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ANALYSIS OF A RANGE OF POLYMERS BY AUTOMATED PYROLYSIS GC-MS USING THE GERSTEL PYRO

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INTRODUCTION

Significant media attention has highlighted the issues of single use plastics in the environment. These often get shredded/abraded into microplastic that could be consumed by aquatic organisms. Pyrolysis GC-MS is a technique that allows identification of the polymeric material by subjecting the sample to high temperatures (up to 1000 °C) in an inert atmosphere, the resulting pyrolysis products are transferred to the GC-MS for chromatographic separation and analysis. These pyrograms can be compared with those of standards or literature data to allow the identification of unknown plastics. This application note demonstrated the use of the GERSTEL pyrolysis module to generate pyrograms for standard polymeric samples and unknown polymeric materials provided by the University of Birmingham. Mixtures of the polymer samples were also prepared and the chromatograms interpreted to identify the polymers present.

This approach could significantly aid the speed and identification of microplastics if an appropriate microplastic filter design could be devised.

INSTRUMENTATION

GC-MS: Agilent Technologies 7890A GC and 7000 MS with GERSTEL MPS Robotic autosampler, Thermal Desorption unit and pyrolysis module.

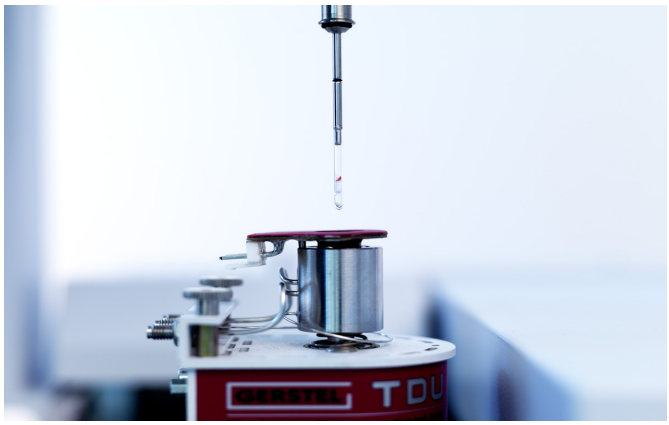

Figure 1: Image of sample tube being loaded into the TDU with pyrolysis module installed

METHOD

Aliquots of the polymer samples (<1 mg) were transferred into pyrolysis sample tubes. The MPS robotic sampler transfers these into the TDU with pyrolysis module. When the samples were loaded the TDU was at 50 °C this was held for 0.33 mins before heating to 300 °C at 720 °C/min. The pyrolysis module was then heated to 600 °C and held for 0.33 mins. The TDU with a split of 100:1, the CIS injector was heated to 300 °C and with a 100:1 split. This gives a combined split of 10000:1 showing the sensitivity of the technique.

Chromatographic separation was on a DB-5MS column of dimension 30 m x 0.32 mm x 0.25 µm. The oven was held at 50 °C for 2 mins then heated at 10 °C/min to 320 °C and held for 3 mins. The MS ran in MS2 scan mode between m/z 10-550.

RESULTS

Each of the provided samples were analysed individually, the resulting chromatograms are shown in Figures 2-11.

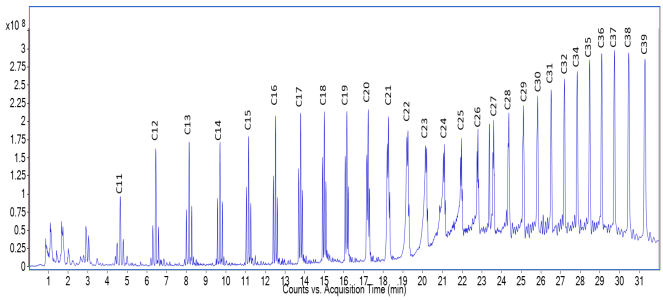

Figure 2: TIC of High-density polyethylene (HDPE) sample, showing peaks consistent with chain length repeating units and degree of unsaturation

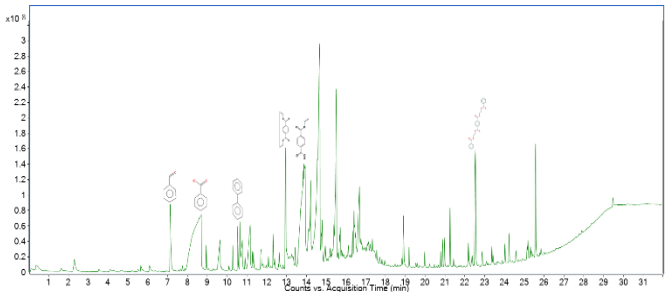

Figure 3: TIC of Polyethylene terephthalate (PET) sample, showing the presence of expected components such as vinyl benzoate, benzoic acid, divinyl terephthalate etc

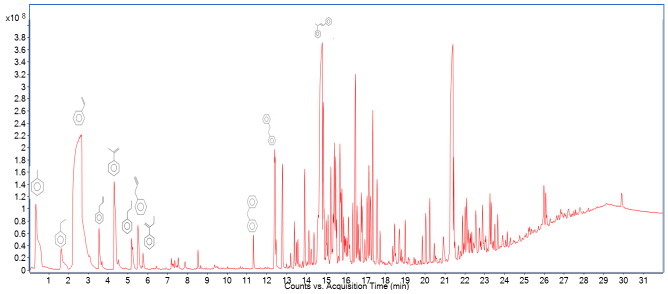

Figure 4: TIC of polystyrene (PS) chip sample, showing pyrolysis products of toluene, styrene, methyl styrene etc consistent with those of the literature

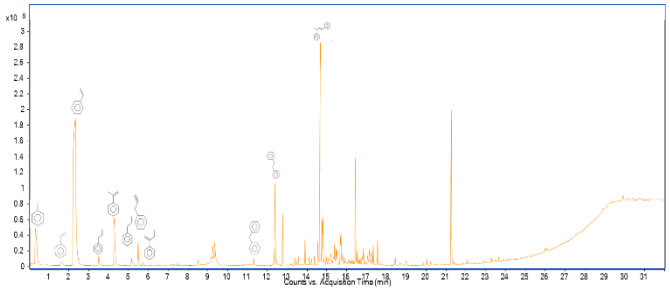

Figure 5: TIC of expanded polystyrene (EPS) sample, as with figure 4 this pyrogram shows the pyrolysis products consistent with polystyrenes

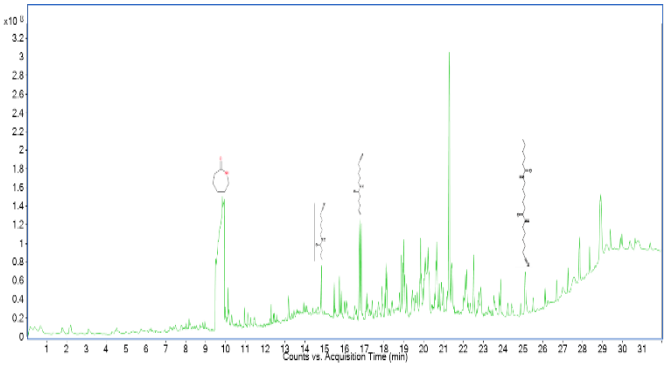

Figure 6: TIC of nylon 6 sample, with the major component matching caprolactam

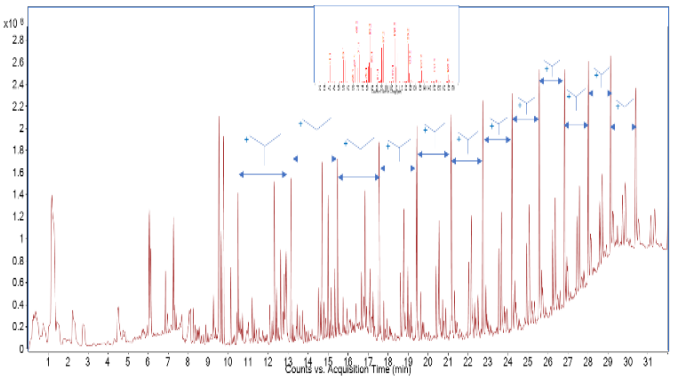

Figure 7: TIC of polypropylene (PP) sample, showing peaks consistent with chain length repeating units and degree of unsaturation

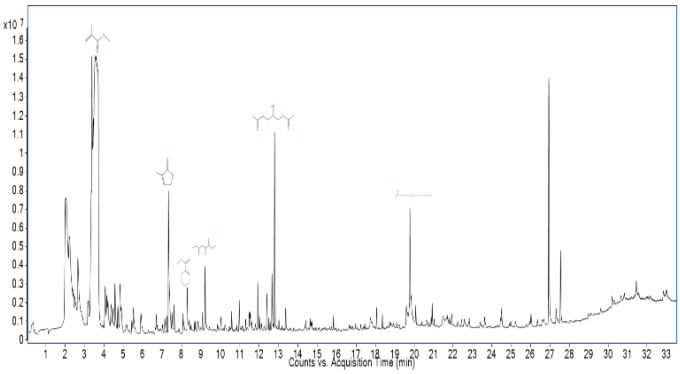

Figure 8: TIC of poly(methyl methacrylate) (PMMA). Showing the major component of methyl methacrylate as expected

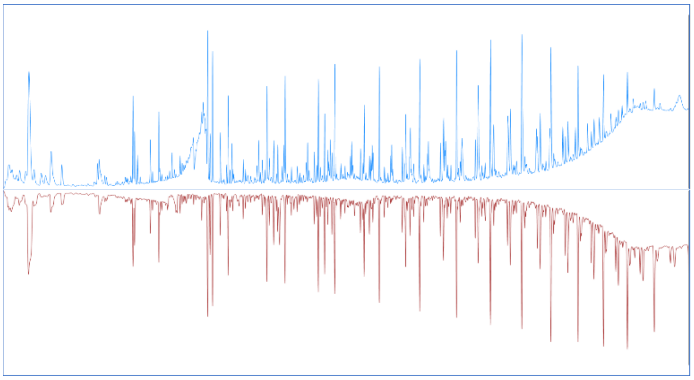

Figure 9: Comparison of the TIC of the unknown polymeric sample of blue rope and a PP standard

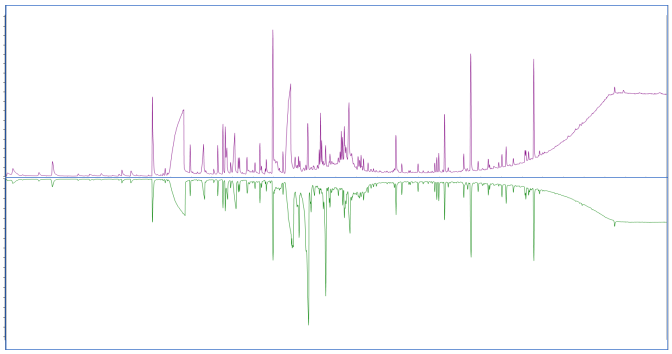

Figure 10: Comparison of the TIC of the sample of unknown polymeric pink string and PET sample

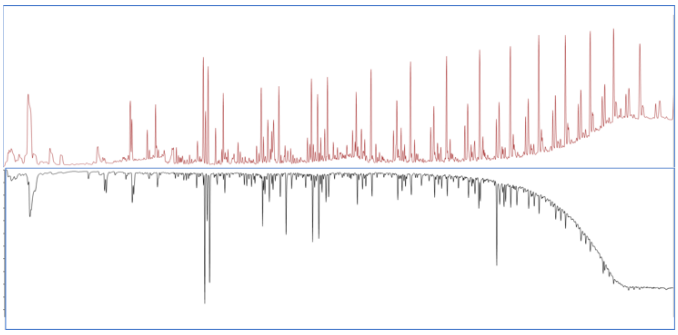

Figure 11: Comparison of the TIC of an unknown polymer chip and a PET standard. This shows a match for the major peaks but with different intensities due to differing sample quantities

Mixtures of samples were also prepared to ascertain if individual polymers could be identified from the features in the chromatogram. Examples of these can be seen in Figures 12 and 13.

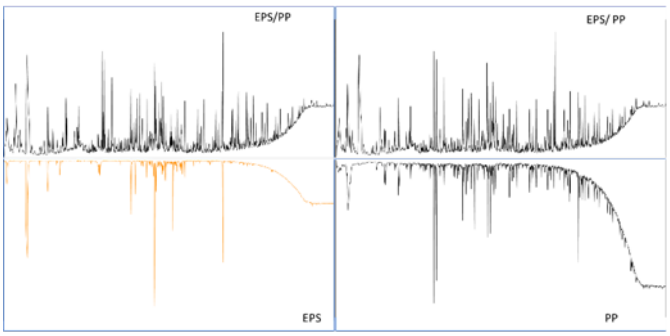

Figure 12: Mixture of EPS and PP compared with the individual components

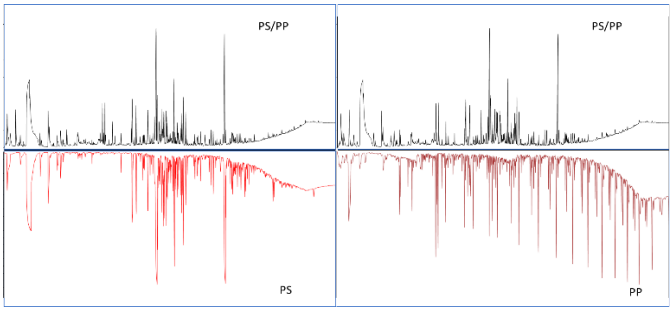

Figure 13: Mixture of PS and PP compared with the individual components, these show the same peaks but due to sample size change different intensities

DISCUSSION

On comparison of individual provided polymer standard's chromatograms with that of literature data, the major components shown in the literature were all present.

Among the samples provided were two typically found environmental contaminant products. One was a piece of blue rope, the pyrogram for this sample shows a close match to that of PP. The other typical environmental sample was a piece of pink string, this gave a profile similar to that of PET.

Of the evaluated mixtures there were sufficient discriminating peaks to allow identification of the component polymers present.

Pyrolysis GC-MS has been shown to be a sensitive technique capable of identification of very low quantities of polymeric materials. This could greatly aid in the identification of microplastics from environmental samples. We are interested in further developing the application and are seeking partners to collaborate with.

REFERENCE

Pyrolysis-GC-MS Data book of synthetic polymers: Pyrograms, Thermograms and MS of Pyrolyzates, Tsuge Shin, Ohtani Hajime & Watanabe Chuichi, 2011.