ANALYSIS OF POLYETHYLENE BY PYROLYSIS-GC×GC-MS

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Pyrolysis-gas chromatography-mass spectrometry (py-GC-MS) is a very useful technique for polymer characterization. The carefully-controlled pyrolysis heating step provides informative and specific products that can be separated and identified by GC-MS to estimate the polymeric composition/structure. However, these profiles are sometimes too complex to be characterized properly by conventional GC, leading to loss of information.

Comprehensive two-dimensional gas chromatography (GC×GC) provides enhanced resolving power and peak capacity by combining two different separation mechanisms in one analysis. This allows for more detailed separations and more complete characterization of complex matrices. Here we show the py-GC-MS and py-GC×GC-MS profiles of polyethylene (PE) to prove the advantages arising from coupling pyrolysis and GC×GC.
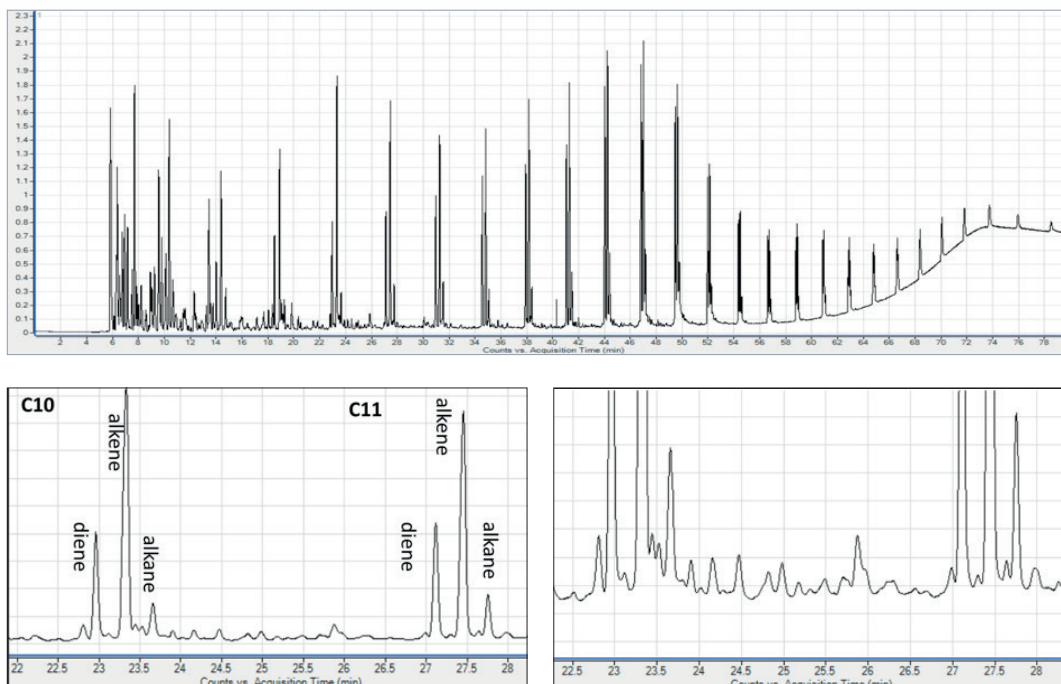
Instrumentation and software
CDS Pyroprobe 5200 coupled to an Agilent 7890B GC equipped with a Zoex ZX2 cryogen-free thermal modulator and a 5977A Agilent Mass Selective Detector (MSD).

Results
Fig. 1 shows the GC-MS chromatogram of a PE sample subject to pyrolysis at 750C° and separated on a non-polar column. The characteristic PE pyrolysis profile shows a repeating unit of triplets of paraffins (diene-alkene-alkane) for every carbon number. Between these major peaks, there are a number of smaller, unresolved peaks commonly identified as branched paraffins.

Fig. 1
Py-GC-MS chromatogram of PE. The zoom-ins show a detail of the profile and an example of complex area.
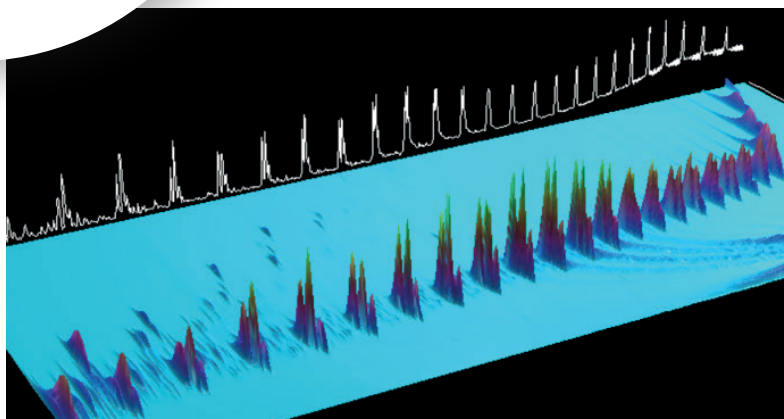
SHARPER PEAKS, BETTER SEPARATIONS

The two-dimensional separation of the same pyrolysis profile with is shown in Fig. 2. The second dimension separation based on polarity grants additional composition information. Several peaks are visible between the triplets, providing a better idea of the number of branched paraffins present. Additionally, there are a number of polar compounds more retained on the second dimension (Fig. 3). These analytes are not visible at all in the GC-MS analysis due to their small abundance and the co-elution with the aliphatic components, like in the case of naphthalene and C12 triplet. In the 2D plot they are fully separated and show clean MS spectra that allow for easy identification.
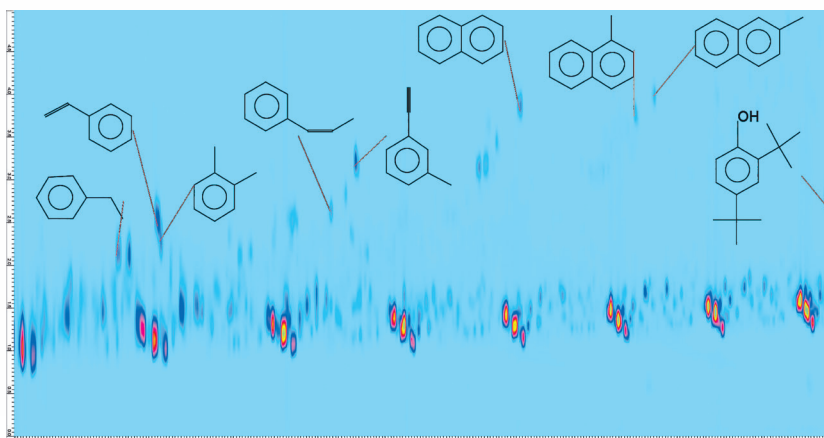

Fig. 3
Py-GC×GC-MS
chromatogram of PE.

CONCLUSIONS

- Py-GC-MS analysis of polyethylene shows a characteristic pattern of paraffin triplets for every carbon number. However, the separation is not sufficient to unravel the sample complexity.
- The characterization obtained by coupling pyrolysis with GC×GC is much more informative.
- Several aromatic compounds are identified in the 2D pyrogram of polyethylene which are not detected in the mono-dimensional separation.

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