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A CRITICAL REVIEW ON FUNDAMENTAL AND PHARMACEUTICAL ANALYSIS OF FT-IR SPECTROSCOPY

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ABSTRACT

Fourier transform infrared spectroscopy *(FTIR)* is a technique which is used to obtain an infrared spectrum of absorption, emission, photoconductivity or Ramanscattering of solid, liquid or gas. An *FTIR* spectrometer simultaneously collects spectral data in a wide spectral range. An *FT-IR* Spectrometer is an instrument which acquires broadband NIR to FIR spectra. Unlike a dispersive instrument, i.e. grating monochromator or spectrograph, *FT-IR* Spectrometers collect all wavelengths simultaneously. *FT-IR* (Fourier Transform Infra Red) is a method of obtaining infrared spectra by first collecting an interferogram of a sample signal using an interferometer, and then performing a Fourier Transform (FT) on the interferogram to obtain the spectrum. The main goal of *FTIR* spectroscopic analysis is to determine the chemical functional groups in the sample. Using various sampling accessories, *FTIR* spectrometers can accept a wide range of sample types such as gases, liquids, and solids. Thus, *FTIR* spectroscopy is an important and popular tool for structural elucidation and compound identification.

Keywords: *FT- IR* – Fourier Transform Infra red spectroscopy, Structure Elucidation, Functional group Identification.

INTRODUCTION

Fourier transform spectrometers have recently replaced dispersive instruments for most applications due to their superior speed and sensitivity. They have greatly extended the capabilities of infrared spectroscopy and have been applied to many areas that are very difficult or nearly impossible to analyze by dispersive instruments. Instead of viewing each component frequency sequentially, as in a dispersive IR spectrometer, all frequencies are examined simultaneously in Fourier transform infrared (*FTIR*) spectroscopy.

Spectrometer Components: There are three basic spectrometer components in an FT system: radiation source, interferometer, and detector. The same types of radiation sources are used for both dispersive and Fourier transforms spectrometers. However, the source is more often water-cooled in *FTIR*

instruments to provide better power and stability. *FTIR* spectrometer to differentiate and measure the absorption at component frequencies[1]. The monochromatic is replaced by an interferometer, which divides radiant beams, generates an optical path difference between the beams, and then recombines them in order to produce repetitive interference signals measured as a function of optical path difference by a detector. As its name implies, the interferometer produces interference signals, which contain infrared spectral information generated after passing through a sample.

So, what information can *FT-IR* provide?
• It can identify unknown materials
• It can determine the quality or consistency of a sample
• It can determine the amount of components in a mixture

Infrared Spectroscopy

Infrared spectroscopy has been a workhorse technique for materials analysis in the laboratory for over seventy years. Each of different material is a unique combination of atoms; no two compounds produce the exact same infrared spectrum. Therefore, infrared spectroscopy can result in a positive identification (qualitative analysis) of every different kind of material. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present. With modern software algorithms, infrared is an excellent tool for quantitative analysis. 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).

Because all compounds show characteristic absorption/emission in the IR spectral region. And based on this property they can be analyzed both quantitatively and qualitatively using *FT-IR* spectroscopy. Today *FT-IR* instruments are digitalized and are faster and more sensitive than the older Ones. *FT-IR* spectrometers can detect over a hundred volatile organic compounds (VOC) Emitted from industrial and biogenic sources. Gas concentrations in stratosphere and Troposphere were determined using FT-IR spectrometers. In case of environmental studies FTIR Spectroscopy is used to analyze relevant amount of compositional and structural information concerning environmental samples [2] the analysis can be performed also to determine the nature of pollutants, but also to determine the bonding mechanism in case of pollutants removal by sorption processes.

Advantages of *FT-IR*

Some of the major advantages of *FT-IR* over the dispersive technique include:

Speed: Because all of the frequencies are measured simultaneously, most measurements by FT-IR are made in a matter of seconds rather than several minutes. This is sometimes referred to as the Felgett Advantage.

Sensitivity: Sensitivity is dramatically improved with FT-IR for many reasons. The detectors Employed are much more sensitive, the optical throughput is much higher (referred to as the Jacquinot Advantage) which results in much lower noise levels, and the fast scans enable the coaddition of several scans in order to reduce the random measurement noise to any desired level (referred to as signal averaging).

Mechanical Simplicity: The moving mirror in the interferometer is the only continuously Moving part in the instrument. Thus, there is very little possibility of mechanical breakdown.

Internally Calibrated: These instruments employ a HeNe laser as an internal wavelength Calibration standard. These instruments are self-calibrating and never need to be calibrated by the user. These advantages, along with several others, make measurements made by FT-IR extremely Accurate and reproducible. Thus, it a very reliable technique for positive identification of virtually any sample. The sensitivity benefits enable identification of even the smallest of contaminants. This makes FT-IR an invaluable tool for quality control or quality assurance applications whether it is batch-to-batch comparisons to quality standards or analysis of an unknown contaminant. Quantitative methods can be easily developed and calibrated and can be incorporated into simple procedures for routine analysis. Thus, the Fourier Transform Infrared (FT-IR) technique has brought significant practical advantages to infrared spectroscopy. It has made possible the development of many new sampling techniques which were designed to tackle challenging problems which were impossible by older technology. It has made the use of infrared analysis virtually limitless. [3]

INSTRUMENTATION

The building blocks of an F-T are very different from the predecessor, the double beam (diffraction) infrared spectrometer. In an F-T you have the chain –

Source ➞ Interferometer ➞ Sample ➞ Detector

Each building block varies from manufacturer to manufacturer but basically they all obey the same laws of physics. I can't be exhaustive, but I will try to cover most of the bits and pieces used in contemporary instruments.

Sources

All the manufacturers use a heated ceramic source. The composition of the ceramic and the method of heating vary but the idea is always the same, the production of a heated emitter operating at as high a temperature as is consistent with a very long life. Historically, people have achieved this objective in almost bizarre ways e.g. using an old fashioned gas mantle, or the Nernst Glower. These days, the manufacturers tend to go for either a conducting ceramic or a wire heater coated with ceramic. Now, as I explained recently when talking about hot samples in Raman spectroscopy, heated objects emit, the emission occurs at all wavelengths and the emission at any wavelength increases with temperature.

Interferometers

The interferometer is the bit that analyses the infrared

or near infrared and hence enables us to generate a spectrum. Most of us will have at one time or another seen the classical diagram of an interferometer and had it explained to us. Let's go through this again.

The classic Michelson Interferometer involves a beam splitter – a component which reflects about ½ of the path. The two bundles are then recombined and pass out of the device. Now, one path is radiation that hits it and transmits the rest. One bundle of radiation follows one path and the remainder a different changed in length allowing radiation to interfere with that following the fixed path. In the following Figure-2, I show the classical diagram of the Michelson Interferometer.

DETECTORS:

Various detectors are encountered in *FTIRs*, FTNIRs and F-T Raman instruments. The vast majority act as photo resistors i.e. they have a very high resistance in the dark and this falls as light falls on them. The most sensitive are the Gee and InGaAs semi-conductor devices. In the dark, they can have resistance as high as 3×10^8. Measuring resistance at these high values and doing so rapidly requires the use of very clever electronics if spurious signal (noise) is not to be added to the detected signal. All semi-conductor detectors show an 'absorption edge' i.e. they will ignore radiation longer than a characteristic wavelength. Cooling detectors invariably reduces the amount of noise they develop [we are all familiar with noise. If you listen to your car radio you will be aware that in some areas the sound is clear, in others it is accompanied by hiss – this is "noise" in electronics language. The ratio of signal: noise (S: N) is critical in the measurement of electrical signals and also in the pleasure in listening to your car radio or mobile phone], but unfortunately cooling shifts the absorption edge towards shorter wavelength. Some detectors give adequate performance (an acceptable useful S: N ratio) at room temperature but others must be cooled.

In an FTIR, one normally finds a TGS or similar detector for ordinary use. If better results [or more often, you need results on samples or sample accessories that transmit very little light] are required, one then resorts to the use of a cryogenically cooled mercury cadmium telluride semi-conductor detector. Thus, these are invariably used in infrared microscopy and very often in diffuse reflection experiments. The output from the detector goes to a preamplifier where it is converted into a voltage signal varying with time. This signal has to be digitized and the job is usually done with a dedicated 'analogue to digital' converter chip. These devices will measure the input voltage in binary numbers with 8, 16, 20 or 32 or more digits. Clearly,

the number of useful digits is governed by the quality (S: N ratio) of the signal. 16 and 20 bit devices are frequently used.

SIGNAL-NOISE RATIO

Once your instrument has generated a spectrum and put it up on the screen, you will be aware of the S: N ratio. In theory a spectrum should consist of bands (signal) against a smooth background (i.e. N=zero). In reality this is not so, the background varies at random and the peak height jitters up and down (or will vary in height when you measure it again and again).

Noise in spectra stops you detecting weak bands and also restricts you in making reliable quantitative measurements. You can reduce the noise i.e. enhance the S: N ratio by co-adding scans. The improvement you can achieve is by a factor of n2 where 'n' is the number of scans. So, the noise in a spectrum can be reduced by a factor of 10 by adding 100 spectra and dividing the summed intensities by 100 [this is the co-addition process]. Many users simply set the instrument to scan once or 4 times or some other "house style". This is not very logical. Some spectra appear against strong backgrounds and tend to be noisier than when the bands stand against a low flat background. I advise setting the instrument to run to the maximum sensible (say 20) scans and that you examine the co-added spectra as they appear on the screen. Once you see what you want – stop the scanning. Now "see what you want" sounds very subjective – very unscientific, but this really is the way we all work. There is no 'ideal' or 'acceptable' signal: noise ratio.

RECORDING SPECTRA

This instrument covered the wavelength range from 2.5 μm to 15 μm (wavenumber range 4000 cm^{-1} to 660 cm^{-1}). The lower wavelength limit was chosen to encompass the highest known vibration frequency due to a fundamental molecular vibration. The upper limit was imposed by the fact that the dispersing element was a prism made from a single crystal of rock-salt (sodium chloride) which becomes opaque at wavelengths longer than about 15 μm; this spectral region became known as the rock-salt region. Later instruments used potassium bromide prisms to extend the range to 25 μm (400 cm^{-1}) and caesium iodide 50 μm (200 cm^{-1}). The region beyond 50 μm (200 cm^{-1}) became known as the far-infrared region; at very long wavelengths it merges into the microwave region. Measurements in the far infrared needed the development of accurately ruled diffraction gratings to replace the prisms as dispersing elements since salt crystals are opaque in this region. More

sensitive detectors than the bolometer were required because of the low energy of the radiation. One such was the Golay detector. An additional issue is the need to exclude atmospheric water vapour because water vapour has an intense purerotational spectrum in this region. Far-infrared spectrophotometers were cumbersome, slow and expensive.

Resolution

The interferogram belongs in the length domain. Fourier transform (FT) inverts the dimension, so the FT of the interferogram belongs in the reciprocal length domain, that is the wave number domain. The spectral resolution in wave numbers per cm is equal to the reciprocal of the maximum retardation in cm. Thus a 4 cm−1 resolution will be obtained if the maximum sretardation is 0.25 cm; this is typical of the cheaper FTIR instruments. Much higher resolution can be obtained by increasing the maximum retardation. This is not easy as the moving mirror must travel in a near-perfect straight line. The use of corner-cube mirrors in place of the flat mirrors is helpful as an outgoing ray from a corner-cube mirror is parallel to the incoming ray, regardless of the orientation of the mirror about axes perpendicular to the axis of the light beam. Connes measured in 1966 the temperature of the atmosphere of Venus by recording the vibration rotation spectrum of Venusian CO2 at 0.1 cm−1 resolution.[4]

Michelson himself attempted to resolve the hydrogen Hα emission band in the spectrum of a hydrogen atom into its two components by using his interferometer[5]. A spectrometer with 0.001 cm−1 resolution is now available commercially. The throughput advantage is important for high-resolution FTIR as the monochromator in a dispersive instrument with the same resolution would have very narrow entrance and exit slits.

FT-IR SAMPLE PREPARATION

1. LIQUIDS:

Place a small drop of the compound on one of the KBr plates. Place the second plate on top and make a quarter turn to obtain a nice even film. Place the plates into the sample holder and run a spectrum. If the sample is too concentrated, separate the plates and wipe one side clean before putting them back together.

The KBr plates must be thoroughly cleaned after this procedure to prevent contamination of future samples. Wipe the windows with a tissue, then wash several times with methylene chloride (or another solvent that will take off you sample), then ethanol. Use the polishing kit in the lab to polish the window surface. Wear gloves to prevent fogging. The cleaned surface should be clear and free from scratches.

2. SOLIDS (in solution):

Prepare a concentrated solution of your compound in a suitable solvent (e.g. CH_2C_{l2}).

The all solvents containing water will either dissolve the KBr plates or make them fog up. The broad water band might also mask important bands of your compound.

There are several ways to do this depending how much material you have at hand: either you place a small amount (2-5 mg) of your compound directly on the plates and add one drop of solvent, or you dissolve it in a small test tube first and transfer this solution with a pipet onto the IR plates.

The KBr plates must be thoroughly cleaned after this procedure to prevent contamination of future samples. Wipe the windows with a tissue, and then wash several times with your solvent, then ethanol. Use the polishing kit in the lab to polish the window surface. Wear gloves to prevent fogging. The cleaned surface should be clear and free from scratches.

3. SOLIDS (as Nujol mulls)

Alternative methods to obtain IR spectra of solids are Nujol (mineral oil) mulls between KBr plates.

Take 5 to 10 mg of finely ground sample are then placed onto the face of a KBr plate, a small drop of mineral oil is added and the second window is placed on top. With a gentle circular and back-and-forth rubbing motion of the two windows, evenly distribute the mixture between the plates. The mixture should appear slightly translucent, with no bubbles, when properly prepared.

Place the sandwiched plates in the spectrometer and obtain a spectrum. Ideally, the strongest band should have a transmission ob 0 to 10% and should not be totally absorbing for more than 20 cm-1.

4. KBr pellets/disks (for solid samples)

The concentration of the sample in KBr should be in the range of 0.2% to 1%. The pellet is much thicker than a liquid film, hence a lower concentration in the sample is required (Beer's Law). Too high a concentration usually causes difficulties obtaining clear pellets. The IR beam is absorbed completely, or scattered from the sample which results in very noisy spectra.

Sample preparation

Although a homogeneous mixture will give the best results, excessive grinding of the potassium bromide is not required. The finely powdered potassium bromide will absorb more humidity (it is hygroscopic) from the air and therefore lead to an increased background in certain ranges. Transfer some KBr out of the oven (the oven is at 100^0C) into a mortar. Add about 1 to 2 % of your sample, mix

and grind to a fine powder. For very hard samples, add the sample first, grind, add KBr and then grind again.

The sample must be very finely ground as in the Nujol mulling technique to reduce scattering losses and absorption band distortions.

Take two stainless steel disks out of the desiccator. Place a piece of the precut cardboard (in the tin can next to the oven) on top of one disk and fill the cutout hole with the finely ground mixture. Put the second stainless steel disk on top and transfer the sandwich onto the pistil in the hydraulic press. With a pumping movement, move the hydraulic pump handle downward. The pistil will start to move upward until it reaches the top of the pump chamber. Then, move the pump handle upwards and pump until the pressure reaches 20,000 prf. Leave for a few seconds and with the small lever on the left side, release the pressure (hold until the sample and pistil are all the way down). Remove the disks and pull apart. Remove the film, which should be homogenous and transparent in appearance. Insert into the IR sample holder and attach with scotch tape. Run the spectrum. [6]

After use, the mortar and pistil should be cleaned with acetone and double distilled water, and be put back on top of the oven for drying.

REASONS FOR CLOUDY DISKS
1. KBr mixture not ground enough
2. Sample was not dry
3. Sample: KBr ratio high
4. Pellet too thick
5. Bolts not tightened sufficiently.
6. Sample has low melting point

Interpretation for *FTIR* spectroscopy
Every part of the molecules has different atoms and are connected by bonds. Each bond requires different IR region for absorption and so characteristic peaks are observed.

Group frequency region, the peaks corresponding to different functional groups can be observed.

Applications of FTIR
1. Identification of simple mixtures of organic and inorganic compounds both as solids or liquids [7].
2. Identification of polymers and polymer blends.
3. Indirect verification of trace organic contaminants on surfaces.

4. Routine qualitative & quantitative FTIR Analysis.
5. Thin film analysis.
6. Analysis of adhesives, coatings and adhesion promoters or coupling agents.
7. Small visible particle chemical analysis.
8. Analysis of stains and surface blemishes remnant fromcleaning and degreasing processes combined withoptical microscopy, SEM/EDX, XPS and SIMS tec hniques.
9. Analysis of resins, composite materials and release films.
10. Solvent extractions of leachable or contaminants, plasticizers, mould release agents and weak boundary layers coupled with XPS surface chemical analysis techniques.
11. Identification of rubbers and filled rubbers.
12. Determination of degrees of crystallinity in polymers (eg LDPE and HDPE).
13. Compararive chain lengths in organics.
14. Extent of thermal, UV or other degradation or depolymerisation of polymers and paint coatings.
15. Analysis of gaseous samples using a gas cell for headspace analysis or environmental monitoring.
16. Analysis of unknown solvents, cleaning agents and detergents.

CONCLUSION

The review article discussed about the basic fundamental technique of Fourier Transform Spectroscopy has become more and more important as an instrument for analytical research to determine the chemical functional groups in the sample. It producing routine spectra in shorter times and of better quality than those from conventional grating systems and the extension of the possibilities of performing measurements.Superior sensitivity and resolution, rapid sample measurement, absolute wavelength accuracy, versatile spectra processing.
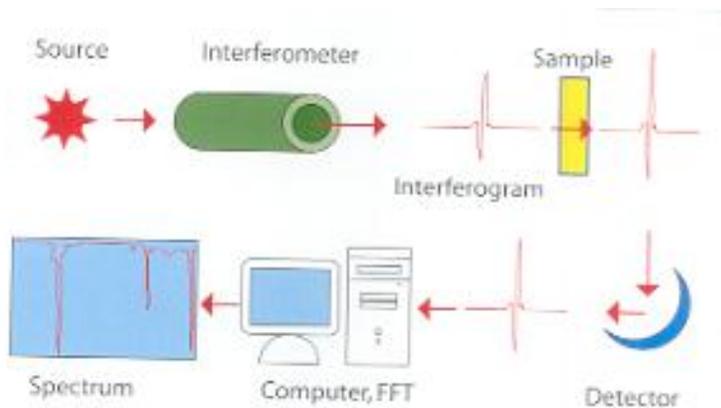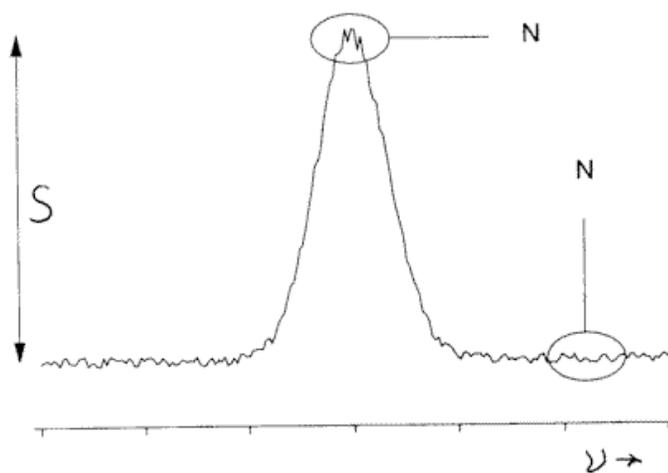
Figure-1shows Instrumentation for *FTIR*
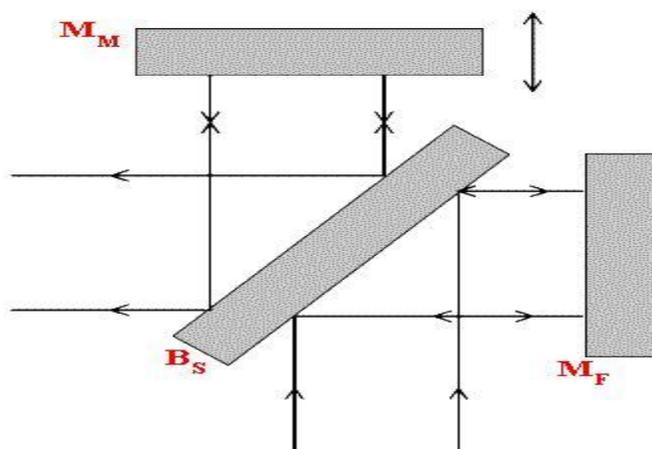

Figure 2 SIGNAL: NOISE RATIO

Figure 3.Show the classical diagram of the Michelson Interferometer.

Table No 1 Absorption of Common Functional Groups

Group	Range cm-1
C-H stretching(alkane)	2960-2850
C-H stretching(alkene)	3040-3010
C-H stretching(aromatic)	3030
C-H bending(alkane)	1340
C-H bending(aromatic)	700-850
C=C stretching(alkene)	1680-1620
C=C stretching(alkyne)	2100-2200
C=C stretching(aromatic)	1450-1600
C=O stretching(ketone)	1705-1725
C=O stretching(aldehyde)	1720-1740
C=O stretching(ester)	1735-1750
C=O stretching(acid)	1700-1725
C=O stretching(amide)	1650-1700
O-H stretching(free)	3590-3650
O-H bending(alcohols)	1050-1150
O-H bending(phenols)	1200
C-O stretching(alcohols)	1250-1350
C-O stretching(phenols)	1310-1410
N-H stretching	3400-3500
N-H bending	1500-1650
C=S stretching	1050-1200
S=O stretching	1050-1400
S=H stretching	2500-2600
C-N vibrations	1000-1400

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