Application Note AN # 79

Attenuated Total Reflection (ATR) – a versatile tool for FT-IR spectroscopy

Introduction

Since the dispersive systems were superseded by the much more powerful FT-IR (Fourier-Transform-Infrared) spectrometers IR-spectroscopy developed into a widely used routine analytical tool. FT-IR spectroscopy's strength is the structural identification of functional groups like for instance C=O, C-H or N-H. Furthermore, most substances exhibit a characteristic spectrum and can be identified by this similar to the human fingerprint.

FT-IR spectroscopy allows measuring all types of samples whether they are solid, liquid or gaseous. Yet, the preparation of the sample for a transmission measurement is a rather complex task. Liquid samples need to be filled into a liquid cell with suitable path length; solids typically have to be diluted with the IR-inactive KBr and pressed to the well-known "KBr-pellet". However, both types of measurement techniques have their drawbacks:

- Liquid cells need to be filled without air bubbles and are not easy to clean.
- KBr is hygroscopic, hence not easy to handle and to store.
- A good KBr pellet is difficult to make, time consuming and requires a special tool kit including a hydraulic press (see Figure 1).
- Too much sample in a pellet will result in total absorption.

Figure 1: KBr tool kits

- Handling and measurement of the KBr pellets itself requires skill.
- Homogenization of sample and KBr is for some substances like rubbers or other elastomers hard to achieve.

In summary the making and measurement of a suitable KBr pellet are time-consuming and only experienced operators will get good results. In many cases, the pellet will be turbid and the baseline of the resulting spectrum will drift due to the influence of the resulting stray light. Furthermore, the possibility of interactions between the polar KBr and the sample has to be mentioned.

In order to overcome these disadvantages of KBr pellets and liquid cells nowadays IR-measurements are mainly performed in ATR (Attenuated Total Reflection) mode as this technique is much more comfortable to use than the conventional transmission mode. All types of samples (e.g. solids, liquids, powders, pastes, pellets, slurries, fibers etc.) are placed undiluted on the ATR crystal. The measurement then is typically performed within seconds

ATR principle

As already mentioned, the great advantage of ATR is the possibility to measure a wide variety of solid and liquid samples without any complex sample preparation. The basic principle is shown in Figure 2.

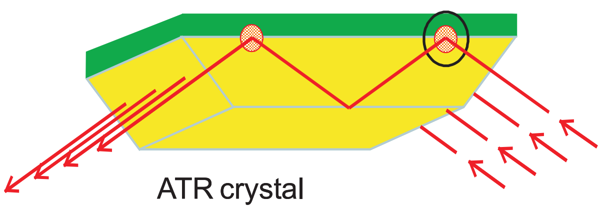
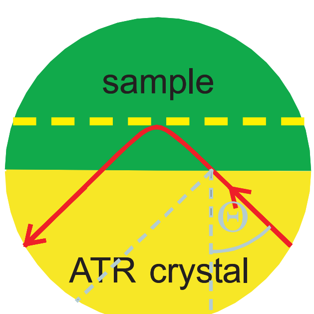


Figure 2: ATR principle

The ATR crystal consists of an IR transparent material with a high refractive index and has polished surfaces (Figure 2). As shown in the image, the infrared beam enters the ATR crystal at an angle of typically 45° (relative to the crystal surface) and is totally reflected at the crystal to sample interface. Due to its wave like properties, the light is not reflected directly on the boundary surface but by a virtual layer within the optically less dense sample (Goos-Hänchen effect; see Figure 3, dotted yellow line). The fraction of the light wave that reaches into the sample is called the evanescent wave. Its penetration depth is depending on the wavelength, the refractive indices of ATR crystal and sample and the angle of the entering light beam. Typically it amounts to a few microns (ca. 0.5 - 3 µm). In those spectral regions where the sample absorbs energy, the evanescent wave will be attenuated. After one or several internal reflections, the IR beam exits the ATR crystal and is directed to the IR-detector.



Refractive index
Crystal > Sample

Figure 3: ATR effect

To achieve a high quality spectrum some requirements must be fulfilled:

- Good contact between sample and ATR crystal has to be ensured as the evanescent wave penetrates only up to some microns into the sample.
- The refractive index of the crystal must be considerably higher than that of the sample (see table of ATR crystals).

As the typical refractive indices for ATR crystals are between 2 to 4 and typical values for organic substances (e.g. polymers) range from ca. 1.2 to 1.5 a large majority of IR-active samples can be measured.

Instrumentation

Most ATR units are designed as horizontal crystals with a type of clamping utility to ensure good sample contact of solids. For liquids and pastes, it is sufficient to put a drop on the crystal and directly start the measurement.

Figure 4: Diamond ATR accessory in Bruker Optics' ALPHA

With modern small ATR crystals and robust pressure clamps good sample contact can be obtained with samples like elastomers and fine powders, even with glass fibers reinforced polymers or minerals. Available crystal materials include diamond, zinc selenide (ZnSe) and germanium. Their properties are listed in the following table:

Material	Spectral region (cm^{-1})	Refractive index	Depth of penetration at 45°, 1000cm^{-1} (µm)	Hard-ness (Knoop)
ZnSe	20,000-500	2.43	1.66	130
ZnS	22,000-750	2.25	1.54	355
Ge	5,000-600	4.01	0.65	550
Si	10,000-100	3.42	0.81	11150
Diamond	45,000-10	2.40	1.66	9,000

ZnSe is a common low-cost material and ideal for analyzing liquids and "soft" samples. However, ZnSe is prone to scratches and can only be used between pH 5 to pH 9. Germanium with its high refractive index is used to analyze highly absorbing samples like carbon-black colored rubbers. If the highest surface sensitivity is required like for thin layers, Ge yields good results due to the low depth of penetration. Diamond is very robust and chemically inert making it an ideal crystal material for routine measurements with a wide range of possible samples. Even though the initial investment is higher, the cost of ownership over the instrument lifetime is often lower since diamond cannot be scratched and is completely insoluble.

The procedure of an ATR-measurement is very easy:

- Clean the crystal (e.g. cellulose tissue with isopropanol).
- Measure the background with the ATR unit.
- Place the sample on the crystal ensuring good contact.
- Measure sample

Bruker's spectroscopy software OPUS offers a "preview mode" that shows a live spectrum during sample preparation on the ATR-crystal. This allows a real time monitoring of the "spectral quality" after applying pressure on a solid sample. Once a satisfactory quality is achieved, the spectrum is measured after just one click. In ATR measurements, the thickness of the sample does not affect the intensity of the absorbance bands; in transmission mode however, too thick samples lead to "total absorbance". The effective path-length through the sample is influenced by the penetration depth of the evanescent wave. This fact results in similar spectral intensities for samples of various thicknesses. The wavelength dependency of the penetration depth into the sample and the anomalous dispersion of the IR-light result in some systematic differences between spectra measured using the ATR- and the transmission-technique. To obtain a better comparability of ATR and transmission spectra OPUS provides the "Extended ATR correction" function. A sophisticated algorithm corrects the position and intensity of the absorption bands in an ATR-spectrum to match them with a transmission spectrum of the same sample. As an example, this correction improves the hit quality when performing a library search using an ATR-spectrum in combination with a library built from transmission spectra.

ATR materials – Diamond and Germanium

In case of hard or reinforced materials, a higher pressure must be used to obtain a good spectrum. For samples like the very rigid glass fiber reinforced polyamide granules, high pressure clamping devices have to be applied. Furthermore, a higher optical path length is of benefit. The spectra displayed in the following figure were both measured with a Bruker ALPHA spectrometer with the same measurement conditions by using a diamond- and a Ge-ATR unit respectively:
As expected, the diamond ATR spectrum shows stronger signals due to the higher penetration depth.

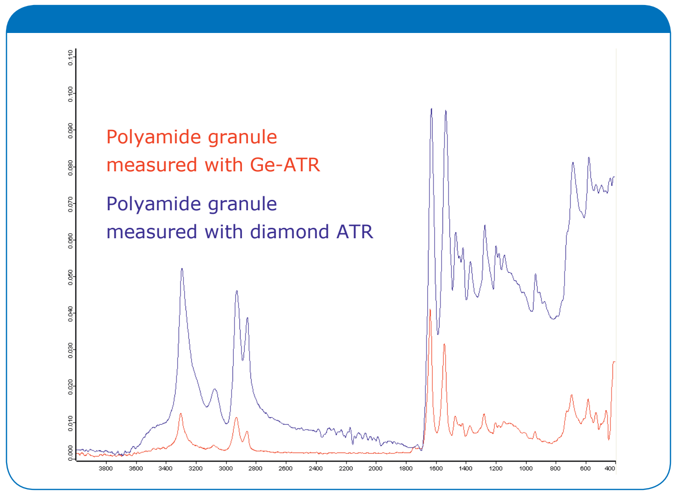


Figure 5: Polyamide measured with Germanium- and diamond ATR.

Example application Black Rubber

Rubber is a widely used material in the automotive industry. Elasticity and stability are the most prominent features of this material. To regulate the elasticity plasticizers are added. Frequently, wrong amounts or insufficient mixing may lead to Inapprpriate the formation of "greasy" films or crystalline "blooming's" on the surface of the rubber. Faced with such a defect, the analytical question is whether the substance

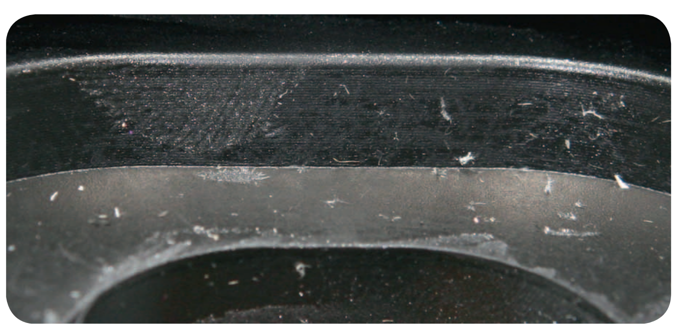


Figure 6: Black rubber

can be identified. Mostly the rubber will have a strong IR-absorbance due to embedded carbon black particles. As already outlined above, a Ge-crystal is the best choice for this spectroscopic task.

Figure 6 shows a black rubber with white crystalline substance on the surface. To identify the white substance, a spectrum from a clean area of the surface was taken as a reference. Then an area with the white substance was placed on the ATR crystal and measured:

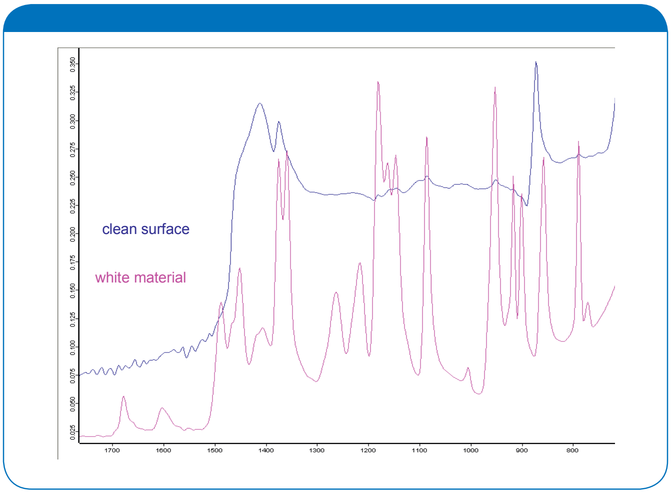


Figure 7: IR-spectra of a black rubber polymer (blue) and white particles (pink) on its surface. Spectra were measured in ATR mode usind a Ge crystalplate.

The two spectra in figure 7 show:

- The white substance was measured without interference of the rubber matrix.
- Rubber and the substance exhibit very different spectra.

A library search clearly reveals the white substance to be a commonly used plasticizer (Figure 8).

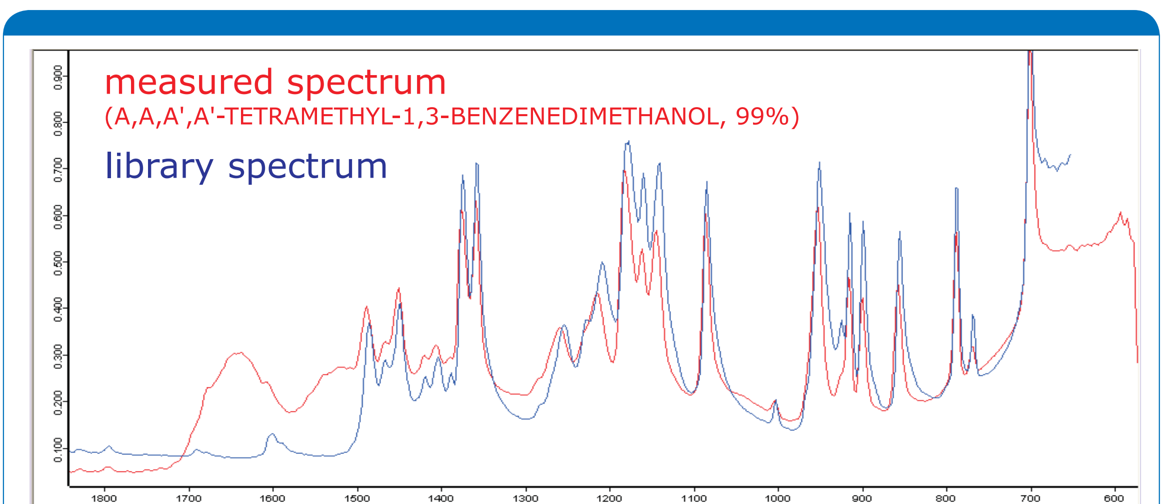
In this case, germanium is the ideal crystal material. The low penetration depth of germanium allows the measurement of the highly absorbing black rubber and the thin white film on the rubber without showing any spectral traces from the rubber matrix.

Summary

ATR has advanced to be THE standard FT-IR sampling technique, providing excellent data quality combined with highest reproducibility. Major advantages are:

- Faster sampling with no preparation.
- Excellent sample-to-sample reproducibility.
- Minimal operator induced variations.

In conclusion, most samples can be handled with a diamond ATR-crystal that is almost universally applicable due to its chemical and mechanical robustness. Germanium can be used for special purposes e.g. for measuring highly absorbing samples or thin layers. Finally, the crystal material ZnSe is a very cost-efficient option for the analysis of liquids and soft solid samples.



30 Hits	Hit Quality	Compound Name	Entry No.	Molecular formula	Molecula
1.	598	A,A,A',A'-TETRAMETHYL-1,3-BENZENEDIMETHANOL, 99 %	10617	C12H18O2	194.3
2.	598	A,A,A',A'-TETRAMETHYL-1,3-BENZENEDIMETHANOL, 99 %	10617	C12H18O2	194.3
3.	598	A,A,A',A'-TETRAMETHYL-1,3-BENZENEDIMETHANOL, 99 %	10618	C12H18O2	194.3

Figure 8: Result of a library search of the wihte materail on the black rubber polymer sample.

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