Chapter 3

MICRO-THERMAL ANALYSIS AND RELATED TECHNIQUES

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1. 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 behaviour 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.

It is not surprising, therefore, that many investigators have combined studies by thermal analysis with such techniques as optical [1] or electron microscopy. For example, Price and Bashir [2] studied the thermal behaviour of poly(acrylonitrile) which had been compression moulded in the presence of water. Under conditions of high pressure, water acts as a solvent for this otherwise intractable polymer (which normally degrades on melting) allowing the material to flow. On cooling, the specimen has an open structure with the water trapped in pores within the polymer mass. Differential scanning calorimetry (DSC) was used to study the formation of ice within the pores on cooling. Analysis of the shape of the DSC curves show that the pore size followed an approximately bimodal distribution, whereas scanning electron microscopy indicated that a third category of larger pores existed which could not be detected due to the fact that they were incompletely filled with water [2].

Thermomicroscopy is the direct observation of a sample (usually) by optical microscopy (often with polarised light) as a function of temperature [1]. Frequently called “hot-stage (optical) microscopy”, this is a relatively common
technique which is used widely for the study of historical artefacts [3], polymorphic transitions in drugs [4], pyrotechnics [5], and also for following the crystallisation of polymers [6,7]. Other forms of high-resolution imaging such as electron and scanning probe microscopies have been combined with the use of a variable temperature sample stage. Of particular relevance to this discussion is the use of atomic force microscopy at temperatures other than ambient [8,9]. Studies by Grandy et al. [10] illustrate the potential of mechanical property imaging above and below transition temperatures of two phase polymer systems. Particularly novel is the application of a method of image analysis which seeks to assign a statistical probability of each pixel comprising the image to be one phase or the other (or an interphase). This is based upon the assumption that the contrast can be described using overlapping distributions of signal intensity arising from each component. Fasolka et al. [11] have published similar work using resonant frequency (rather than forced oscillation) non-contact atomic force microscopy where they also obtain images at a temperature between the glass-rubber transitions of a diblock polymer system.

The major disadvantage of any method of thermomicroscopy (whether optical, electron or scanning probe technique) is that the whole sample is heated at the same time. Changes in the sample which occur outside the field of view are not observed and if these changes are irreversible (e.g. the sample crystallises, degrades, two phases mix or separate) then a new sample must be prepared. Ideally, one would desire a means to obtain a high-resolution image of a specimen under ambient conditions and then carry out thermal analysis of a specific region, phase or contaminant identified using the image as a guide. Reading [12], in a patent application filed in May 1992, proposed an instrument based upon a scanning thermal microscope modified to perform spatially resolved modulated(-temperature) differential thermal analysis. Although such an apparatus was never constructed, subsequent development in a collaboration with Pollock and Hammiche resulted in a working instrument and three more patents [13-15]. Development and prototyping of this concept took place through collaboration between Loughborough and Lancaster Universities in the UK in conjunction with commercial and UK Research Council support. TA Instruments Inc. (Newcastle, Delaware, USA) launched this equipment as a commercial product in 1998. The instrument received the Gold Award at the 1998 PittCon analytical instrumentation conference and the R&D 100 award for innovation. In addition, the UK government awarded the instrument “Millenium Product” status.

Before considering the development of what has become known as “micro-thermal analysis”, it is appropriate to review the history, technology and
applications of scanning thermal microscopy so as to place this family of techniques in context.

2. SCANNING THERMAL MICROSCOPY (STHM)

The inventions of the scanning tunnelling microscope (STM) [16] and the atomic force microscope (AFM) [17] have allowed sub-micrometre and, at times, atomic-scale spatially-resolved imaging of surfaces. Spatially-resolved temperature measurements using optical systems are diffraction limited by the wavelength of the radiation involved, which is about 5-10 µm for infrared thermography and about 0.5 µm for visible light [18]. The spatial resolution of near-field techniques (such as AFM) is only limited by the active area of the sensor (which in the case of STM may be only a few atoms at the end of a metal wire).

The first experiments in scanning thermal microscopy (SThM) were carried out by Williams and Wickramasinghe [20] who employed a heated thin-film thermocouple fabricated from a conventional STM tip. As the tip approached a surface, it was cooled due to tip-substrate heat transfer. By using the temperature sensed by the thermocouple as a feedback to maintain a constant tip-substrate gap, this scanning thermal profiler could overcome the limitations of STM and be used to image electrically insulating surfaces with a lateral resolution of 100 nm. Since the feedback signal was based on maintaining a constant probe temperature, this device could not be used to obtain true thermal images of surfaces. Instead, the system measured a convolution of topography of the specimen and its thermal conductivity in a non-contact mode by means of heat leak from the thermocouple to the sample through a small air gap.

In an attempt to overcome the limitations of this method of SThM, Majumdar [21] described the use of an AFM cantilever fashioned from a pair of dissimilar metal wires (chromel and alumel) which met to form a thermocouple junction at the tip. In this way, the conventional AFM force feedback mechanism could be used to measure surface topography whilst at the same time mapping the temperature distribution of energized electronic devices with sub-micrometre resolution. Since this demonstration, a number of different probe designs have been developed and progress has been made towards the measurement of absolute thermal conductivities and 3-dimensional tomographic imaging. A general discussion of SThM can be found in the reviews by Gmelin [22] and Majumdar [18,19].
2.1. Instrumentation for SThM

The atomic force microscope forms the basis of both scanning thermal microscopy and instruments for performing localised thermal analysis. A schematic diagram of an AFM is shown in Figure 1 [23]. The instrument consists of a sharp tip mounted on the end of a cantilever which is scanned across the specimen by a pair of piezoelectric elements aligned in the x-y plane. As the height of the sample changes, the deflection of the tip in contact with the surface is monitored by an optical lever arrangement formed by reflecting a laser beam from the back of the cantilever into a photodetector [24]. The tip is then moved up and down by a feedback loop connected to a z-axis piezo which provides the height of the sample at each x,y position. Besides the topographic information provided by rastering the tip across the sample, other properties can be obtained by measuring the twisting of the cantilever as it is moved across the sample (lateral force microscopy) [25]. This provides image contrast based on the frictional forces generated from the sample-tip interaction. Other imaging modes, such as force modulation and pulsed force modes can indicate the stiffness of the sample [26]. An advantage of the AFM over the scanning electron microscope is that little sample preparation is required because the sample is not exposed to a high vacuum and electrically insulating materials can be examined.

Figure 1. Atomic force microscope (schematic) [23]. (With permission from Elsevier.)
2.2. **Probe design**

Three methods have been used to combine the conventional AFM cantilever with a means of localised thermometry.

2.2.1 **Thermocouple cantilevers**

The use of AFM with a thermoelectric element at the tip has been described above. In an effort to improve the performance of a bare thermocouple tip, Majumdar *et al.* [27] cemented a diamond shard to the junction so as to give a harder tip with improved spatial resolution and reduced thermal resistance. The same group also describe depositing successive layers of different metals so as to make thermocouple pair on top of a standard “A-frame” AFM cantilever [28]. Fish *et al.* [29] borrowed technology from near-field scanning optical microscopy to make a thermocouple derived from gold-coated glass micropipettes containing a platinum core. Workers at Glasgow University [30,31] have fabricated thermocouple probes using electron beam lithography and silicon micromachining in order to deposit one or more thermocouple junctions at the AFM tip. Such work leads to the possibility of building thermopile sensors (with the incorporation of a heater) analogous to a miniature heat flux calorimeter [32,33].

2.2.2 **Resistance thermometry**

![Figure 2. Schematic diagrams of resistive SThM probes: a) Wollaston wire type [34,35], b) micro-machined coated Si cantilever [37] and c) “data storage” doped Si probe [55].](image)

In 1994, Dinwiddie and Pylkki [34,35] described the first combined SThM/AFM probes that employed resistance thermometry to measure thermal properties. These were fashioned from Wollaston process wire. This consists of a thin platinum/5% rhodium core (about 5 µm in diameter) surrounded by a thick (about 35 µm) silver sheath. The total diameter of the wire is thus about
75 µm. A length of wire is formed into a “V” and the silver is etched away at the apex to reveal a small loop of Pt/Rh which acts as a miniature resistance thermometer (Figure 2(a)). A bead of epoxy resin is added near the tip to act serve as mechanical reinforcement and sliver of silicon wafer is glued to the top of the probe to act as a target mirror for the laser employed in the cantilever deflection detection mechanism [36]. This can be operated in two modes: a) as a passive thermo-sensing element (by measuring its temperature using a small excitation current) or b) as an active heat flux meter. In the latter case, a larger current (sufficient to raise the temperature of the probe above that of the surface) is passed through the wire. The power required to maintain a constant temperature gradient between the tip and sample is monitored by means of an electrical bridge circuit. In essence, this is equivalent to a power compensation calorimeter. Mills et al. [37] describe similar probes in which the resistance element is deposited across the apex of a silicon nitride pyramid similar to a conventional AFM cantilever (Figure 2(b)).

In a passive mode, such devices function like thermocouple probes described above. These can be used (for example) to map the temperature distribution in energised electronic devices simultaneously with their topography [38,39]. If the surface is illuminated with infrared radiation, the photo-thermal effect arising from the absorption of energy specific to the infra-red (IR) active modes of the specimen may be used to obtain the sample’s IR spectrum [40-47]. In the active mode, the heat flow from the tip can be used to detect surface and subsurface defects of different thermal conductivity than the matrix [48,49].

Other resistive probe designs have been reported. For example, Li and Gianchandani [50] have fabricated SThM probes using polyimide rather than silicon as a substrate in a process similar to that of Mills et al. [37] except that it exploits the mechanical flexibility of the polyimide to implement an assembly technique that eliminates the need for probe removal or wafer dissolution. Use of polyimide rather than silicon as a substrate offers a greater degree of thermal isolation since its thermal conductivity is three orders of magnitude lower than silicon [51]. These probes have been manufactured in a differential arrangement with one probe being used as a reference. Edinger et al. [52,53] describe a sensor consisting of a nanometre-sized filament formed at the end of a piezoresistive atomic force microscope type cantilever. The freestanding filament is deposited by focussed electron beam deposition using methylcyclopentadienyl trimethyl platinum as a precursor gas. The authors claim a spatial resolution of < 20 nm and, due to its small thermal mass, a high sensitivity and fast response time. Leinhos et al. [54] have fabricated thermal elements from silicon with a Schottky diode integrated into the probe tip. One design of such a probe may also be used for simultaneous scanning near-field optical microscopy as well as SThM and AFM.
Chui et al. [55] also describe high resolution silicon (piezo)resistive cantilevers designed not for SThM, but for high-density data storage. An array of probes are used to “write” 10-50 nm diameter pits in a spinning polymer coated silicon disc [56]. Read-back is achieved by making use of the increased cooling of the tip when it encounters the indentations when the probes are operated in SThM mode. Such an approach is essentially the reverse of micro-thermal analysis in that the marks produced as a consequence of localised thermomechanical experiments are detected by the effect of their topography on the heat flux rate between the probe and the sample [57]. Schematic diagrams of the Wollaston, micromachined silicon and “data storage” probes are shown in Figure 2(a-c). The spatial resolution of these probes is of the order of 2, 0.2 and 0.02 µm respectively. All of these designs are now commercially available.

2.2.3 Bimetallic sensors

Nakabeppu et al. [58] describe the use of composite cantilevers made from tin or gold deposited on conventional silicon nitride AFM probes to detect spatial variations in temperature across an indium/tin oxide heater. Differential thermal expansion of the bimetallic elements causes the beam to bend. This movement is monitored using the AFM optical lever deflection detection system. In order to separate thermal deflection of the beam from displacement of the cantilever caused by the sample topography, an intermittent contact mode of operation is employed. Measurements were made under vacuum so as to minimize heat loss. A more practical use of this technology is in the form of miniature chemical and thermal sensors [59]. This approach has been used to perform thermal analysis on picolitre volumes of material deposited on the end of a bimetallic cantilever [60]. Arrays of such devices have applications as highly sensitive electronic “noses”.

2.3 Quantitative SThM

Small-scale measurements of thermal conductivity and thermal diffusivity would benefit the semiconductor and other industries where thermal transport properties are significantly different to, and cannot be inferred from, measurements at higher scales. Examples of key areas of modern technology and science which might be expected to benefit include microelectronics, cellular biology, forensic, pharmaceutical and polymer science etc. In theory, heated thermal probes are capable of measuring the absolute thermal conductivity of materials by the heat flux between the tip and the surface. In practice, heat losses also occur both within the probe and to the atmosphere. Furthermore, the contact area between the tip and the specimen is usually unknown. Ruiz et al. [61] developed a simple method for converting heat flux to
thermal conductivity by using hard materials of known thermal conductivity to calibrate the system. This procedure was used to determine the thermal conductivity of diamond-like nanocomposites to a precision of ±15%. Gorbunov et al. [62-64] measured the change in heat flux as the probe approached the sample surface, or was ramped in temperature in contact with the specimen, so as to derive its thermal conductivity – again by calibration with samples of known response. This approach has been used to study IR receptors in snakes with a view towards designing artificial sensors which mimic those found in nature [65]. Fiege et al. [66] used AC heating of the tip to measure the thermal conductivity of silver and diamond, using gold as a single-point reference material in order to estimate the contact area of the tip. Blanco et al. [67] have used SThM to investigate qualitative differences in thermal conductivity of carbon-carbon composites arising from different processing histories.

Figure 3. Illustration of the convolution of surface roughness on the apparent thermal conductivity (k) measured by the tip during a line scan. Darker coloured material (left) has lower bulk thermal conductivity than lighter coloured material. See text for additional explanation.

The thermal conductivity contrast image obtained by scanning thermal microscopy represents a convolution of the true thermal transport properties of the specimen with artefacts arising from changing tip-sample thermal contact
area caused by any surface roughness of the specimen [48]. When the probe encounters a depression on the surface, the area of contact between the tip and sample increases, resulting in increased heat flux from the tip to the sample. More power is required to maintain the tip temperature at the set-point value and this is recorded on the image as an apparent increase in the local thermal conductivity. The opposite is true when the probe meets an asperity. Visual comparison of the thermal image with the topographic image (recorded simultaneously) often shows that “features” in the former are correlated with changes in height of the specimen – particularly at edges of such features where the surface relief changes rapidly. Even with careful sample preparation (e.g. cutting or polishing) it is almost impossible to avoid artefacts in the thermal image not attributable to topography. In cases where there is little inherent thermal contrast between parts of a heterogeneous specimen, interpretation of the thermal image can be problematic. An example of this is illustrated in Figure 3 for three cases: 1 – a homogenous material flat surface; 2 – the same material with a depression and an asperity; 3 – a smooth interface between low thermal conductivity and high thermal conductivity phases & 4 as 3, but with added surface roughness.

In theory, it would be possible to construct an analytical model of the probe-surface interaction based upon the local geometry of the probe tip and surface [62-64]. Rather than develop a general model for heat transfer, an alternative approach can be developed using a neural net algorithm [68]. Each digitised image consists of a grid of points (pixels) which define the height of the sample and the heat flux from the probe to the sample. For each pixel the local topography is characterised by subtracting its height from the heights of the surrounding points. This defines whether the probe rests in a depression, asperity, flat surface, etc. The training set for the neural network comprises images acquired on materials of homogeneous thermal properties with a range of surfaces roughnesses. From these samples a table of topographic parameters correlated with the thermal measurement is obtained for a wide range of surface roughness. The ‘true’ thermal measurement is the value obtained on a perfectly smooth surface. In practice, an average value from the smoothest available surface can be taken as the ‘true’ value. In each case, the required value is given as the measurement on a smooth surface.

The usual procedures for training, testing and validation of a neural network can be applied to result in a method to take a pair of images (thermal and topographic) and effectively “subtract” artefacts arising from surface roughness. As an alternative to lengthy training with a variety of specimens, it is feasible to use the images of a test specimen itself to train the network. This method relies upon the sample having discrete areas of homogenous thermal conductivity to provide internal calibration values for network training. Figure 4 shows the
results of carrying out this type of image processing on a sample of polyolefin packaging film. Despite careful sample preparation, differences in mechanical properties result in a non-flat sample after cutting with a microtome. This generates false contrast in the raw thermal conductivity image which is largely eradicated by processing with a neural net which was trained using a series of polymers of differing surface roughnesses.

Figure 4. Left – topography of microtomed cross-section through a multi-layer polyolefin packaging film. Centre – raw thermal conductivity contrast image. Right – thermal conductivity image post-processing with trained neural net program.

Other methods of image processing have been devised which apply a statistical analysis of pixel intensity distribution to enhance image contrast. Royall et al. [69] have used such a method to discriminate between the substrate and coating of a pharmaceutical compact whereby each pixel is defined to be one or the other component according to the heat flux from the tip to the sample. This simple “on/off” data treatment can be extended to assign a probability (displayed as a grey-scale level) of being a certain component based upon the position of the pixel’s intensity within the total distribution of values. This procedure is illustrated using a non-prescription analgesic tablet containing paracetamol (acetaminophen) described below.
Figure 5. (a) Raw thermal conductivity contrast image of an analgesic tablet containing paracetamol [70], (b) histogram showing distribution of pixel intensity fitted to two overlapping Gaussian peaks assigned to the drug and filler components.

Figure 5(a) shows the raw thermal conductivity image of an analgesic tablet containing the drug paracetamol (acetaminophen). Localised thermal analysis of the sample indicates that the bright area in the bottom right of the image is some form of thermally inert filler whereas the dark regions comprise the drug [70]. Inspection of a histogram of pixel distribution in Figure 5(b) shows that the shape of this distribution can be modelled using two overlapping Gaussian peaks corresponding to the drug and filler responses.

Figure 6. (a) Simple black and white separation of image shown in Figure 5(a) using a threshold of 1.66 mW, (b) Grey-scale separation of image shown in Figure 5(a) using a more complete statistical analysis of the original histogram distribution in Figure 5(b).

A simple means of highlighting the two phases might be to assign a zero grey-scale intensity to pixels with an original value below the cross-over between the two peaks at 1.66 mW and a grey-scale intensity of unity to all the pixels above this threshold. Thus, points which are statistically more likely to be comprised of the drug appear black and those which are more likely to be the filler appear white (Figure 6(a)). This is the same, simple method of image processing that has also been found to be particularly applicable to mechanical property imaging modes (pulsed force mode atomic force microscopy) in combination with a variable temperature sample stage [10]. A more refined approach is to generate a grey-scale value for each pixel based upon the probability of it belonging to the drug or filler component derived from the ratio of the value of the fitted
peak height assigned to the filler to the total fitted histogram intensity. The resulting transformation of the thermal image in Figure 5(a) via this process is shown in Figure 6(b) and exhibits a more satisfactory discrimination of phases – particularly at the interface between the two domains where there exists some uncertainty over their assignment.

De Cupere and Rouxhet [71] have recently published a similar method of image contrast enhancement based upon splitting a surface friction image into two components using the pixel intensity histogram. The resulting image was cleaned by selectively erasing any foreground pixel in contact with a background pixel (“erosion”) and the final image was obtained by reconstruction of the objects left after erosion. This procedure, which is similar to that described above, was used to measure the surface fraction of spherulites grown on amorphous poly(ethylene terephthalate) film after different annealing times.

2.3 Other SThM techniques

2.3.1 3-D tomographic imaging

The decay length of thermal waves produced by AC heating of a tip varies as a function of the reciprocal of its frequency [72]. Thus, it is possible to detect variations in thermal response at shallower depths by using a high frequency temperature modulation superimposed on the conventional DC heating of the tip. Several groups have employed this technique to study the thermal diffusivity variations in materials [49,73,74]. Gomès et al. have examined this process theoretically [75] and there is potential for the use of multiple frequency modulated-temperature SThM as a means to provide non-destructive three-dimensional imaging of optically opaque samples using similar principles to those employed for medical imaging by electrical impedance tomography [76-79].

2.3.2 Thermal expansivity imaging

An additional imaging mode has been demonstrated whereby the thermal expansion of a specimen is detected whilst AC heating is applied to the probe as it is scanned over the surface [23,70,80,81]. The resulting z-axis modulation of the probe arising from thermal expansion and contraction of the surface is detected and used to construct an image based on the thermal expansivity of the sample. Although Majumdar [82-84] has also described similar measurements, this approach does not require electrically conductive specimens and employs the same configuration used for thermal conductivity imaging. Again, there is the potential for using this approach for tomographic imaging.
3. LOCALISED THERMAL ANALYSIS

3.1 Principles

Active, resistively-heated, thermal probes readily lend themselves to localised thermal analysis. Although it is feasible to control the temperature of a thermocouple-based probe by passing a current through it [86], the simultaneous measurement of its temperature is non-trivial and requires filtering out of the current providing the heating. Probes based on resistance thermometers are more readily controlled and this technology forms the basis of the well-known power-compensation differential scanning calorimeter [87]. Using a previously acquired topographic and/or thermal image obtained by the SThM facility, it is possible to place the probe at one or more selected locations in sequence on the sample and program the tip’s temperature in order to make localised measurements of transition temperatures. By monitoring the power required to follow the temperature programme, a form of spatially resolved calorimetry may be carried out [49,89]. In addition, since the vertical deflection of the tip can be determined using the AFM stage, localized thermomechanical analysis (TMA) may be performed concurrent with the calorimetry [72,90]. A linear temperature ramp of the order of tens of degrees Celsius per second is the most commonly employed programme, often with a superimposed sinusoidal modulation of the probe temperature at kilohertz frequencies about the mean set-point. The use of AC heating allows two extra calorimetric signals to be obtained – the AC power and phase difference between the applied modulation and probe response – akin to AC calorimetry [88]. Such high heating (and cooling rates) are possible as a consequence of the small size of the probe and the region (typically a few μm square) of material that it contacts. The apparatus developed by Fryer [91] employs lower heating rates (of the order of a few degrees Celsius per minute) because of manual control of the probe set-point temperature and lack of automatic data logging.

At present, only the analogues of DSC and TMA are commercially available. Localised dynamic mechanical analysis (DMA) has also been demonstrated [23,70,72,80,92]. Here, the force between the thermal probe is modulated during the temperature ramp. Such a procedure may also be used as an imaging mode in order to obtain a map of variations in mechanical properties across the specimen [80,92]. Localised modulated-temperature TMA has been performed whereby the amplitude and phase difference of the modulation in z-axis displacement of the probe is detected whilst a temperature ramp with overlaid AC modulation is applied to the tip [81]. An indirect form of thermogravimetry has been reported whereby the mass of material remaining adhered to the tip was monitored indirectly using the AC calorimetric signal [70]. By employing...
stiffer cantilevers with integrated heaters, the mechanical resonance frequency of the beam has also been used to measure the mass of material on the tip during heating [93].

3.2 Calibration [94]

Localised thermal analysis has generally been used as a qualitative tool; that is, it is primarily used to identify the material being examined or for examining compositional gradients within materials. The temperature at which a transition takes place is often of primary interest, although it may be possible to add further semi-quantitative interpretation of the data from the magnitude of the change (e.g. amount of probe penetration) observed. Like all thermal analysis techniques, interpretation of results requires detailed temperature calibration procedures and an understanding of the precision of the temperature measurement.

A good reference material has a number of desirable properties including a well-documented value, availability in a suitable form for analysis, homogeneity, stability, low toxicity, and traceability to a national reference laboratory (NRL). In traditional DSC and TMA, metals like indium, tin, and zinc meet these criteria. These metals are not suitable for temperature calibration for localised thermal analysis, however, as they may contaminate the probe tip thus changing its resistance and defeating the object of calibration. Organic calibration materials are more suitable for calibration as they do not react with the probe and the tip may be easily cleaned at the end of an experiment by heating to above 500 °C in air. This is sufficient to decompose most organic substances. The British Laboratory of the Government Chemist (LGC), a national reference laboratory, conveniently offers eleven organic reference materials with melting temperatures ranging from 41 to 285 °C. However, in these materials are generally unsuitable to be used directly and large flat polycrystalline surfaces must be prepared by melting a small amount of substance in a suitable holder (such as small cup aluminium foil) and then cooled.

Many investigators, particularly those working in the field of polymer science, prefer to use films of semi-crystalline thermoplastics such as poly(caprolactone or polyethylene terephthalate) as melting point standards. Whilst less desirable from a theoretical standpoint, temperature calibration with polymeric films offers a number of ease-of-use advantages. Moreover, many polymers have high melting temperatures that provide a calibration range of nearly 300 °C, a range difficult to achieve with organic chemicals. Generally, a two point temperature calibration is carried out spanning the experimental range of interest. Whatever protocol the investigator adopts, it is essential that the method is well-documented so that it can be replicated.
3.3 Features

There are several important differences between the localised calorimetric and thermomechanical measurements and their more conventional “bulk” analogues. Firstly, for the calorimetric measurements, the sample size is poorly defined. This is because the contact area between the tip and specimen is ill-defined. Furthermore, should the sample soften during the measurement, the probe will sink into the specimen thus aggravating this effect. Therefore, there is often a strong correspondence between the shape of the calorimetric response and the displacement of the probe [95]. A second-order effect, not often considered, is that the temperature gradient extending away from the heated tip will be affected by the properties of the specimen and the heating rate employed during the measurement. This is analogous to the modulated temperature SThM mode of imaging which has been considered by Pollock and Hammiche [85] whereby the depth of penetration of the thermal wave emanating from the tip decays more rapidly for higher modulation frequencies. Slough [96] has considered the case of a heat pulse lasting the duration of the temperature programme of the probe for a typical polymeric sample. His calculations suggest that for an instantaneous heat pulse of 200°C delivered for one second to the surface of a sample of polystyrene at 25°C, the specimen’s temperature is not significantly affected 10 μm from the probe. Inoue and Uehara [97] have modelled this process at a more sophisticated level in the context of data writing and erasing in a phase-change optical disk. Melting of a crystalline material at a part of the surface causes surface rippling around the molten area and subsequent rapid cooling generates an amorphous spot. This amorphous material is maintained at low temperature and subsequent localised thermal analysis can be used to determine the glass-rubber transition temperature of this region.

The way in which localised thermomechanical measurements are performed also differs from conventional measurements. In the usual implementation of these measurements, the feedback loop between the cantilever force and the z-axis piezo control is disabled at the start of the experiment. Thus, the probe is initially applied to the surface with a user-defined cantilever deflection which will change (thus giving the displacement of the tip by means the optical lever formed by reflecting a laser spot from the back of the probe into a photodetector) during the course of the measurement. Should the specimen soften during the experiment, the probe will indent into the sample and the force on the tip will decrease (possibly to the extent of losing contact with the sample).

A final effect often observed during localised thermal analysis arises from the high heating-rates that can be employed. Many thermal transitions are governed by kinetic laws which define the time dependence of such processes as
devitrification and thermal degradation. As a consequence of this, some transitions can appear at elevated temperatures when compared to bulk measurements at more modest heating rates - even after careful calibration of the instrument. This effect is not generally seen for melting phenomena, and the rapid heating affords a means of measuring the melting temperature of metastable materials without them undergoing rearrangement to more stable forms [98].

Figure 7. Localised thermal analysis of semi-crystalline poly(ethylene terephthalate) showing two consecutive measurements at the same location (solid line is the probe displacement, broken line is the probe power, filled symbols denote first upwards temperature scan, open symbols denote second upwards temperature scan, heating rate 10 °C s⁻¹).

Some of the above aspects of the technique are illustrated in Figure 7. This shows two measurements performed consecutively on the same region of a sample of poly(ethylene terephthalate) of approximately 40% bulk crystallinity at a heating rate of 10 °C s⁻¹. During the first upwards temperature scan, very little effect is seen in the probe displacement until melting of the polymer occurs around 250 °C. This is mirrored by an increase in probe power which is largely arises from the increased contact area between the tip and the sample as it indents the surface. A small decrease in probe power occurs around 125 °C, well above the "normal" glass-rubber transition temperature of this polymer of 70-80 °C. This feature might be ascribed to devitrification of amorphous material present. Immediately the first measurement was completed, the tip was lifted clear of the (now molten) material. The polymer in this area is rapidly quenched to room temperature by the surrounding specimen. On carrying out a second scan of the same region, the glass-rubber transition is observed readily in
both signals, without any evidence for further rearrangement to crystalline material above this temperature or subsequent melting of any crystals so formed.

### 3.4 Terminology

The nomenclature of this new method of analysis is still under development. The originators (Hammiche, Pollock and Reading) devised the terms “Calorimetric Analysis by Scanning Microscopy” (CASM) as a name for the measurement of probe power, and “Mechano-thermal Analysis by Scanning Microscopy” (MASM) as part of an effort to coin a systematic hierarchy of terms for this family of techniques [72]. The commercial term for this field is “μTA” which is a registered trade mark of TA Instruments Inc. (Newcastle, Delaware, USA) who also holds trademarks on the terms “μDTA” and “μTMA” corresponding to the calorimetric and thermomechanical methods [99]. Many authors have used the terms: “micro-thermal analysis” (with or without the hyphen, abbreviated to “micro-TA”) and corresponding terms “micro-DTA” and “micro-TMA”. Such usage goes against the recommendations of the International Confederation of Thermal Analysis and Calorimetry nomenclature committee who claim that there is ambiguity over the term “micro” because it is not clear whether the term is related to sample size (mass, volume), the size of the instrument, or the value of the measured signal (which may be amplified) or quantity detected [100]. (At least one company markets a “micro-DSC” which is a high sensitivity instrument for measuring heat flow in the μW range.) The general term which seems to be gaining popularity is “local(ised) thermal analysis” and the derivations “local(ised) calorimetry” and “local(ised) thermomechanical analysis” in order to differentiate this technique from traditional forms of thermal analysis which measure the global response of the sample [101]. In this discussion, the term “micro-thermal analysis” (or “micro-TA”) is used to denote SThM and localised measurements, whereas the individual measurements are described in full. Until there has been time for the terminology to develop and become accepted, searching the growing literature on this subject will be difficult.

### 3.5 Applications

Since its development and subsequent commercialisation, localised thermal analysis has been employed in a number of different disciplines. A review by Pollock and Hammiche [85], summarises the wide range of materials which have been studied by these techniques. An earlier paper by Price et al. [102] describes measurements on polymers, electronic components and biological specimens in the same publication as an illustration of the wide applicability of
such measurements. Articles in popular technical publications have also served to illustrate this point [72, 90, 103-105].

3.5.1 Polymers

Localised thermal analysis has been used for the characterisation of multi-component polymer thin films [101,109,110] or polymer blends [102,111-113], for the investigation of surfaces and interfaces between materials [92,98,114-126], and compositional gradients brought about by the specimen’s processing history [90,126-131]. In particular, localised thermal analysis is useful for probing the behaviour of polymers used for the fabrication of microelectronic components, where the bulk response of the polymer may not be representative of the same material when it is present in thin layers [126,132-136]. However, care must be taken to ensure that an apparent elevation in transition temperature is not due to the substrate acting as a heat sink, thus leading to errors in temperature measurement [137]. One interesting application of localised thermal analysis is to use the thermal probe for in-situ processing of materials, whereby heat is used to cross-link or decompose the substrate [126,138,139]. Again, this technology lends itself to data storage and micro-machining [140].

![Figure 8](image)

**Figure 8.** Localised thermal analysis of multi-layer polyolefin film shown in Figure 4 [105].

Two examples of the use of localised thermal analysis are provided in order to illustrate the generic applications of this approach. Figure 8 shows localised thermomechanical analysis of the surface of the multi-layer film in Figure 4. Measurements were made at points within this image describing the bulk
polymer, the central gas-barrier layer and the thin tie-layer between this and the bulk film. The melting transition temperatures are consistent with high density polyethylene, poly(ethylene-co-vinyl alcohol) and medium density polyethylene for the bulk, gas barrier and tie layers, respectively [101].

![500 µm](image)

Figure 9. Optical micrograph of the cross-section “gel” particle embedded in a 75 µm low density polyethylene film. Also visible are craters remaining following localized thermal analysis of the specimen.

Another example is illustrated in Figures 9 and 10 for a blemish or “gel” particle in a blown polyethylene film. Figure 9 shows an optical micrograph of the film which has been carefully cross-sectioned across the feature. Also visible are small craters in the film which are a consequence of a series of localised thermal analyses along the specimen. These also serve to illustrate the potential spatial resolution of the technique. Whilst the Wollaston wire probe has a diameter of 5 µm at the tip and is capable of detecting thermal transitions in the order of a few square micrometres, heat from the measurement process spreads out and disrupts a large region (about 20 µm square) around the tip. This ultimately restricts the proximity of a sequence of measurements on a specimen. For the analysis of the sample shown in Figure 9 the specimen was translated under the instrument using a micrometer stage. Over an order-of-magnitude improvement (both in terms of sampling area and proximal placement of multiple analyses) can be achieved using semi-conductor probes such as those shown in Figure 2(c). These have recently become commercially available and promise to move localised thermal analysis into the nano-scale with sub-micrometre resolution.
Figure 10. Results from localised thermal analysis of the specimen shown in Figure 9. The solid symbols denote measurements on the normal film whereas the open symbols denote measurements made in the “gel” particle [103].

Figure 10 shows results measurements made on the bulk film and in the region of the defect. Whilst it can be observed that the temperatures of the onset of probe penetration into the low density polyethylene film are broadly similar for all measurements. The degree of penetration into the sample into the “gel” particle is much lower. This implies that the material here has a much higher melt viscosity than the normal perhaps as a consequence of some problem during polymer synthesis [104].

3.5.2 Pharmaceuticals

The applications of micro-thermal analysis within the pharmaceutical industry have been reviewed by Craig *et al.* [141]. Most tablets are not composed of the pure active ingredient, but contain the drug dispersed within an excipient package (such as micro-crystalline cellulose, starch, glucose *etc.*) with added processing aids (such as magnesium stearate) which act as fillers and lubricants for the formation of a mechanically stable compact. Furthermore, the tablet may be coated with a polymer or sugar film to prevent the drug being released into the body before it enters the stomach [142]. Imaging by SThM can be used to identify discrete phases containing these ingredients and their identification can be confirmed by localised thermal analysis [23,69,70, 104,143-147]. Figure 11 illustrates this by means of measurements on the specimen shown in Figure
Localised thermal analysis detects the melting of the drug paracetamol (acetaminophen) around 180 °C for the low thermal-conductivity region of the image. No change in response is observed when an area from the high thermal-conductivity region of the same image is examined. This suggests that the material here is comprised of a filler or excipient - most probably micro-crystalline cellulose. The distribution of drug within a pharmaceutical compact can have very important implications for the dissolution of the tablet within the digestive system and micro-thermal analysis is a useful characterisation tool.

Many drugs can be produced in more than one crystalline modification. Micro-thermal analysis has been shown to be a viable means of differentiating between such polymorphs [148,149], or between crystalline and amorphous regions in drugs [150,151]. Royall et al. [152] have employed localised thermal analysis to detect surface segregation of progesterone encapsulated in poly(lactic acid) microspheres (thus confirming earlier work by DSC), while Zhang et al. have studied the distribution of poly(ethylene glycol) in the same polymer [153].

![Figure 11. Localised thermal analysis of the analgesic tablet shown in Figure 5(a) with measurements made in the low thermal conductivity (dark) region (solid line) and the high thermal conductivity (bright) region (broken line) of the image [70].](image)
3.5.3 Biology

Micro-thermal analysis has been used to examine a number of specimens of biological origin. Gorbunov et al. have reported the study of the infrared receptors of snakes using SThM and localised thermal analysis, whereby the thermal transport properties of the receptors were found to be lower than the surrounding skin [65]. The surfaces of plant leaves have also been examined by localised thermal analysis, to study the waxy coating which protects the leaf from water loss. Melting of the cuticular wax has been detected [102] and the effect of surfactant packages on this behaviour investigated as a means of improving the absorption of agrochemicals [154]. Studies of historical parchment derived from the dermis of animal skin have been employed to measure the softening temperature of the material. It is a particular advantage of the technique to be able to examine small quantities of material [155]. SThM has been used in food science to image the surface of caramel [156]. In this instance pulsed-force microscopy and infrared spectroscopy were employed to characterise surface structures, although it would be a natural extension to use the SThM to study local thermal transitions.

3.5.4 Inorganic materials

This category includes metals, ceramics and electronic materials which are typically of high thermal conductivity whereby the discrimination between phases afforded by SThM can be compromised [157]. Furthermore, it is difficult to envisage that point-source heating afforded by active thermal probes would be sufficient to heat highly-conductive bulk specimens such as metals. However, thin-film NiTi shape-memory alloys have been studied by localised thermal analysis, whereby measurements of the martensitic to austenitic transformation were made and the spatial variation in transition temperature corresponding to compositional variations within the specimen identified [158]. Micro-thermal analysis has also been employed to resolve differences in thermal conductivity and softening temperatures that arise during the processing of carbon fibres [67,129,159]. These were related to the local oxygen content of the fibre measured by electron probe micro-analysis.
Figure 12. Shaded topography (left) and thermal conductivity contrast (right) images of a light emitting diode. Reproduced from reference [102] with the permission of Akadémiai Kiadó.

Figure 13. Localised thermal analysis of the LED shown in Figure 12. The upper set of curve show measurements made within the high thermal conductivity central region and the lower set of curves show measurements made outside this area [102].

As described earlier, passive SThM techniques have proven popular in the microelectronics industry for the identification of hot-spots within components. For example, Boroumand et al. have made measurements of the temperature distribution across a polymer light-emitting diode (LED) [160]. Figure 12 shows the topography and thermal conductivity contrast image of a silicon-based LED from a batch of components which had failed under testing.
Localised thermomechanical measurements of the centre and outside of specimen are shown in Figure 13. Although no thermal transitions are observed, the thermal expansivity is different between the two areas. This would lead to thermal stresses building up when to the device was energised. This could ultimately lead to failure of the LED. Measurements on a LED which passed testing showed no variation in properties [102,104].

4. LOCALISED CHEMICAL ANALYSIS

The measurements physical properties afforded by existing forms of micro-thermal analysis can be insufficient to discriminate between different materials. Incorporation of some means of chemical analysis of the specimen is therefore highly desirable. This has been achieved by two processes; localised pyrolysis-evolved gas analysis, and near-field photothermal spectroscopy.

4.1 Localised evolved gas analysis

It has been demonstrated that the Wollaston wire probe tip used for localised thermal analysis measurements can be heated rapidly and repeatedly to temperatures in excess of 600°C. This is sufficient to bring about localised pyrolysis of most organic materials [72,157]. This process generates a small plume of gaseous decomposition products characteristic of the substrate. Chemical analysis of these products can be performed via two alternative routes: by absorbing them on a suitable substrate and subsequent investigation using thermal desorption gas chromatography-mass spectrometry (td-GC-MS), or by direct sampling by mass spectroscopy (MS) [23,70,106,162-165]. Furthermore, the thermal probe may be used to soften and remove material from the surface of the specimen for subsequent characterisation [70]. These approaches are described in more detail in the following sub-sections.

4.2.1 Offline localised pyrolysis-td-GC-MS

Realisation of the first approach – trapping and offline analysis – employs a miniature gas-sampling tube packed with a mixture of Tenax® (molecular sieve) and Carbopak® (activated charcoal) absorbent material. Such tubes are routinely used for environmental monitoring of hazardous industrial atmospheres whereby operators during the normal course of their duties carry a small tube (about the size of a pen) clipped to their clothes. 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-pyrolysis-td-GC-MS, the sorbent tube is modified to end in a short section of stainless steel hypodermic tubing the open end of which can be placed immediately adjacent to the heated thermal probe using a micro-manipulator. As the tip is heated, a pump is used to draw gas through the tube. After sampling, the tube is placed in a suitable carrier that fits into a standard thermal desorption unit interfaced to a GC-MS system. Blank desorption runs of the sorbent tube are carried out before and after each pyrolysis experiment to confirm the cleanliness of the detection system. Such tubes are re-usable since the thermal desorption process cleans them of trapped material. The lifetime of such tubes is at least 1000 cycles.

A dedicated design of micro-manipulator is used for positioning the sampling tube which can be interfaced with a variable-temperature sample stage upon which the microscope is placed. Thus, the sample can be cooled or heated independently of the thermal probe, using a small heated sample holder coupled to a Dewar vessel containing liquid nitrogen for cooling the specimen. Generally, the specimen is only required to be under ambient conditions. Therefore, an x-y-z translator can be used in place of the heated stage. This configuration is very versatile and affords independent positioning of the sampling tube, microscope and sample.

One of the obvious benefits of off-line 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 can 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 [165]. This approach has particular benefits for filled systems, such as paints and coatings, which may contain only a small fraction of organic binders.

Another benefit of analysis by GC-MS is to use the ability of 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 [166]. Alternatively, one may only be interested in the presence (or absence) of a particular component at a specific location. For example, this technique has been used to locate the source of camphor extracted from plant leaves [164].

It is possible to exploit this technique as a means of surface-specific pyrolysis. For example, Figure 14 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 (about 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 × 50 µm 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 [165].

Figure 14. Comparison of evolved gases from bulk (macro-EGA) and surface (micro-EGA) of paint film [165].

4.2.2 Online localised pyrolysis-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 reducing the time for analysis. One of the drawbacks of the td-GC-MS 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. Furthermore, it is advisable to conduct a “blank” experiment with the tube prior to sampling in order to ensure that no residues are present in the system.

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 can be achieved by using a small-bore silica-glass capillary transfer line which also serves to reduce the pressure from atmospheric to that which could be accommodated by the ion source of the mass spectrometer. The capillary tube must be surrounded by a heated jacket for most of its length in order to prevent condensation of volatiles on the walls of the tube. Only a few centimetres of the end of the capillary are left unheated – these were passed through an empty micro-sorbent tube (described above) so as to enable the same micro-manipulator 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 have been 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 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 of depth-profiling though the sample so as to reveal buried layers beneath the surface [106,164]. Alternatively, successive pyrolysis measurements may be made using either of the first or second methods of heating the probe with either direct sampling to the mass spectrometer, or the more time-consuming offline td-GCMS sampling [106].

As stated earlier, online MS sampling of evolved gases lacks the separation stage afforded by td-GC-MS and is unsuitable for complex systems. Furthermore, the sensitivity of the technique 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. These may be detected by monitoring single-ion masses rather than acquiring a full mass spectrum. 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 [165].
An example of this is shown in Figure 15 for a poly(methyl methacrylate)/polystyrene laminate. Data from a 6 × 6 array of pyrolysis measurements were used to reconstruct images based upon the ion 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 [167]. Three-dimensional tomographic imaging may also be considered by using the probe to ablate the surface.

Figure 15. Left: topographic image of poly(methyl methacrylate)/polystyrene laminate – polystyrene layer is to the right of the image. Centre: 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) [165].

4.2 Near-field photothermal spectroscopy

When a material is illuminated with infrared radiation it will tend to absorb energy corresponding to specific infra-red (IR) active modes and increase in temperature. This is known as the “photo-thermal effect” and can be exploited to obtain the IR spectrum of a specimen. Passive temperature-sensing SThM probes can be used to measure the specimen response to IR radiation over a very small area below that realisable using conventional optics because the spatial resolution is limited largely by the contact area of the tip and the thermal diffusivity of the specimen being of the order of 1 µm which is at least one order-of-magnitude improvement over conventional techniques. Near-field photothermal spectroscopy using resistive probes of the types shown in Figure 2(a-b) has been exploited by Hammiche and co-workers [40-47], who used a mirror system to bring the IR beam to focus on the specimen surface while it was in the SThM. Two approaches have been used to generate the spectrum. In the first method a high-intensity tunable IR source has been used to scan the spectrum in a manner analogous to dispersive IR spectroscopy [42]. The
second approach uses a broadband source in an interferometer and subsequent Fourier transform analysis to obtain the spectrum [40]. The results of this method, in addition to the work described above, have also been combined with measurements by SThM and localised thermal analysis. Polymers [106] and pharmaceuticals [23] represent the largest classifications of materials that have been investigated, although this technique has been used in cellular biology to monitor the life-cycles of cells [168].

4.3 Thermally-assisted micro-sampling

![Figure 16](image-url)

Figure 16. Online MS single-ion monitoring for methyl methacrylate monomer (using the CH₂C(CH₃)CO⁺ ion fragment m/z = 69) removed from the surface as a consequence of heating the probe in contact with the specimen.

The ability of the heated thermal probe to soften the surface of a specimen and remove a small amount of material has also been demonstrated. By placing the probe on the sample and raising its temperature, the substrate is softened [70]. As the probe is withdrawn from the sample, some material adheres to tip. This residue can then be characterised by pyrolysis-evolved gas analysis (td-CG-MS or MS). Figure 16 illustrates this process using online-MS monitoring for the evolution of monomer from a specimen of poly(methyl methacrylate). The tip is first heated rapidly to 1000 °C to ensure that it is free of any contaminants. Then, the probe is brought into contact with the specimen and the tip is heated to
400 °C at 10 °C s⁻¹, whereupon a small amount of monomer is evolved as the hot tip is removed from the surface. A second probe-cleaning cycle results in a larger amount of monomer being detected as a result of the decomposition of material adhering to the tip. Subsequent cleaning of the tip by heating to 1000 °C does not result in the detection of any residue. Experiments indicate that it is only necessary to heat the specimen above its glass-rubber transition or melting temperature in order to transfer material from the surface to the tip. Analogous measurements have been demonstrated using photothermal IR spectrometry to detect material removed in this way [169]. Thermal dip-pen nanolithography using a heated AFM tip has also been developed [170]. In this case, the tip is coated with an organic material which is transferred to the surface by heating the tip so as to melt the “ink”. This is essentially the inverse of the micro-sampling process described above.

5. CONCLUSIONS

This chapter presents an overview of micro-thermal analysis. Scanning thermal microscopy has gained acceptance in many areas of physical science. The commercial availability of instrumentation will continue to broaden its scope of usage into more areas of characterisation of materials. A better understanding of the mechanisms of heat transport from the tip to the surface can be expected to make routine measurements of absolute thermal properties via scanning thermal microscopy possible. The thermodynamic limit of measurement \((kT)\) is about \(10^{-21}\) J at room temperature [27]. The current spatial resolution of scanning probe microscopy is around \(10^{-10}\) m. The maximum temperature resolution of the most sensitive thermal probes (bimetallic cantilevers) is \(10^{-5}\) K with an estimated sensitivity limit of \(\approx 10^{-12}\) J and a spatial resolution of \(\approx 10^{-7}\) m. There is, therefore, plenty of room for improvement. Advances in thermal probe design are also expected to lead to applications for localised thermal analysis, thus enabling the behaviour of materials to be investigated over even smaller dimensions. The integration of chemical analysis (by pyrolysis and/or near-field photothermal infrared microscopy) raises the possibility of constructing a versatile instrument capable of performing a wide range of analyses that exploits abilities of the thermal probe to act as a very small heater and thermometer. Such an instrument might well be termed “the laboratory on a tip”.

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