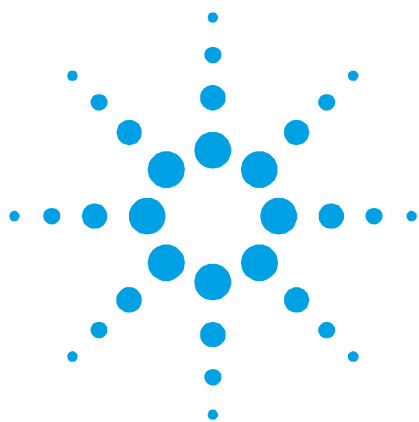




Infrared imaging – the evolution of infrared microscopy

Application Note

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Introduction

For a number of years infrared (IR) microscopy has been an important tool for IR spectroscopists. The IR microscope has developed considerably over the past few years and can now be considered a multifunctional accessory suitable for a wide variety of measurements in transmission, reflectance, grazing angle, and attenuated total reflectance (ATR) modes. IR microscopy is a powerful investigative technique and can be used to solve problems in fields as diverse as mineralogy (oil inclusions in rocks), polymer manufacturing (surface defects) and forensics (identification of paint chips). In fact, IR microscopy has almost become the ubiquitous trouble shooting technique when it comes to surface defects and contaminants, and wherever small samples are encountered. Using a conventional IR microscope it is possible to collect an IR spectrum from an area as small as 7-10 μm in transmission and reflection, or $\sim 20 \mu\text{m}$ using an ATR contact technique. The minimum area from which a sample can be measured is defined by the diffraction limit. That is the minimum area from which a measurement can be made approaches the wavelength of light with which the spectral analysis is made.

An intrinsic application of IR microscopy is the determination of the chemical distribution of a compound, component or defect, on or within a sample. To date, much of this work has been done by IR mapping. In a mapping experiment, a grid or line is defined across a sample surface and a series of spectra collected sequentially. Using these sequential spectra, a map of the sample can be generated and, from the spectral information obtained, a contour or 3D map depicting the distribution of a chemical functional group and/or component can be prepared.



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Whilst still a powerful investigative technique, IR mapping suffers from a number of disadvantages and, whilst still useful in many cases, is limited with respect to time and efficiency. In a mapping experiment, data is collected sequentially and, with each data point requiring several minutes to co-add spectra, even relatively small maps can require long acquisition times (~1 hr). Using a smaller sampling area, and/or higher spectral resolution further increases the analysis time required, meaning detailed investigations can require 8 hours (or more) scanning time (introducing additional problems where liquid nitrogen cooled detectors are concerned).

Since the launch of the first FTIR microscope in the early 1980's (Digilab UMA-100), continuous innovation and development has extended the functionality and efficacy of IR microscopy. The late 1990's saw the release of the first FTIR imaging system using focal plane array (FPA) detector technology (Digilab Stingray). In combination, FTIR microscope and FPA detector make for a powerful analytical tool. FTIR imaging provides all the functionality of mapping, but does so faster and with better spatial resolution, and most importantly, with considerably better sensitivity.

Focal plane arrays

Based on technology first developed with astronomy and military applications in mind, an FPA essentially performs like a camera – but with a spectral advantage. Instead of collecting one data point at a time, or collecting a row of data points (as is the case with linear arrays), the imaging is accomplished by collecting spectra from all detector pixels simultaneously. Less time consuming and more efficient than mapping, true FPA imaging permits the fast acquisition of a spectrochemical snapshot of the sample being investigated.

Spectrochemical imaging

IR imaging (or spectrochemical imaging as it has become known) employs a focal plane array detector consisting of a square array of Mercury Cadmium Telluride (MCT) detector elements (Figure 1). Using an IR microscope, an image of the sample is imaged onto the MCT detector array and, at each element of the array a complete IR spectrum of the corresponding region of the sample is obtained (Figure 2).

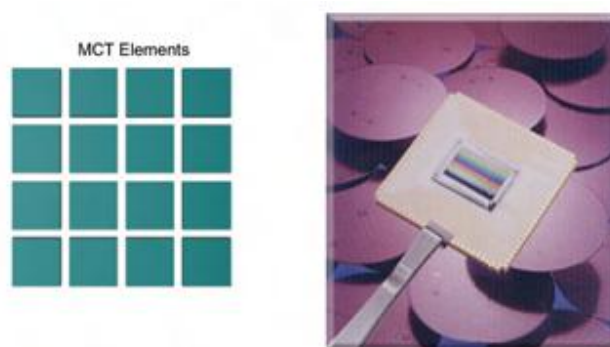


Figure 1. The Focal Plane Array detector: square grid of MCT detector elements (left) and finished FPA detector assembly (right)

The total IR energy across the array (or total IR response at each detector element) is used to create the primary IR image of the sample, with this IR image corresponding to the visible image of the sample. The power of the technique stems from the fact that from each pixel of the array an entire infrared spectrum can be extracted. Each individual spectrum can then be used to create secondary (or functional group) images of the area sampled. There may be as many as 200 secondary images behind the primary image, with spectral information extractable as peak heights, peak areas or peak ratios within each separate spectrum.

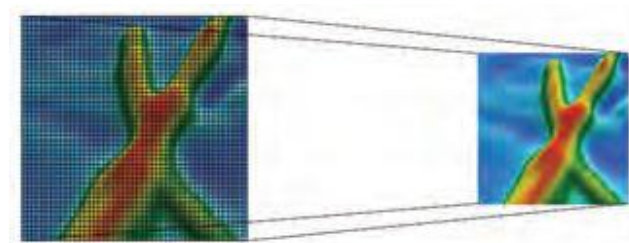


Figure 2. The sample is imaged on to a detector array, with each detector pixel collecting a full infrared spectrum

Arrays can range in size from 16 x 16 MCT pixels up to 256 x 256 pixels, and comprise between 256 and 65,536 individual IR spectra. The area of sample imaged is dependent on the size of the array used, with areas between 88 μm^2 and 1.2 mm^2 typically measurable in a time span of approximately 0.5 to 9.0 seconds (at 8 cm^{-1} spectral resolution).

The sheer speed of data collection offers enormous advantages over conventional IR mapping, with sample throughput increased at least fifty-fold. Combined with improved spatial resolution and signal-to-noise, FTIR imaging is a technology with wide ranging applications. In fact, wherever an IR microscope is being used today, FTIR imaging will offer significant advantages to the analyst.

Applications of spectrochemical imaging

FTIR imaging is an information-rich investigative technique and, as such, finds application in many branches of the physical sciences. Be it semiconductor defect analysis or biomedical bacterial screening, spectroscopists and non-spectroscopists alike are quickly discovering the power of FTIR imaging. In some cases it is simply the increased speed of analysis that sets imaging apart from mapping. In others it is the improved spatial resolution and signal-to-noise that, in combination, provide new insights into areas as diverse as drug dissolution and the science of adhesion, or simply permit the acquisition of an infrared spectrum of a sample that has previously proved 'unanalysable'.

An indicative example of the power of spectrochemical imaging is the identification of surface contamination. Figure 3 shows the visible image of a metal surface with an unidentified surface defect.

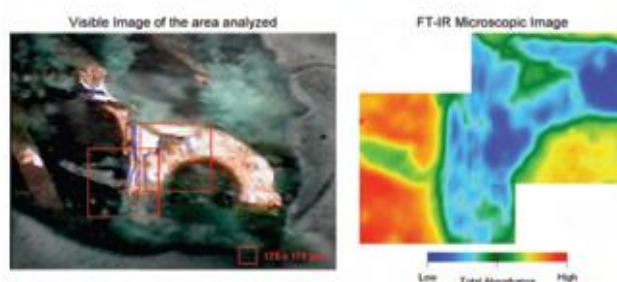


Figure 3. Defect on a metal surface: visible image (left) and total infrared image (right) of the sample

In a matter of seconds the surface defect can be imaged using the focal plane array, and an IR map of the sample surface displayed. As described previously, the IR image is created from the total IR reflection across the area of the sample imaged.

At each point (or pixel) on the IR image (corresponding to a 5.5 μm^2 point on the sample), an entire infrared spectrum is available. In this particular image, there are 4096 (64 x 64) points with 4096 associated spectra. The area of the image is 35 μm^2 and, at a spectral resolution of 8 cm^{-1} , a single image is collected in less than one second. From the individual spectra, peak heights can be used to generate the secondary images shown in Figure 4.

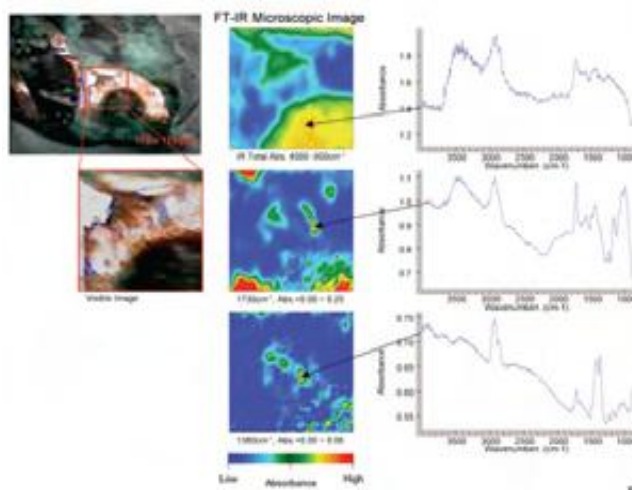


Figure 4. Defect on a metal surface: a complete infrared spectrum is recorded at each point on the detector array. From these individual spectra, functional group images (centre) can be generated

These secondary images allow the analyst to determine the nature of the defect or contaminant and/or image the distribution of the contaminant (in this case organic) across the surface in question.

An extension of FTIR imaging involves the use of attenuated total reflectance (ATR). ATR imaging has a number of advantages over conventional FTIR imaging, the most significant of these being the ability further improve spatial resolution. ATR is a contact sampling technique which requires the use of an IR transparent, high refractive index medium (such as Germanium). Where imaging is concerned, this has the double advantage of reducing the diffraction limited minimum area from which a sample can be measured whilst also simplifying sample preparation.

Figure 5 shows the visible image of a number of polystyrene beads known to have an approximate diameter of 15 μm .



Figure 5. Visible image of a number of polystyrene beads known to have an approximate diameter of 15 μm

The corresponding ATR image of one of these beads (Figure 6), confirms (a) the chemical identity of the bead and (b) the diameter of the bead. Where samples are too thick for transmission and/or poor reflectors, ATR imaging is the tool of choice.

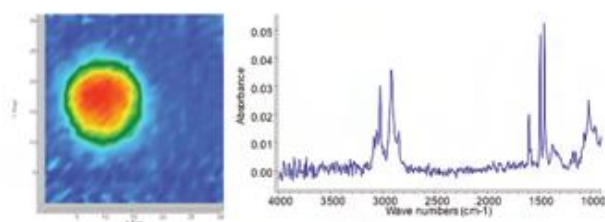


Figure 6. ATR image of polystyrene bead confirming chemical identity (left – total IR image; right – spectrum of bead centre region) and diameter (bead is 13 pixels wide, equating to 18.2 μm).

Conclusion

Spectrochemical imaging is a powerful and information rich technique applicable to a variety of disciplines and applications. The combination of FTIR microscopes with focal plane array detectors overcomes many of the limitations of IR mapping, and the use of square arrays greatly reduces the time required to perform imaging analyses.

Once solely the domain of the 'nuts & bolts' spectroscopist, the IR microscope has now become an almost ubiquitous FTIR accessory, finding application in laboratories the world over. Taking the power of IR microscopy one step further, FTIR imaging using FPA technology is poised to do the same. The software allows the user to include PCR/PLS methods to measure oil parameters and convert the units of spectral absorbance into physical results (ppm, wt.%, cSt, mg KOH/g oil, etc.) applying spectral subtraction if needed.

About the authors

Andrew Hind has a PhD in physical/analytical chemistry, using predominantly FTIR, and more than 10 years experience using molecular spectroscopy in fundamental and applied research and industrial problem solving.

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