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PYROLYSIS-GC×GC-MS FOR EASIER AND MORE EFFECTIVE ANALYSIS OF ADDITIVES IN POLYPROPYLENE (PP).

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Pyrolysis-gas chromatography-mass spectrometry (py-GC-MS) is a powerful technique for polymer characterization. Pyrolysis thermally decomposes the material into smaller units (e.g. monomers, dimers) suitable for GC-MS. The degradation profiles, or pyrograms, elucidate polymeric composition and structure. On the other hand, due to the elevated complexity the profiling of minor yet key components such as additives (e.g. antioxidants, light stabilizers, plasticizers) is often challenging. Comprehensive two-dimensional gas chromatography (GC×GC) combines two separation mechanisms to achieve superior separation power. Coupling pyrolysis to GC×GC can allow for easier and more confident additives profiling in polymers. In this work we present as case study the py-GC×GC-MS analysis of polypropylene (PP) materials with different additive content.

Experimental details

PP samples: material A (Irganox 1010: 0.025%, Irgafos 168: 0.11%) and B (Irganox 1010: 0.08%, Irgafos 168: 0.1%). Measurements are performed with a CDS 5200 Pyroprobe coupled to an Agilent 7890B GC equipped with a Zoex ZX2 thermal modulator and an Agilent 5975C MSD with Triple-Axis Detector. Data are processed with GC Image.

Results

When pyrolyzed, Irganox 1010 and Irgafos 168 break down to several aromatic fragments that can be used as markers. Fig. 1 shows an example of py-GC×GC analysis with pyrolysis at 750°C for 15 seconds.

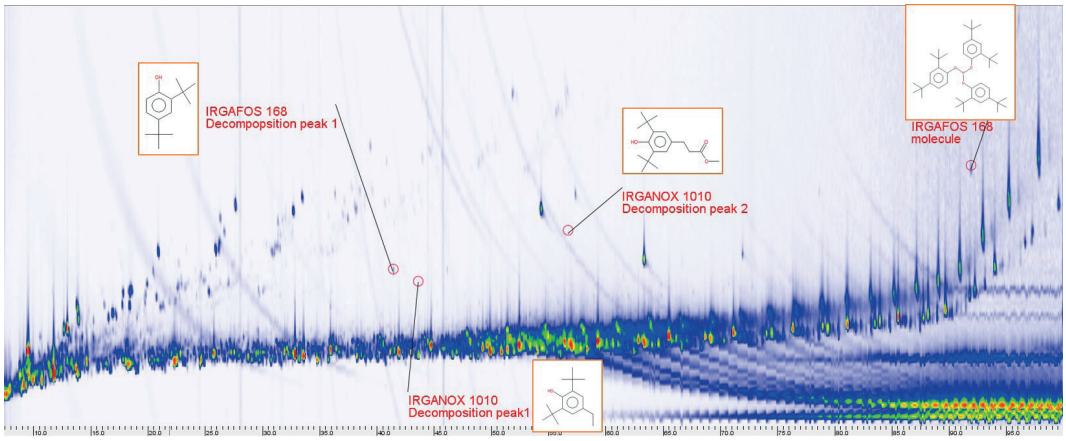

Fig. 1
2D pyrogram for sample B with illustrative identification of some markers for the target additives.

This 2D pyrogram of sample B clearly shows the benefits of the enhanced chromatographic resolution. The aromatic markers are separated from the aliphatics generated by the PP matrix, so they can be found with a simple and quick workflow based on integration and library search. All target markers are successfully detected also in sample A, which has a lower content (especially for Irganox 1010, 250 ppm or 0.025 % w/w).

Confident identity confirmation is possible thanks to the clean spectra obtained as a result of the good separation (Fig. 2). In addition to the targets, other additives (and/or pyrolysis products) can be detected and identified in both samples with relative ease and satisfactory confidence. The peak capacity offered by GC×GC, in combination with the consequent spectral quality not compromised by co-elution, are in fact ideal features for general screening.

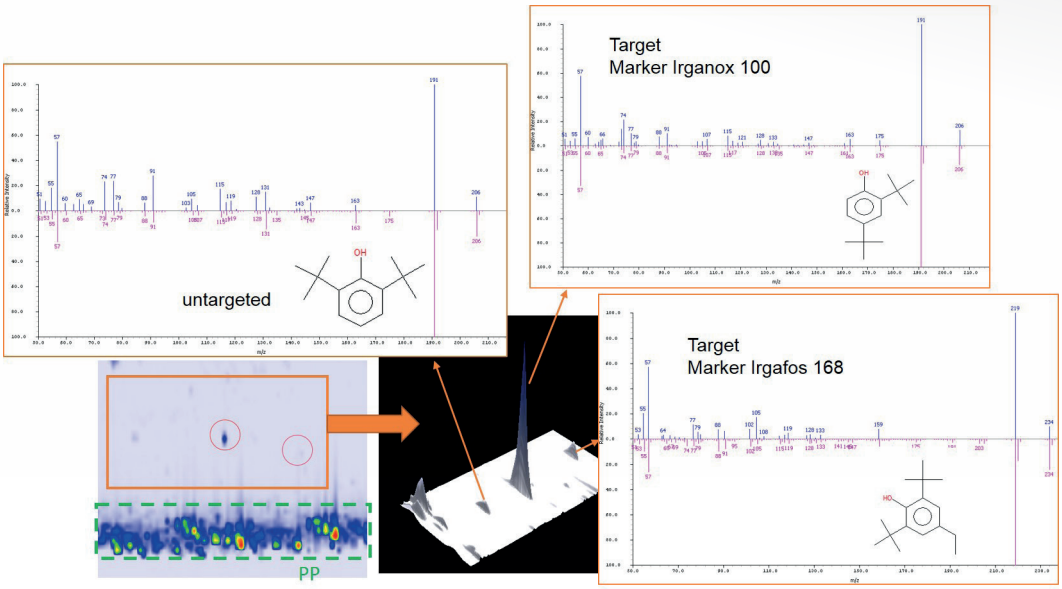

Fig. 2
Zoom-in for sample A and examples of NIST library search for targeted pyrolysis markers and an untargeted UV light stabilizer

These results are a very significant improvement compared to standard py-GC-MS. The automated search for the markers by deconvolution in the 1D pyrogram is not successful. The reasons for this are the poor response and the co-elution with the much more abundant and complex aliphatic group, which make the task highly challenging at best. The additives can be found by searching manually for known selective mass fragments and assessing the presence of consistent MS pattern, so the process relies heavily on the operator and is thus time-consuming and laborious.

CONCLUSIONS

- Py-GC×GC-MS is a very powerful analytical tool for the analysis of additives in polymeric materials.
- Targets can be found in an automated way without need for time-consuming deconvolution or laborious manual steps.
- The aromatic fragments of the target additives are efficiently separated by the aliphatic PP and identified with good confidence thanks to the clean spectra.
- The number of peaks fully resolved makes it possible to find and identify potentially interesting unknowns, providing a more complete composition overview of the sample.