

CHARACTERIZATION OF INDUSTRIAL PLASTICS USING PYROLYSIS WITH ATMOSPHERIC PRESSURE GAS CHROMATOGRAPHY COUPLED TO HIGH-RESOLUTION MASS SPECTROMETRY

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INTRODUCTION

With the implementation of strategies in the EU to move towards a circular plastic economy¹, there is a drive to reduce or reuse plastic waste leading to the adoption of recycled and reclaimed materials into different industrial applications. Therefore, there is a greater need to be able to characterize these recycled materials to ensure they are safe to use.

Pyrolysis coupled to gas chromatography-mass spectrometry (GC-MS) is often utilized for materials such as plastics.² However, the high energy of electron impact (EI) ionization can lead to insufficient sensitivity and selectivity for undertaking full characterization.

Pyrolysis-GC with soft ionization and high-resolution mass spectrometry (HRMS) is a complementary technique to help address this challenge. Atmospheric Pressure Gas Chromatography (APGC) is an ionization technique which uses a corona discharge enabling softer ionization. This results in molecular ion detection which can help with the confirmation of a molecular formula for identification. APGC can be coupled to a quadrupole time-of-flight mass spectrometer (QToF MS) which can acquire data in MS^E mode, whereby both low and high collision energy spectra are simultaneously acquired.³ Using this technique, the accurate mass of both precursor and fragment ions are available, both of which aid structural elucidation and, ultimately, compound identification.⁴ To further understand the differences between virgin and recycled materials, statistical analyses can be used in conjunction with the data acquired from these analytical instruments.⁵

In this study, an analytical workflow was developed to analyze virgin and recycled industrial plastics (Figure 1). Simple steps were undertaken to characterize these complex materials including data acquisition, screening against a library, statistical analysis, and structural elucidation.

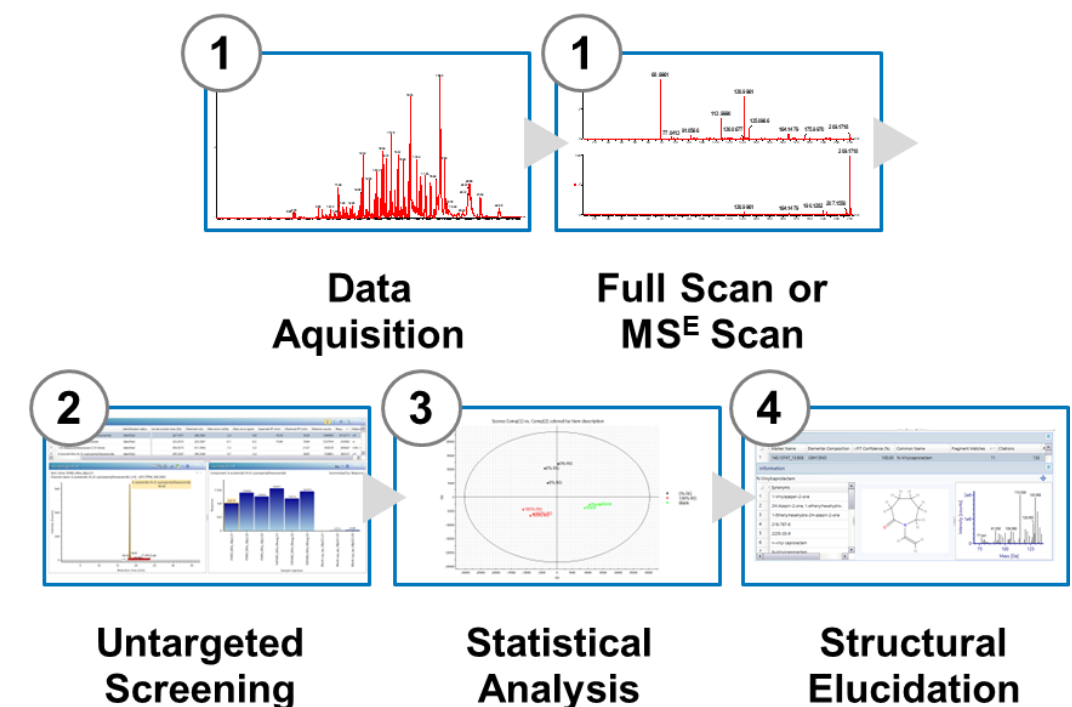


Figure 1. The analytical approach used for the analysis of virgin vs. recycled plastics and the determination of chemical markers responsible for differences.

METHODS

Sample Preparation

Samples were prepared from virgin and recycled molded gears made from PrestaAmid™, which consists of 95% high-molecular-weight polyamide (thyssenkrupp Presta, Liechtenstein). The recycled plastics were regrinds from reclaimed plastic off cuts. Approximately 0.2 mg of each sample was loaded into a stainless steel sample cup with a plug of quartz wool. Triplicates of each sample were prepared, and sample cups filled with quartz wool alone were used as blanks. The sample list was randomized before the samples were placed into the autosampler.

Sample Type	Percentage Recycled	Label
Virgin Gear	0%	0% RG
Recycled Gear	100%	

Pyrolysis Conditions	
Pyrolyzer	EGA/PY-3030D (FrontierLab)
Interface Temp.	320 °C
Pyrolyzer Temp.	600 °C
Analysis Type	Single-shot

GC Conditions	
GC Oven	Agilent 7890
Inlet Mode	Split/Splitless
Inlet Temp.	310 °C
Septum Purge Flow	3 mL/min
Split Ratio	50:1
Split Flow	50 mL/min
GC Interface Temp.	300 °C
Column	Rtx-5MS, 30m x 0.25 mm x 0.25 µm (RESTEK)
Column Flow	1.4 mL/min
Oven Gradient	45 °C for 5 min, up to 300 °C at 20°C/min, 18 min final hold
Total GC Run Time	37.25 min

MS Conditions	
Instrument	Xevo™ G2-XS QToF*
Ionization Mode	APGC™
Corona current	3 µA
Sampling cone	40 V
Source Temp.	150 °C
Mass Range	m/z 10-1200
Scan Time	0.2 s
Cone gas	150 L/h
Auxiliary gas	350 L/h
MS ^E collision energy	Low 6 V High 15 to 35 V

*(Equivalent or better performance is expected with the Xevo G3 QToF mass spectrometer.)

Data Management

Data were acquired using Waters MassLynx™ 4.2. software. Data processing and reporting were performed using the UNIFI™ application within the waters_connect™ platform. All statistical analyses were undertaken with EZInfo™ 3.0.

RESULTS

1 Data were acquired using pyrolysis-APGC-QToF MS in MS^E mode. Base peak intensity (BPI) pyrograms were obtained for all samples (Figure 2). The pyrograms below demonstrate the complexity of these materials.

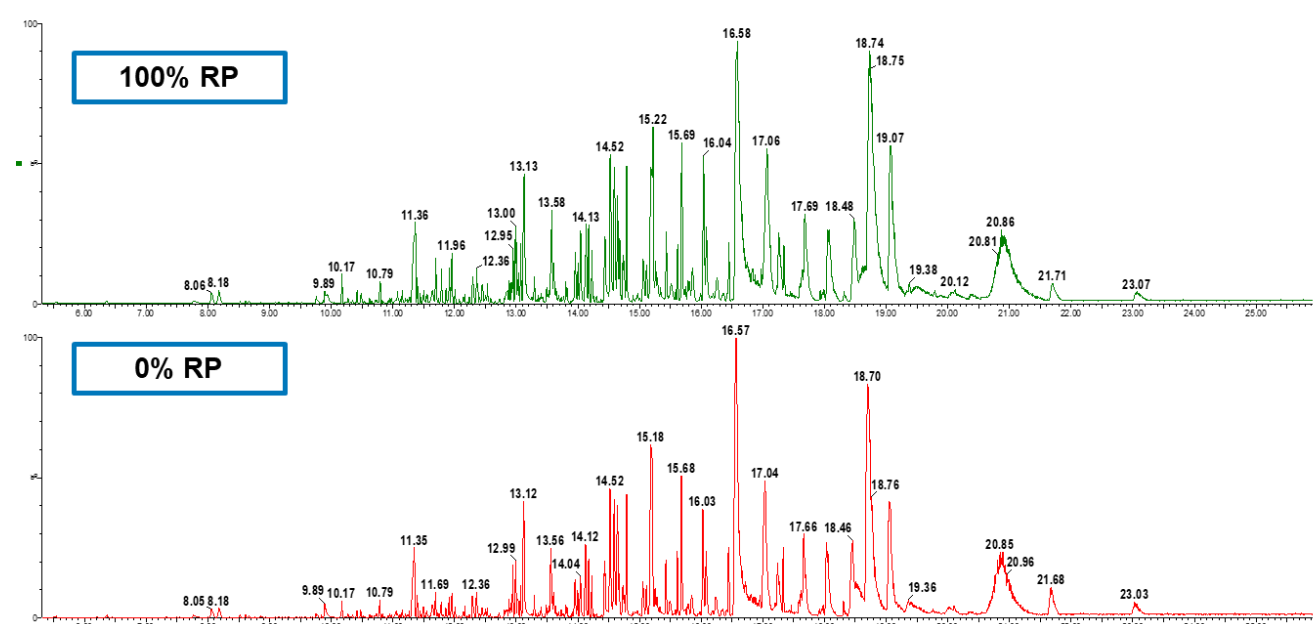


Figure 2. Base peak intensity (BPI) pyrograms from full scan data of 100% recycled gear (top) and 0% recycled gear (bottom), between 6 and 26 minutes.

2 A library containing 24 typical pyrolyzates of these types of polymer^{2,6} was created by importing .mol files into the UNIFI application. The samples were screened against this library for accurate mass matches to evaluate any trends across the dataset. Figure 3, for example, shows that 6-acetamido-N-(5-cyanopentyl)hexanamide was detected in each sample of the 0% and 100% recycled gears. This is a tentative identification because the match was made based on the accurate mass alone.

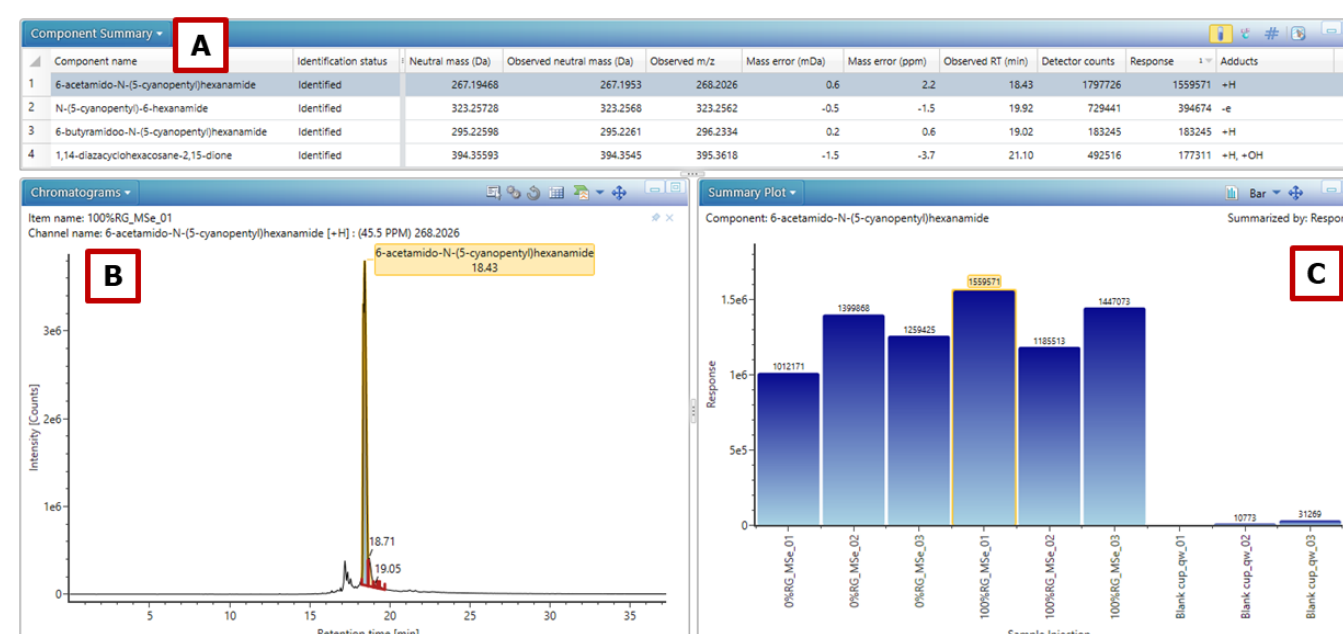


Figure 3. Screening workflow in the UNIFI application highlighting the results for 6-acetamido-N-(5-cyanopentyl)hexanamide. [A] Component summary table including mass error (ppm), retention time, and response. [B] Extracted ion chromatogram for 6-acetamido-N-(5-cyanopentyl)hexanamide. [C] Trend plot of the response for this compound across all injections.

3 To find differences between the virgin and the recycled materials, the data were transferred to EZInfo, and Principal Component Analysis (PCA) was performed. Figure 4A shows the data from the blanks, 0%, and 100% recycled gear samples in a PCA scores plot. There is clear separation between the three groups of samples, which highlights that there are differences between the samples.

To establish the markers responsible for the differences between the 0% and 100% recycled gears, an Orthogonal Projections to Latent Structures Discriminant Analysis (OPLS-DA) was performed on data from these groups of samples. The resulting S-Plot is shown in Figure 4B, and the markers highlighted in the red regions are up-regulated in one of the sample types. These markers were selected and transferred back into the UNIFI application for further investigation.

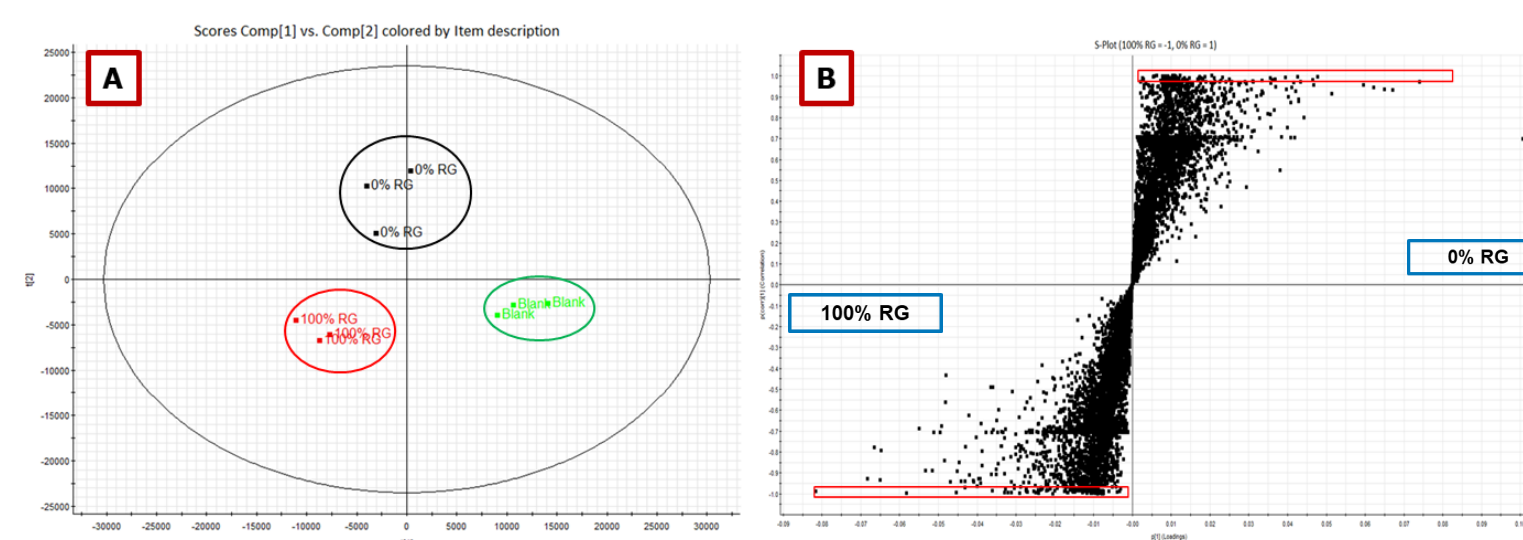


Figure 4. [A] PCA scores plot of the blanks, 0%, and 100% recycled gears. [B] S-plot from the OPLS-DA, indicating statistically significant markers for the 0% recycled (upper right) and the 100% recycled (lower left) material.

4 The selected markers were investigated using the Discovery Tool in the UNIFI application's elucidation toolkit.⁷ Since the pyrolysis data were collected in MS^E mode, where high and low collision energies are alternated, the accurate mass of both precursor and fragments ions were available for the interpretation of each marker. Figure 5 demonstrates the information displayed by the Discovery Tool for an elucidated marker.

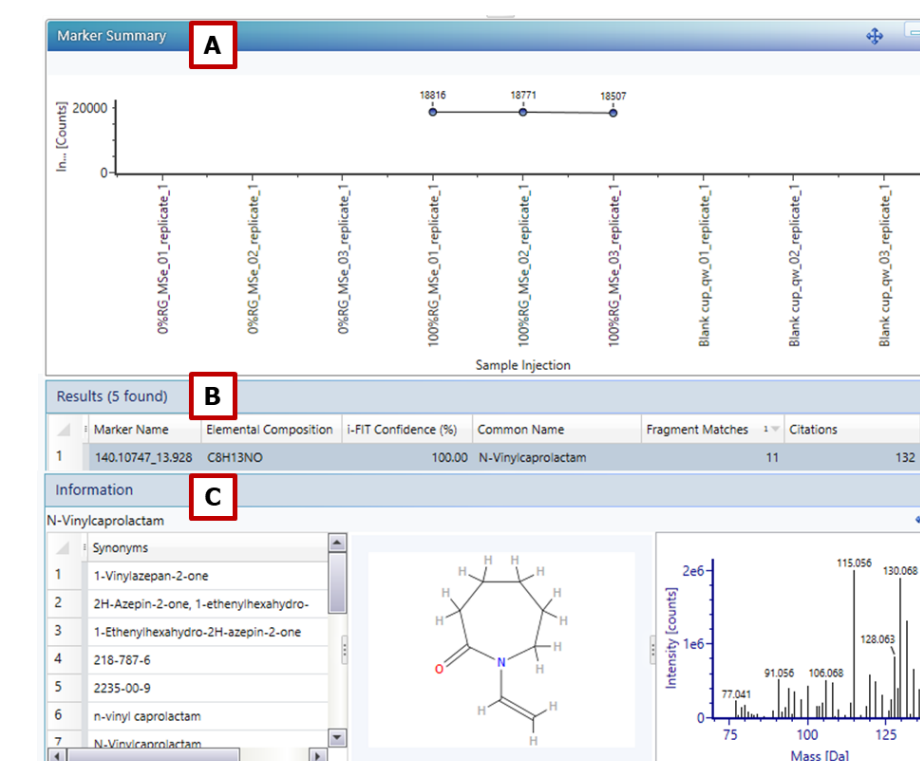


Figure 5. Putative identification of a marker unique to the 100% RG sample as N-vinylcaprolactam with protonated m/z 140.1075 ([C₈H₁₃NO]⁺ mass accuracy 0.2 ppm). [A] Marker abundance (response) across all samples. [B] The predicted elemental composition for this marker, i-FIT confidence, common name for the compound, number of fragment matches, and the number of citations. [C] Synonyms and structure for this compound and high energy spectrum.

The markers of interest were isolated using statistical analysis and identified with different levels of confidence. Whilst a reference standard would be needed for full confirmation of an identity, the UNIFI software utilizes a complete workflow that significantly reduces the burden of lengthy manual data interrogation. Figure 6 indicates the tentative identity of a selection of markers from the 100% recycled gears together with the corresponding level of confidence (explained below) for each assignment.

Sample	m/z	Retention Time (min)	Common Name	Chemical Formula	Fragment Matches	i-FIT Confidence (%)	Level
100% RG	182.1541	12.27	4-(2-Pyrrolidinyl)-1,6-heptadien-4-ol	C11H19NO	21	83	2
100% RG	187.1452	13.54	(4-Isopropyl-1-piperazinyl)acetic acid	C9H18N2O2	7	100	3
100% RG	140.1075	13.93	N-Vinylcaprolactam	C8H13NO	11	100	3
100% RG	186.1467	14.56	(2R)-N-(1-Aminoethyl)-2,2,4,5,3H(4Z)-	C9H15N7	5	100	3
100% RG	166.1586	18.39	10-Undecanenitrile	C11H19N	5	100	3
100% RG	256.2017	19.9	1,1-Dimethylethyl 2-[1-(cyclopropyl)imino]	C13H25N3O2	3	54	2
100% RG	166.1593	19.29	1-Piperidino-1-cyclohexene	C11H19N	9	100	3
100% RG	156.1384	18.92	1-tert-butyl-4-piperidone	C9H17NO	2	100	3
100% RG	224.176	18.74	4-(1-Methyl-1H-pyrazol-4-yl)-4-propo	C12H21N3O	8	35	2

Figure 6. Putative identifications by the Discovery Tool of a selection of chemical markers unique to the 100% recycled gears. In this case, level 1 is accurate mass alone (m/z tolerance 2 mDa), level 2 is accurate mass and fragment matches, and level 3 is accurate mass, fragment matches, and a high i-FIT confidence.

Once confirmed, chemical components can be added into the screening library in the UNIFI application for future analyses, such as targeted screening or targeted quantitation. The experimental data obtained, for example the retention time and the m/z values of fragment ions, can also be incorporated. As an example, a chemical marker that was found to be unique to the 100% recycled gear through the statistical analysis, and elucidated using the Discovery Tool, was added to the library. The results of screening for this compound in the 0% and 100% recycled gears are shown in Figure 7.



Figure 7. 4-(1-Methyl-1H-pyrazol-4-yl)-4-propoxy piperidine screening results after being added to the library.

CONCLUSION

- Py-APGC-QToF HRMS in combination with multivariate statistical analysis is a powerful tool for screening compounds specific to a sample group and differential characterization.
- The analytical workflow described encompasses simple steps to characterize complex industrial plastics, including data acquisition, screening against a library, statistical analysis, and structural elucidation to putatively identify chemical components.
- Utilizing PCA reveals the clustering of sample types and the OPLS-DA S-plot highlights significant markers responsible for differences between the virgin and 100% recycled plastic.
- The Discovery Tool within the structural elucidation toolkit of the UNIFI application can be utilized for tentative compound identifications. Compounds are identified using the accurate mass information of both precursor and fragment ions acquired with soft ionization and MS^E data acquisition.
- Confirmed compounds can be added to an in-house library or database with their associated experimental data. This enhances the scope of such libraries for future screening analyses of a multitude of sample types in routine workflows, reducing the time and complexity of analysis.

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