Introduction

One of the most powerful developments in mid-infrared spectroscopy (MIR) in the last 10 years was the introduction of the Diamond ATR (DATR) technique. It allows collection of good-quality infrared spectra from virtually any solid or liquid sample with almost no sample preparation. One of the prerequisites of the ATR measurement is good contact between the sample and the crystal. Due to its hardness, diamond is an ideal ATR crystal material as it allows good sample contact even with extremely hard solids by applying very high pressures to a small crystal. Consequently, the DATR technique has become the most important sampling technique in the mid-infrared. In addition, due to the small size of the crystal, the amount of sample required is often quite small compared to other ATR techniques. Using diamond as the ATR element, cleaning of the crystal is relatively easy and can be done quickly.

For routine FT-IR analysis in the MIR that involves, for example, raw material identification or even quantitative analysis, DATR is the most convenient sampling method provided the pathlength achieved is appropriate.

However, for a laboratory that would like to make decisions on samples based on infrared spectra, as is done in a QA/QC environment, we should aim to measure these spectra with high repeatability. Unfortunately, in ATR spectroscopy, this is not easily achieved for a variety of samples. While with liquid samples, there is good, constant contact between the sample and the crystal due to the properties of a liquid, this is not the case for solid samples. Here, the intensities of ATR spectra can vary considerably when applying different pressures to the sample as this is directly influencing the contact of the sample with the crystal. Therefore, it is important to control the contact in a DATR accessory.
As long as the sample is larger than the crystal, only the force that is used needs to be adjusted. But force control is not the only key to good reproducibility. There are other influences from the design of a DATR accessory that can reduce the contact and not only give rise to spectral ordinate variations, but also to spectral distortions with changes of the line shape. Therefore, a careful design of the mechanics in such an accessory is very important to guarantee good quality spectra.

The Frontier UATR Accessory
The Universal ATR accessory (UATR) for the Frontier Spectrometer (Figure 1) is an improved version of the diamond ATR accessory that was developed for the Spectrum One spectrometers.

The design of the UATR enables higher spectral reproducibility, signal-to-noise performance and ease-of-use. Key design enhancements follow.

Positive locations of the movable arm
The UATR accessory uses a movable arm that swings in to clamp the sample and moves out to allow better access to the crystal during cleaning or changing of the crystal plate. This design approach is common to most DATR accessories. However, there is always the danger that the arm does not adequately engage the sample due to mechanical tolerances in the arm mechanism, resulting in possible spectral reproducibility problems. With this UATR design, this is overcome by using an arm with two positive locations at the end stops that are permanently aligned, giving the user a tactile feeling for the correct position when moving the arm to the sampling end stop.

Improved rigidity of the movable arm
Another source of intensity variations is related to the bending of the arm when applying high force to it. The result of this bending is that the surface of the pressure shoe is no longer parallel to the crystal surface, i.e. the direction in which the force is applied is no longer perpendicular to the crystal. This has the effect that the contact of the sample is no longer uniform over the crystal, resulting in not only a reduced intensity of the spectrum but also generating additional intensity variations depending on the bending of the arm. With this new design, the movable arm is much more rigid and these bending effects are totally removed. Figure 2 demonstrates the improved sampling performance of the new accessory based on these design changes. In order to test these changes, 15 replicate spectra of the same polystyrene film were measured with the old and the current design UATR accessory (1 bounce) by using the 0.5 mm UATR shoe and a force gauge of 120 units. Between each measurement, the sample was removed and the crystal cleaned. The top plate was not changed between samples.

Figure 2 shows the strongest band in the polystyrene spectrum of approximately 695 cm⁻¹. The left graph shows the band intensity variation due to the lower rigidity of the arm in the old accessory. The largest difference between the absorbance of this polystyrene band here is 30.8% of the average absorbance. The design improvements achieved with the new accessory are demonstrated in the right graph where this deviation is only 3%. In addition to this improved ordinate reproducibility by one order of magnitude, an increase in band intensity by a factor of 2.5-3.0 can also be observed. It is important to note that this improved contact is not achieved through changing the force. With both accessories, the same force was applied, but the sample was pressed more perpendicular to the surface of crystal with the new UATR.

Figure 1: UATR accessory for the Frontier FT-IR.

Figure 2: Intensity variation of 15 replicate measurements of a poly-styrene film on the previous UATR (left) and the new UATR accessory (right).
This performance improvement has been further demonstrated using a powder sample that should show even larger variations due to different particle sizes or different packaging. Figure 3 shows the result of 15 replicate measurements of caffeine powder with the previous and the new design UATR accessory (1 bounce) by using the 0.5 mm UATR shoe, the UATR Sample position plate 3 mm diameter and a force gauge reading of 100 units. Between each measurement, the sample was removed and the crystal cleaned. The top plate was not changed between samples.

As expected, the enhanced repeatability of the new design is clearly proven in the right graph with less absorbance variations of one of the strong caffeine bands around 742 cm⁻¹, but also with less variations in the baseline. The improved uniformity of the pressure of this powder sample can be observed during cleaning of the crystal. With the new accessory, the compacted powder was covering the whole crystal, while on the old accessory, only half of the powder on the crystal was compacted. In addition, we observe increased intensities and therefore an improved signal-to-noise performance compared to the old design. This performance gain could be used to allow a shorter measurement time and, therefore, a higher sample throughput.

One could argue that these kind of variations observed are not so critical in qualitative analysis; for example, in the identification of a raw material by doing a COMPARE™ of the sample spectrum against a reference spectrum. Due to the filters applied in the COMPARE algorithm, these variations are reduced and still allow the discrimination between samples that have quite different infrared spectra. However, with these variations, more subtle changes of the line shape of bands can also occur that can make it difficult to discriminate materials with very similar spectra – especially if we use chemometric methods.

Kinematic mount of the top plate
A kinematic mount ensures that the top plate is always in the same position independent of how often the top plate is touched, removed and put back. In order to demonstrate the improvement in repeatability achieved with this design, an experiment was chosen where any variation due to sample contact was excluded by using a liquid sample (Nujol). Fifteen replicate spectra were measured, and in between each measurement, the top plate was cleaned, removed and put back. A background was only measured once at the beginning of the experiment. Figure 4 highlights the improved stability of the beam geometry with the kinematic mount. With the old design, the variation of the transmittance of the strongest Nujol band is 0.32 %T, while with the kinematic mount, this is reduced to 0.084 %T. At the baseline of the Nujol spectrum (1800 cm⁻¹), the corresponding variations are 0.606 %T and 0.082 %T.

This kinematic mount does not only reduce baseline effects (that could be largely removed by applying an offset correction); it also prevents the situation where the beam is passed through different parts of the ATR crystal, helping to avoid small changes of the line shapes of the sample bands.

Figure 3: Intensity variation of 15 replicate measurements of a Caffeine powder sample with the previous (left) and the new (right) UATR accessory.

Figure 4: Transmittance variation of 15 replicate measurements of a Nujol sample when changing the top plate in between with the previous (left) and the new (right) UATR accessory.
In order to compare these results with a competitive DATR accessory, the previous experiment was repeated with a third party DATR accessory, where the top plate was not removed but the crystal was cleaned between each sample and the bridge closed and screwed down. In Figure 5, the spectra are displayed. The mounting of the third party accessory crystal is obviously very sensitive to touching – the cleaning of the crystal is generating a big variation of the beam geometry resulting in strong transmittance changes. Here the variation of the transmittance is 2.89 %T at the strongest Nujol band and 4.17 %T at the baseline of the Nujol spectrum (1800 cm⁻¹). In addition, there is a distortion observed of the Nujol spectra at the baseline.

Force restrictor

In this design, the head of the screw that is used to apply pressure to a sample contains a built-in slipping clutch that works as a force restrictor. So, in addition to the force gauge in the software which changes its color to red when the maximum force is reached, this device further prevents any damage of the crystal due to overpressure.

Improved sealing of the top plate

The UATR accessory has a seal between the top plate and the upper part of the accessory body. This sealing prevents solvent vapors generated during cleaning from diffusing into the beam. With some designs, this is sometimes observed as additional solvent bands in the sample spectra.

Summary

These results show that the design of a DATR accessory strongly influences the spectral quality. With its improved design, the UATR accessory for the Frontier FT-IR is capable of generating spectra with an improved ordinate repeatability by up to one order of magnitude and an improved signal-to-noise by a factor of 3 compared to the previous version. Therefore, it is predestined for routine applications where these benefits will allow higher sample throughput or improved quality of the results achieved.

Figure 5: 15 replicate measurements of a Nujol sample with the Golden Gate accessory (left) and the new UATR accessory (right).