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Energy

Pyrolysis gas chromatography - high resolution Orbitrap mass spectrometry as a tool for Li-ion battery shred material forensics

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Keywords

Pyrolysis gas chromatography, lithium-ion battery shred material, high resolution mass spectrometry, Orbitrap, organic binders, fingerprinting

Goal

The goal of this application note is to demonstrate the identification of organic binders in lithium-ion battery shred material using pyrolysis as a sample introduction technique together with high mass resolution analysis with the Thermo Scientific™ Orbitrap Exploris™ GC 240 mass spectrometer.

Introduction

The invention of the lithium-ion battery (LIB) has had an unprecedented impact on our society, leading to the development of powerful and versatile portable electronics (e.g., smart phones, laptop computers). However, with the exponential increase in demand for LIBs to drive electrification of the automotive sector, greater stress is being placed on the finite resources of metals. Thus, recycling of LIB material will be critical to maintain the supply of essential minerals while reducing both economic and environmental costs associated with battery production.

Due to the complexity of LIBs, efficient separation of the various components is critical to maximize recovery of essential metals needed for battery production. This is of particular importance for organic binders, as their presence in LIB shred material can reduce the extraction efficiency of essential metal components during the recycling process.[1] This highlights the need for binder identification in LIB material to optimize recycling processing.

The complexity of the aged electrode matrix in which the binders are present requires selective separation and detection techniques for accurate identification. The combination of pyrolysis (Py) with gas chromatography-mass spectrometry (GC-MS) facilitates polymer analysis by overcoming the limitations of high molecular mass and low volatility while allowing for direct material analysis without pretreatment. Compositions of polymers can be thermally decomposed with subsequent analysis of their fragments by Py-GC-MS to provide reproducible chromatograms (pyrograms) as a recognizable fingerprint.[2,3]

In this study, the high selectivity of the Orbitrap Exploris GC 240 mass spectrometer in combination with pyrolysis gas chromatography is demonstrated for the direct analysis of LIB shred material for organic binder identification. Minimal sample material was needed due to the high selectivity and sensitivity of the Orbitrap Exploris GC 240 mass spectrometer, helping instrument performance remain robust during repetitive analyses. Specific binder marker molecules could be easily identified with the high selectivity of the instrument, enabling reliable binder identification.

Experimental

Standard and sample preparation

A small mass of industrially produced LIB recycling shred (approximately 0.3–0.5 mg) was measured and used without any further pretreatment. Reference standard materials of polyvinylidene fluoride (PVDF, Kureha, Japan) and styrene butadiene (SBR, Synthomer, United Kingdom) were measured as standard reference materials for binder identification.

Instrument and method setup

Analysis was carried out using an Orbitrap Exploris GC 240 mass spectrometer coupled to a Thermo Scientific™ TRACE™ 1610 gas chromatograph, fitted with a Thermo Scientific™ TraceGOLD™ TG-5SilMS 30 m × 0.25 mm i.d. × 0.25 µm film capillary column with 5 m SafeGuard (P/N 26096-1425). A Thermo Scientific™ iConnect™ split splitless (SSL) injector module was equipped with an adapter for gas injection (P/N 19050733) to perform direct sample injection using the Frontier Laboratories™ Multi-Shot Pyrolyzer™ (EGA/PY-3030D) with Auto-Shot Sampler™ (EGA/PY-3030D). Double shot analysis at 200 °C and 600 °C was performed. The thermal desorption step at 200 °C performs an initial pretreatment step by removing residual electrolyte components and decomposition products to help simplify the chromatographic data for binder identification at 600 °C. Information on electrolyte/decomposition products was also collected during the initial thermal desorption step but will not be further discussed as the focus of this application was on binder identification. Injection and chromatographic separation parameters are given in Table 1.

Table 1. Pyrolysis and GC injection parameters and separation conditions for battery shred material analysis

Multi-Shot Pyrolyzer parameters	
Analysis type	Double shot analysis
First desorption temperature (°C)	200 °C
First desorption time (min)	0.2
Pyrolysis temperature (°C)	600
Pyrolysis time (min)	0.2
Interface temperature (°C)	300
TRACE 1610 GC parameters	
Injector type	SSL with gas injection adapter
Injection mode	Split
Injection temperature (°C)	300
Split ratio	200
Carrier gas (mL·min^{-1})	He (1.0)
Oven temperature program	
Initial temperature (°C)	40
Hold time (min)	2
Heating rate (°C/min)	20
Final temperature (°C)	320
Hold time (min)	5

Data acquisition was performed initially using electron impact (EI) followed by positive chemical ionization (PCI) for molecular ion confirmation and structural elucidation. Initial EI analysis was performed in full scan mode at a mass resolution of 60,000 (Full width at half maximum (FWHM) at *m/z* 200) using selected column bleed ions for internal calibration purposes.

Additional details of the MS scan parameters are displayed in Table 2.

Table 2. Mass spectrometer parameters for EI and PCI analysis

Orbitrap Exploris GC 240 MS parameters	
EI analysis	
Transfer line temp. (°C)	300
Thermo Scientific™ ExtractaBrite™ ion source temp. (°C)	200
Electron energy (eV)	70
Acquisition mode	Full scan
Mass range (*m/z*)	30–500
Resolving power	60,000
Lock masses for internal calibration	133.01356; 207.03235; 225.04292; 281.05114; 299.06171; 355.06993
PCI analysis	
Transfer line temp. (°C)	300
ExtractaBrite ion source temp. (°C)	180
Reagent gas (mL·min^{-1})	Methane (1.0)
Acquisition mode	Full scan
Full scan mass resolution	60,000
Full scan mass range (*m/z*)	30–500

Results and discussion

Identification of binder pyrolysis products

The various binders, electrolyte residues, and electrolyte decomposition products present in shredded LIB material create a complex sample matrix for investigation with pyrolysis, as thermal degradation produces a broad variety of pyrolyzates. A quick and simple identification of PVDF from such a complex LIB shred sample is demonstrated by using the selectivity of the Orbitrap Exploris GC 240 mass spectrometer. PVDF decomposes to a variety of pyrolyzates, including fluoroalkenes with various chain lengths under temperature conditions for pyrolysis (Table 1).[2,3] Within the MS source, fluoroalkenes undergo in-source fragmentation to produce specific molecular markers, such as 1, 1, 3, 3-tetrafluroallylium ($C_3HF_4^+$, *m/z* 113.0009). Figure 1 shows the extracted ion chromatogram (EIC) of $C_3HF_4^+$ at a mass accuracy of 500 milli mass units (mmu, unit mass resolution) and 5 ppm (60,000 mass resolution) in LIB shred material with comparison to a PVDF reference standard using electron impact ionization.

An immediate noticeable difference between the EICs in Figure 1 is the elevated baseline observed between 1.25 to 5 minutes using a mass accuracy of 500 mmu. However, this isobaric interference from the sample matrix was easily filtered away at higher mass resolution (60,000) and accuracy (5 ppm) settings. This highlights the selectivity advantage of high resolution accurate mass, where such interferences can be easily filtered, simplifying fingerprint matching of binder materials. Another advantage is less sample material is required due to the enhanced sensitivity gained by the Orbitrap Exploris GC 240 mass spectrometer. As hydrofluoric acid (HF) is produced during pyrolysis of PVDF-containing material, using less sample material will result in less HF being introduced into the GC system, helping to minimize GC maintenance and maximize analysis robustness.

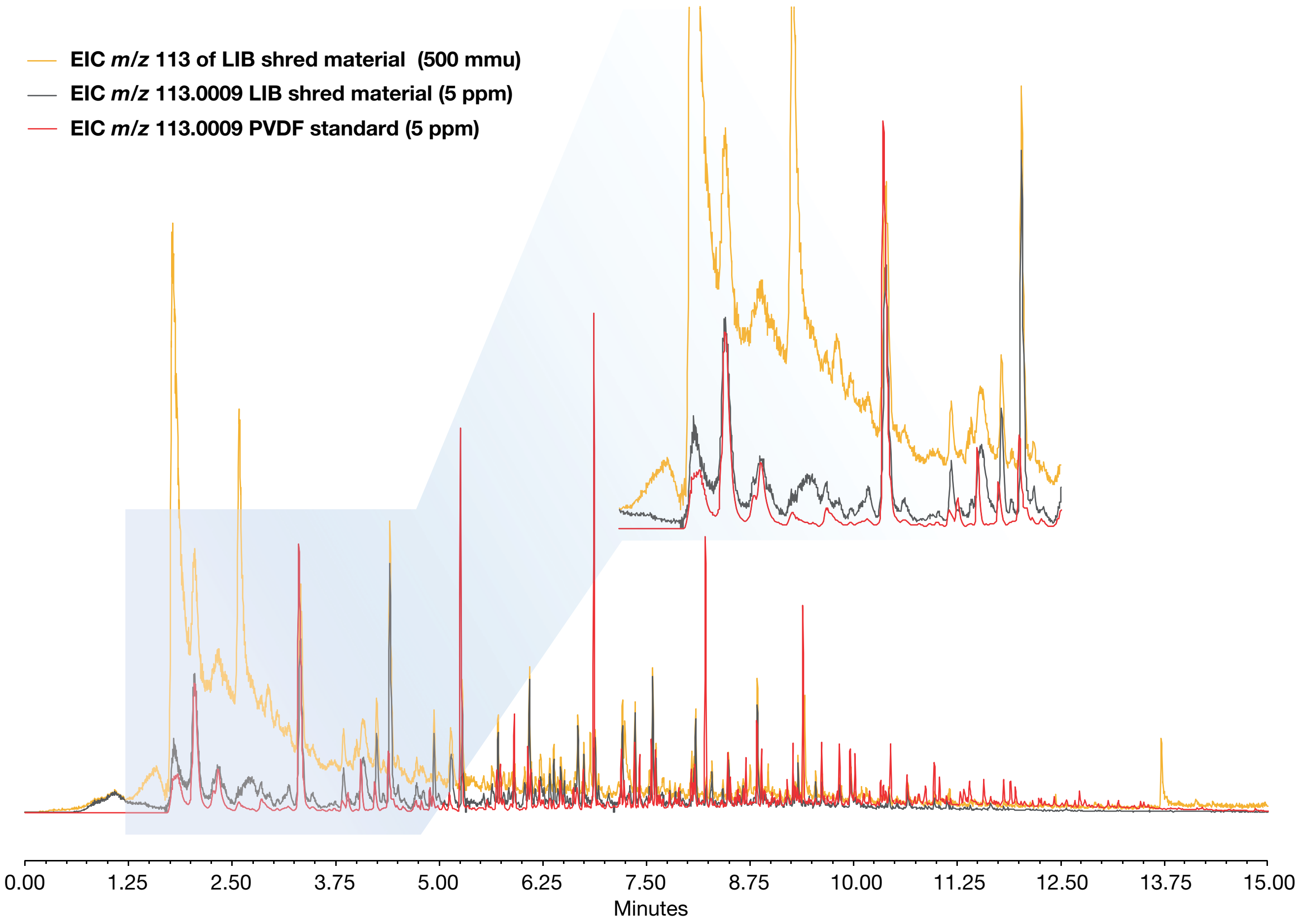

Figure 1. The extracted ion chromatograms (EIC) of $C_3HF_4^+$ at a mass accuracy of 500 mmu and at 5 ppm in LIB shred material and of the PVDF reference standard with electron impact ionization

Depending on the complexity of the sample matrices, analysis in PCI mode can offer advantages in fingerprint identification due to its softer ionization. The source exchange from EI to CI is performed without breaking vacuum and the system is operational within minutes using the vacuum probe interlock (Thermo Scientific™ NeverVent™ technology). Figure 2 shows the TIC and EIC of $C_3HF_4^+$ (*m/z* 113.0009) in the same LIB shred material shown in Figure 1 using PCI mode. Similarities between the EIC of $C_3HF_4^+$ between the LIB shred material and the PVDF reference standard using PCI confirm the presence of PVDF. Additional information regarding the molecular ion (M^+) of the various fluoroalkenes detected can also be obtained compared to analysis in EI where severe fragmentation of the fluoroalkenes occurs (Figure 3). Although this is not useful for binder identification, such information can be beneficial for material research, where insight into binder degradation during battery cycling is important for future material development.

Several binders may be incorporated into electrode materials to improve their stability and performance. Styrene butadiene rubber (SBR) provides flexibility and high thermal resistance to the polymeric matrix while offering higher binding affinity compared to PVDF.[4] Pyrolysis of SBR produces a reproducible fingerprint characterized by aromatic compounds (i.e., benzene, toluene, styrene). Although such compounds can be easily identified using low mass resolution quadrupole instruments, the selectivity provided by high-resolution techniques helps simplify identification. Figure 4 displays the EIC of the toluene from the same LIB shred material at both 500 mmu and 5 ppm mass accuracy settings.

Using just visual inspection, the extracted exact mass of toluene (*m/z* 92.0621) from the LIB shred at 5 ppm mass accuracy displayed a more simplified pyrogram compared to unit mass (*m/z* 92) observed with unit mass resolution (500 mmu). Additional peaks observed at unit mass resolution acquisition indicate isobaric interference, making fingerprint identification not intuitive. This highlights the advantage of high mass resolution selectivity for fast and accurate binder identification.

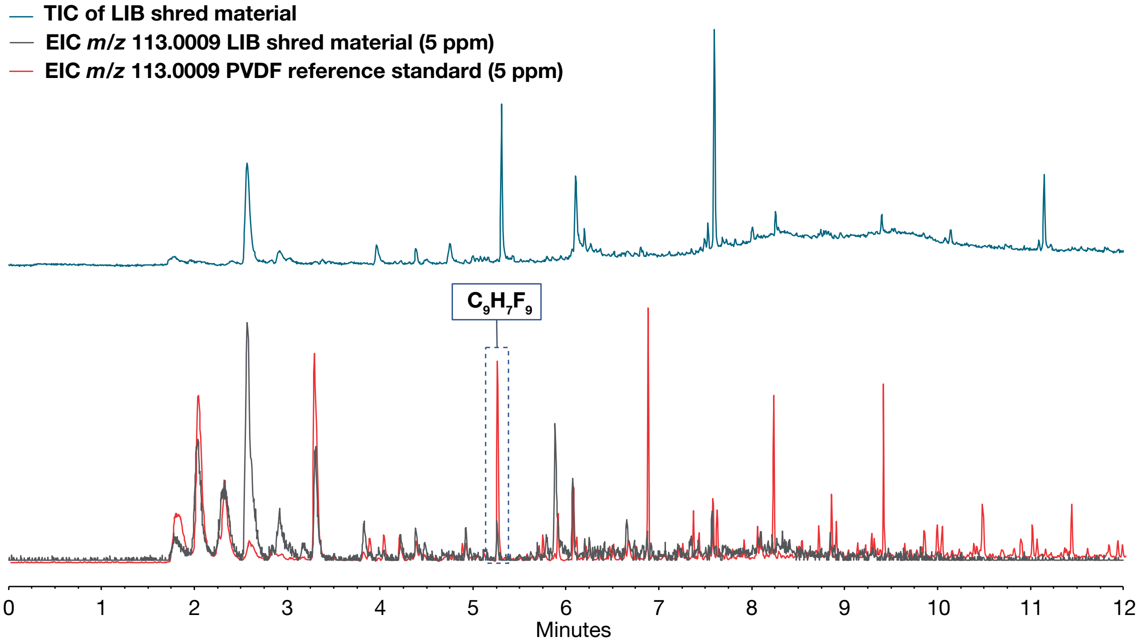

Figure 2. Comparison of TIC and EIC of $C_3HF_4^+$ in LIB shred material and PVDF reference standard using positive chemical ionization

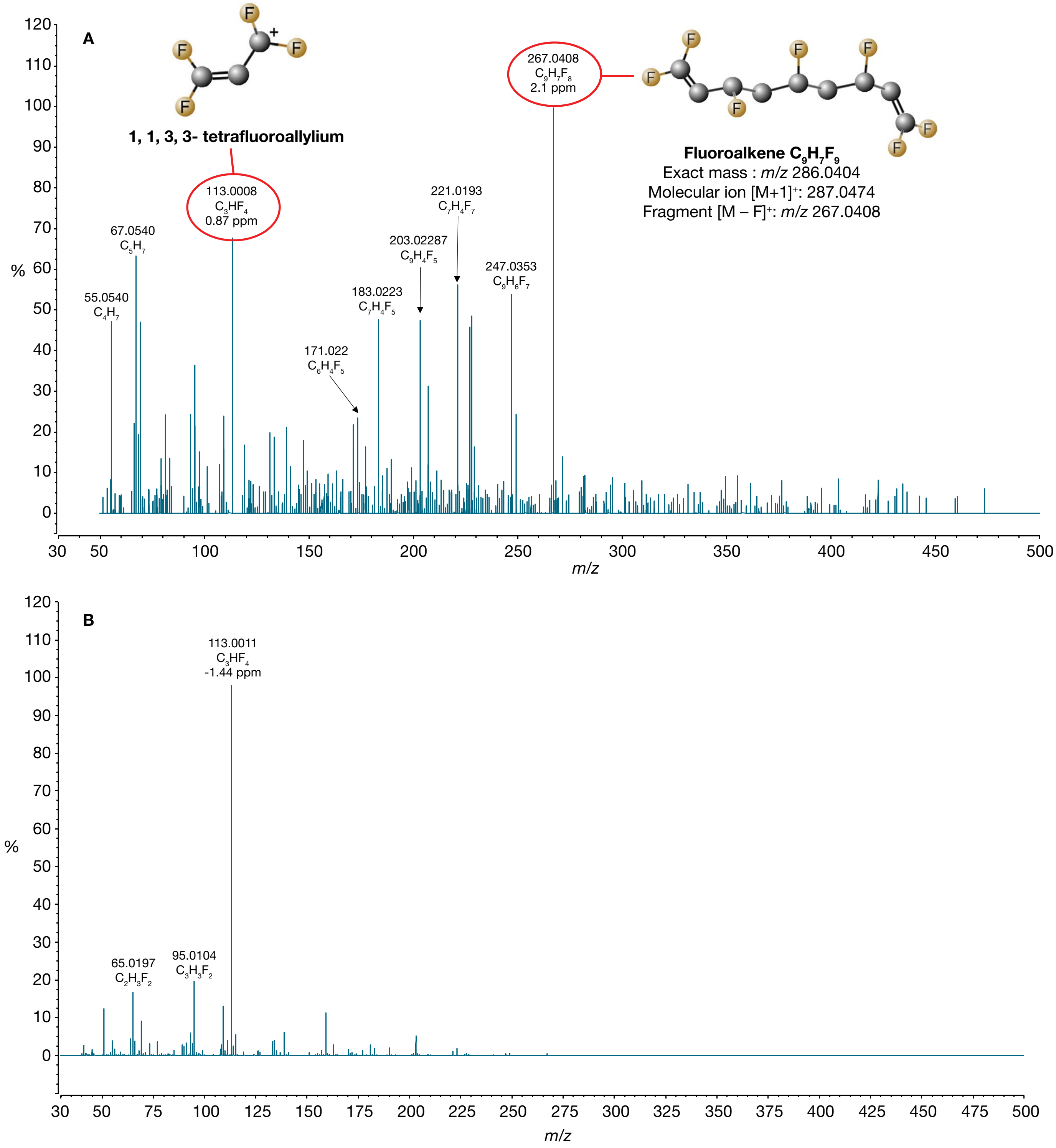

Figure 3. PCI mass spectrum (A) and EI mass spectrum (B) of fluoroalkene $C_9H_7F_9$ detected at 5.24 min in LIB shred material. Mass accuracy for both $C_9H_7F_9$ and C_3HF_4 ions displayed are obtained at high mass resolution settings.

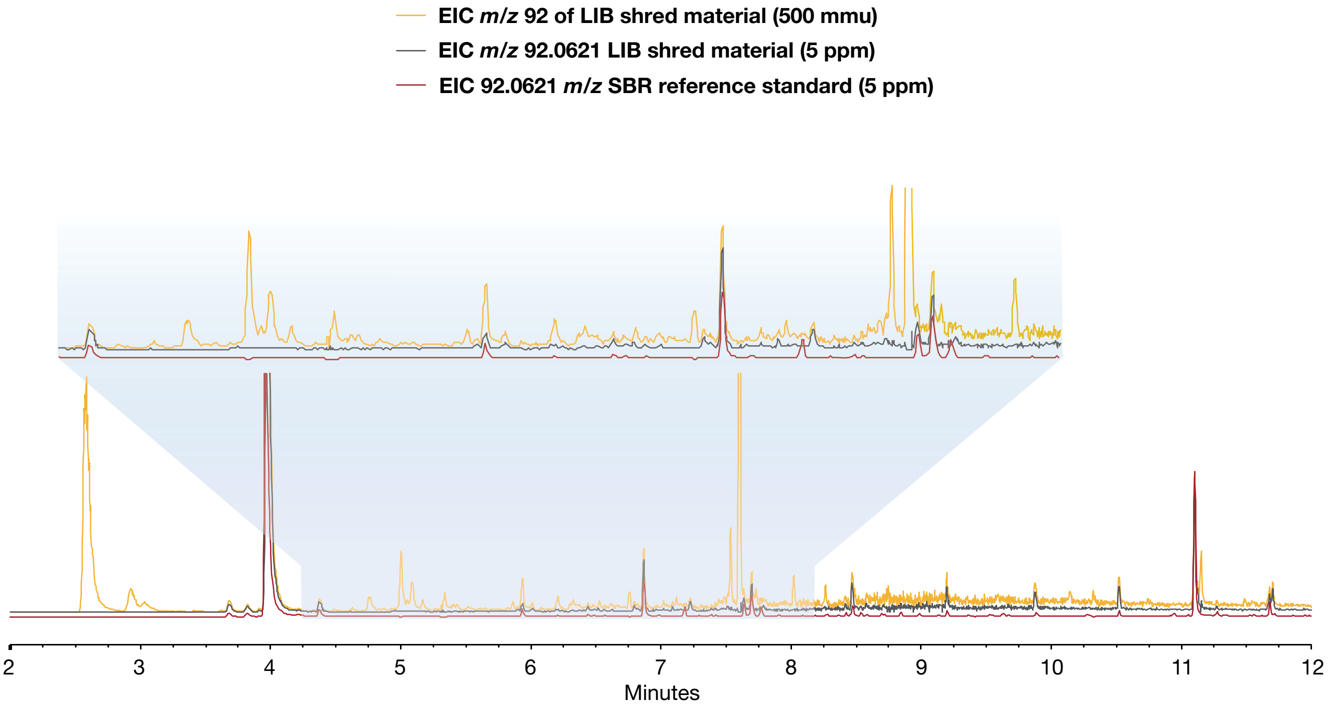

Figure 4. Extracted ion chromatogram of toluene in LIB shred material at 500 mmu and 5 ppm mass accuracy and SBR reference standard

Conclusion

This application note demonstrates the advantage of using the high mass resolution and accuracy power of the Orbitrap Exploris GC 240 system for fast and accurate binder identification.

- Direct sample introduction of LIB shred material using pyrolysis to overcome challenges in sample matrix volatility
- Rapid switching between EI and CI ionization techniques with NeverVent technology for binder identification and degradation mechanisms
- Fingerprint matching of binder materials in LIB shred material facilitated by selective removal of isobaric interferences/distortions at sub ppm mass accuracy

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