Attenuated Total Reflection (ATR) Mode – Advantages for FT-IR Spectroscopy

By AZoM

Table of Contents

Introduction

As the dispersive systems were superseded by the much more powerful FT-IR (Fourier-Transform-Infrared) spectrometers, IR spectroscopy progressed into a widely used analytical tool. One of the advantages of FT-IR spectroscopy is its capability to identify functional groups such as C=O, C-H or N-H. Most substances show a characteristic spectrum that can be directly recognized. FT-IR spectroscopy enables measuring all types of samples: solids, liquids and gases.

Sample Preparation

Preparing samples for a transmission measurement is a rather complex task. Liquid samples must be poured 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 technique have their drawbacks:

- Liquid cells must be free of air bubbles and are not easy to clean.
- KBr is hygroscopic and therefore not easy to handle and store.
- A good KBr pellet is rather hard to make. The operation is time consuming and requires a special tool kit including a hydraulic press (Figure 1)
- Any excess of sample material in the pellet results in total absorption.
- Handling and measuring the KBr pellets require specific skills.
- The homogenization of the sample and KBr is hard to achieve for some substances such as rubbers or elastomers. The making and measurement of suitable KBr pellets are time-consuming and only experienced operators are able to obtain good results. In many cases, the pellet is turbid and the baseline of the resulting spectrum is drifted due to the influence of the stray light.
- Also, interactions between the polar KBr and the sample are possible

Figure 1. *KBr tool kits.*

To overcome the disadvantages of KBr pellets and liquid cells, nowadays IR-measurements are mainly performed in ATR (Attenuated Total Reflection) mode as this technique is simpler 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 is typically performed within a few seconds

ATR Principle

As mentioned, the major benefit of ATR is the ability to measure a wide variety of solid and liquid samples without requiring complex preparations. The basic principle is shown in Figure 2. The ATR crystal comprises an IR transparent material with a high refractive index and polished surfaces as shown in Figure 2.

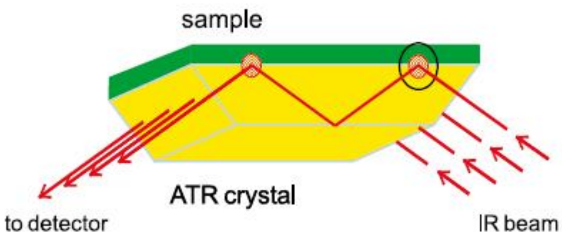

Figure 2. *ATR principle.*

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. Because of its wave-like properties, the light is not reflected directly by the boundary surface but by a virtual layer within the optically less dense sample (Goos-Hänchen effect, Figure 3 dotted yellow line). The fraction of light reaching into the sample is known as evanescent wave. Its penetration depth depends on the wavelength, the refractive indices of the ATR crystal and the sample and the angle of the entering light beam. It is typically of the order of a few microns (ca. 0.5 - 3 μm). In the spectral regions where the sample absorbs energy, the evanescent wave is attenuated. After one or several internal reflections, the IR beam exits the ATR crystal and is directed to the IR-detector.

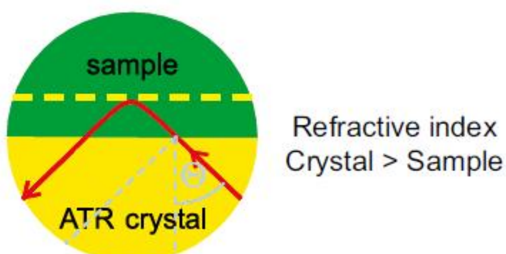

Figure 3. *ATR effect.*

In order to achieve a high quality spectrum some requirements must be fulfilled. They are as follows:

- Good contact between sample and ATR crystal has to be ensured as the evanescent wave penetrates only up to a specific number of microns into the sample.
- The refractive index of the crystal must be significantly higher than that of the sample, as shown in the table of ATR crystals. Since the typical refractive indices for ATR crystals are between 2 and 4 and typical values for organic substances such as polymers range from ca. 1.2 to 1.5, a large number of IR-active samples can be measured.

Instrumentation

Most ATR units are designed as horizontal crystals with a type of clamping utility that ensures good sample contact for solids. For liquids and pastes, it is sufficient to put a drop on the crystal and start the measurement. With modern small ATR crystals and robust pressure clamps good sample contact can be obtained even for samples such as elastomers, fine powders, glass fibers reinforced polymers or minerals. Available crystal materials include diamond, zinc selenide (ZnSe) and Germanium.

Figure 4. *Diamond ATR accessory in Bruker Optics' ALPHA.*

The properties are listed in the following table:

Material	Spectral region (cm^{-1})	Refractive index	Depth of penetration at 45°, 1000cm^{-1} (µm)	Hardness (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 an inexpensive material; it is suitable for the analysis of liquids and "soft" samples. However, ZnSe is prone to scratches and can only be used between pH 5 and pH 9.

Germanium has a high refractive index and is used to study highly absorbing samples like carbon-black colored rubbers. If high surface sensitivity is required, like for thin layers, Ge is ideal due to a low penetration depth. Diamond is very robust and chemically inert making it an ideal crystal material for routine measurements on a wide range of samples. Although the initial investment is higher, the costs over the instrument lifetime are often lower due to the high resistance of diamond to scratches and its complete insolubility. The procedure of an ATR-measurement is straightforward, the steps are listed below:

- Cleaning the crystal (e.g. with a cellulose tissue and isopropanol).
- Measuring the background with the ATR unit.
- Placing the sample on the crystal ensuring good contact.
- Measuring the sample

Bruker's spectroscopy software OPUS offers a "preview mode" that displays a live spectrum during sample preparation on the ATR-crystal. This enables real time monitoring of the "spectral quality" after applying pressure on a solid sample. Once a satisfactory quality is reached, the spectrum can be directly measured. In ATR measurements, the sample thickness of the sample does not affect the intensity of the absorbance bands; in transmission mode however, very thick samples lead to "total absorbance".

The effective path-length through the sample is impacted by the penetration depth of the evanescent wave. This can result in similar spectral intensities for samples of different thicknesses. The wavelength dependency of the penetration depth into the sample and the anomalous dispersion of the IR-light result in typical systematic differences between spectra measured using the ATR- and the transmission-technique. To obtain a better comparison of ATR and transmission spectra OPUS provides the "extended ATR correction" function. A sophisticated algorithm optimizes the position and intensity of the absorption bands in an ATR-spectrum to match them with a transmission spectrum of the same sample.

ATR Materials – Diamond and Germanium

In the case of hard or reinforced materials, a higher pressure must be used to obtain a good spectrum. For samples such as rigid glass fiber reinforced polyamide granules, high pressure clamping devices have to be employed. Furthermore, a high optical path-length is ideal. The spectra displayed in the figure 5 were both measured with a Bruker ALPHA spectrometer; the measurements were taken under the same conditions but using a diamond- and a Ge-ATR unit, respectively. As expected, the diamond ATR spectrum shows a higher signal due to the higher penetration depth.

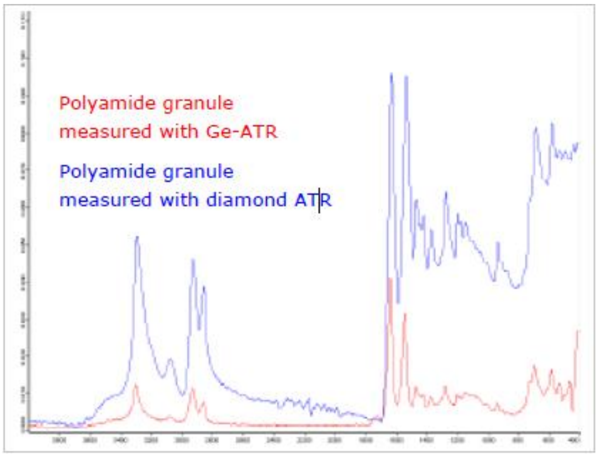

Figure 5. *Polyamide measured with Germanium- and Diamond-ATR.*

Example Application Black Rubber

Rubber is a widely used material in the automotive industry. Elasticity and stability are the most peculiar features of this material. To monitor the elasticity, plasticizers are added. Frequently, incorrect quantities or insufficient mixing lead to undesired effects such as the formation of "greasy" films or crystalline "blooming" on the rubber surface. This can result in the incapability of identifying the substance. Generally rubber has a strong IR-absorbance due to embedded carbon black particles.

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 (a Ge-crystal was used, being it ideal for such spectroscopic task). Then an area with the white substance was placed on the ATR crystal and measured.

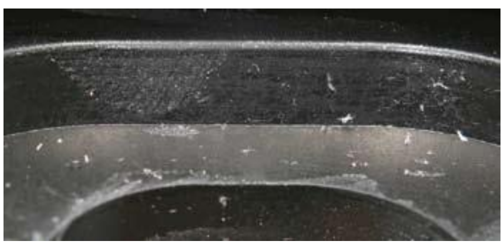

Figure 6. *Black rubber.*

The results are shown in figure 7:

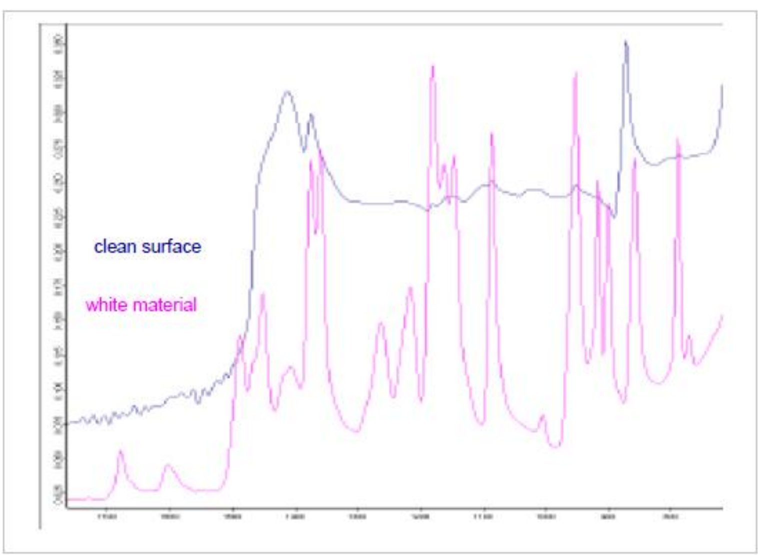

Figure 7. *IR-spectra of a black rubber polymer (blue) and white particles (pink) on its surface. Spectra were measured in ATR mode using a Ge crystal-plate.*

- The white substance was measured without interference of the rubber matrix.
- The rubber and the other substance exhibit very different spectra.
- A library search clearly reveals the white substance being a commonly used plasticizer

(Figure 8).

- In this case, Germanium is the ideal choice as crystal material. The low penetration depth of Germanium allows the separate measurement of the highly absorbing black rubber and of the thin white film on the rubber.

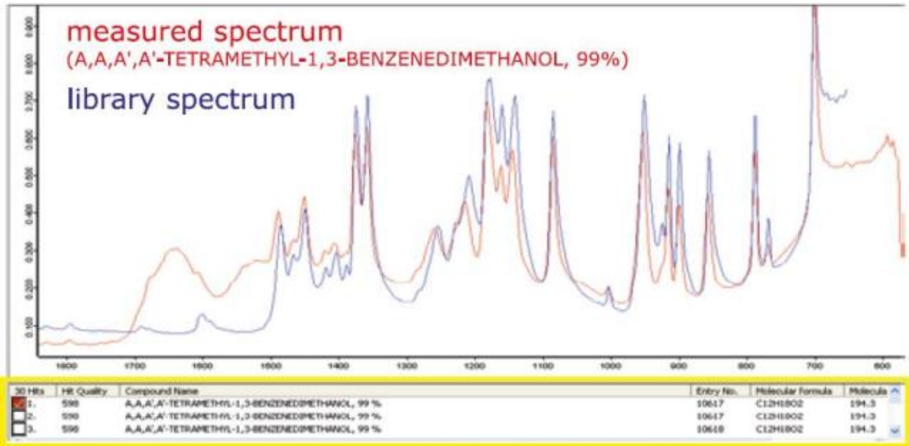

Figure 8. *Result of a library search of the white material on the black rubber polymer sample.*

Advantages of ATR

A list of the major advantages of ATR are listed below:

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

Summary

ATR has advanced to become the standard FT-IR sampling technique, providing excellent data quality combined with high reproducibility. Most samples can be analysed with a diamond ATR-crystal which possesses extreme chemical and mechanical robustness, while Germanium can be used for special purposes, e.g. for measuring highly absorbing samples or thin layers. Using ZnSe as the crystal material is a very cost-efficient option for the analysis of liquids and soft solid samples.

About Bruker Optics

Bruker Optics, part of the Bruker Corporation is the leading manufacturer and worldwide supplier of Fourier Transform Infrared, Near Infrared and Raman spectrometers. Their product line includes FT-IR, NIR, Raman, TD-NMR, TeraHertz spectrometers and imaging spectrographs for various markets and applications.

This information has been sourced, reviewed and adapted from materials provided by Bruker Optics.

For more information on this source, please visit Bruker Optics.

Date Added: Feb 13, 2012 | Updated: Sep 16, 2013

Comments

Alaa Mahrath says:
September 24, 2014 at 2:50 PM
sometimes the solid or liquid material stick with ZnSe crystal can I use a spatula to clean ZnSe .

Reply 0 0

Ask A Question

Do you have a question you'd like to ask regarding this article?

Leave your feedback

Login

Public Question Private Question to Supplier

Submit