

## Hyphenated micro-TA techniques

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### ABSTRACT

Micro-thermal analysis (micro-TA) combines the imaging capabilities of the atomic force microscope with the ability to perform localized thermal analysis (calorimetry and thermomechanical measurements). This affords a means of physical characterization of different areas of a specimen by their thermal properties (eg. melting point or softening temperature). Localized chemical composition cannot be obtained directly by thermal analysis and is usually inferred by some *a priori* knowledge of the sample. In order to overcome this drawback we are developing hybrid instrumentation which interfaces the micro-TA system to a gas chromatograph-mass spectrometer, mass spectrometer or a FTIR spectrometer. For GC-MS and MS the thermal probe is used to pyrolyze a region of the sample. The evolved gases can be trapped for subsequent thermal desorption into a GC-MS or passed directly to the MS via a heated capillary transfer line. The ability of the thermal probe to act as a passive temperature sensor (rather than an active heater/heat flow meter) is exploited for FTIR measurements. In this mode the sample is irradiated by a broadband IR source focused on its surface by reflective optics and the temperature rise due to absorption of the radiation is detected by the probe and used to reconstruct its IR spectrum.

### INTRODUCTION

The major difficulty with conventional thermal analysis techniques is that they measure the response of the whole sample. If one observes a broad change in behavior on heating a specimen this could be the result of a genuine effect in a homogeneous system or be due to a series of overlapping responses from a heterogeneous system where there may be a gradation in properties throughout the sample. Alternatively, a weak effect seen in the entire sample could arise from a strong response from a minority component (e.g. an impurity) within in the bulk of the material. The same statements are true of other classical analytical techniques which require moderately sized amounts of material for sampling.

Micro-thermal analysis (micro-TA) is a form of analytical microscopy that affords the ability to perform calorimetric and thermomechanical measurements in a localized way so as to characterize the nature and distribution of thermal transitions in a specimen (1,2). Scanning probe microscope technology is used to move an ultraminiature heater/thermometer sensor across the specimen's surface so as to obtain images representing the sample's topography and apparent thermal conductivity. Other imaging modes are possible which can be used to generate

image contrast on the basis of thermal expansivity or to obtain 3-dimensional tomographic mapping of buried structures. These images can then be used as a guide to position the sensor over areas of interest and record its vertical displacement and thermal flux whilst it is heated in contact with the sample. These measurements represent the micro-analogues of TMA and DSC and can be used to establish the temperatures of thermal transitions of a region less than 5  $\mu\text{m}$  square.

The physical property measurements afforded by existing forms of micro-TA may, however, be insufficient to discriminate between different materials. Our aim therefore is to develop the means to add chemical analysis via two routes:

1. micro-TA-evolved gas analysis (Micro-TA-EGA)
2. micro-TA-infrared spectroscopy (Micro-TA-IR)

This opens up the possibility of imaging a specimen and performing a wide range of physical and chemical characterization using one versatile instrument.

### **MICRO-TA-EGA**

The standard probe tip used for micro-TA measurements can be heated rapidly and repeatedly to temperatures in excess of 600°C sufficient to bring about localized pyrolysis of organic materials. This process generates a small plume of gaseous decomposition products characteristic of the substrate. Chemical analysis of these products by either trapping and subsequent investigation using thermal desorption gas chromatography-mass spectrometry (td-GCMS) or direct sampling by mass spectroscopy (MS) are both potential methods for evolved gas analysis (1-4).

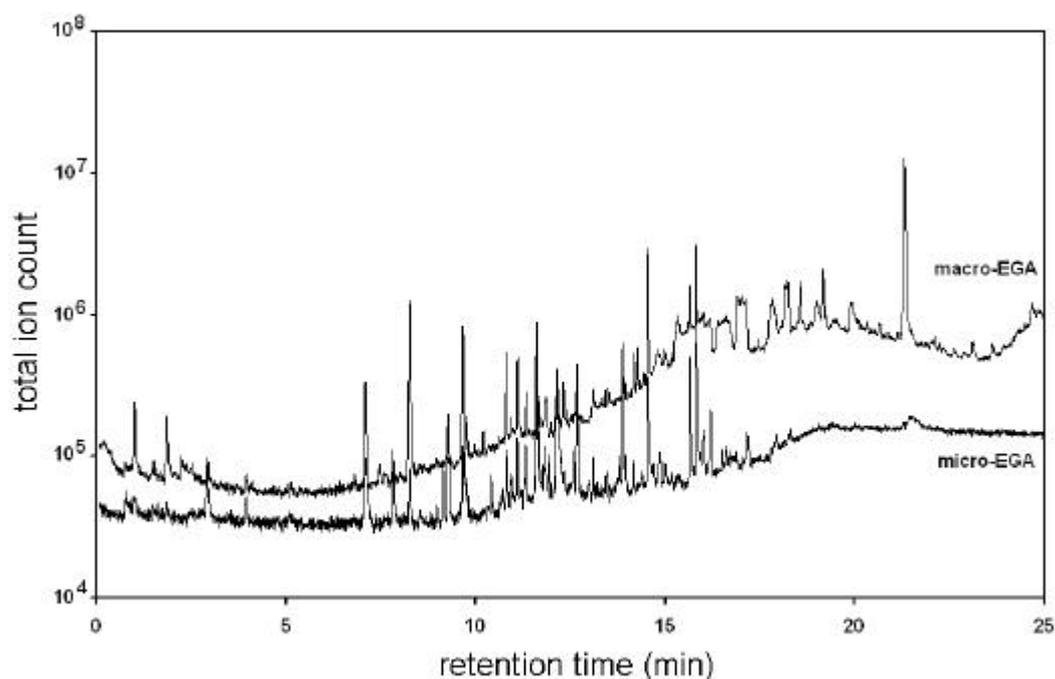
#### Micro-TA-GCMS

Development of the first approach – trapping and offline analysis – was facilitated by the design and construction of a miniature gas sampling tube packed with a mixture of Tenax (molecular sieve) and Carbopak (activated charcoal) adsorbent material. Such tubes are routinely used for environmental monitoring of hazardous factory atmospheres whereby operators during the normal course of their duties carry a small tube (about the size of a pen) clipped to their workwear. A pump may be used to draw gas through the tube at a controlled rate and at the end of the work period the tube is sealed and sent for analysis. Heating the sorbent tube drives off the trapped material into a gas chromatograph for separation and quantification.

For micro-TA-GCMS, the sorbent tube was modified to end in a short section of stainless steel hypodermic tubing (0.8 mm o.d., 0.4 mm i.d.), the open end of which was placed immediately adjacent to the heated thermal probe using a micro-manipulator. As the tip was heated, a pump was used to draw gas through the tube which was then placed in a suitable carrier that fitted in a standard thermal desorption unit interfaced to a GCMS system. Blank desorption runs of the sorbent tube were carried out before and after each experiment to confirm the cleanliness of the detection system. Such tubes are reusable since the

thermal desorption process cleans them of trapped material. The lifetime of such tubes is at least 1000 cycles.

One of the obvious benefits of offline trapping and analysis of pyrolysis products is the ability to take samples of evolved gases from more than one location on the sample. For example, if the region of interest covers a sufficiently wide area then multiple points may be selected for pyrolysis and the evolved gases gas be trapped in the same tube thus increasing the yield of material for subsequent analysis. Alternatively, line or area scans of surfaces may be made with a heated probe to drive off any volatiles into the tube. This approach has particular benefits for filled systems such as paints and coatings which may contain only a small fraction of organic binders. For example, figure 1 shows total ion chromatograms for the decomposition products from samples of the same household paint. The top curve (“macro-EGA”) shows material collected from a bulk sample (ca. 1 mg) of paint using a thermobalance to decompose the material and gas sampling tube in the purge gas outlet to collect the evolved gases. The lower curve (“micro-EGA”) shows material collected by scanning a hot thermal probe over at  $25 \times 50 \mu\text{m}$  area of the surface of the paint. Both curves show common features arising from the binder in the paint (polyamide and acrylic polymers), but also differences between the surface and the bulk indicating a reduction in antioxidants and volatile plasticisers (particularly the peak at 21.3 min due to dibutyl phthalate) at the exposed surface.



**Figure 1.** Comparison of evolved gases from bulk and surface of paint film.

Another benefit of analysis by GCMS is to use the ability gas chromatography to separate the mixture of decomposition products yielded by all

but the simplest of substrates. This allows complex systems (such as paints and coatings described above) to be identified or at least “fingerprinted” by the characteristic mixture of volatile materials formed during thermal degradation.

#### Micro-TA-MS

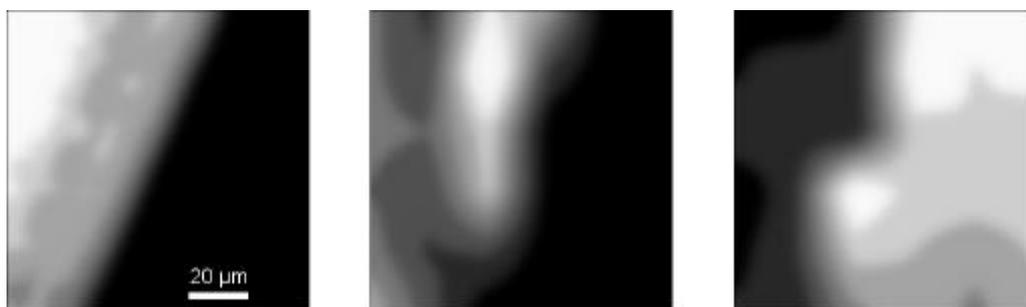
As an alternative to analysis of evolved gases by GC-MS, mass spectroscopy by itself can be used. This has the disadvantage of lacking the specificity given by the chromatographic separation but the advantage of considerably reduced time for analysis. One of the drawbacks of the td-GCMS approach is the time taken for the analysis of collected gases from the micro-pyrolysis experiment. The thermal probe itself may be heated at over 100°C/s to the required pyrolysis temperature and several locations may be examined within a few minutes. Desorption and separation of the trapped material is limited by the cycle time of the GC-MS system. Even with an optimised oven programme for the GC, a typical analysis can take 30 minutes. The need for a “blank” experiment with the tube prior to sampling in order to ensure that no residues are present in the system adds a further time penalty to the technique.

One way around this problem is to dispense with the trapping and separation stage by continuous sampling of the atmosphere around the thermal probe. This was achieved by using a small bore silica glass capillary transfer line (10 µm i.d., 1 m long) which also served to reduce the pressure from atmospheric to that which could be accommodated by the ion source of the quadrupole mass spectrometer. The capillary tube was surrounded by a heated jacket for most of its length in order to prevent condensation of volatiles on the walls of the tube. It was demonstrated that adsorption and desorption of material in an unheated transfer line lead to peak broadening and chromatographic separation of gases from the pyrolysis experiment. Only a few centimetres of capillary were left unheated – these were passed through an empty micro-sorbent tube (described above) so as to enable the same micromanipulator assembly to be used to position the end of the transfer line close to the thermal probe.

For online micro-pyrolysis-MS, three modes of pyrolysis were developed. Firstly, the temperature of the probe may be rapidly pulsed to the required temperature – the amount of material liberated depending upon the duration and temperature of the heat pulse. Secondly, a conventional temperature ramp can be applied to the probe whilst monitoring for evolved species. This approach has the benefit that the operator can select several locations within the 100 x 100 µm field of view of the microscope in order to carry out compositional mapping via evolved gas detection. Finally, a heated thermal probe may be brought into contact with a specimen whilst monitoring gas evolution. As the heat source nears the surface, material is progressively decomposed affording a means to depth profile through the sample so as to reveal buried layers beneath the surface.

As stated earlier, online MS sampling of evolved gases lacks the separation stage afforded by td-GCMS and less suited for analysis of complex systems. Thus, the two approaches can be used in tandem: td-GCMS for initial characterisation and direct MS for mapping. The sensitivity and speed of MS sampling is improved by monitoring for specific species rather than collecting mass spectra across a wide mass range during pyrolysis. For example, materials

containing aromatic species often evolve benzene amongst their decomposition products whereas aliphatic materials often give alkene fragments. The ability to examine a succession of points within a few minutes can enable a compositional map of the specimen to be obtained which shows the spatial distribution of phases in a specimen via its pyrolysis products. An example of this is shown in figure 2 for a poly(methyl methacrylate)/polystyrene laminate. Data from a  $6 \times 6$  array of pyrolysis measurements were used to reconstruct images based upon the yield of the respective monomers. Unlike similar methods of chemical imaging (e.g. secondary ion mass spectrometry and laser ionisation mass spectrometry), the sample is examined under ambient conditions rather than high vacuum. Three-dimensional tomographic imaging may also be considered by using the probe to ablate away the surface and reveal buried structures.



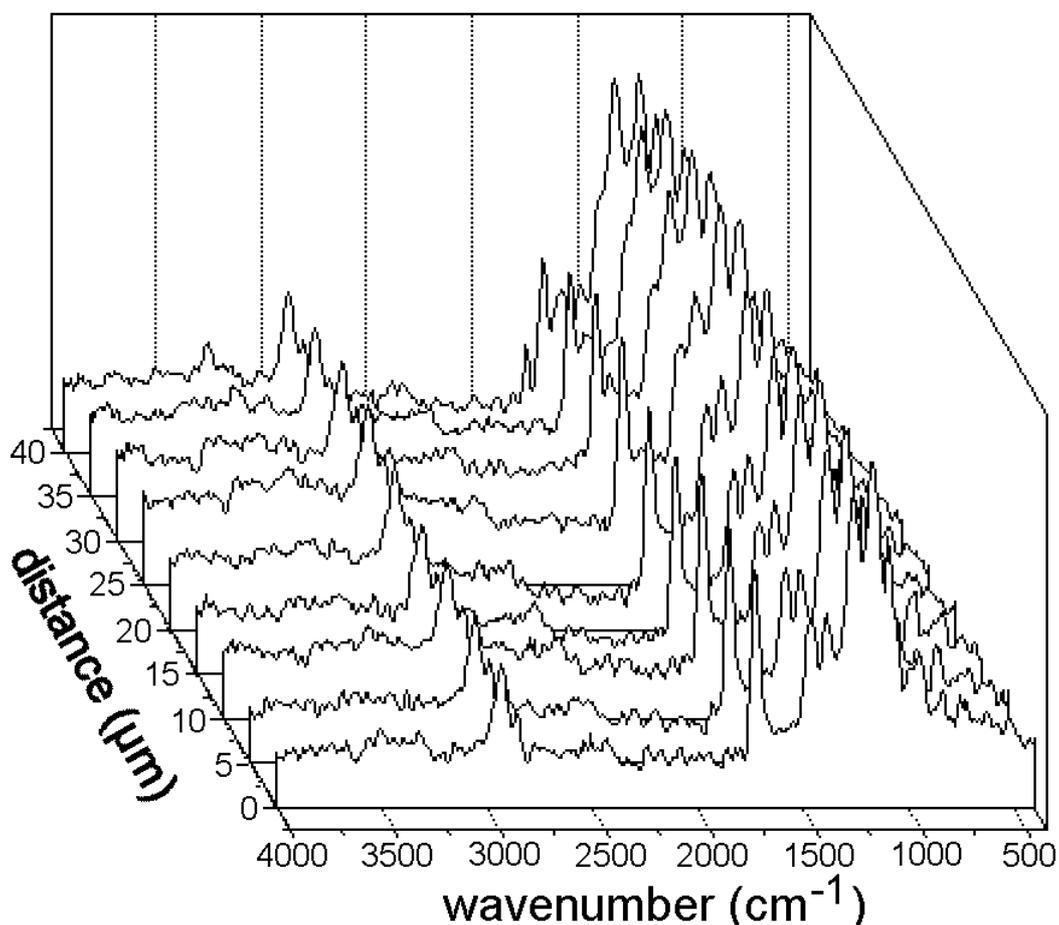
**Figure 2.** Left: topographic image of poly(methyl methacrylate)/polystyrene laminate – polystyrene layer is to the right of the image. Center: evolved gas “image” reconstructed from multiple pyrolysis measurements monitoring for methyl methacrylate monomer (molecular ion  $m/z$  100). Right: similar image reconstructed for styrene ( $m/z$  104).

### MICRO-TA-IR

This technique exploits the ability of the thermal probe to act in a purely passive mode as a localized temperature sensor. An interface has been designed which allows the micro-TA system to be mounted in the sample compartment of a standard FTIR spectrometer (2). IR radiation from interferometer is focused onto as small a spot as possible with the thermal probe located in the area of highest flux. The temperature change of the surface arising from the absorption of infrared radiation is detected (photothermal effect), amplified and used as the input into the spectrometer (5,6).

Unlike conventional IR microspectrometry, the spatial resolution of the technique depends upon the contact area between the tip and the surface rather than the diffraction limit imposed by the wavelength of the radiation used. Sub-micron spatial resolution should be possible and we have demonstrated the potential of the technique to characterize very small amounts of material extracted from the surface following a localized thermal analysis measurement. Nano-sampling may offer the benefit of improved lateral resolution compared with contact mode spectroscopy in that the contribution of material remote from the

immediate probe-sample contact zone is completely eliminated. Like micro-TA-MS, the technique also lends itself to imaging as shown in figure 3.



**Figure 3.** Stacked plot of photothermal IR spectra across the interface of a sample of nylon (at the back) embedded in an acrylic resin (front).

## CONCLUSIONS

The development of spatially resolved chemical analysis complements the imaging and physical characterization afforded by micro-TA. Particularly interesting is the possibility of chemical mapping of species by these techniques. All of these techniques can be integrated into a single versatile instrument that can truly be described as a "laboratory on a tip".

## REFERENCES

1. H. M. Pollock and A. Hammiche *J.Phys. D* **2001** 34, R23
2. M. Reading et al., *Macromolecular Symposia* **2001**, 167, 45
3. D. M. Price et al., *Thermochimica Acta* **2001** 367/368 195.
4. D. M. Price et al., *J. Thermal Anal. Cal.* **2001** 64 309.
5. A. Hammiche et al., *Appl. Spectroscopy* **1999** 53, 810.
6. A. Hammiche et al., *J. Vac. Sci & Technol B* **2000** 18 1322