Application News

GCMS-QP™2020 NX, HS-20 NX

Analysis of Volatile Compounds in Recycled Lithium-Ion Battery Material using HS-GCMS

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User Benefits

- Simple screening of volatile compounds in black mass (recycled lithium-ion battery material)
- User-friendly monitoring of the quality of black mass recycling
- Reliable quantitative analysis of remaining organic carbonates in black mass

Introduction

Organic carbonates play a significant role in the recycling of lithium batteries, particularly in the recovery of valuable materials such as lithium, cobalt, and nickel. These compounds are commonly used as solvents in the electrolytes of lithium-ion batteries. When batteries reach the end of their life cycle, the recycling process aims to extract these organic carbonates alongside other critical metals.

The recycling of lithium batteries involves several stages, including disassembly, shredding, and chemical processing. During these stages, organic carbonates can be recovered and purified for reuse in new battery production or other applications. This not only reduces waste but also minimizes the environmental impact associated with the extraction of raw materials.

By integrating these compounds into the recycling workflow, companies can improve the general recovery rates of LIB materials, ensuring that valuable resources are not lost. Within this application a method utilizing a Shimadzu GCMS-QP2020 NX + HS-20 NX is presented to demonstrate the potential of this technology for the quantitation of the remaining carbonates and the screening of black mass material in general.

Sample preparation and measurement

Approximately 5 mg of each sample was placed in 20 ml headspace vial. This sample can be directly used for the HS-GCMS analysis. For the quantitative analysis stock solutions of ethylene carbonate (181 mg/ml) and propylene carbonate (240 mg/ml) in acetonitrile were prepared. The standard addition was done by addition of 20 µl, 40 µl, 60 µl and 80 µl of a stock solution containing 5 mg/mL of EC and PC.

Method details

A Shimadzu GCMS-QP2020 NX with headspace sampler HS-20 NX was used for the analysis of black mass (Figure 1).

Figure 1 Shimadzu GCMS-QP2020 NX with HS-20 NX

The Package

The recommended analytical hardware and software configuration is listed below.

❑ *Main Unit*

Nexis GC-2030 with QP2020 NX: Gas chromatograph plus mass spectrometer detector

❑ *Accessory*

HS-20 NX sampler: headspace autosampler with 90 vials capacity

❑ *Main Consumables*

SH-I-5MS, 30m × 0.25mm × 0.25µm; P/N 221-75940-30

❑ *Software*

GCMSSolution and GCMS Insight Software

Results and Discussion

Qualitative Screening

The obtained results of black mass analysis with Shimadzu GCMS-QP2020 NX + HS-20 NX are shown in the Figure 2.

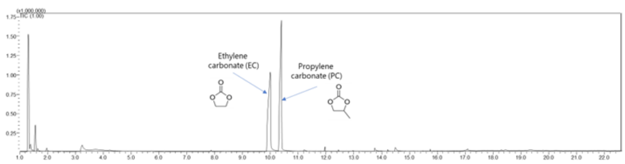

Figure 2 Chromatogram of a black mass sample

The two dominating peaks in the chromatogram could be identified as ethylene carbonate (EC) and propylene carbonate (PC). Both compounds are quite typical for the LIB electrolyte, whereas EC is present nearly in all electrolytes, PC may be replaced by other carbonates and their mixtures. In black mass samples, it is not surprising to see a mixture of carbonates which are not typically found in any individual LIB but originate instead from the mixture of different LIBs during the recycling process. In the presented case only EC and PC could be detected. As black mass includes electrolytes from aged LIBs, a huge variety of different destruction/reaction byproducts and diverse additives can be observed, as shown in the zoomed chromatogram in Figure 3.

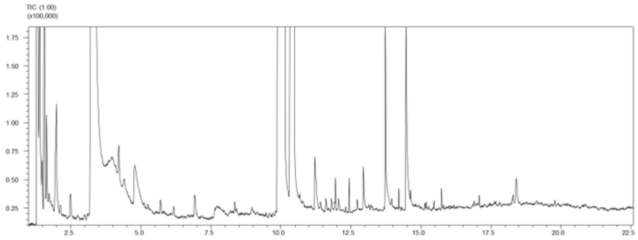

Figure 3 Zoomed in chromatogram of the black mass sample shown in Fig. 2

The composition of black mass is generally more complex than that of lithium-ion battery (LIB) electrolytes, as it consists of a mixture of various electrolyte types and the recycling processes can lead to the formation of additional byproducts. A significant challenge in identifying these compounds lies in the fact that similarity searches often yield unreliable results due to the low amounts present and that available libraries on the market do not include most of these substances. In contrast to the unpredictable nature of the byproducts found in black mass samples, the additives used in LIBs are typically consistent, allowing for a more reliable identification.

In the analyzed sample, four different additives were clearly identified: gamma-butyrolactone, delta-valerolactone, 1-methylpyrrolidinone, and tert-amylbenzene. The first two additives were present only in trace amounts, thus filtering the selective m/z was needed for a clear identification. The latter two were clearly visible in the TIC. The resulting spectra of these compounds and their corresponding extracted ion chromatograms are shown in Figure 5.

■ Quantitative analysis of the remaining carbonates

The content of the remaining organic carbonates in black mass is important for evaluating the effectiveness of the recycling process and determining the purity of the final recycled product for its potential reuse. Within this application a standard addition using carbonate standards was carried out. The calibration curve is shown in the Figure 4 and the quantitative results in the Table 1.

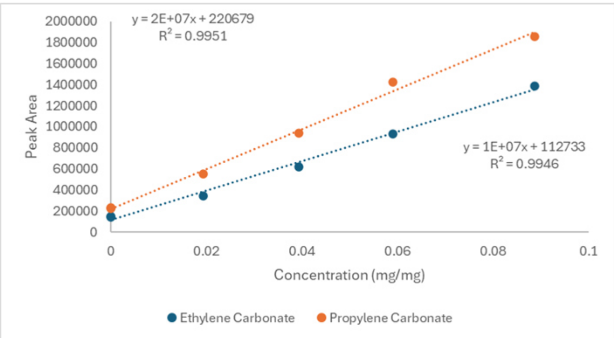

Figure 4 Calibration curves for organic carbonates

Table 1 Quantitative results for organic carbonates

Component	Conc. as w% in black mass
EC (Ethylene carbonate)	1.1 %
PC (Propylene carbonate)	1.2 %

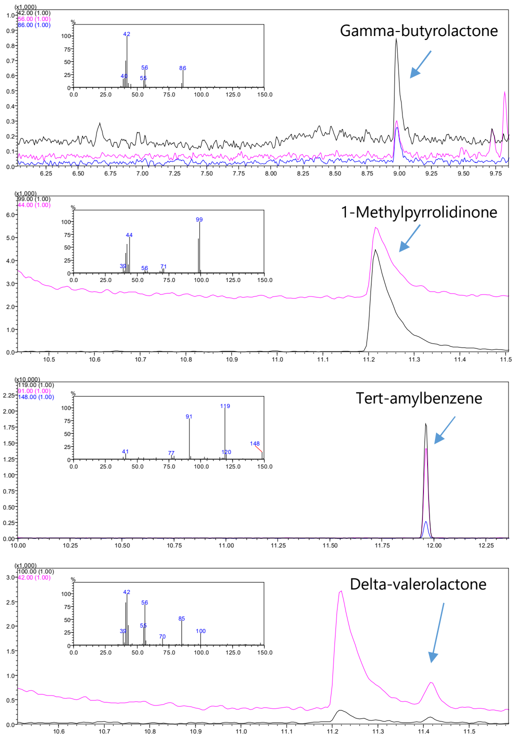

Figure 5 The obtained spectra and extracted ion chromatograms for gamma butyrolactone, 1-methylpyrrolidinone, tert-amylbenzene and delta-valerolactone

■ Conclusion

This application demonstrated the suitability of the Shimadzu GCMS-QP2020 NX + HS-20 NX to analyze remaining organic carbonates and additives in black mass samples. This technology facilitates the optimization of the recycling conditions and enables the assessment of the recycling process effectiveness. The new regulation for LIB recycling in Europe (EU) 2023/1542 [1] demands very high recovery rates for the battery interior materials, and the GCMS-QP2020 NX + HS-20 NX can support the establishment of the highest standards in LIB recycling processes.

■ Literature

[1] Regulation (EU) 2023/1542 of the European Parliament and of the Council of 12 July 2023 concerning batteries and waste batteries, amending Directive 2008/98/EC and Regulation (EU) 2019/1020 and repealing Directive 2006/66/EC.
http://data.europa.eu/eli/reg/2023/1542/oj

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