IMPROVED POLYMER ANALYSIS BY USING PYROLYSIS-GC×GC-MS: DIVERSE POLYETHYLENE (PE) MATERIALS.

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Pyrolysis-gas chromatography-mass spectrometry (py-GC-MS) is a technique widely used for polymer analysis. Pyrolysis provides precise and carefully-controlled heating of the solid sample, leading to the formation of GC-amenable units (e.g. monomers, dimers, etc.). These are analyzed by GC-MS to give chromatographic patterns, or "pyrograms", specific to the polymeric composition and structure. However, pyrolysis profiles are often too complex and accurate profiling is difficult at best. Typical workflows involve material identification based on the pyrogram average MS spectrum (with the aid of dedicated libraries) or focusing on a few diagnostic compounds. A great deal of information is thus overlooked.

In comprehensive two-dimensional gas chromatography (GC×GC) two different separation mechanisms are coupled in one analysis to give improved resolving power and unmatched peak capacity. Thanks to these features, GC×GC has found increasing acceptance and widespread use and nowadays can be considered the method of choice for the analysis of highly complex samples. As a result, GC×GC is the logical candidate to unravel highly complex pyrolysis profiles.

In this work we show the benefits of coupling pyrolysis to GC×GC-MS with thermal modulation for the analysis of diverse polyethylene (PE) materials, a polymer commonly encountered in daily life in different forms. The 2D pyrograms are shown to allow for more detailed characterization and easier, more informative comparison.

Experimental details

The test materials are two polyethylene standards with low (LD-PE) and high (HD-PE) density. The real-life samples are 6 packing materials. All materials undergo direct pyrolysis at 700°C for 15 seconds.

All measurements are performed with a CDS 5200 Pyroprobe coupled to an Agilent 7890B GC equipped with a Zoex ZX2 cryogen-free thermal modulator and an Agilent 5975C Mass Spectrometer with Triple-Axis Detector. All 2D data are visualized and processed with the *GC Image* software package.

Results

At first the standards are analyzed. Fig. 1 shows an example 3D view of a chromatographic section obtained for the LD-PE standard. The well-known structure typical of PE, with repeated n-dialkene/n-alkene/n-alkane triplets for the different carbon numbers, is of course still predominant. In addition, several compounds co-eluting on the non-polar primary column are resolved based on polarity on the second dimension.
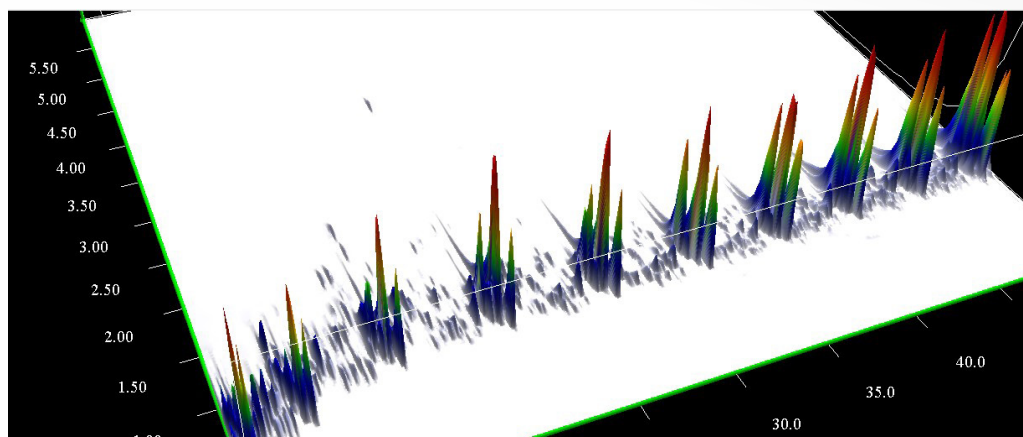
With py-GC-MS, LD-PE materials normally exhibit higher response than HD-PE between the triplets that is commonly attributed to a higher branched hydrocarbons content. However actual characterization is neglected due to the elevated number of isomers present and their similar MS spectra.

GC×GC provides more insight (Fig. 2): for both materials between the triplets branched alkanes are hardly present, while naphthenes and olefins are predominant. Numerous compounds are present and the composition differs in terms of individual components as well as groups. For instance, LD-PE has a higher content of branched alkenes, which can thus be linked to higher response typical of LD-PE in these areas.

SHARPER PEAKS, BETTER SEPARATIONS
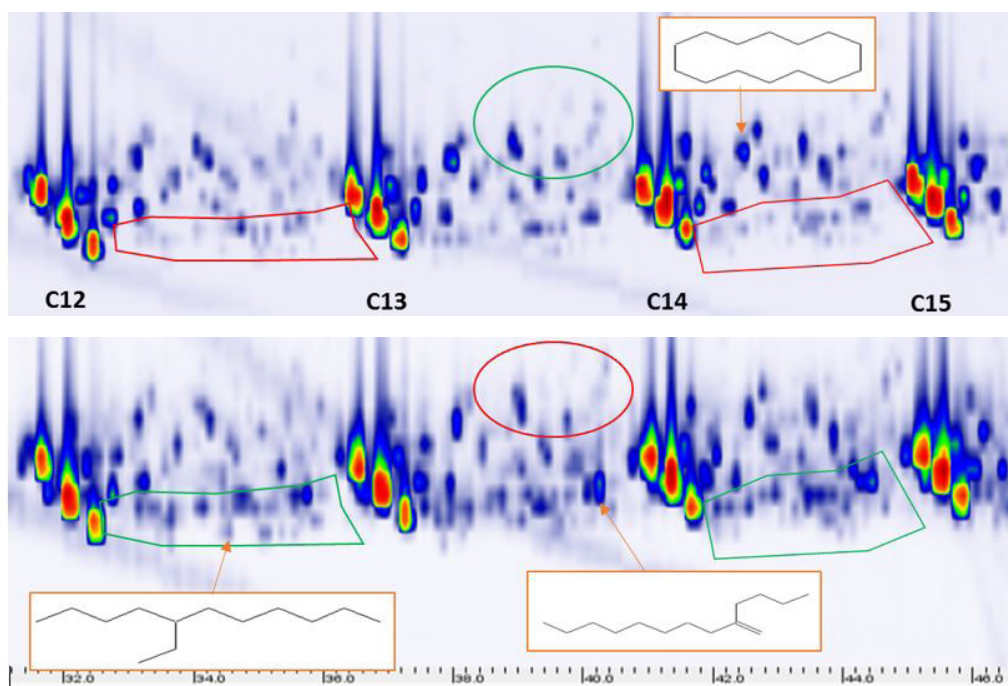
A number of aromatic compounds are also present and, also in this case, differences are present between the standards (Fig. 3). The untargeted profiling of these compounds, which is quite simple in a 2D separation space, would be hardly possible in 1D-GC due to the co-elution with the much more abundant aliphatic groups.

Fig. 3 — Example of separation and identification of diverse aromatic compounds for the PE standards.
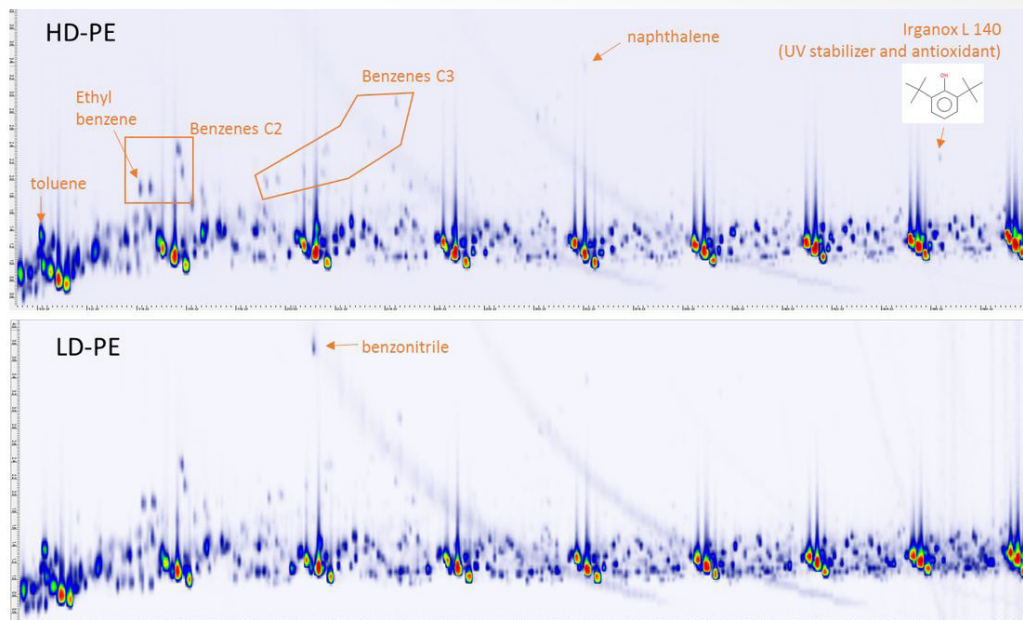
Next, the 6 real-life samples are analyzed. The sample set is composed by 3 LD and 3 HD PE packing materials. The *Image Investigator* part of the *GC Image* software package is used to compare the 2D plots in an automated way. The data processing is here focused at finding class-based similarities and differences. The result of the PCA analysis is shown in Fig. 4. The two classes can be effectively distinguished, suggesting that correct, automated grouping of unknown materials should be feasible.

Fig. 4 — PCA analysis of the real-life samples performed with Image Investigator.
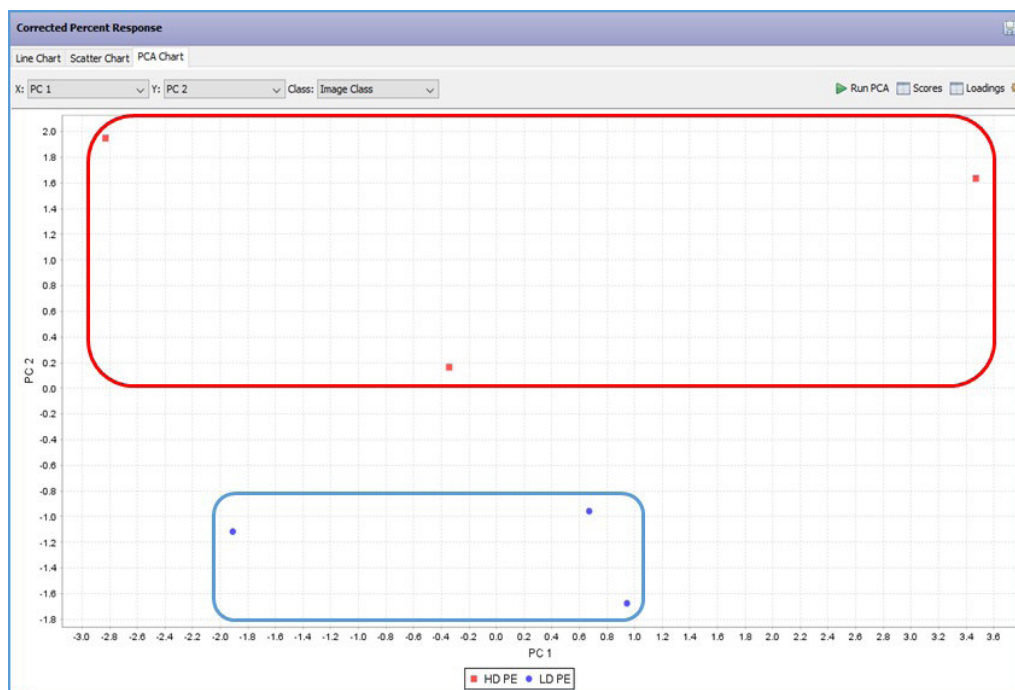
Fig. 5 shows the aromatic profiles for 2 different HD-PE samples. As can be seen one sample hardly exhibit any response while the other has a number of different aromatics. Thanks to the efficient separation and the resulting clean spectra, several of these are confidently identified. Among this, it is worthy to mention the presence of styrene, which could indicate the presence of polystyrene in the material, and few known additives.

Fig. 5
Example of separation and identification of diverse aromatic compounds for two real-life HD-PE samples.
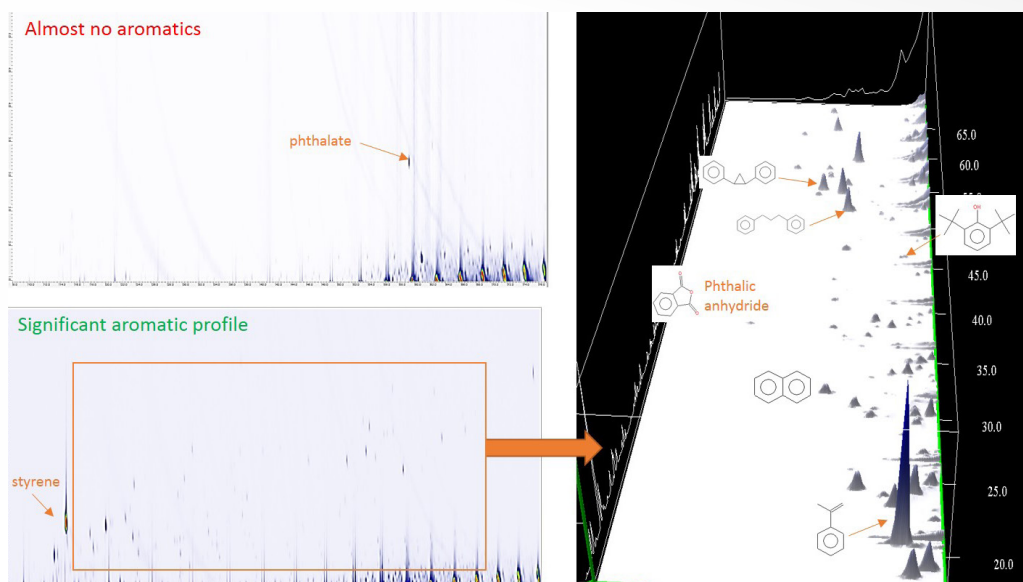
CONCLUSIONS

- Py-GC×GC-MS is a very powerful analytical tool for improved polymer analysis.

- 2D pyrograms deliver more accurate and detailed sample characterization and are remarkably effective for sample comparison and fingerprinting.

- The differences in the pyrolysis profiles of LD-PE and HD-PE standards and samples are highlighted with a level of detail that would not be possible by py-GC-MS.

- The real-life PE samples are effectively grouped as LD or HD materials with PCA analysis.

- It is possible to detect and identify unknowns of possible interest, such as antioxidants and UV light stabilizers, in an easier and more confident way.

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