A guide to the history and practice of ATR FTIR (Attenuated total reflection Fourier Transform Infrared) spectroscopy

The storyline behind the development of the present generation of ATR FTIR (Attenuated total reflection Fourier Transform Infrared) spectroscopes is impressive and intriguing. The broad interest in the analysis technique and the universal adoption of FTIR spectroscopy is a testament to all the engineers and scientists that have contributed to the development over the past 60 years (1). In addition, the growing number of applications of this analytical technique, in several diverse fields from civil defense, (2-4) plastics, (5) geology, (6-8) environmental, (9) biological, (11) medical, (12) heritage, (13-15) timber, (16) oils, (17) pharmaceuticals, (18) drugs, (19) and for both organic and inorganic chemicals is a key endorsement of the accuracy and versatility of this method of analysis.

The science associated Infrared Spectroscopy covers many aspects of any science syllabus;

- Understanding of electromagnetic radiation and middle infrared and the absorption by molecular bonds.
- Sources of IR radiation and detectors.
- Michelson interferometer (1887) which was used to measure the speed of light. Michelson's earliest attempts, made with materials costing barely ten dollars, measured the speed of light at 186,508 miles per second, or within two hundred miles of the current accepted value. In 1907 he was awarded a Nobel prize in physics for measuring the speed of light, the first Nobel prize in science awarded to an American.
- Fourier transform to convert time domain data to frequency domain data and the development of the important computer algorithm by Turkey and Cooley developed during the cold war as part of a top secret project to monitor the Russian nuclear weapons test program
- Lasers. He-Ne laser are used due to their excellent wavelength stability to calibrate the wave number.

The background to Infrared Spectroscopy

The electromagnetic spectrum consists of different regions corresponding to different energy (E), frequency (v), and wavelength (λ) ranges as seen in Figure 1. The unit for near-, mid-, and far-infrared, the wave number (cm-1), is derived from the inverse relationship between wavelength and frequency.
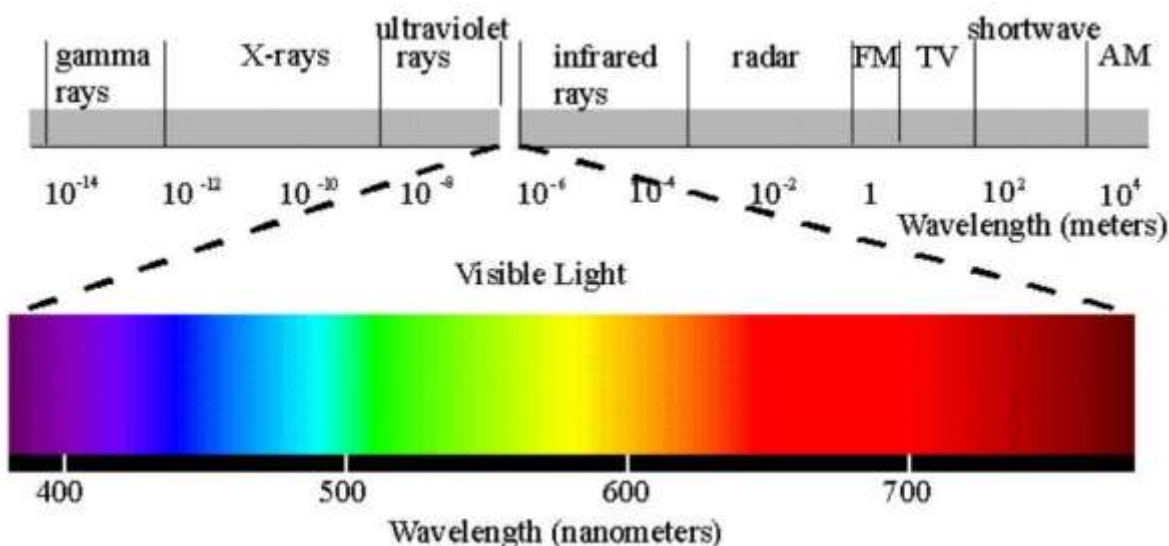
Infrared radiation is divided into:

- near (NIR, v = 10,000 – 4,000 cm^{-1});
- middle (MIR, v = 4,000 – 200 cm^{-1}) and
- far (FIR, v = 200 – 10 cm^{-1}).

The principles of IR spectroscopy are illustrated in Figure 2. All compounds show characteristic absorption/emission in the IR spectral region and based on this property these compounds can be analysed both quantitatively and qualitatively using IR spectroscopy. IR spectroscopy takes advantage of how IR light changes the dipole moments/vibration in molecules (Figure. 2) that correspond to a specific vibrational energy.

IR spectroscopy can be used for the quantification of known compounds or for determining the molecular structure of unknown molecules. An IR source emits infrared radiation towards a sample of chemical compounds. Some of the IR radiation is absorbed by the chemical molecules as motion/vibration energy. Compounds that do not react to the infrared radiation do not have a suitable molecular structure and are classed as IR inactive. However, in the case of an IR active compound functional groups can be identified by their characteristic absorption bands, and thus give information to identify compounds. This is often referred to as the "unique characteristic absorption fingerprint".
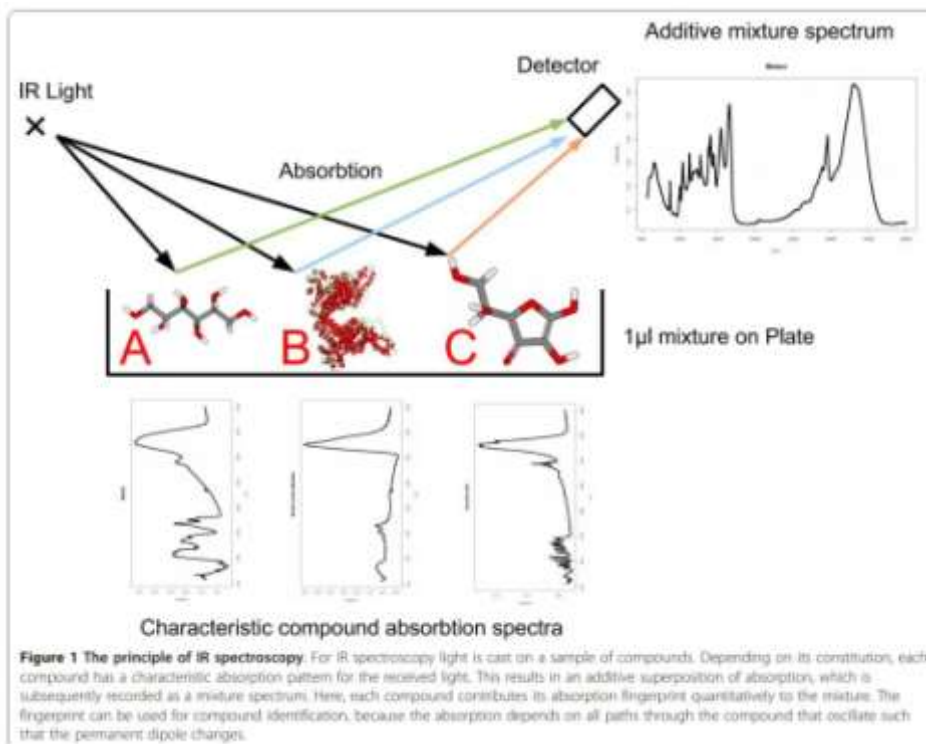
Figure 2 The principle of IR Spectroscopy (Ref 12)

The first simple and basic instruments used gratings to generate infrared spectra, slits to isolate spectral lines, and thermopiles for the detection of infrared light. These instruments were available in the 1940's. In recent decades, a very different methods of obtaining an infrared spectrum have been developed. Fourier-transform infrared spectrometers are now predominantly used and have improved the speed of acquisition and accuracy of infrared spectra dramatically.

Fourier Transformation

A major innovation in the history of IR Spectroscopy was the adoption of the Fourier transformation to convert time domain data to the frequency domain. This algorithm was invented around 1805 by Carl Friedrich Gauss, who used it to interpolate the trajectories of the asteroids Pallas and Juno, but his work was not widely recognized (being published only posthumously and in neo-Latin). FFTs became popular after James Cooley of IBM and John Tukey of Princeton published a paper in 1965 reinventing the algorithm and describing how to perform it conveniently on a computer.

This was done using the Tukey Cooley algorithm. Wikipedia has the fascinating background to the development of this algorithm. It was reported that Tukey came up with the idea during a meeting of President Kennedy's Science Advisory Committee discussing ways to detect nuclear-weapon tests in the Soviet Union by employing seismometers located outside the country. These sensors would generate a seismological time series. However, analysis of this data would require fast algorithms for computing DFT (Discrete Fourier Transform- is the equivalent of the continuous Fourier Transform for signals known only at instants separated by sample times) due to number of sensors and length of time. This task

was critical for the ratification of the proposed nuclear test ban so that any violations could be detected without need to visit Soviet facilities.

To keep secrecy Tukey told Cooley that this was needed to determine periodicities of the spin orientations in a 3-D crystal of Helium-3. Cooley and Tukey subsequently published their joint paper, and wide adoption quickly followed due to the simultaneous development of Analog-to-digital converters capable of sampling at rates up to 300 kHz.

Design of an ATR FTIR Spectrometer

The three major parts of an FTIR are the source, interferometer, and detector (Figure 3).
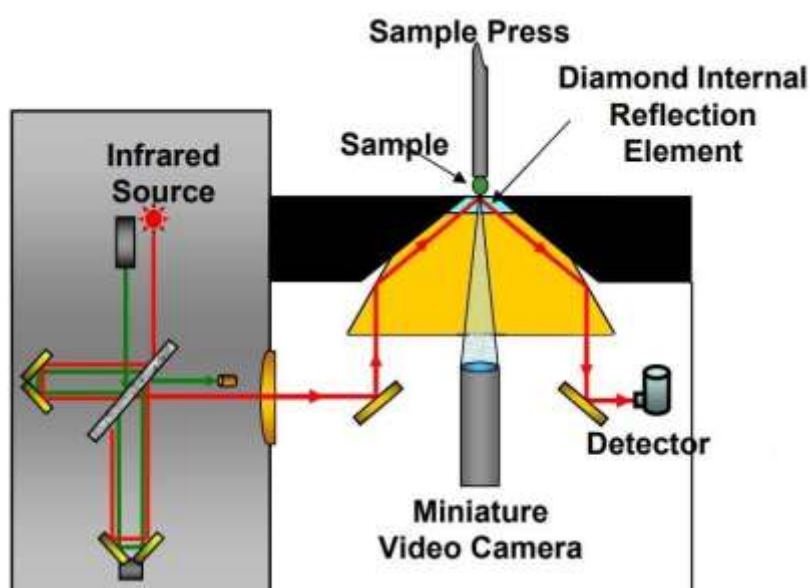

Figure 3 - Parts of an ATR-FTIR spectrometer with source, interferometer, diamond. sample press and detector (Ref 27)

The source is typically a broadband emitter such as a mid-IR ceramic source (50-7,800 cm^{-1}). The Michelson interferometer is the heart of FTIR and consists of a beam splitter, a stationary mirror, a moving mirror, and a timing laser (typically He-Ne). All FTIR instrument use the Michelson interferometer, which was invented in 1887, and became a key part of the FTIR instrument in the 1960s. The beam splitter splits the light from a source into two paths with half the light going to a stationary mirror and the other half going to a moving mirror. The difference in the path of the mirrors causes constructive and destructive interference over the course of time it takes for the moving mirror to make a pass. The signal versus mirror position (and, thus, time) is called an interferogram. A laser is used to determine the position of the moving mirror using the precisely known wavelength of a He-Ne laser. The He-Ne lasers are the industry norm due to their excellent wavelength stability compared to solid-state or diode lasers. The use of the He-Ne laser allows the high accuracy needed to produce the spectra that can allow library searches that need high wavenumber accuracy (often referred to as Connes Advantage)

Laser Reference (or Connes) Advantage

An FT-IR spectrometer determines frequencies by direct comparison with the output of a He-Ne laser. Potentially, this offers an improvement in frequency accuracy which was determined by Connes and therefore, it is known as Connes advantage. The use of the laser to calibrate the output represents an advantage for the FT-IR spectrometers over dispersive spectrometers. With dispersive instruments, the precision and accuracy depend on:

- Calibration with external standards and;
- Ability of electromechanical mechanisms to uniformly move gratings and slits.

By contrast, in FT-IR spectrometers the direct laser reference has the advantage that no calibration is required. Here, both the mirror movement and detector sampling are clocked by the interferometer fringes from the monochromatic light of laser. All frequencies in the output spectrum are calculated from the known frequency of the laser light. Thus, the wave number calibration of interferometers is much more accurate and has much better long-term stability than the calibration of dispersive instruments.

Principles of attenuated total reflectance (ATR)

In ATR FTIR spectroscopy the sample is in contact with the ATR crystal (diamond). The sample can be either liquid, solid, powder or gas. The IR radiation travels through the crystal and interacts with the sample on the surface in contact with the ATR crystal. Because of the differences in refractive indices of both materials, total internal reflection occurs. This reflection forms the so-called "evanescent wave" which extends into the sample. Based on the sample's composition, a small part of the infrared light is absorbed when the evanescent wave interacts with the sample, resulting in a slightly attenuated total reflection.

Total internal reflection

When the infrared radiation meets the surface between two optical media which have different refractive indices at a certain angle of incidence, the light is totally reflected. The angle is called the critical angle and can be calculated using Snell's law. Snell's law states that the ratio of two refractive indices is equal to the inverse ratio of the angle of incidence and the angle of refraction.

To obtain total internal reflection, ATR crystal materials must have a higher refractive index than the tested sample material. The angle of incidence of the IR beam has to match the calculated critical angle for each cell material in order to create total internal reflection.

The formation of an evanescent wave

When total internal reflection occurs, it is difficult to explain the interaction of the IR beam and sample because the IR beam never leaves the ATR crystal. The answer to the problem is that the interaction of the IR beam and sample occurs due to an evanescent field, often called "evanescent wave"(see Figure 4)

When total internal reflection of the infrared radiation occurs at the interface a small fraction of the infrared extends into the sample as an evanescent wave. Under these

conditions the infrared entering the sample decays exponentially and the depth of penetration is limited to a few microns.

In areas where the sample is in contact with the evanescent wave specific parts of the infrared beam are absorbed based on the sample's composition. The totally reflected infrared radiation is depleted of the part of the spectrum/intensity absorbed by the sample molecules and thus the reflected infrared radiation is attenuated. This effect results in the name "attenuated total reflectance" (ATR).
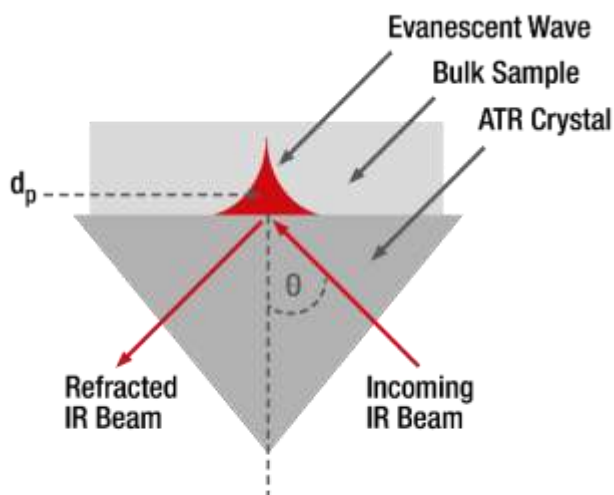

Figure 4 - Evanescent wave resulting from total internal reflection

The depth of penetration of the evanescent wave into the sample

The penetration depth is a measure of how far the evanescent wave extends into the sample. Its exact value is determined by the wavelength of radiation, the angle of incidence on the interface between crystal and sample, and the indices of refraction for the ATR crystal and the sample medium. The depth of penetration is defined as the distance to the point at which the evanescent wave's amplitude has decreased to about 37 % of its maximum value. This can be calculated with the following equation:

Calculation of penetration depth:

$$d_p = \frac{\lambda}{2\pi n_1 \sqrt{sin^2\theta - (\frac{n_1}{n_2})^2}}$$

d_p – Penetration depth

λ – Wavelength of incident light in vacuum

n_1 – Refractive index of ATR crystal (dense medium)

n_2 – Refractive index of sample (rare medium)

Θ – Angle of incidence

According to the above equation the penetration depth for an ATR cell made of zinc selenide, a sample with a refractive index of 1.5 and a wavelength of 10 μm is approximately 2.0 μm. Most organic samples have a refractive index of 1.5; therefore, this value is widely used for calculation.

How does ATR FTIR identify chemicals?

Recall that an infrared spectrum has peaks where light energy is absorbed by molecular bonds

Bonds between particular atoms (functional groups) occur at characteristic wavenumbers

Let's look at the effects some functional groups have on infrared spectra.
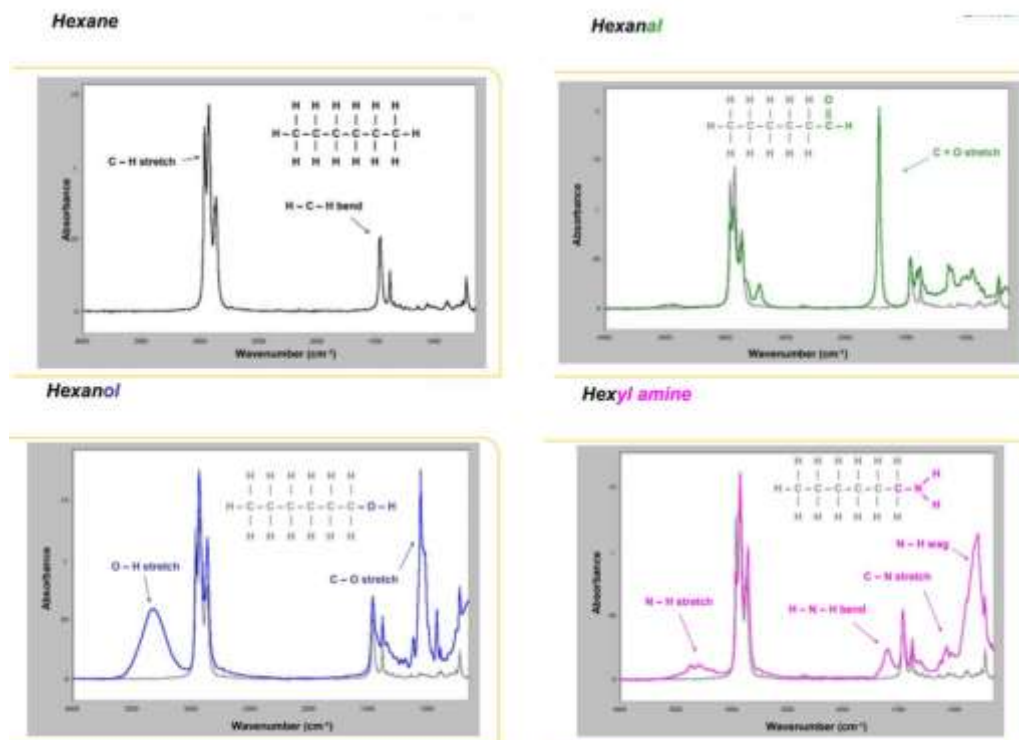
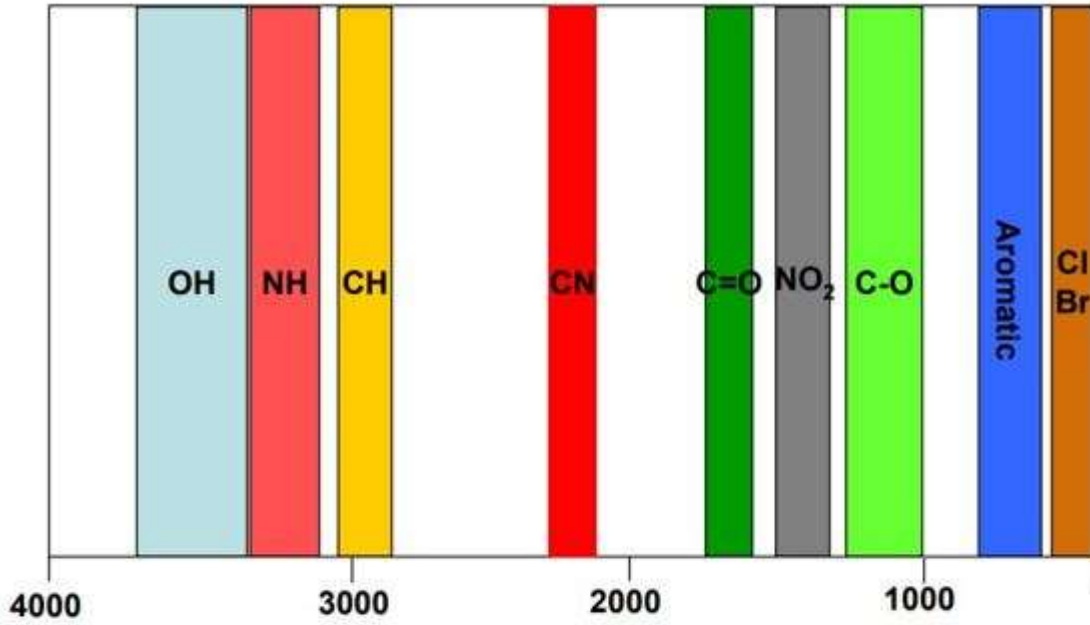Function group peaks of Hexane, Hexanal, Hexanol and Hexyl Amine (Ref 27)

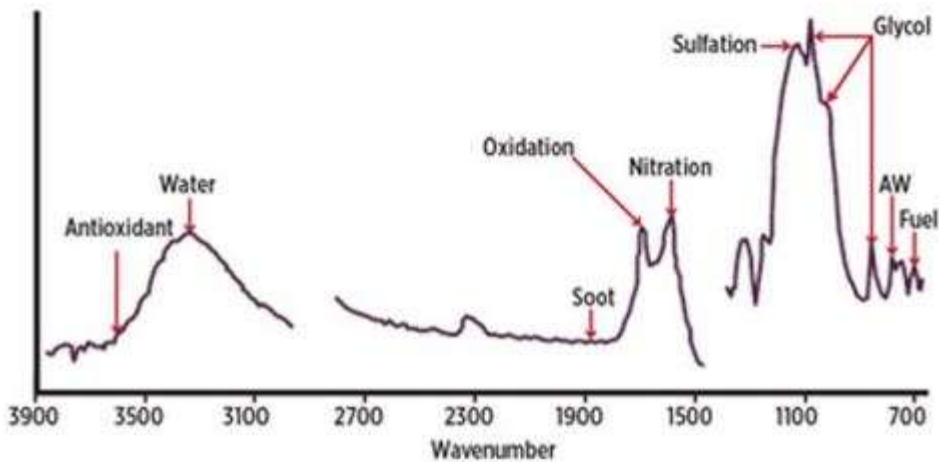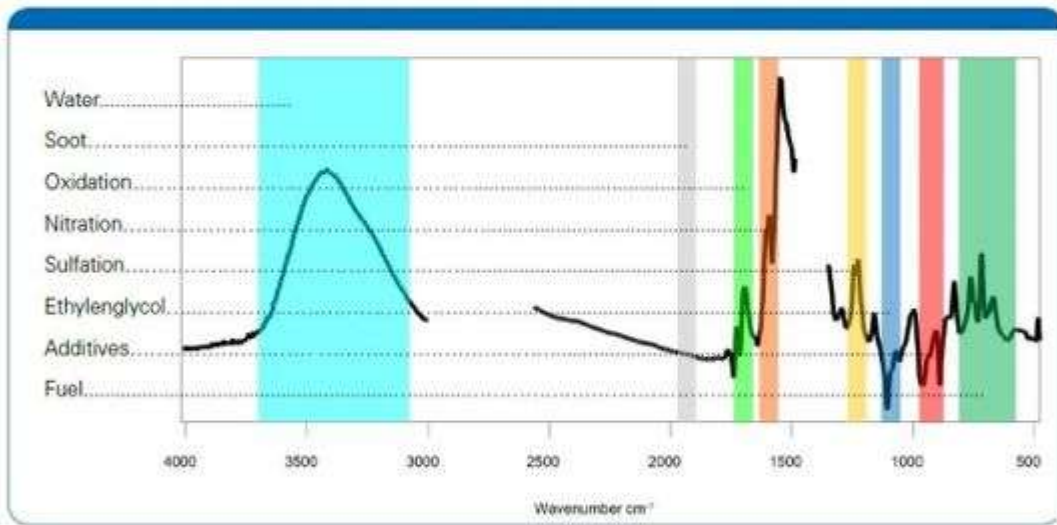Figure 6 – Absorption Landmarks (Ref 27)

Figure 7 Diagrams showing the interpretation of FTIR curves

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