commercial vendor and a customer production facility, summarized in Table 2.

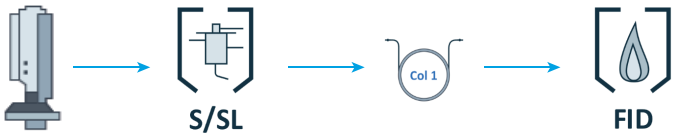


Figure 2. Agilent 8850 GC flow path.

Table 1. Instrument acquisition parameters and consumables.

Parameter	Value
Liquid Autosampler	1 µL injection
Inlet (S/SL)	230°C Split, 100:1 Gas saver 20 mL/min at 2 min Septum purge 5 mL/min
Column Flow	2.5 mL/min (He)
Oven (120 V, Slow)	45 °C, hold 0.5 min Ramp 8 °C/min to 155 °C, hold 1 min Ramp 30 °C/min to 230 °C, hold 5 min
FID	275 °C Air 400 mL/min H_2 30 mL/min Make-up gas (N_2) 25 mL/min
GC Run Time	22.75 min

Consumable	Description
Syringe	10 µL Agilent ALS syringe, Blue Line, PFTE-tip plunger (p/n G4513-80203)
Liner	Agilent inlet liner, low pressure drop with wool (p/n 5183-4647)
Column	Agilent J&W DB-23, 30 m × 320 µm, 0.5 µm (p/n 123-2332E)
Single-Component Material	NMS (≥ 99%), 2PYR (99%), Sigma-Aldrich

Table 2. NMP solvent sample details.

Source	Description
Sigma-Aldrich	NMP, 99.7+%, purchased 2019
Sigma-Aldrich	NMP, 99+%, purchased 2019
Sigma-Aldrich	NMP, 99+%, purchased 2024
Customer Sample	Sample A, 99.8+%, GC Analysis
Customer Sample	Sample B, 99.70+%, GC Analysis
Customer sample	Sample C, 99.7+%, GC Analysis

Results and discussion

The separation study evaluated several columns, and the following criteria were considered: void time, peak shape, baseline consistency, and operating temperature range. While NMP, NMS, and 2PYR all have boiling points exceeding 200 °C, they also have favorable vapor pressures to consider higher polarity columns with lower maximum operating temperatures. Single-component standards were prepared at 0.1% (w/v) from neat NMS (≥ 99%) and 2PYR (99%), both from Sigma-Aldrich (Milwaukee, WI, U.S.) to verify compound identification and retention time.

The evaluated column chemistries included polyethylene-glycol-based columns such as the Agilent DB-WAX Ultra Inert (UI) and Agilent J&W HP-INNOWax, cyanopropyl columns such as the Agilent J&W DB-624 and DB-23, and apolar columns such as the Agilent J&W DB-5. The data were most consistent and comprehensive with a 30 m × 320 µm, 0.5 µm DB-23. Most column selections eventually resulted in an adequate separation under optimized conditions, but the DB-23 was selected because the separation demonstrated less void time, better peak shape for NMS and 2PYR, and lower baseline bleed over time. Although both DB-624 and DB-WAX UI column chemistries are typically used to quantify residual NMP, the injections in this study contained NMP as the primary component of the injection, which impacts the separation. The unidentified impurity that eluted at 18 minutes under the conditions in Table 1 was used as a marker for the end of the GC run, as this compound was highly retained on some columns.

Figure 3 displays stacked runs of three commercially available NMP solvents. As shown in Table 2, a 99+% option was purchased at the beginning of this study and was used as a reference. The other two Sigma-Aldrich solvents were purchased five years ago and were used in this study to investigate the effect of time on the impurity profile. The presence of NMS is significantly more apparent in lower-purity and aged sources of solvent, indicating degradation in the bottle. Monitoring expected impurities generates valuable supplemental data for labs purchasing bulk quantities of NMP, highlighting the need for a separation process that fully resolves all known components.

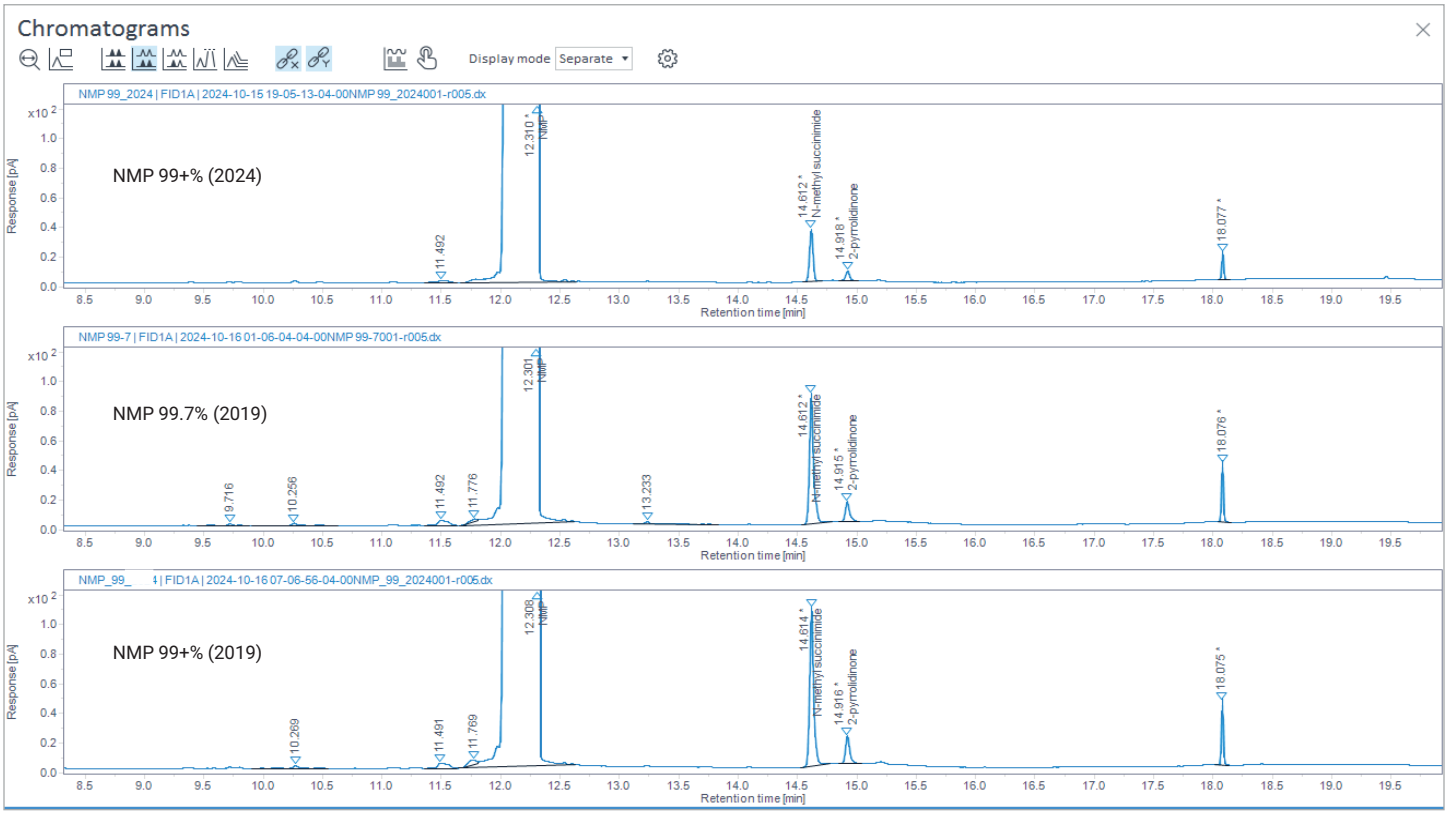
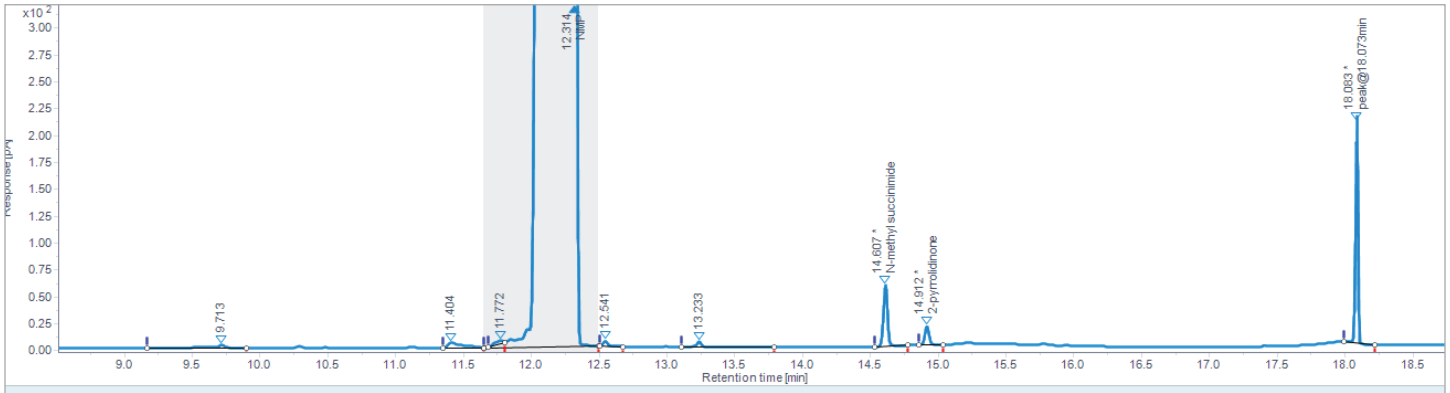


Figure 3. Normalized chromatograms of commercially available solvents, analyzed on an Agilent J&W DB-23 column.

After selecting the column and optimizing the GC parameters to separate expected impurities in commercially available solvents, customer samples were analyzed to compare the results with existing methodologies for NMP purity analysis. Three customer samples with established purity results were tested against the new conditions. These samples were each run in a replicate series of 10, and were statistically evaluated in the same manner as the commercial solvents. These results are also shown in Table 3. An example chromatogram of customer sample B is shown in Figure 4, along with software-calculated purities of each compound based on percent area. The most apparent difference between the commercially available samples and the customer samples is the abundance of the late-eluting peak. The customer samples show a significant increase in this compound compared to the commercial options. Overall, the DB-23 separation results in a lower NMP purity when compared to the reported result, indicating an improved separation. Integration thresholds and quantitation methods may also contribute to the small discrepancy. Identifying all impurity peaks was not within the scope of this work.



Injection Results

Peaks | Summary

#	Name	Signal description	RT (min) △	Area (pA·s)	Area%	Height (pA)	Height%	Amount	Concentration	Start time (min)	End time (min)
1		FID1A	9.713	15.919	0.013	3.006	0.02			9.167	9.902
2		FID1A	11.404	34.723	0.029	5.040	0.04			11.346	11.646
3		FID1A	11.772	14.117	0.012	2.921	0.02			11.684	11.804
4	NMP	FID1A	12.314	119314.347	99.579	12147.304	97.58			11.651	12.495
5		FID1A	12.541	11.137	0.009	4.762	0.04			12.500	12.672
6		FID1A	13.233	15.773	0.013	5.509	0.04			13.110	13.792
7	N-methyl succinimide	FID1A	14.607	119.780	0.100	56.868	0.46			14.532	14.773
8	2-pyrrolidinone	FID1A	14.912	38.272	0.032	17.313	0.14			14.856	15.034
9	peak@18.073min	FID1A	18.083	254.555	0.212	205.964	1.65			17.990	18.217

Figure 4. Agilent OpenLab CDS software screenshot of customer sample B with area percent purity.

Table 3. Calculated percent area results of NMP samples, as well as the three most prevalent impurities: NMS, 2PYR, and the unknown peak at 18 minutes. The NMP purity result for the method is highlighted in gray, and can be compared against the value in the column header.

	Sigma-Aldrich ACS Grade 2024 (99+%)	Sigma-Aldrich Biotech 2019 (99.7+%)	Sigma-Aldrich ACS Grade 2019 (99+%)	Customer Sample A (99.83%)	Customer Sample B (99.7%)	Customer Sample C (99.77%)
NMP						
RT %RSD	0.05%	0.05%	0.03%	0.03%	0.05%	0.03%
Area %RSD	3.49%	3.52%	2.11%	2.48%	3.95%	2.36%
% Composition	99.84	99.72	99.68	99.60	99.51	99.75
NMS						
RT %RSD	0.03%	0.01%	0.01%	0.00%	0.01%	0.00%
Area %RSD	15.80%	3.93%	4.06%	8.29%	7.83%	7.00%
% Composition	0.11	0.19	0.22	0.09	0.11	0.10
2PYR						
RT %RSD	0.03%	0.00%	0.01%	0.00%	0.00%	0.00%
Area %RSD	16.64%	4.29%	4.66%	5.95%	4.67%	8.00%
% Composition	0.02	0.03	0.04	0.03	0.04	0.02
Unknown						
RT %RSD	0.02%	0.00%	0.00%	0.00%	0.00%	0.07%
Area %RSD	28.30%	13.26%	10.23%	4.76%	5.71%	8.91%
% Composition	0.04	0.04	0.04	0.23	0.27	0.08

The OpenLab CDS software generates the percent composition calculations and does not consider response factors or other adjustments under default settings. These results are simply the percentage area compared to the total integrated area of all peaks in the chromatogram. Integration set points have a significant impact on the number of peaks, so these must be adjusted carefully to ensure that relevant data are captured and stored with the file.

The area precision results shown in Table 3 were certainly affected by the response of each individual compound. The impurities were expected to be much lower in response than NMP, but the lower responses were often accompanied by a higher variability across the series of runs. Precision was also found to be influenced by the autosampler wash program, specifically after injection. These compounds exhibit unacceptable carryover results when a minimal wash program was employed. The 7650 ALS used in this experiment has two wash locations and one waste location for each row of 25 vials.[4] The wash program used in this study included:

- Five pre-injection sample washes
- Four sample pumps
- A 1 µL injection of sample
- Four postinjection washes of both A and B wash vials, each containing acetone

The increased wash solvent use requires the user to empty waste and refill wash vials often to avoid contaminating the system. NMP will also affect the syringe lifetime, resulting in restricted movement or damage to the plunger. More washes significantly improve the syringe lifetime. The time to execute a longer wash program need not affect run-to-run timeliness negatively. Agilent autosamplers include a method feature to minimize the impact. Sample Overlap (Figure 5) is a set point that instructs the autosampler to begin preparing a sample at a prescribed time. In this case, the sample washes were programmed to occur at the end of the GC run, as washing the syringe five times with the sample took approximately the same amount of time as the oven cooldown. If no sample overlap is enabled, the autosampler will begin the wash program when the GC reaches Ready status. Sample Overlap is a useful and intuitive feature that can minimize the idle time of the GC between runs.

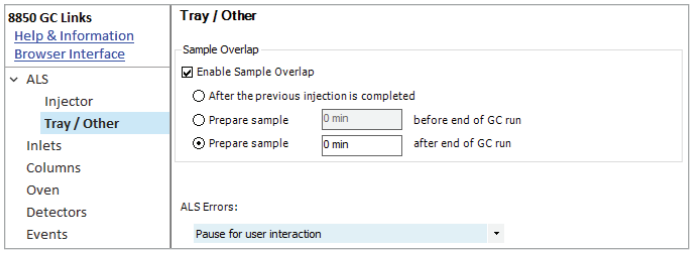


Figure 5. Screen capture of the Sample Overlap settings in Agilent OpenLab CDS 2.7 Method Editor.

Retention time precision results were exceptional, demonstrating that the 8850 GC is a high-performance instrument capable of producing reliable results. User-enabled GC features such as Peak Evaluation[5] and Early Maintenance Feedback trackers are embedded in the 8850 GC for convenience. Peak Evaluation tasks the GC with monitoring attributes such as retention time consistency or impurity presence. Under these customizable settings, the GC will alert the user if an injection produces an atypical result, effectively delegating workload tasks from the operator to the instrument. EMF trackers can be applied to alert the user when maintenance is due, or to review the frequency of maintenance on a specific system.

Conclusion

The Agilent 8850 GC, 7650 ALS, and J&W DB-23 column together deliver exceptional performance for separating common impurities in NMP solvent. With intelligent features such as Sample Overlap and Peak Evaluation, as well as a compact design that conserves lab space, the 8850 GC is essential for high-throughput labs requiring consistency in results. The DB-23 column's excellent separation capabilities, demonstrated through comparative analysis of customer samples, make it ideal for workflows seeking detailed impurity information alongside the overall solvent purity results.

References

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DE-004358

Printed in the USA, April 7, 2025
5994-8126EN

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