INFRARED SPECTROMETER ACCESSORIES

Measurement of ATR Spectra of Hard and Irregular Shaped Solid Samples Using the Quest ATR Accessory

Introduction

Infrared spectroscopy can be used as an analytical measurement technique to identify the molecular constituents (chemical groups) of an extremely wide range of solid, liquid and gaseous sample types.

Certain plastics and polymer type samples in a raw, bead or pellet shaped form can be classified as irregular shaped, hard solid samples. Due to their physical nature small quantities of these sample types cannot be ground with KBr powder to form a homogenous mix of the sample suspended in the KBr matrix for infra red spectral analysis using a transmission technique. Traditionally a plastic or polymer sample type can be melted and then compressed into the formation of a uniform thickness of film (circa 50 microns in depth) that allows for infra red spectral collection via transmission spectroscopy.

However, a plastic or polymer sample type can be analysed “as is” using the ATR spectroscopic technique for collection of a representative IR spectrum. This obviates the need for a timely sample preparation method for a thin film production for a transmission spectral measurement, if the reflection technique for qualitative and quantitative analysis of the sample is sufficient.

Application

ATR measurement of an irregular shaped, hard solid sample in order to try and obtain as wide a spectral transmission range of light frequency collection for the sample as possible.

Specac’s Quest ATR Accessory

Equipment and Method

For the ATR measurement of a plastic or polymer bead material to obtain a full spectral range for the sample between 4000cm^{-1} and 400cm^{-1}, the Quest ATR Accessory P/N GS10801-B was used with the single reflection diamond extended range ATR crystal puck option on the black surface coloured optical unit. Both the stainless steel flat and pellet anvil options from the anvil arm assembly were used for an appropriate sample type to cover over the sample when in contact with ATR crystal for correct and consistent positioning.

The spectra were collected on a Thermo Nicolet iS5 instrument using the standard room temperature detector system set at a resolution of 4cm^{-1} for 16 scans.

The following plastic and polymer bead samples studied were:-
PET (Polyethylene Terephthalate) 100% as small, hard, short rod type fragments.
Blue Coloured Plastic Pen Cap (Polypropylene) as small, hard, shards of material.
Grey Plastic Construction Brick (Acrylonitrile Butadiene Styrene) as small, hardish fragments.
PVA (Polyvinylacetate) as softish beads.
PolyB (Polyethylene) as hard beads.

For preparation of each sample for the ATR spectral measurement, a particular example of the sample was taken "as is" and placed over the diamond ATR crystal of the Quest ATR puck assembly option.

A new example of the same sample was repeated for a couple of further spectral collections to check for consistency of result. A set load from either the flat or pellet anvil option from the anvil arm assembly was used to cover over the sample when in contact with the ATR crystal for correct positioning of the sample and application of a constant and reproducible force to obtain an acceptable IR ATR spectrum.
The sample was then ready for spectral data collection.

Spectral Data

The Infra red spectra collected for the samples studied are presented as Figures 1 to 6.

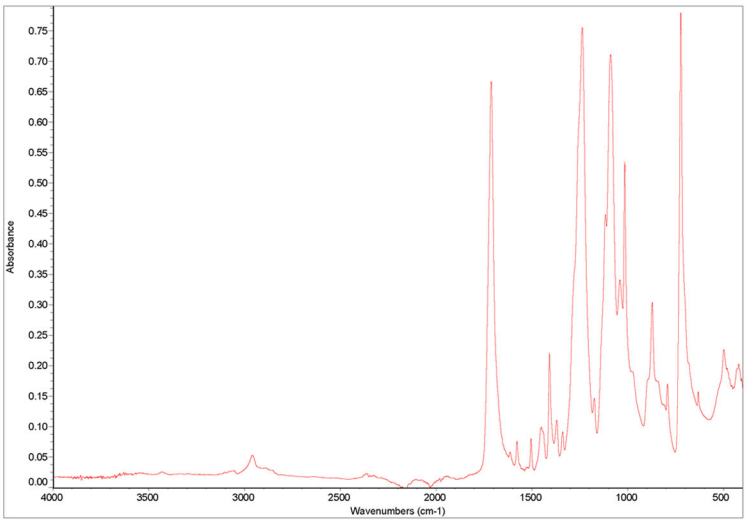


Fig. 1. PET (Polyethylene Terephthalate) 100% hard, "rod" with Flat Anvil on diamond ATR puck of Quest ATR Accessory

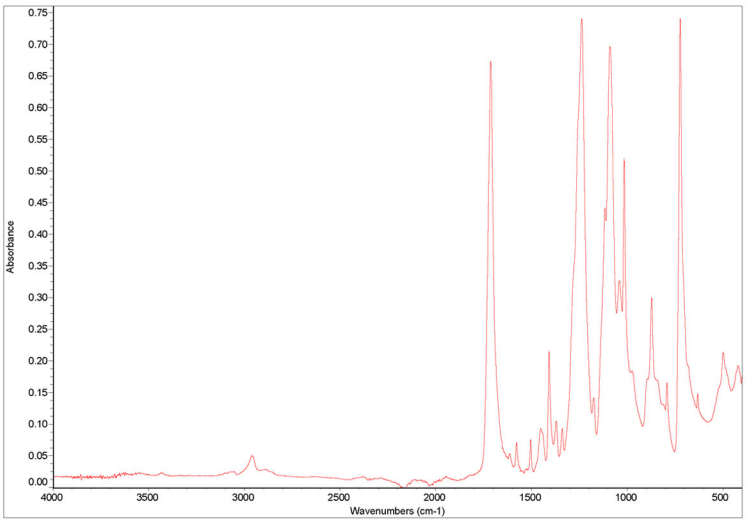


Fig. 2. PET (Polyethylene Terephthalate) 100% hard, "rod" with Pellet Anvil on diamond ATR puck of Quest ATR Accessory

Discussion

One of the objects of this exercise has been to try and determine which of the two anvil options (flat or pellet stainless steel) might be considered best to use for a particular polymer/plastic type.

In the case of the PET (Polyethylene terephthalate) sample there appears to be very little difference in whether the flat or pellet anvil is used to bring the sample into contact with diamond for a consistent ATR spectrum to be collected. (See Figures 1 and 2). It is the actual sample shape and its relative hardness that has determined the type of contact that can be made resulting in any difference for absorption intensity characteristics between the three similar sample like determinations in collection of the spectra. Because of the shape of the PET polymer rod and its overall hardness, the pellet anvil is the preferred option though, to keep the rod consistently in position over the diamond ATR crystal surface during spectral acquisition. The spectra shown as Figures 1 and 2, are typical examples of this sample type when using the flat and pellet anvil respectively for the contact force.

For the Blue Coloured Plastic Pen Cap sample, the ATR spectra indicate this material to be generally of a form of polypropylene. Similar to the PET samples, fragments of the pen cap that had been cut for sampling were locally harder than some other

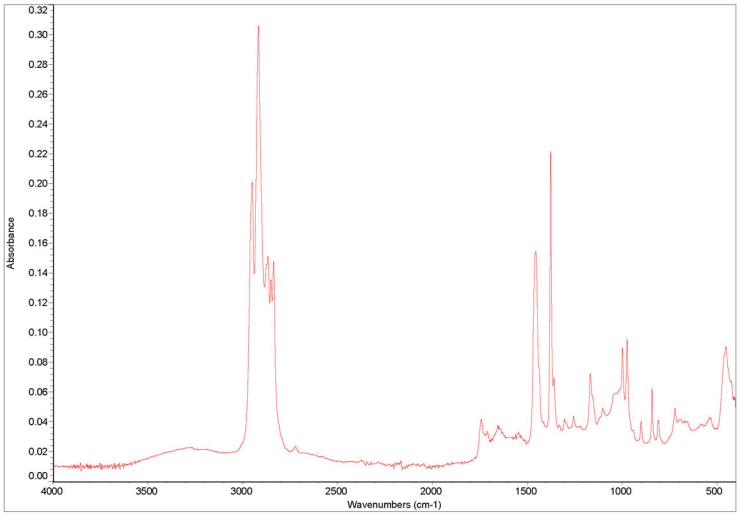


Fig. 3. Blue Pen Cap (Polypropylene) hard, "shard" with Flat Anvil on diamond ATR puck of Quest ATR Accessory

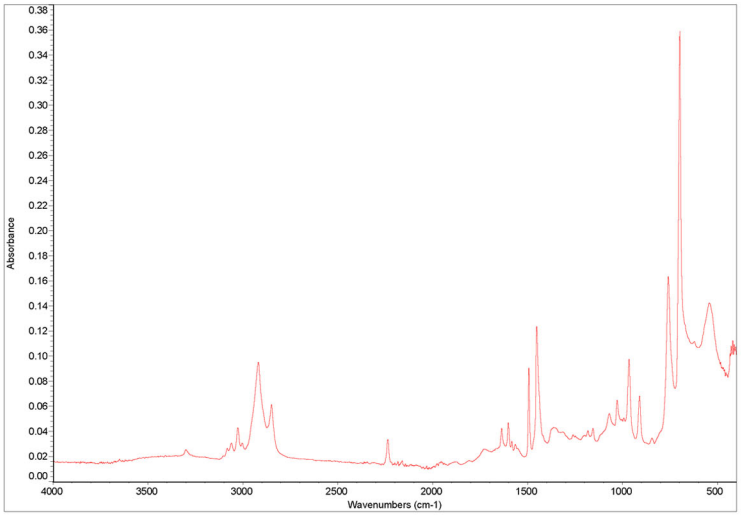


Fig. 4. Plastic Construction Brick (Acrylonitrile Butadiene Styrene) small, hardish fragment with Pellet Anvil on diamond ATR puck of Quest ATR Accessory

pieces and so consequently from the example sample chosen for pressing, its contact has lead to the variability in overall sensitivity of signal absorption. However, there is consistency between the overall spectral profiles and relative peak intensities from the individual sample pieces analysed. The spectrum presented as Figure 3. is an example of the spectrum collected for this sample type using the flat anvil for the load force against the diamond crystal.

The Grey Plastic Construction Brick sample shows very consistent spectra for the examples of sample run using the pellet anvil to provide the contact force. The spectrum shown as Figure 4. is a typical example for the sample type. The spectra are quite consistent in sensitivity from goodish contact (the polymer is hardish by nature) and the polymer material is identifiable as acrylonitrile butadiene styrene. An interesting spectral feature of this molecule is the nitrile (-CN) anti-symmetric stretch vibration seen circa 2235cm^{-1} which although weak, is real. This chemical group frequency spectral vibration is close to the natural diamond vibration region and the fact that this spectral feature can be seen for this sample helps to demonstrate that a Quest diamond ATR accessory can be used to determine the presence of such chemical groupings in a molecule from its IR spectrum.

Fig. 5. PVA (Polyvinylacetate) softish bead with Pellet Anvil on diamond ATR puck of Quest ATR Accessory

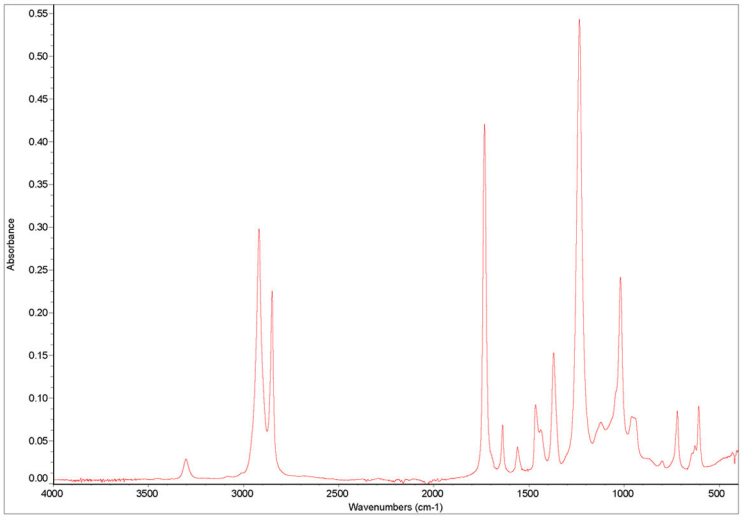
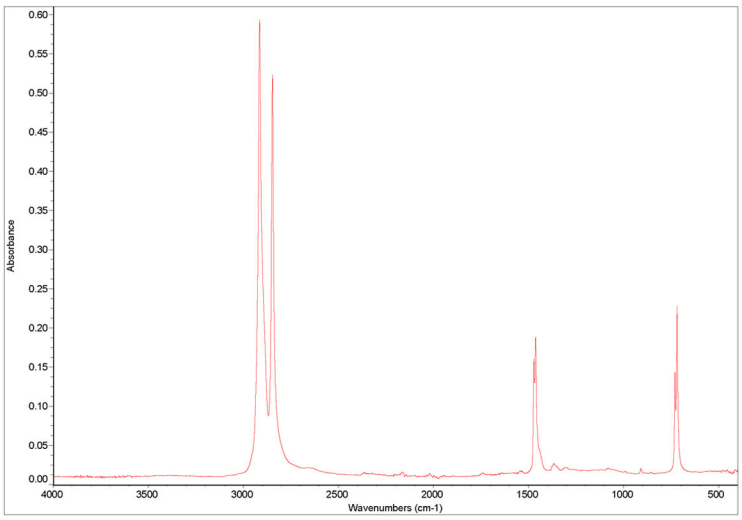


Fig. 6. PolyB (Polyethylene) hard bead with Pellet Anvil on diamond ATR puck of Quest ATR Accessory



For the PVA (polyvinylacetate) sample shown as Figure 5. these polymer beads were quite soft and so all three sample examples gave consistent PVA IR spectra using the pellet anvil, but a user might be able to decide that for such softish polymer bead types the flat anvil would also work just as well (if not better) for consistent pressing.

Finally, the PolyB (polyethylene) sample shown as Figure 6. was in a solid bead form and similar to the PVA sample gave consistent spectra for the three sample examples chosen when the pellet anvil was used.

Conclusion

In conclusion, a fairly broad spread of plastic and polymer types in various shapes, forms and hardness have produced good reproducible spectra, very easily, when using the Quest ATR with a diamond ATR puck. It is a matter mostly of discerning the sample type for its shape, size and hardness to know if the flat or pellet anvil may be better employed to allow for the force needed to bring the sample type into close contact with ATR crystal, but this could be learnt with experience of use.

With use of the diamond crystal ATR top plate option of the Quest ATR accessory, the widest range of IR spectrum for the mid infra region (e.g. 4000cm^{-1} to 400cm^{-1}) has been obtained for each of the sample types chosen for measurement.

Traditionally for the ATR spectroscopic technique, use of a ZnSe crystal will only allow for spectral transmission to circa 600cm^{-1} whereby certain spectral features for a given sample type between 600cm^{-1} and 400cm^{-1} cannot be observed unless a diamond ATR crystal has been used.

Additionally, use of a diamond ATR crystal instead of the choice of a ZnSe ATR crystal has allowed for the measurement of the hard, sample types, with the minimum of risk for potential damage to the ATR crystal from the sample contact force required for excellent ATR spectral reproducibility.

Acknowlegement

The study was carried out by: C. Moss, Specac Limited, Orpington, Kent, UK.

Specac Ltd
River House, 97 Cray Avenue, Orpington
Kent BR5 4HE UK
T: +44 (0) 1689 873134 F: +44 (0) 1689 878527
E: sales@specac.co.uk W: www.specac.com

Specac Inc
301 Berkeley Drive, Swedesboro, NJ 08085 USA
T: Toll Free +1 800 447 2558
E: sales@specac.com W: www.specac.com
Specac is part of Smiths Group plc