MASS SPECTROMETRY TOOLS FOR CONFIDENT DISCRIMINATION OF DIFFERENT QUALITIES OF POST-CONSUMER RECYCLED PLASTICS

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INTRODUCTION

Plastic is present in every aspect of our lives and thus creates a big portion of our waste. Fossil-fuel derived plastic can remain intact for decades or centuries. To reduce the environmental impact, plastic waste could become a valuable resource when recycled.

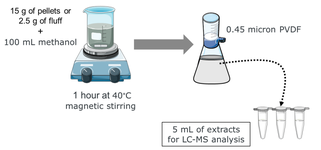
To successfully reintroduce post-consumer recycled plastics (PCR), PCR needs to comply with quality and safety standards. Therefore, there is a need for analytical methods to characterize and guarantee PCR quality and safety.

This work demonstrates a flexible workflow using LC-HRMS for the characterisation of different batches of recycled low-density polyethylene (rLDPE). An unbiased approach was adopted for the characterisation and identification of impurities in rLDPE. Herein, key compounds characteristic for quality grades of the studied rLDPE batch were identified.

SAMPLE PREPARATION

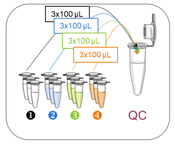
1 Methanol extraction protocol:

Samples consist of four groups, three replicates in each: virgin low density polyethylene (vLDPE), virgin LDPE with additives (vLDPE+), good and poor quality recycled LDPE (good rLDPE, poor rLDPE, respectively).



Scheme 1: Extracts were prepared by submerging the pellets or fluff with 100% methanol. The extraction was performed at 40°C under magnetic stirring. The beaker was closed to avoid evaporation. The mix was then filtered. Samples were stored in glass vials at 4°C until analysis.

2 Quality control preparation:



Scheme 2: A quality control (QC) was prepared by mixing 100 µL of each of the extracts. The samples were randomised and injected twice. The QCs were injected in between five sample injections, at the beginning and at the end of the sequence to ensure consistent instrument performance across analysis.

LC-MS METHOD

3 Liquid chromatography:

Samples, QC, and blanks were analysed using ACQUITY™ Premier Liquid Chromatography System couple to Xevo™ G3 QTof mass spectrometer using the following conditions:

Mobile phase A: H_2O + 0.1% CH_3COOH

Mobile phase B: 100% Methanol

Flow rate: 0.3 mL/min

Injection volume: 5 µL

Column: CORTECS™ C18, 1.6 µm, 2.1x100mm, 90Å (p/n: 186007095)

Column temperature: 50 °C

Sample temperature: 6 °C

Gradient :

Time (min)	%A	%B
0	98	2
0.5	98	2
8.5	2	98
13.5	2	98
13.5	98	2
16	98	2

4 MS source parameters:

Instrument	Xevo G3 QTof
Desolvation temp.	600 °C
Desolvation Gas	150 L/h
Source Temp.	150 °C
Cone Gas	150 L/h
Source offset	80
Sampling cone	30 V
Capillary voltage	1 kV

5 MS acquisition parameters are:

Instrument	Xevo G3 QTof
Ionisation mode	ESI-/+
Mass range	*m/z* 50—1200
Acquisition rate	5 spectra per second (Hz)
Lock mass	Leucine enkephalin (m/z 556.276 and m/z 554.262, for ESI+ and ESI- modes, respectively).
Acquisition mode	$HDMS^E$
Collision energy	Low collision energy: 0 eV High collision energy: ramp from 20-40 eV and 20-50 eV for ESI+ and ESI– modes, respectively.

6 Software tools and data process:

Data acquisition: MassLynx™ v4.2

Statistical analysis: Progenesis™ QI (Version 3.0.7929.47290)

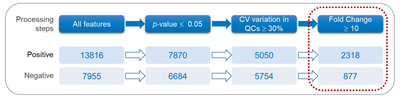
Data processing steps:

The data processing steps:

1. Peak picking by deconvoluting the detected ions
2. Grouping the adducts when present into one compound. For the positive mode, $[M+H]^+$ and $[M+Na]^+$ molecular ions were grouped as one compound. And for the negative mode $[M-H]^-$ and $[M-CH_3COO]^-$ were grouped as one compound
3. Mass and retention time alignment
4. Data normalisation
5. Multivariate analysis. Only compounds with with *p*-value ≤ 0.05 are retained
6. Removing compounds with > 30% variation in QC injections
7. Keeping compounds with > 10 fold intensity compared to vLDPE

Each of the described processing steps helped in reducing the feature list and focusing on the fundamental difference between the groups. The final list (highlighted in red in Scheme 3 below) contained **2318 and 877** features. These features will be the focus of the statistical analysis.

The different steps and their corresponding number of compounds are illustrated in Scheme 3.



Scheme 3: Summary of the data processing steps and the resulting number of compounds in positive and negative modes. The data analysis was performed using Progenesis QI

RESULTS AND DISCUSSION

1 Can we distinguish the different types of plastics?

The list of 2318 and 877 compounds in positive and negative modes, respectively are used for principal component analysis (Figure 1).

PCA plots point out:

- Clear separation between vLDPE and rLDPE (ESI -/+)
- In ESI+ good and poor quality rLDPE can be distinguished

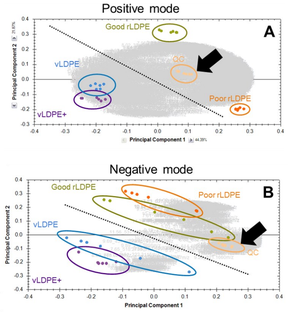


Figure 1: PCA for the ESI+ (A) and ESI- (B) compounds. PCA components capture the maximum variation in the data. Components 1 and 2 are 44.39% and 21.87% for ESI+ and 41.17% and 20.86% for ESI- data, respectively.

2 What are the markers of poor quality rLDPE?

To identify markers of poor quality rLDPE a correlation analysis was performed on the 2318 compounds detected in ESI+ (Figure2).

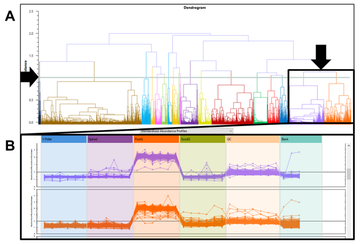


Figure 2. Correlation analysis. 2A: Dendrogram with a threshold distance selected at 1.0. 2B: Abundances of the compounds within the same tree branch in the different sample injections. Each sample group is distinguished by a different column colour. From left to right: Blue: vLDPE, Violet: vLDPE with additive, Orange: poor-quality rLDPE, Green: good-quality rLDPE, light orange: quality control sample, and turquoise: blank samples.

3 Can we identify the markers?

The correlation studies in figure 2 point out two branches with strong correlation (distance >0.85). The two branches are composed of 457 compounds either unique or highly abundant in poor quality rLDPE. To annotated the distinctive compound in poor quality rLDPE we have searched in two published databases: Food Contact Chemicals (FCCdb, 3237 entries) and Chemicals associated with Plastic Packaging (CPPdb, 7149 entries) databases, respectively[1, 2].

Among the list of compounds of interest is ***m/z* 441.2978** detected at 9.89 minutes (Figure 3). $HDMS^E$ acquisition increased the level of confidence in the identification. The accurate mass, isotopic distribution, and the fragmentation information pointed out that *m/z* 441.2978 corresponds to the [M+Na]+ of $C_{24}H_{38}O_4$ with mass accuracy ±0.56 ppm (Figure 4).

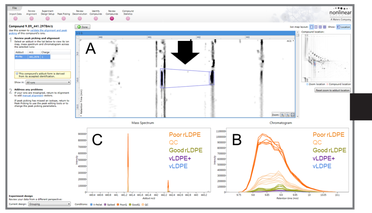


Figure 3: A: Heat map of m/z vs retention time. 3B and 3C: Overlay of Extracted ion chromatogram (EIC) ofm/z 441.2978 and mass spectra in 24 injections, respectively. Each colour represents a sample group.

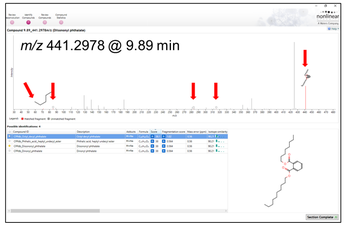


Figure 4: The fragments obtained by MS^E are annotated by comparison with in silico generated fragmentations. These fragments are common to the four suggested isomers of phthalates.

4 How confident can the identification be ?

Level 1 identification is obtained by comparing the retention time and fragmentation patterns of the chemical standard and sample[3]. By analysing the standard of a pure chemical standard of di-isononyl phthalate (DINP) and LDPE samples we confirm the identity of *m/z* 441.2978 (and *m/z* 419.3161). Figures 5 illustrate the EIC and fragmentation spectra of *m/z* 441.2978 in the standard and the LDPE extracts.

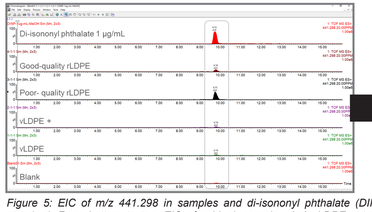


Figure 5: EIC of m/z 441.298 in samples and di-isononyl phthalate (DINP) standard. From bottom to top, EIC of a blank sample, virgin LDPE extracts (vLDPE), virgin LDPE extracts with additives (vLDPE+), poor-quality rLDPE, good-quality rLDPE, and a standard of 1 µg/mL of di-isononyl phthalate (DINP).

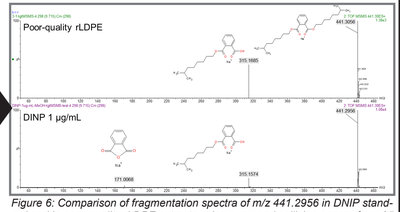


Figure 6: Comparison of fragmentation spectra of m/z 441.2956 in DNIP standard and in poor-quality rLDPE extracts using a ramped collision energy from 25 –90 eV.

CONCLUSIONS

- One integrated, streamlined instrument and software solution with MassLynx™ and Progenesis™ QI used to distinguish between different qualities of post-consumer recycled material (PCR)
- At least 4 significant marker compounds were detected and identified in positive ESI mode characteristic of poor-quality rLDPE.
- This workflow can be applied to other types of PCR such as high density polyethylene (HDPE), polyethylene terephthalate (PET), polypropylene (PP).

References

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2. K. J. Groh, T. Backhaus, B. Carney-Almroth, B. Geueke, P. A. Inostroza, A. Lennquist, H. A. Leslie, M. Maffini, D. Slunge, L. Trasande, A. M Warhurst, J. Muncke. Overview of Known Plastic Packaging-Associated Chemicals and Their Hazards. Science of the Total Environment. 651: 3253–3268 (2019).
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