Gas Chromatography Nexis™ GC-2030

Application News

Analysis of battery electrolytes and N-methyl-2-pyrrolidone (NMP) via headspace GC-FID

R. Kelting [1], M. Moragues [2]
1 Shimadzu Europa GmbH, 2 Shimadzu France

User Benefits

- Analysis of battery electrolytes and N-methyl-2-pyrrolidone (NMP) without tedious sample preparation using HS-20NX
- Automatic switching of the carrier gas type for full flexibility and gas consumption control can be realized using the gas selector for Nexis GC-2030

Introduction

The increasing demand for electronic portable devices and electronic vehicles makes production and performance monitoring of batteries a major task these days. Lithium-ion battery electrodes are created using dispersions, so-called slurry compositions, which consist of the active material for the electrode and other ingredients such as binders and conductive agents [1]. The solvent widely used for basic slurry compositions is N-methyl-2-pyrrolidone (NMP), as this dissolves polyvinylidene fluoride (PVDF), the most frequently utilized binder in the cathode slurry formulation [1,2]. The lithium-ion battery itself does not contain NMP as it is recovered from the exhaust gases and re-used [3].

Consequently, the degree of purity of NMP and the absence of it in the battery electrolyte is important to produce a high-performance battery. Additionally, knowing the general composition of the electrolyte is essential to improve ion transport and monitor the related battery life. The analysis of battery electrolytes regarding their composition and NMP content as well as purity testing of 2-methyl-2-pyrrolidone via headspace GC-FID are presented.

Measurement Conditions and Samples

The headspace approach allows for direct use of various samples, eliminating the need for tedious sample preparation. For purity testing of N-methyl-2-pyrrolidone (NMP) 5 µL of the solution were put into a 20 mL headspace vial, whereas for trace determination of NMP in the electrolyte 20 µL of the electrolyte solution were added to the vial. To quantify potentially found NMP in the electrolyte, a 5-point calibration curve of NMP standard solution in the range of 14 to 342 mg/L was created. For analysis of the major volatile compounds in the electrolyte, 1µL of the electrolyte solution was placed in the vial. The analyses was carried out using Nexis GC-2030 equipped with HS-20 NX headspace sampler and FID-2030 flame ionization detector (Fig. 1).

Fig. 1 Nexis™ GC-2030 equipped with FID-2030 detector and HS-20 NX autosampler

Results

The investigation of N-Methyl-2-pyrrolidone revealed four impurity peaks (Fig. 2) in the quantities summed up in table 1. The NMP purity was determined to be 99.82 %.

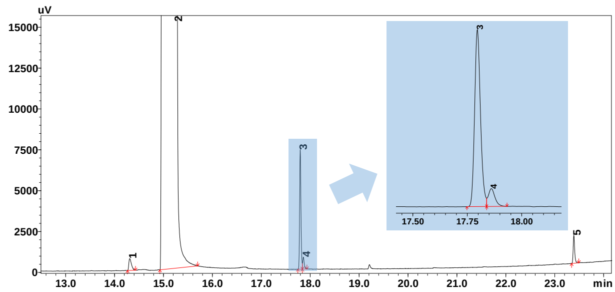

Fig. 2 Chromatogram of N-methyl-2-pyrrolidone (NMP) solution for purity testing

Table 1 Quantification of the impurities in NMP

Peak #	Ret. Time (min)	Area	Area %
1	14.31	2685	0.02
2 (NMP)	15.25	12173851	99.82
3	17.80	13681	0.11
4	17.86	1546	0.01
5	23.39	3671	0.03
Total		12195433	100

Four major volatile compounds were found in the electrolyte solution analyzed (Fig 3). The quantification results based on area% of the respective component are summarized in table 2. Reproducibility of the analysis gave %RSD values below 2.4 for all four compounds (n=5).

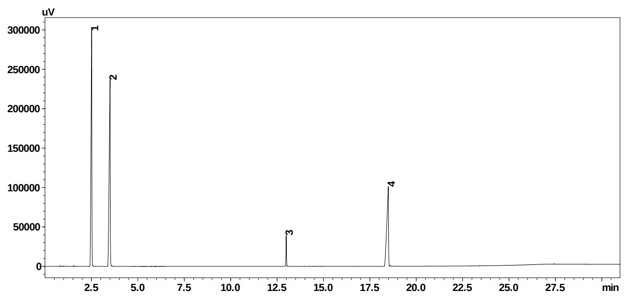

Fig. 3 Chromatogram of volatile compounds in electrolyte solution

Table 2 Quantification of the major volatile compounds in the electrolyte

Peak #	Ret. Time (min)	Area	Area %
1	2.50	842982	36.89
2	3.49	801013	35.05
3	12.99	60980	2.67
4	18.48	580471	25.40
Total		2285446	100

The 5-point calibration curve created to quantify trace levels of NMP in the electrolyte showed very good linearity (Fig. 4).

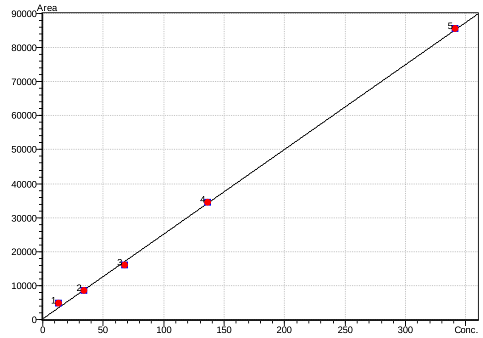

Fig. 4 Calibration curve of NMP standard solution

A carryover test performed after the injection of a NMP standard solution at a concentration of 650 mg/L revealed perfect inertness of the system with a negligible carryover of 0.01% (Fig. 5).

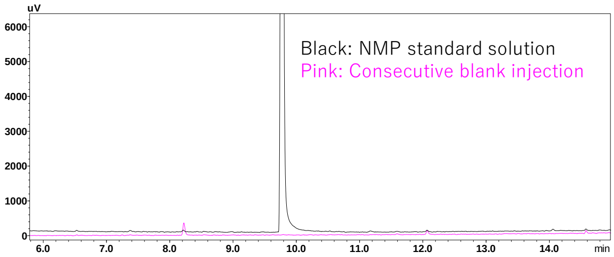

Fig. 5 Chromatogram comparison of NMP standard solution at 650 mg/L and consecutive blank injection

The analysis of an electrolyte real sample showed a negligible NMP amount present (Fig. 6).

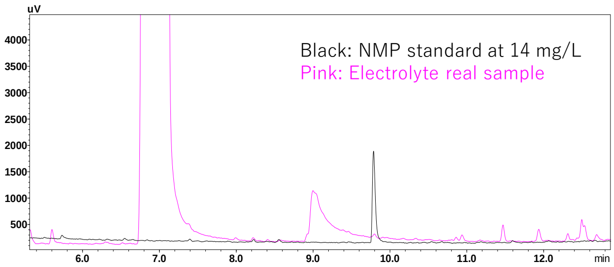

Fig. 6 Chromatogram comparison of NMP standard solution at 14 mg/L and the electrolyte real sample

■ Conclusion

The Nexis GC-2030 coupled to a HS-20NX headspace sampler offers a suitable solution for the analysis of battery electrolytes, both at the level of major compounds quantification and for the search for traces of contamination in the electrolyte solution. Additionally, it allows for purity testing of the NMP used during electrode production, offering full flexibility for various analyses, thanks to its ease of implementation and the absence of sample preparation.

■ References

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[3] Recharge, Eurobat, ”Recommendation about n-methyl-pyrrolidone (NMP; CAS no. 872-50-4) proposal for inclusion in Annex XIV for authorization,”, Position Paper, May 2017. Available: [2017-05-24-RECHARGE-position-NMP.pdf (rechargebatteries.org)]

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