Attenuated total Reflectance FTIR

R Swetha sri[1], K.Bhavya sri[2] and Bima Benazir[3]

[1]Department of Pharmaceutical Analysis , Raja Bahadur Venkata Rama Reddy Women's College of Pharmacy, Hyderabad, India
[1]siri.pharma86@gmail.com

Abstract: Attenuated total internal reflectance (ATR) is based on the phenomenon of total internal reflectance. In this and IR beam enters the ATR element (e.g. a diamond ATR crystal) at a particular angle corresponding to the critical angle between the ATR element and the sample. The beam then undergoes total internal reflection and this total internal reflection creates an evanescent wave that stretches above the ATR element into the sample where some of the evanescent wave is absorbed by the sample. Since the sample absorbance attenuate the intensity of totally reflected infrared beam the term ATR is used. It sometimes becomes unavoidable to measure the absorption spectra of material that cannot be put inside a infrared cell such as paint on a door/wall or a piece of art, these type of samples can therefore be analyzed by using a ATR. This system is an attachment that can be added to a conventional IR system and is used only in sampling.

***Keywords*:** Attenuated total reflectance, total internal reflectance, refraction, diamond, selenium

1. INTRODUCTION

Mid infrared spectroscopy is a highly credible and well acceptable fingerprinting method. By using this spectroscopy many substances can be identified and quantified. IR spectroscopy has the ability to analyse wide variety of solids, liquids and gases but in many cases sample preparation is required to get a good quality spectrum. Conventionally IR spectrometers analyse the sample by passing the IR radiation directly through the sample and when the sample is solid or liquid the intensity of spectral features is determined by thickness of the sample which cannot be more than few tens of microns and preparing such samples involves skill an expenditure of time and even after skilfully performing and spending time ,it is not guaranteed to get a good quality spectrum and even if a good quality spectrum is obtained it is not guaranteed whether it will be reproducible or not in future. Therefore in cases of solids and liquids where sample preparation and spectral reproducibility becomes a challenge ATR can be used as an effective tool to overcome such challenges.

1.1. Principle Of Atr-Ftir [1]

Attenuated total reflectance is based upon internal reflectance. In this a beam of light travels through a crystal of high refractive index (n_c) into a sample of lower refractive index (n_S). The angle of incidence of the beam plays a very important role in this, if the angle of incidence is small, some of the beam will reflect of the internal surface of the crystal and some beam will refract out of the crystal into the sample giving the refracted beam. According to the laws of refraction as the angle of incidence (θ_i) increases angle of refraction (θ_r) also increases therefore at some angle of incidence the angle of refraction will become 90° and then the infrared beam will no longer leave the crystal but will remain within it reflecting itself along the walls of the crystal, hence the term total internal reflection. The minimum angle of incidence at which the total internal reflectance occur in a material is called its critical angle (θ_c). Total internal reflection will take place at θ_c at and at all angles of incidence greater than θ_c .The critical angle depends upon the refractive indices of the crystal and sample as follows :

$$\theta_c = \sin^{-1}(n_s/n_c)$$

Where

θ_c = Critical angle

n_s = Refractive index of sample

n_c = Refractive index of crystal

At the point of internal reflectance the incoming and outgoing infrared beam occupy the same volume. Under the right conditions these two beams undergo constructive interference. We know that in constructive interference the amplitude increases therefore the enhanced amplitude has nowhere to go but up which results in infrared light sticking up into the space above the crystal surface which is called evanescent wave,

which are also called "hotspots" it by less than a micron to upwards of 10 microns depending upon the experiment carried out. To take the spectrum of a sample it is brought in contact with the hotspot and then some of the beam is absorbed by the sample, the beam is the focussed onto the detector. The background spectrum is obtained of the clean, dry crystal beforehand and then this sample spectra is taken. As the sample absorbance attenuated the intensity of totally reflected beam, the term attenuated total reflectance is used.

1.2. Types Of Crystals Used In Atr-Ftir [1-2]

Types of Crystal used in ATR are

KRS-5

KRS-5 is a mixture of thallium bromide and thallium iodide and was one of the first materials used as an ATR crystal.

Advantages: Its one advantage is that it works over a wide wavenumber region, including the entire mid-infrared.

Disadvantages: However, it is soft and easily scratched so

it cannot be used with powders and many other solids, and it is highly toxic and should never be handled with bare hands.

Zinc selenide (ZnSe)

Zinc selenide (ZnSe) was for many years the most popular ATR crystal material.

Advantages: It is tougher and harder than KRS-5, and is transparent throughout most of the mid-infrared. This material

Works well with liquids, polymers, and soft solids but has difficulty with powders.

Disadvantages: However, hard powders and solids will scratch it, it will break if too much pressure is applied, and it is attacked by strong acids and bases

Silicon and germanium(Ge)

Silicon and germanium are useful ATR crystals because they are hard, durable, and not that sensitive to pH.

Diamond

The use of diamond as an ATR crystal began in the mid-1990s and has increased exponentially since then. Diamond is in some ways the perfect ATR crystal material.

Advantages: Its refractive index is almost identical to that of ZnSe, which means the two crystals produce similar-looking spectra, which is very useful when performing spectral comparisons or library searching. Diamond is chemically inert; it will not react with most samples, and it is impervious to strong acids and bases. Diamond is the hardest substance known to man, so samples will not scratch it. Finally, diamond is tough. A lot of pressure can be applied to it to flatten any manner of samples and the crystal will not break.

Disadvantages: Diamond ATR's cost several thousand dollars more than other ATR accessories. It absorbs strongly in the mid-infrared between 2200 and 2000 cm−1.

Table I-The types of crystals used in ATR and their properties

Crystal material	Refractive index	Wave number range(cm^{-1})	color	pH range
KRS-5	2.37	20,000–250	Red	5–8
ZnSe	2.42	15,000–600	Yellow	5–9
Si	3.42	8900–660	Grey	1–12
Ge	4.0	5500–600	Grey	1–14
Diamond	2.42	30,000–2200, 2000–400	Clear	1–14

1.4. Single Vs Multiple Reflection Atr [3-4]

There are two types of reflection single as well as multiple reflection. For hard solids and powders typically single reflection ATR with small surfaces used as it results in stronger absorbance bands when compared to multiple reflection ATR whereas for liquids and semi solids multiple reflection ATR is suitable.

For example the spectral differences (Fig-1) of a powder taken through single reflection ATR and multiple reflection ATR can be seen. In single reflection the absorption bands are stronger than multiple reflection ATR.

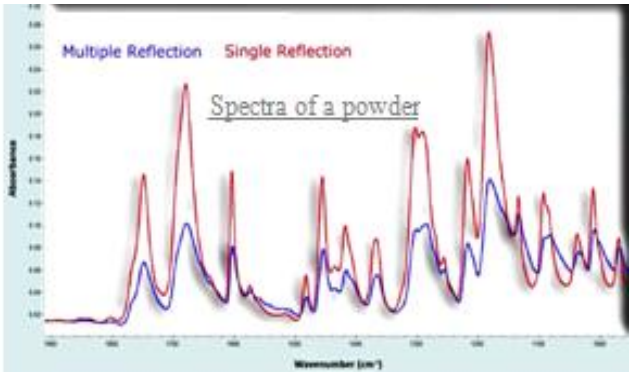

Figure 1- Spectra of a powder

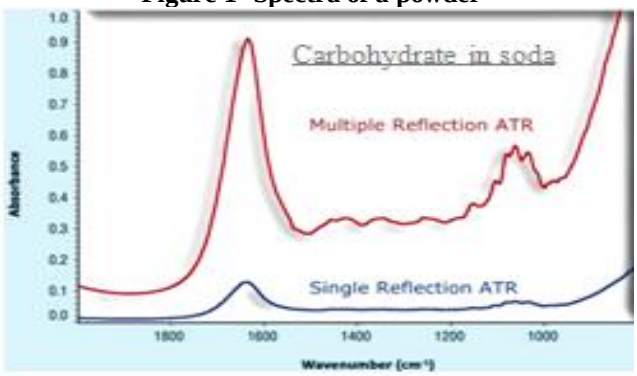

Figure 2- Spectra for detecting the carbohydrate

In liquids the multiple reflection ATR has an upper hand when compared to the single reflection ATR as it can be seen in the below spectra taken for detecting the presence of carbohydrate in soda (Fig-2) .It was observed that carbohydrates are nearly undetectable by single reflection ATR but in multiple reflection they are not only detectable, the absorbance bands magnitude is also increased.

1.5. Types of sample that can be used in ATR

There are 4 types of sample that can be used in ATR they are solids (powder), polymer, and semi solid and liquid

1.6. Difference In Sample Preparation Method Between Ftir And Atr-Ftir [5-6]

1.6.1. Sample preparation in FTIR

1. sampling of solids
a) Nujol mull b) Pressed pellet technique
2. Sampling of liquids a) NaCl / KBr cell
3. Sampling of gases a) Gas sample cells

1.6.2. Sample preparation in ATR-FTIR

The best part of using ATR is that there is no sample preparation needed for any kind of sample, if it is solid, polymer or powder they just need to be directly placed in contact with the crystal and then they must be pressed against the crystal by using the pressure tower If they are liquid sample ,the sample must first be withdrawn by using a Pasteur pipette few drops according to the crystal surface must be placed on to it, when it comes to liquid there is no necessity of applying pressure, they can be directly analysed without applying pressure. When it comes to semisolid samples they just need to be smeared onto the crystal. Gas samples cannot be analysed using ATR-FTIR. The application of pressure and change in particle size has a significant importance when it comes to sample analysis. Coarse sample do not give good quality spectrum, therefore grinding the sample for as less as 1 minute will significantly impact the spectrum quality .In few instances, it was observed that coarse sample spectrum quality was not as good as the fine powdered spectrum. Even though this technique is known for no sample preparation but the grinding of coarse powder for 1 minute is extremely less when compared to other sample preparation technique used in FTIR. Application of pressure onto the sample increases spectrum quality, as increase in pressure increases the contact of the sample with the crystal and also more sample surface comes in contact with the crystal which increases the spectrum quality.

1.7. Advantages And Disadvantages Of Atr Sample Preparation Method[7]

Advantages

In this technique there is very little grinding, pressing and diluting needed to prepare a sample for ATR analysis. For many samples there is little sample preparation, in this ATR crystal is cleaned, the the sample is placed as it is (in case of solid, powders and polymers) and clamped and sometimes there is no clamping necessary (in case of liquids and semi-solids),then the sample is analysed. Later the sample is removed and the crystal is carefully cleaned and then it is ready for next use. Such preparation makes it a easy technique and as the time for analysis is less it is a fast technique. It analyses solid, powders, polymer, liquids and semisolid, therefore many different types of sample can be analysed. Only gas sample cannot be analysed by this method. As it does not involve sample destruction, it is a non-destructive technique, it becomes an important factor when the sample is valuable. As long as the refractive index of the sample is less than the refractive index of the crystal, quantitation of the sample can be done easily unlike other technique where dilution of sample, sample quantity and other factors determine whether the sample can be quantified or not.

Disadvantages

The technique lacks sensitivity as its depth of penetration is sometimes less than 1 micron and rarely greater than 10 micron this makes this technique less sensitive. The accessory used for the analysis is usually costly. The crystals used for the analysis are not cheap, crystals like diamond are far more costly than other crystals. Also crystal care must be taken for crystals like ZnSe the must be carefully cleaned as some of the tissue paper used contain wood fibres and they may scratch the crystal and this may ultimately affect the analysis as they disturb the hotspot formed, if the hotspots are disturbed the analysis will give wrong results which is not our aim. The crystals must be carefully handled and they must not be dropped as this may break the crystal and broken crystals cannot be used for analysis. Another issue with ATR is its wavenumber range. Many ATR crystals absorb in the mid-infrared. Specifically, diamond absorbs between 2200 and 2000 cm^{-1} and ZnSe absorbs below 700 cm^{-1}, masking sample features in these regions. Some diamond ATRs use ZnSe lenses to focus the infrared beam; for these accessories sample peaks between 2200 to 2000 cm^{-1} and below 700 cm^{-1} will be hidden. It is a good idea to have two crystals with complimentary wavenumber ranges to cover the entire mid-infrared. For example, diamond and Ge together are transparent from 4000 cm^{-1} down to 600 cm^{-1}. Before measuring any samples you should know what type of ATR crystal you have and what wavenumber regions it masks so you can take that into account when interpreting your sample spectra.

Table 2-Table showing Advantages over disadvantages of ATR

ADVANTAGES	DISADVANTAGES
Fast and easy sample analysis	It lacks of sensitivity when compared with other techniques
Analysis of different types of samples	The ATR accessory is costly
Non-destructive technique	Crystal care should be taken in case of crystals like ZnSe
Straight forward quantitation	Limited cm^{-1} range

2. CONCLUSION

The other sample preparation technique like nujol mull and pressed pellet technique were developed many years ago, it involved skilled people and the samples were manually prepared. In those days labour was cheap, and it made sense to spend minutes or hours in sample preparation. However, in the 21st century, labour costs are significantly higher, and all labs are under pressure to do more with less to increase profitability, so the old sample preparation technique were not as profitable to begin with. Therefore, there was

necessity to develop technique which was easy to use and gives rapid result in less time. The introduction in the mid-1990s of diamond ATR accessories has revolutionized FTIR sample preparation. The toughness and durability of diamond meant that materials that which would have been formerly scratched and broken under pressure can be omitted. Diamond can tolerate all manner of liquids, semi-solids, solids, and powder. It is also used as it is easy to used and faster in analysis. For these reasons diamond ATR is the premier type of sample preparation in use today and also with many application for it today it is the most used sample preparation. As we need the crystal refractive index to be high than the sample, germanium is considered the best,as its refractive index is the highest. On the whole different crystal comes to play their role at different condition which is needed, therefore the ATR-FTIR is considered best and is now widely used in analysis of sample.

3. RECENT APPLICATIONS OF ATR-FTIR

3.1 Pharmaceutical applications

A. Pre and post formulation compatibility study of diacerein based on ATR-FTIR study for the design of transfersomal carriers
B. Use of ATR-FTIR Spectroscopy to Study the Diffusion of Ethanol Through Glycerogelatin Films

3.2 Differentiating tool

A. ATR-FTIR spectral discrimination between normal and tumorous mouse models of lymphoma and melanoma from serum samples

B. ATR-FTIR Spectroscopy for the Assessment of Biochemical Changes in Skin Due to Cutaneous Squamous Cell Carcinoma

3.3 Diagnostic tool

A. ATR-FTIR Spectroscopy for determining the glucose levels in healthy patients

3.4Forensic analysis

A. FTIR-ATR Spectroscopy for Identification of Illicit.
B. Soft and Robust Identification of blood ageing over several months Using Fourier Transform Infrared Spectroscopy for Forensic Analysis
C. Differentiation of Hair Using ATR FT-IR Spectroscopy: A Statistical Classification of Dyed and Non-dyed Hairs

3.5 Food analysis

A. Use of ATR-FTIR spectroscopy to detect the changes in extra virgin olive oil by adulteration with soybean oil and High temperature heat treatment
D. Preliminary Discrimination of Butter Adulteration by ATR-FTIR Spectroscopy
E. Application Of FTIR-ATR Spectroscopy for Quantification Of Sugar In Honey

3.6 Quantitative estimation

Application of ATR-FTIR spectroscopy in quantitative analysis of deuterium in basic solutions

A. Quantitative analysis of ATR-FTIR water-soluble vitamins by spectroscopy

3.7 Forensic analysis

A. FTIR-ATR Spectroscopy for Identification of Illicit Drugs Seized From Clandestine Laboratories
B. Soft and Robust Identification of blood ageing over several months Using Fourier Transform Infrared Spectroscopy for Forensic Analysis
C. Differentiation of Hair Using ATR FT-IR Spectroscopy: A Statistical Classification of Dyed and Non-dyed Hairs.

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