

## MICRO-THERMAL ANALYSIS AND EVOLVED GAS ANALYSIS

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### ABSTRACT

We have developed a thermal desorption method of trapping the gases that are evolved when a thermal probe is used to pyrolyze a sample. The trapped gases can then be desorbed and passed into a GC-MS system for separation and identification. With this system it is possible to ablate a small (<10 x 10  $\mu\text{m}$ ) area of a sample and elucidate its identity. When the thermal probe is used as part of a Micro-TA system, this capability expands the normal visualization and characterization of the sample to include the possibility of analyzing the sample (or a domain, feature or contaminant) as well. Here we will present our initial results when using this technique to analyze and identify a range of homo- and heterogeneous materials.

### INTRODUCTION

Microthermal analysis (micro-TA) combines the imaging capabilities of atomic force microscopy with the physical characterization capabilities of thermal analysis (1-3). Specimens may be visualized by means of their topography and ability to conduct heat. The images so obtained can then be used as a guide for the scientist to select areas and perform localized equivalents of the "macro-TA" techniques such as TMA and MTDSC. With some knowledge of the components in the sample and their likely thermal responses (*e.g.* melting point, softening temperature *etc.*) it is possible to use the results from such experiments to elucidate the nature and distribution of different phases within the bulk. Where the chemistry of the sample is unknown however, one may be forced to resort to the more traditional methods of analysis capable of providing spatially-resolved compositional information (such as X-ray photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS) and infrared microspectrometry).

Surface analysis methods such as XPS and SIMS are often inconvenient techniques to employ since they require the sample to be analyzed under high vacuum. The chemical information that they produce can be limited – especially in the case of complex mixtures. Infrared microspectrometry is difficult to use in a mapping mode and, like the aforementioned techniques, is easily defeated by the presence of multi-component systems.

In the “macro-world” there is a long history of using analytical pyrolysis methods to probe the nature of complex substances. Samples are simply heated so as to decompose them into small fragments which are then analyzed by mass spectrometry (MS) or capillary Gas Chromatography-MS (GC-MS). A number of systems have been described whereby the sample is heated in a thermobalance and the evolved gases trapped and analyzed (4). In the realms of micro-TA it is easy to use the resistively heated probe as a means of locally ablating material from the surface. We have now combined this into a system whereby the evolved gases are captured and then analyzed by GC-MS. Furthermore, the ability to perform localised pyrolysis experiments within a small volume of material enhances the value of the technique.

## EXPERIMENTAL

Measurements were carried out on a TA Instruments 2990 Micro-Thermal Analyzer based on a ThermoMicroscopes Explorer Scanning Probe Microscope with the addition of an active thermal probe and associated electronics. Imaging and localised thermal analysis can be carried out in the usual way. For pyrolysis experiments the probe is placed close to the region of interest and rapidly heated to 600°C. The evolved gases are trapped in a specially designed tube packed with a suitable sorbent such as Tenax or Carbopak. The tube comes to a fine point which is placed immediately adjacent to the heated tip using a micro-manipulator. As the tip is heated a syringe is used to draw gas through the tube which is then placed in a thermal desorption unit (TA Instruments Evolved Gas Collector) for analysis of the trapped volatiles by GC-MS (Hewlett-Packard 6890 Gas Chromatograph with HP5973 Mass Selective Detector). The GC was fitted with a HP-5 MS capillary column (30 m x 0.25 mm i.d. x 1.0 µm d.f.) and held at 40°C for 5 minutes following desorption and then heated at 15°C/min to 250°C. Mass spectra ( $m/z$  45-350) were acquired every 0.5 s. A blank desorption run was carried out before and after each experiment to confirm the cleanliness of the detection system. A photograph of the microscope and micro-manipulator is shown in figure 1. Figure 2 shows a view of the thermal probe and end of the sorbent tube as seen by the operator via a CCD camera attached to the microscope.

## RESULTS & DISCUSSION

An example of a pyrolysis crater on a poly(methyl methacrylate) sheet (ICI Perspex) obtained using the thermal probe is shown in figure 3. Line profiles horizontally and vertically across the image indicate that the pit is 6 µm in diameter and 1.7 µm deep (figure 4). Not all of this volume was pyrolyzed since some of the material flows away from the probe on heating. Figure 5 shows the total ion chromatogram obtained from the material trapped in the sorbent tube. A mass spectrum taken from peak at a retention time of 2.43 minutes corresponds to methyl methacrylate monomer generated by unzipping of the polymer (figure 6). This mode of decomposition is quite common for many addition polymers.

A scanning thermal micrograph of a sample of polystyrene (PS) pressed sheet is shown in figure 7. The raw material was believed to be contaminated with some pellets of poly( $\alpha$ -methyl styrene) (PaMS). DSC scans on the specimen were not conclusive since the glass rubber transition of PaMS is broad (50-60°C) and low intensity – particularly in this case where the PaMS is thought to be a minority component. The image contrast suggests that two phases are present and micro-TMA measurements indicate that the material present in the lower thermal conductivity region (bottom) has a softening temperature consistent with PaMS whereas the material in the higher thermal conductivity region is probably PS (figure 8).

Pyrolysis experiments on areas from the top and bottom of the image demonstrate proof of differences in composition between the two locations. PS and PaMS both decompose to yield monomer ( $m/z$  104 and 118 respectively for their molecular ions) (figure 9). Single ion chromatograms monitoring these masses are shown in figure 10. This confirms that the region at the top of the image is primarily composed of PS and that the region at the bottom of the image is mainly PaMS. There is evidently some cross-contamination of the two polymers (and there is also some contribution to the  $m/z$  104 ion from PaMS due to the 9%  $^{13}\text{C}$  abundance of  $m/z$  103 ( $\text{C}_8\text{H}_7^+$ ) derived from methyl loss from the monomer molecular ion (4)). Mullens *et al.* has used online thermogravimetry-FTIR evolved gas analysis and offline thermal desorption GC-MS to study a similar system (5). In the present study, we are not only able to detect the existence of impurities, but also determine where they are located.

## CONCLUSIONS

The combination of scanning thermal microscopy and localized thermal analysis presents a powerful new form of analytical microscopy, which is able to elucidate the organization and constitution of materials. The addition of a localized form of chemical analysis by pyrolysis-GC-MS to this technique provides an independent means of identification and which is essential in cases where there is no *a priori* knowledge of the specimen's makeup or there is unclear discrimination between phases. This combined approach presents the possibility of visualizing a specimen's structure, characterizing its thermal properties and analyzing its chemical composition.

## ACKNOWLEDGEMENTS

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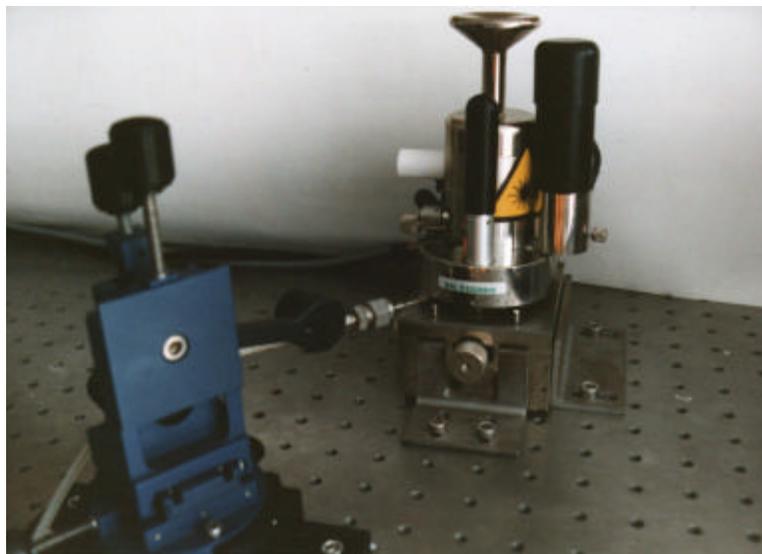


Figure 1. Micro-manipulator and microscope.

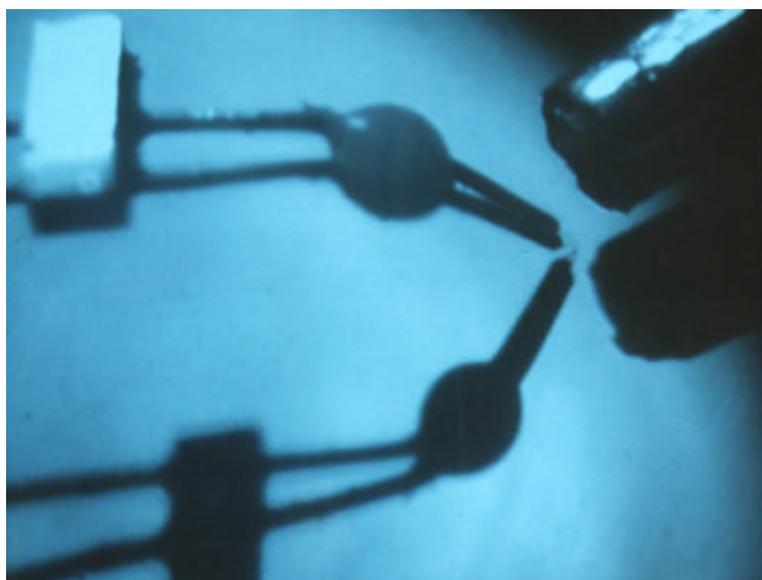


Figure 2. Thermal probe and end of adsorbent tube.

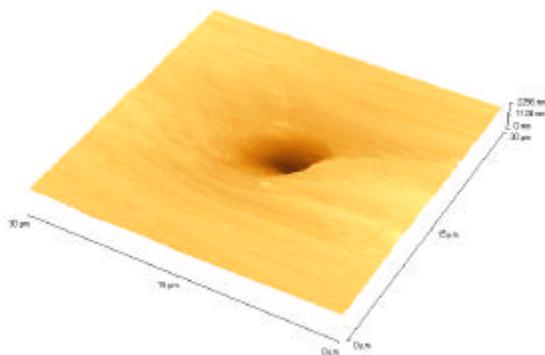


Figure 3. Three dimensional perspective view of a pyrolysis crater on a poly(methyl methacrylate) sheet.

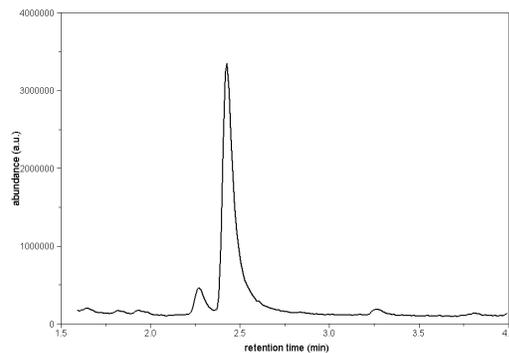


Figure 5. Total ion chromatogram of the pyrolysis products from the crater in figure 3.

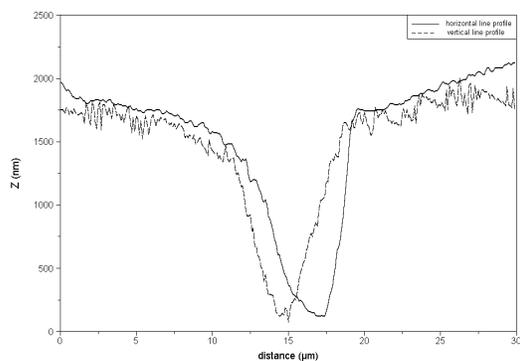


Figure 4. Line profiles horizontally (—) and vertically (-----) across the crater in figure 3.

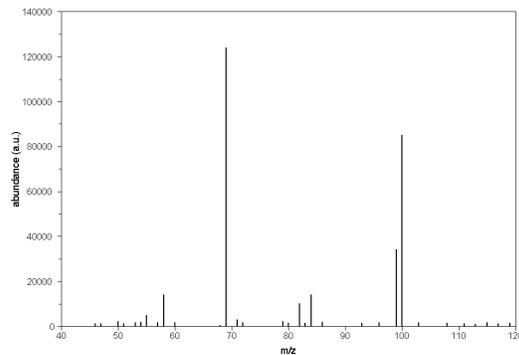


Figure 6. Mass spectrum of methyl methacrylate monomer at retention time of 2.43 minutes in figure 5.

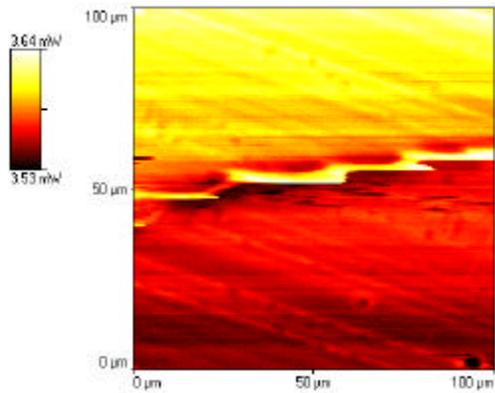


Figure 7. Thermal image of PS sheet containing PaMS (see text)

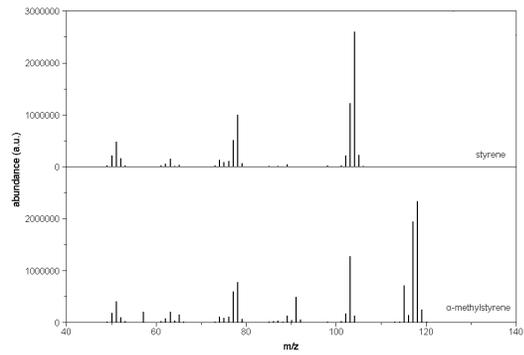


Figure 9. Mass spectra of styrene (top) and a-methyl styrene (bottom) - typical decomposition products of PS and PaMS.

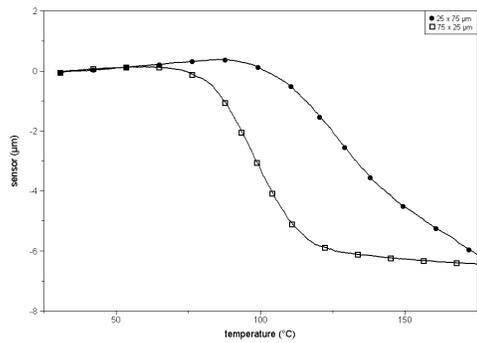


Figure 8. Micro-TMA curves for locations at top left (circles) and bottom right (squares) of the image in figure 7.

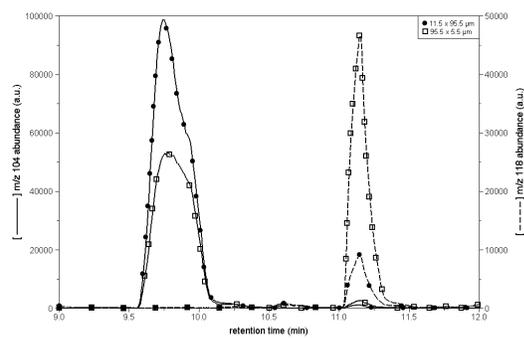


Figure 10. Single ion chromatograms for styrene (m/z 104) and a-methyl styrene (m/z 118) from similar areas as figure 8.