Untargeted screening and identification of substances in plastic food contact materials using an Orbitrap GC mass spectrometer

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ABSTRACT

The objective of this work is to demonstrate the utility of gas chromatography-Orbitrap™ mass spectrometry and Thermo Scientific™ Compound Discoverer™ software for the detection and identification of non-intentionally added substances (NIAS) in a plastic film sample. Due to the wide range of volatility and polarity of such NIAS chemicals, different chromatographic techniques are used to undertake a comprehensive study including LC and GC MS.

INTRODUCTION

In the European Union (EU), plastic materials and articles intended to come into contact with food should comply with the Commission Regulation (EU) No 10/2022 and amendments.[1] This regulation contains a list of authorized monomers, other starting substances, macromolecules obtained from microbial fermentation, additives, and polymer production aids (intentionally added substances, IAS) that can be used for the manufacture of plastic food contact materials (FCM). However, during the manufacturing processes and uses of plastic FCM, the reaction and degradation of products can occur, leading to the formation of other compounds (non-intentionally added substances, NIAS) in the plastic material. For this reason, the risk associated with the presence and potential release of NIAS should be assessed before the authorization of FCM.[2]

Due to the wide range of volatility and polarity of such NIAS chemicals, different chromatographic techniques are used to undertake a comprehensive study. Most reported methods for untargeted analysis of plastic FCM are based on liquid mass spectrometry.

MATERIALS AND METHODS

The sample analyzed in this study was a post-consumer recycled low-density polyethylene (LDPE) film. It was solvent extracted with 20mL acetone and concentrated to 1 mL. Automatic sample injection was performed using a Thermo Scientific™ TriPlus™ RSH SMART autosampler, and chromatographic separation was performed using a Thermo Scientific™ TRACE™ 1310 GC system fitted with a Thermo Scientific™ TraceGOLD™ TG-5SilMS 30 m × 0.25 mm i.d. x 0.25 µm film capillary column. Finally, a Thermo Scientific™ Orbitrap Exploris™ GC 240 mass spectrometer was used for accurate mass measurements in full-scan mode at 120,000 mass resolution (FWHM at *m/z* 200) using both EI and CI ionization. Data processing was performed using Thermo Scientific™ Compound Discoverer™ software.

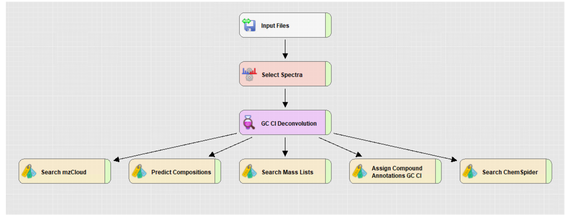
Table 1 & 2. TRACE GC 1610 and mass spectrometer conditions.

TRACE 1610 GC	
Injector	
Injection volume (µL)	1
Inlet liner	Thermo Scientific™ LinerGOLD™ splitless liner, single taper with quartz wool (P/N 453A1925-UI)
Inlet temperature (°C)	280
Inlet module and mode	SSL, Splitless
Splitless time (min)	1
Septum purge flow (mL/min)	5
Oven and column	
Carrier gas, flow rate (mL/min)	He, 1.2
Column	Thermo Scientific™ TraceGOLD™ TG-5SilMS 30 m × 0.25 mm i.d. × 0.25 µm (P/N 26096-1420)
Oven temperature program	
Temperature 1 (°C)	40
Hold time (min)	5
Temperature 2 (°C)	315
Rate (°C/min)	5
Hold time (min)	10
Total GC run time (min)	70

Orbitrap Exploris GC 240 mass spectrometer in EI mode	
Transfer line (°C)	300
Ion source (ionization type)	Thermo Scientific™ ExtractaBrite™ (EI) source
Ion source (°C)	280
Electron energy (eV)	70
Emission current (µA)	50
Acquisition mode	Full scan (FS)
Mass range (*m/z*)	40–500
Orbitrap resolution	120,000
AGC target	Standard
Maximum injection time	Auto
Lock masses	133.01356; 207.03235; 225.04292; 281.05114; 299.06171; 355.06993

RESULTS

Figure 1. The PCI Compound Discoverer software workflow used to confirm the compounds identified in the EI workflow.



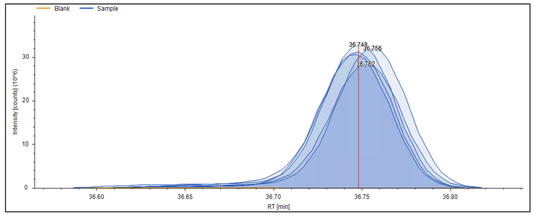
Methyl palmitate was identified with a Total Score of 95.4% and ΔRI 4, as demonstrated in Figure 2a (only data entries relevant to this compound are shown). The total number of the rows was 260 (detected features without the features present in the blank). Beside the Total Score, SI, RSI, HRF, and RHRF (all of them explained above) the results table contains other information on identity.

Figure 2. Identification of methyl palmitate in the EI workflow. a) the corresponding row from the results table. b) extracted ion chromatogram of the reference ion, c) comparison between deconvoluted spectrum (top) and NIST spectrum (bottom)

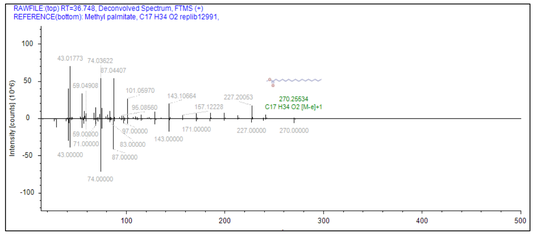
a)

Name	Calc. MW	RT [min]	Reference m/z	Avg TIC	NIST Lib Hit Formula	NIST Theo. Mol. Mass	NIST Observed Mol. Mass	Total Score	HRF Score	SI	Calculated RI	RI Delta	Group Areas (5)	Group CV (%) (5)
Methyl palmitate	270.25589	36.748	55.05414; 27334199	C17 H34 O2		270.25533	270.25534	95.4	99.0	792	1930	4	1.0e8	6

b)

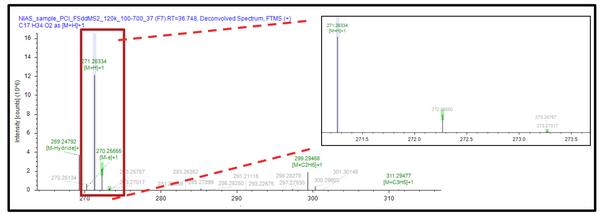


c)



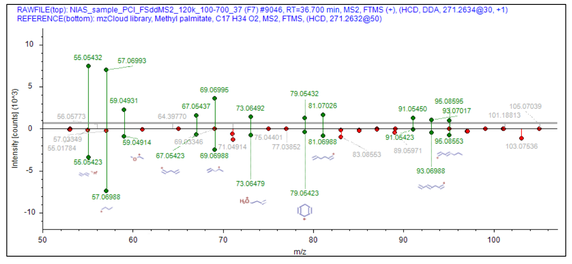
To confirm the identification, the PCI data were revised. Figure 3 shows the PCI MS spectrum at the retention time corresponding to the peak identified in EI as methyl palmitate. Compound Discoverer software found various forms/adducts of the methyl palmitate molecular ion ([M-H-] + ; [M+H]+ ; [M-e]+ ; [M+C2 H5] + ; [M+C3H5] +). Moreover, the isotopic pattern corresponding to the protonated molecule of methyl palmitate was observed.

Figure 3. PCI MS spectrum. The molecular ions and isotopic pattern of methyl palmitate are marked automatically by the software in green.



The availability of the MS2 data provided additional confirmation tools. A search in MS2 libraries and databases is the most straightforward way to utilize MS2 scans. In this study, an mzCloud library search was carried out.. Figure 4 shows a comparison between experimental MS2 spectrum of the compound detected at m/z 271.2634 (presumably protonated methyl palmitate) and a methyl palmitate MS2 spectrum present in the mzCloud library.

Figure 4. Comparison between experimental MS2 spectrum (top) and mzCloud MS spectrum (bottom) for methyl palmitate. MS2 spectrum of methyl palmitate with ions explained by in silico fragmentation



Structure	Name	Formula	Molecular Weight	Best Match
	Methyl palmitate	C17 H34 O2	270.25588	85.9

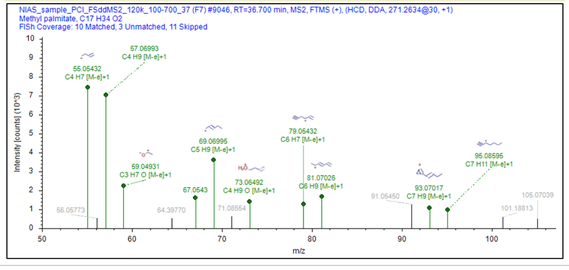
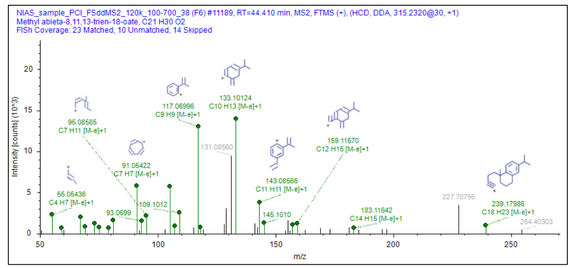


Figure 5. MS2 spectrum of presumably methyl dehydroabietate with ions explained by in silico fragmentation.



In the case of methyl dehydroabietate (methyl abieta-8,11,13-trien-18-oate), identified in the EI and confirmed in the PCI mode by detection of various adducts and expected isotopic pattern, no match was found in the mzCloud spectral library. Thus, the only way to take advantage of the MS2 data was to apply in silico fragmentation (Figure 5). Although, the FISh coverage is slightly lower than in the case of methyl palmitate, it worth noticing that non-explained ions have low intensity. Moreover, many of the explained ions have m/z > 100, which means that they are very selective, and they provide high confidence in the identification.

CONCLUSIONS

Compound Discoverer software is an excellent option for the analysis of packaging migration substances. Consequently, data revision is faster and less complicated. The combination of EI and PCI workflows provides numerous tools for compound identification and confirmation. The EI workflows are compatible with both nominal and exact mass NIST libraries, which facilitates identification of the broadest possible range of substances. The EI identification can be easily confirmed in the PCI mode, which involves MS as well as MS2 data analysis. The MS nodes are focused on the molecular ion and information that is provided by this species (molecular formula prediction, isotopic pattern analysis, ChemSpider search, mass list search), whereas the MS2 data can be used for the mzVault library search, mzCloud search, and FISh scoring. The latter is very helpful in cases where there are no library hits/matches.

REFERENCES

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2. International Life Science Institute (ILSI) Europe. Guidance on Best Practices on the Risk Assessment of Non-Intentionally Added Substances (NIAS) in Food Contact Materials and Articles; ILSI Europe: Brussels, Belgium, 2015.
3. Miralles, P.; Yusà, V.; Pineda, A.; Coscollà, C. A Fast and Automated Strategy for the Identification and Risk Assessment of Unknown Substances (IAS/NIAS) in Plastic Food Contact Materials by GC-Q-Orbitrap HRMS: Recycled LDPE as a Proof-of-Concept. Toxics 2021, 9(11), 283. doi: 10.3390/toxics9110283

TRADEMARKS/LICENSING

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