FTIR micro-spectroscopy for analyzing chemical groups in materials

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Fourier Transform Infra-Red (FTIR) spectroscopy is one of analytical techniques commonly used for analyzing the chemical bonds present in the material [1-3]. This is especially useful for organic materials and their modifications, as the bond formation and its quantification can be carried out by analysis of the FTIR spectrum. These measurements can be done in reflection, transmission and ATR geometries, with each having its own advantages and disadvantages. For example, ATR uses a diamond prism for improving the S/N ratio via increasing the effective volume from which the IR signal is measured. In most cases, a FTIR system acquires a single spectrum from the whole sample and provides the average chemical composition of the sample. Recently, there has been a significant interest towards micro-FTIR based approach wherein a IR microscope is coupled to the FTIR spectrometer enabling the spectral mapping of a sample. This approach can be used for studying samples where the chemical composition distribution is inhomogeneous. Such analysis can provide greater insights into the sample, the chemical composition distribution and also detect the presence of minor inclusions/impurities which might be missed in the macroscopic FTIR measurements.

At the SATHI-CISCoM centre we have a RaptIR+ microscope along with the iS50 spectrometer from TFS. In the spectrometer, we can analyze the chemical composition of both solid and liquid samples. The spectrometer can be operated in both transmission and ATR modes by replacing different compartment modules (these are user switchable). The spectrometer provides a high spectral resolution spectrum of the sample with high S/N. The DLaTGS (Deuterated Lanthanum Alanine-doped Triglycine Sulfate) detector used in the spectrometer which does not require cryogenic cooling, simplifying its use in FTIR instruments. Both the spectrometer and the microscope have a humidity indicator which allows the user to monitor the level of humidity inside the spectrometer.

Equipment in SATHI-CISCoM: TFS Nicolet iS50 with RaptIR+

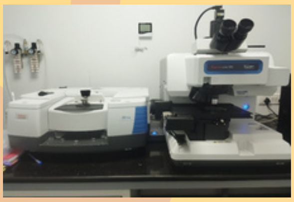

Figure 1. MicroFTIR system in SATHI-CISCoM at IITH

Figure 2. The RaptIR+ microscope with its different components.

The system has the following specifications:
Spectral range– 600-4000 cm^{-1} for the microscope (450 – 6000 cm-1 on the spectrometer)
Spectral resolution – 4 cm^{-1} (microscope); 0.09 cm^{-1} (Spectrometer)
Detector – DLaTGS for FTIR; MCT for Microscope
ATR Crystal – Monolithic Diamond (bulk ATR); Germanium tip (microATR)

This system has the following features:

- **Dual Visualisation Modes:** Optical Brightfield (for visual inspection) and Infrared Visualisation (spectral measurement).
- **High Spatial Resolution:** The system provides near-diffraction-limited resolution and is capable of analysing particles as small as 10–20 µm.
- **Minimal Sample Prep Needed:** The stage can accommodate large samples, and the samples typically require minimal sample preparation (eg, Wet samples need to be dried, etc.). A variety of sample types, including filters (silver membrane, cellulose nitrate), can be mounted directly for analysis.
- Can operate in both reflectance and transmission modes
- Automated mapping of the sample is possible with a designated spatial resolution and step size.
- ·The software for the system can be used for post-processing of the data, especially library-based spectral matching.
- Introduction of Micro-FTIR (TFS Nicolet iS50 with RaptIR+)

Some examples of systems where microFTIR can be employed:

- Microplastics in environmental samples
- Unknown particles in materials (like pharmaceuticals, etc.)
- Defects or inclusions in polymers and coatings
- Contaminants in food, cosmetics, and industrial materials
- Chemical modification of organic samples through reactions
- Material identification and characterisation
- Polymer analysis
- Pharmaceutical and Biopharmaceutical Analysis
- Soil Analysis
- Biomaterials Research
- Hydrogen Bonding Studies
- Forensic Science
- Clinical Diagnostics
- IR response of functional devices

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Application of FTIR analysis for liquid samples in flow conditions:
In most cases, the FTIR analysis is carried out in dry conditions, especially to avoid the strong spectral signatures of solvents. However, in order to use FTIR for monitoring chemical reactions in-situ, it becomes pertinent to carry out the analysis in liquid conditions wherein the contribution of the solvents to the FTIR spectrum becomes extremely crucial [3]. Figure 3(a) shows the design of a homemade liquid which can be used for measuring the IR spectrum using either a gold mirror on CaF2 substrate or with IR metasurfaces. Using this system, it is possible to measure the IR spectrum of solvents (water, acetone and ethanol) as shown in Figure 3(b). We can clearly observe distinct peaks for each of the solvents. In converse, by measuring the spectrum we are able to infer about the composition of the solvent in question. Figure 3(c) shows the timeline of an experiment, wherein the flow cell is first filled with PBS (water based buffer) and then after a certain time point, ethanol is introduced. Using FTIR spectroscopy in real-time, we can observe the replacement of water with ethanol from the IR spectrum as shown in Figure 3(d) and (e). Please note that the measurement volume in this case is extremely low due to the use of metasurfaces required for enhancing the IR signature.

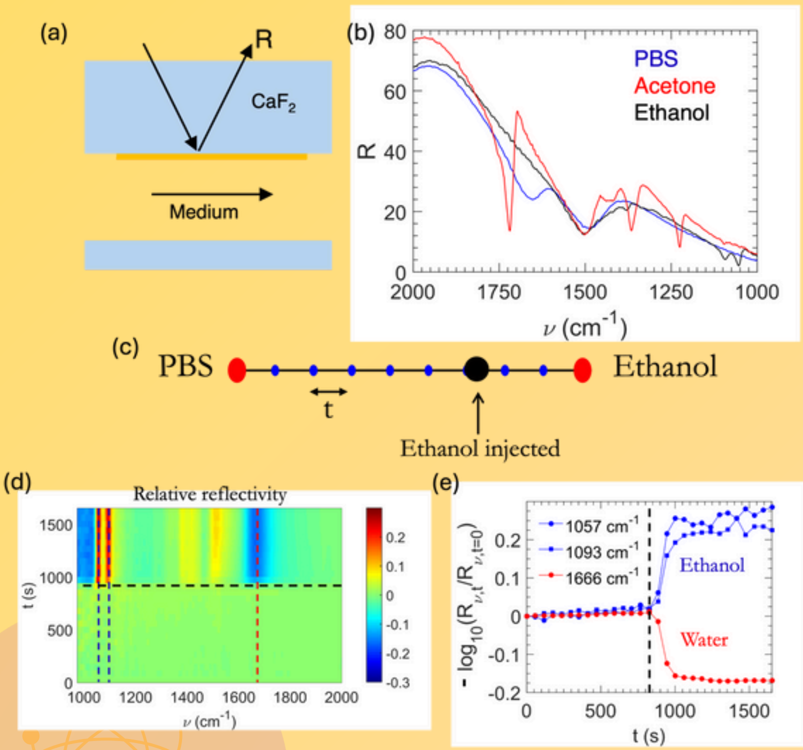

Figure 3. Identification of chemicals in various liquid mixtures. (a) Home made flow cell design wherein a liquid can be injected in to the IR measurement area. (b) FTIR reflection spectrum for three solvents (water, ethanol and acetone). (c) Time line showing the monitoring the exchange of solvents within the flow cell. After a certain time, ethanol is injected in to the flow cell and the FTIR spectrum is monitored in real time. (d) Colormap of change in reflection intensity as a function of wavenumber and time showing the displacement of water. (e) Reflection intensity change as a function of time at three different wavenumbers.

In conclusion, FTIR micro-spectroscopy is a powerful tool that can be used for analying the chemical composition of various materials especially at the microscopic scale. Additionally, combining the microFTIR system with flow cells (with IR transparent windows) allows us to monitor the IR spectrum of samples in in-situ conditions in real-time.

References:
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