

## TUTORIAL :

### Structural Investigation of Ceramic and Polymer Materials at Microscopic Scale

*Abdoulaye Doucoure, Senior Staff Scientist at Pall Corporation;*

*161 Coach Lane, Levittown, New York, 11756 – USA - email:ablodoucoure@hotmail.com*

#### **Abstract:**

This course will provide some examples of methods commonly used to study polymers and ceramics at a submicronic scale. Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Photoelectron Spectroscopy (XPS) are presented with their basic concepts and illustrated with concrete examples. The basic principles, mode of operation and practical use of these spectroscopic methods will be reviewed.

#### Key words

FTIR: Fourier Transformed InfraRed spectroscopy

ATR: Attenuated Total Reflectance

XPS: X-ray Photoelectron Spectroscopy

**Note:** This document is not a research paper but provides some information on spectroscopic techniques widely used in laboratories. This presentation can be understood by someone that has received undergraduate courses in physics and chemistry, and aims to serve students, engineers and researchers generally interested in the characterization of matter. This article is inspired from literature previously published by experts in the field and recognized institutions.

#### **Introduction**

The need for devices that can process information faster and with greater accuracy has greatly favored all efforts towards miniaturization. For instance, this can be seen in microelectronics with the permanent quest for storing more memory on silicon wafers, or in biotechnology where the target is to fabricate lab-on-a-chip elements and improve the research in cell, gene, protein analysis and drug discovery – see table 1. As a result, new analytical tools have emerged to better understand the properties and performances of such materials and improve their

fabrication. FTIR [1] and XPS [2-5] have existed for decades, yet, these versatile techniques are still widely utilized in the field of nanotechnology because of their ability to assess molecular arrangement in small domains.

Table 1: Examples of industries that have heavily relied on miniaturization to save time, space, reduce cost and increase output.

INDUSTRIAL SECTOR	APPLICATION
MICROELECTRONICS	Microchip design: increased memory storage on silicon wafers.
CHEMISTRY	Chemical reactions run with greater efficacy: use of finer catalysts. Purification/concentration of chemicals: finer filters designed to remove smaller contaminants.
BIOTECHNOLOGY	Microarray design: increase storage of biological components on glass, silicon, plastic materials.

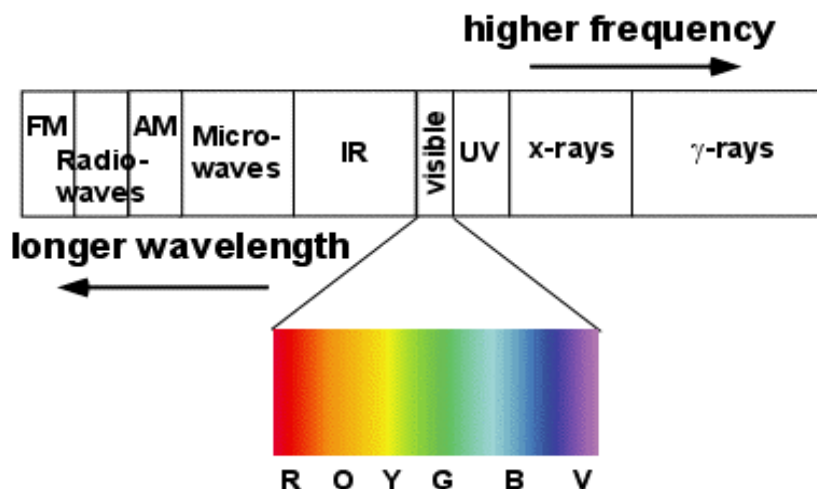
### Fourier Transform Infrared Spectroscopy (FTIR):

#### MODE OF OPERATION [6]:

FTIR spectroscopy analyzes the interaction of IR radiation with a sample (solid, liquid or gas). It measures the frequencies at which the sample absorbs, as well as the intensities of these absorptions. Determining these frequencies allows identification of the sample's chemical make-up, since chemical functional groups are known to absorb radiation at specific frequencies. The intensity of the absorption is related to the concentration of the component. Intensity and frequency of sample absorption are depicted in a two-dimensional plot called a spectrum. For a pure compound, this plot is like a **molecular fingerprint** because of its unique characteristics.

Intensity is generally reported in terms of absorbance (light absorbed by a sample), or percent transmittance (light that passes through it). Frequency is usually reported in terms of wavenumbers or in length unit. Infrared (IR) electromagnetic radiations are located in the middle of the [visible (higher energy) – microwave (lower energy)] region, and is commonly divided in three zones:

Near IR ( $3,600 - 12,800 \text{ cm}^{-1}$ ) - Mid IR ( $200 - 3,600 \text{ cm}^{-1}$ ) - Far IR ( $10 - 200 \text{ cm}^{-1}$ )



The key components of an FT system are the **source**, the **interferometer** and the **detector**. Since no detector can simultaneously sense the intensity and frequency of IR radiation with practical results, one of these two variables (frequency, intensity) must be kept constant in order to perform some measurement. This problem is solved by using an interferometer that modulates the IR source intensity by changing the position of a reflecting mirror – light reflected from the source towards the sample. Thus, the interferometer provides a means for the spectrometer to measure all optical frequencies simultaneously by modulating the intensity of individual frequencies before the detector picks up the signal.

The product of an interferometer scan, termed **interferogram** (a plot of intensity versus mirror position), cannot be interpreted in its original form. By using the mathematical process of FT, a computer converts the interferogram into a spectrum –i.e. intensity versus frequency.

#### PRINCIPLES AND THEORY [7]:

For any given molecular bond, there are several specific frequencies at which it can vibrate. According to quantum mechanics, these frequencies correspond to the ground state (lowest frequency/energy state) and several excited states (higher frequency/energy state). One way to cause the frequency of a molecular vibration to increase is to excite the bond by having it absorb light energy. For any given transition between two states the light energy (determined by the wavelength) must exactly equal the difference in the energy between the two states [usually ground state ( $E_0$ ) and the first excited state ( $E_1$ )].

**Difference in Energy States = Energy of Light Absorbed**

$$E_1 - E_0 = h c / \lambda$$

**Where**      **h = Planks constant**  
                 **c = speed of light, and**  
                  **$\lambda$  = the wavelength of light.**

The energy corresponding to these transitions between molecular vibrational states is generally 1-10 kilocalories/mole ( $200 - 3,600 \text{ cm}^{-1}$ ), which corresponds to the infrared portion of the electromagnetic spectrum.

## APPLICATIONS

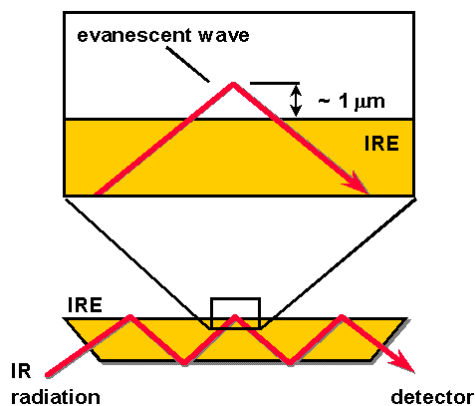
The main technical features of FTIR spectroscopy are summarized below:

- IR is a non-destructive technique;
- IR analysis can be conducted at room temperature;
- Perfect tool for organic analysis (extensive libraries of reference spectra area available to match with unknowns)
- IR can be quantitative (Beer's law).

The interaction between an IR beam and a target sample can occur in many ways, which makes FTIR a versatile tool. The following modes of IR analysis have been developed over the years: IR transmission, IR reflectance, IR specular reflectance, IR diffuse reflectance and ATR-FTIR.

The latter technique is presented below with an application:

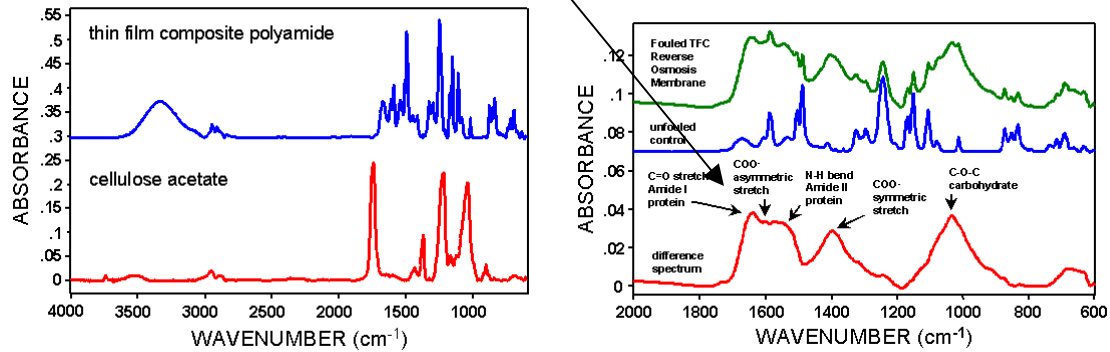
**ATR-FTIR** spectra are obtained by pressing small pieces of a material against an "internal reflection element", IRE, (e.g.: ZnSe)



IR radiation is focused onto the end of an IRE and reflects across the length of the crystal. IR radiation actually penetrates one micron from the surface of the IRE into the material

The following ATR-FTIR spectra are those of a synthetic membrane before (left) and after fouling (right) caused by the formation of a biofilm:

The left image shows the IR spectra of a thin film composite, TFC, polyamide and cellulose acetate polymer membrane. IR spectra on the right correspond to a fouled TFC polyamide membrane. The difference spectrum (red) reveals the spectrum of the fouling layer on the surface of the membrane.

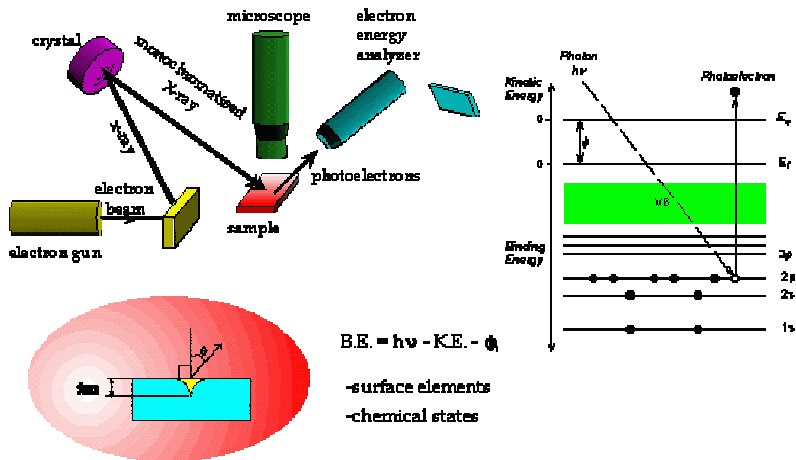


**FTIR LIMITATIONS:**

This technique does not provide elemental information and has a large sampling depth (>100nm). Also, IR does not have an exhaustive library on inorganic compounds; and it mainly operates in transparent or reflective mode.

**X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)**

**MODE OF OPERATION**



X-ray photoelectron spectroscopy works by irradiating a sample material with mono-energetic soft x-rays causing electrons to be ejected. Consequently, surface atomic elements in the sample can be identified directly from the kinetic energies of these ejected **photoelectrons**. The relative concentrations of elements can be determined from the photoelectron intensities.

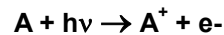
#### PHYSICAL BASIS [9, 10]

In XPS, the photon is absorbed by an atom in a molecule or solid, leading to ionization and the emission of a **core (inner shell) electron**. The energy of the photon (X-ray) is expressed by the Einstein relation:  **$E = h\nu$**

Where:  $h$  - Planck's constant ( $6.62 \times 10^{-34}$  J s) and  $\nu$  - frequency (Hz) of the radiation

The kinetic energy distribution of the emitted photoelectrons can be measured with any appropriate electron energy analyzer; and a photoelectron spectrum can thus be recorded.

The process of photoionization can be considered based on the overall process:



Where:  $A$  is the atom exposed to X-ray and  $A^+$  is its ionized equivalent.

Conservation of energy then requires that:

$$E(A) + h\nu = E(A^+) + E(e^-)$$

Where:  $E(A)$ ,  $E(A^+)$  and  $E(e^-)$  are the state energies for  $A$ ,  $A^+$  and  $E(e^-)$ , respectively.

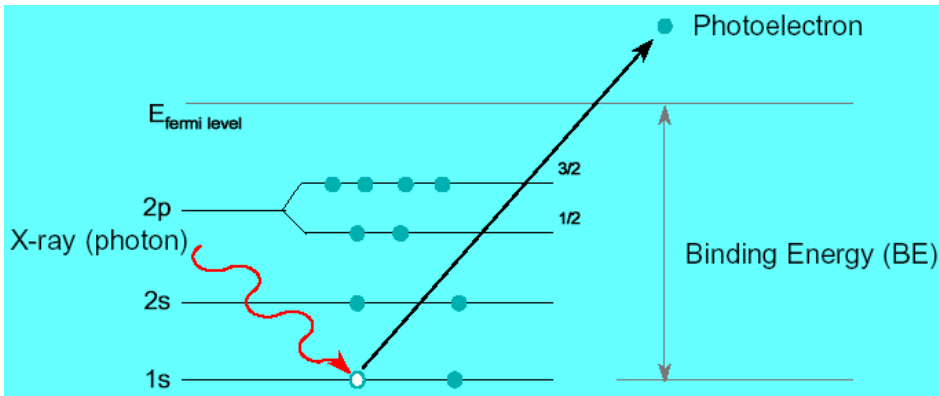
Since the electron's energy is present solely as **kinetic energy (KE)** this can be rearranged to give the following expression for the photoelectron KE:

$$KE = h\nu - (E(A^+) - E(A))$$

The difference  $(E(A^+) - E(A))$  is generally called the **binding energy (BE)** of the electron. This yields the commonly quoted equation:  **$KE = h\nu - BE$**

This formula is further arranged under the following formula:  **$KE = h\nu - (BE + e\Phi)$**

Where  $e\Phi$  = spectrometer work function



### XPS CAPABILITIES:

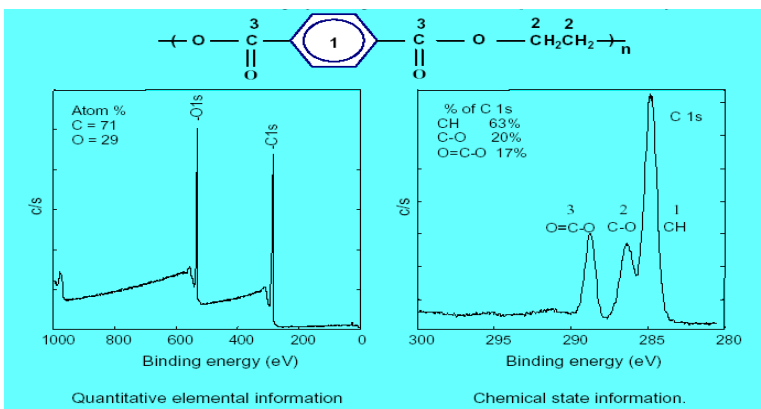
Some main features and benefits specific to XPS spectroscopy are summarized below:

- Elements detected from Li to U.
- None destructive technique (some damage to x-ray beam sensitive materials)
- Chemical state analysis (some exceptions)
- Surface sensitivity from 5-8 nm
- Conducting and insulating materials.
- Detection limits that range from 0.01 to 0.5 atom percent.
- Spatial resolution for surface mapping from >10 nm
- Depth profiling capabilities.

### APPLICATION

With XPS, quantitative data can be obtained from peak heights or peak areas, and the chemical environment can be determined from the chemical states with the exact measurements of peak positions. An accurate quantification is established by a standardized set of sensitivity factors and the transmission function of the spectrometer.

The following plots illustrate how to use XPS for identifying the surface elemental composition (left) and chemical structure (right) of a polymer such as polyethylene terephthalate (PET)



## Conclusion

This tutorial presents basic forms of some important concepts that have helped develop FTIR and XPS techniques. Specific features that characterize each technique have been reported along with a practical illustration. It is our intent to update this course over time and present other techniques aimed at characterizing microscopic materials. Especially, optical such as Atomic Force Microscopy or Field Emission Scanning Electron Microscopy are increasingly used in the field of nanotechnology and will be a good complement to this course.

## References

- [1]: Nicolet, Theory of FTIR, Nicolet Instruments, UK 1991
- [2]: P.R Griffiths, D. Haseth, "Fourier Transform Infrared Spectroscopy", Wiley Interscience, 1986
- [3]: G.E Muilenberg, "Handbook of X-Ray Photoelectron Spectroscopy, Perkin-Elmer Corp., Eden Prairie, 1978
- [4]: H. Yasuda et al., "J. Polym. Sci., Polym. Chem.", vol. 15, 991, (1977)
- [5]: A. Dilks, "X-Ray Photoelectron Spectroscopy for the Investigation of Polymeric Materials, Electron Spectroscopy", vol. 4, C. Bundle and A.D. Baker Ed., Academic Press, London, 1981
- [6]: R. Tapper, PhD thesis "The Use of Biocides for the Control of Biofilms on Stainless Steel", U. of Portsmouth, 1998.
- [7]: West Coat Analytical Service at <http://www.wcaslab.com/index.htm>
- [8]: Ridgway et al., Biofouling of membranes: Membrane preparation, characterization and analysis of bacterial adhesion, p. 463-494. In R. J. Doyle (ed.), Methods in Enzymology, Vol. 310. Academic Press, New York, 1999.
- [9]: M. Engelhard at EMSL: [www.emsl.pnl.gov](http://www.emsl.pnl.gov) (Dpt of Energy/ Pacific Northwest National Lab.)
- [10]: R. Nix at [http://www.chem.qmw.ac.uk/surfaces/scc/scat5\\_3.htm](http://www.chem.qmw.ac.uk/surfaces/scc/scat5_3.htm) (Dpt of Chemistry, Queen Mary, University of London)