

Infrared Spectroscopic Imaging

- identifying small particles
- surface analysis
- imaging chemical composition
- non-destructive

Chemical imaging is a powerful technique that yields spatially resolved chemical information about a surface. This allows for identifying small particles, layered structures and other inhomogeneous materials. The technique combines a Fourier Transform Infrared (FT-IR) instrument with a microscope. A two-dimensional array of detectors allows for parallel acquisition of a large number of IR spectra, yielding short measurement times. The resulting chemical images display the spatial distribution of intensities of preselected IR frequencies.

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Principles FT-IR

FT-IR spectroscopy makes it possible to elucidate the chemical and molecular composition of inorganic and organic compounds. When a sample is exposed to IR radiation ($\lambda = 1\text{-}100\ \mu\text{m}$) part of the radiation will be absorbed by the sample molecules and converted into molecular vibrational energy. As the vibrational energy depends on the mass of the atoms, the force constant of the bonds, the geometry and environment of the molecule, an FT-IR spectrum is characteristic for a complete molecule. With the help of reference samples the amount of absorption at specific frequencies can be used to quantify the chemical composition of a sample. Spectra

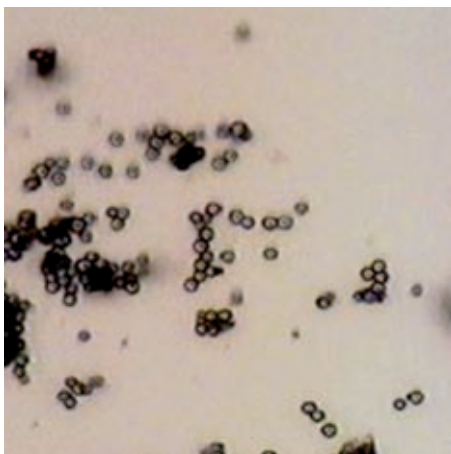
can be recorded in transmission or reflection mode. Attenuated Total Reflection (ATR) is a special reflection technique to analyse surfaces and thin layers.

Principles IR imaging

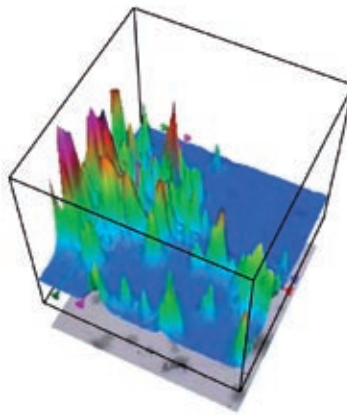
For IR imaging an FT-IR instrument is used, integrated with a microscope. This microscope is equipped with a so-called Focal Plane Array (FPA) detector, consisting of a two-dimensional matrix of 64×64 detector elements. In this way, 4096 spectra can be measured simultaneously, allowing for imaging of a surface area without moving the sample. In combination with ATR it is possible to achieve a resolution better than $2.5\ \mu\text{m}$.

Typical example

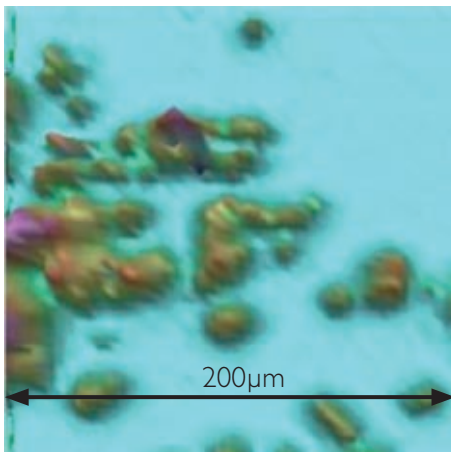
To demonstrate the power of the technique, silicon dioxide spheres with a thin (one mono-layer thick) organic coating were examined using chemical imaging. Figure 1a shows an optical micrograph of a collection of particles on a diamond window. The corresponding X-Y-Z plot in Figure 1b and 1c displays the integrated intensity of the $1200\text{-}1000\ \text{cm}^{-1}$ wavenumber window, i.e. the Si-O stretch vibration in the IR spectrum. The location of the particles is well resolved in this plot. From each point in the X-Y plane a full IR spectrum is available. Figure 1d shows a selected IR spectrum at the position of a sphere. Besides the Si-O band it shows C-H bands of the C-18 coating in the $3000\ \text{cm}^{-1}$ range, proving the presence of the coating on the particles.



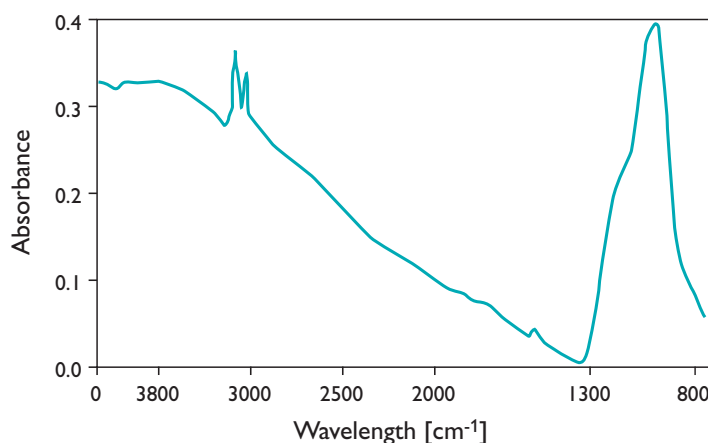
a



b



c



d

Fig. 1: C-18 coated silicon dioxide spheres with $3.5\ \mu\text{m}$ diameter on a diamond window; a) Optical microscopy image; b) X-Y-Z plot, displaying the integrated intensity of the $1200\text{-}1000\ \text{cm}^{-1}$ window (Si-O stretch vibration) as a function of position; c) Contour plot of figure b; d) IR spectrum of a sphere showing the C-H bands of the C-18 coating in the $3000\ \text{cm}^{-1}$ range.

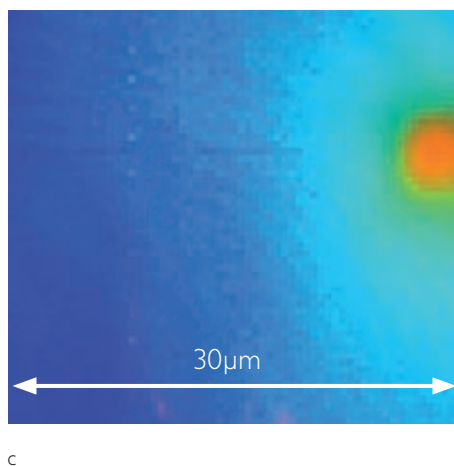
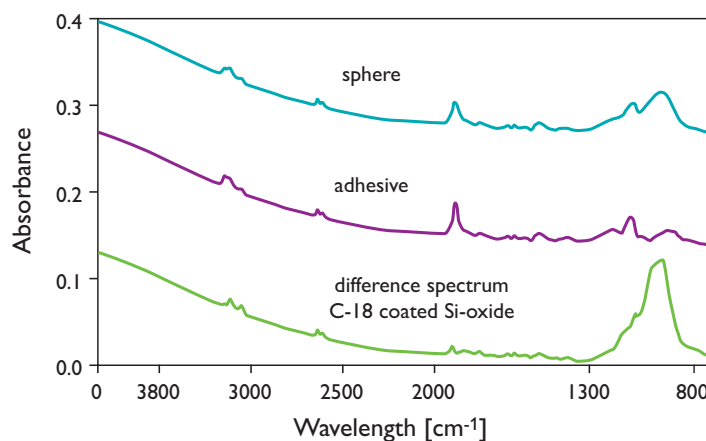
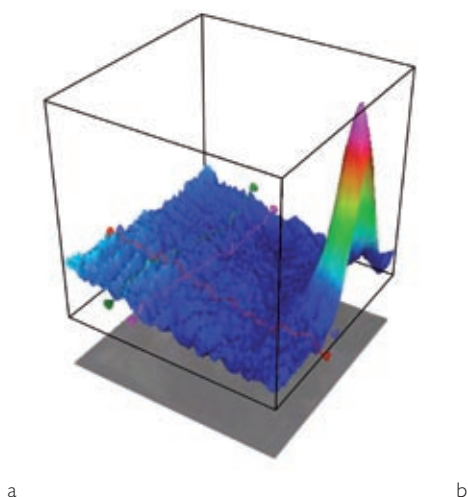


Fig. 2: a C-18 coated silicon dioxide sphere with 3.5 μm diameter deposited on adhesive tape;
 a) X-Y-Z plot of the Si-O stretch vibration, displaying the location of the particle;
 b) IR spectra of sphere, adhesive and a difference spectrum of both showing the C-H bands of the C-18 coating in the 3000 cm^{-1} range;
 c) PCA image displaying the location of the sphere on the adhesive.

Particles transferred to adhesive tape

In most analytical requests, the particles to be studied are not available on an IR transparent window such as mentioned above. More realistically, particles are removed from their substrate using adhesive tape and this tape is submitted for analysis. Although adhesive tape creates a large background signal in the IR spectrum, chemical imaging can still be performed successfully.

As an example, the same C-18 coated silicon dioxide spheres of Figure 1 were deposited on adhesive tape and an ATR chemical imaging dataset was recorded, see Figure 2.

Principal Components Analysis

In many cases, the analyst does not know beforehand at which spatial positions the

species of interest are to be found. Moreover, optical microscopy imaging often does not give sufficient contrast to distinguish between different chemical species. It would be difficult, if not impossible, to manually find all species in the large data set. In such cases, Principal Components Analysis (PCA) becomes very useful. This technique effectively sorts the image spectra into an independent set of sub-spectra (principal components, or factors) from which the image spectra can be reconstructed as pseudo-color maps. Figure 2c shows a PCA image of a sphere in a matrix of adhesive.

Example: polymeric multilayer

Figure 3 shows ATR-imaging of a polymeric multilayer. Actually the selected sample area

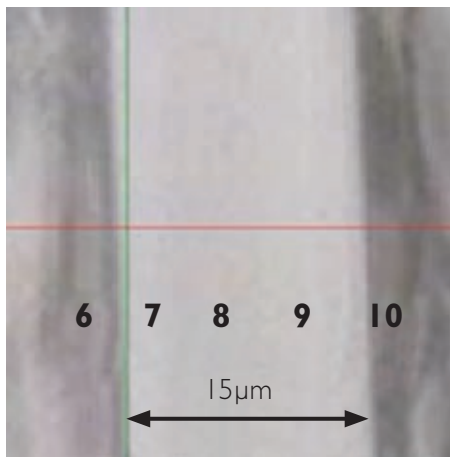
consists of five different polymer layers, but this is visible neither from the visible image (Fig. 3b) nor by an image based on the intensities from only one selected window of wave numbers (Fig. 3c). However, PCA does successfully image the different layers of the foil (Fig. 3d). Subsequently, spectra from selected positions in the five layers provide the detailed chemical information of the PCA separated layers (Fig. 3e).

Applications

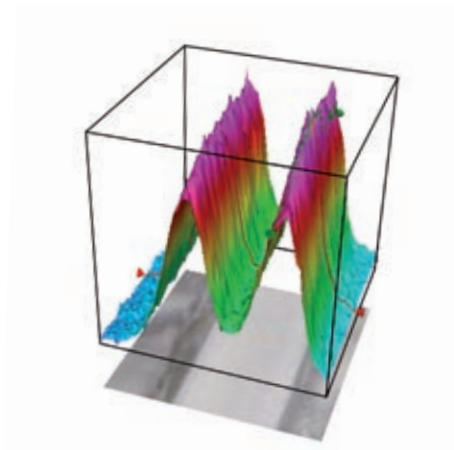
- Identification of unknown materials, particles, surfaces, multi-layers, inclusions
- Trouble shooting
- Contamination control
- In-situ analysis of reaction/polymerization processes



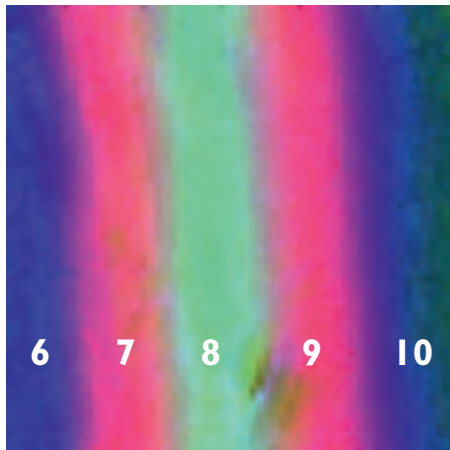
a



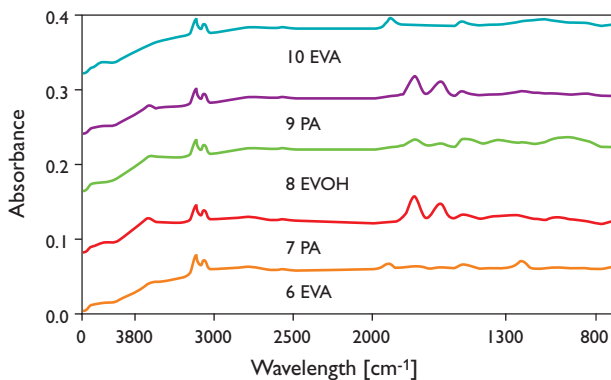
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d



e

Fig. 3: Polymeric foils.

a) Polarized light microscopy image of a complex stack of 12 layers. The area in the rectangle is studied using IR imaging.

b) Optical microscopy image of layer 6 to 10;

c) X-Y-Z plot of the amide vibration (1700 – 1600 cm⁻¹). Only layers 7 and 9 appear to be amides;

d) PCA image, displaying the presence of 5 distinct layers.

e) IR spectra of the individual layers as separated in the PCA analysis.

EVA = poly (ethylene vinyl acetate), PA = poly amide, EVOH = ethyl vinyl alcohol copolymer.



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Characteristics IR Imaging

Obtained information

- Functional groups, identification, orientation, crystallinity, molecular structure
- Qualitative and quantitative when calibration standards are available

Sample type

- Solids and liquids
- Organic and inorganic
- Bulk and thin films (monolayer)
- Powder, single crystals

Sample requirements

- No or little sample preparation required

Spatial resolution

- Transmission and reflection imaging: 10 μm
- ATR imaging: better than 2.5 μm

Detection limit

- Strongly dependant on material and matrix (1%)

Accuracy

- Quantitative 1-5% when calibration standards are available

Analytical range

- Main components

Data acquisition

- Measuring time: minutes
- Interpretation takes more time
- Surface area of 200 * 200 μm² (ATR image 30 * 30 μm²) without moving the sample