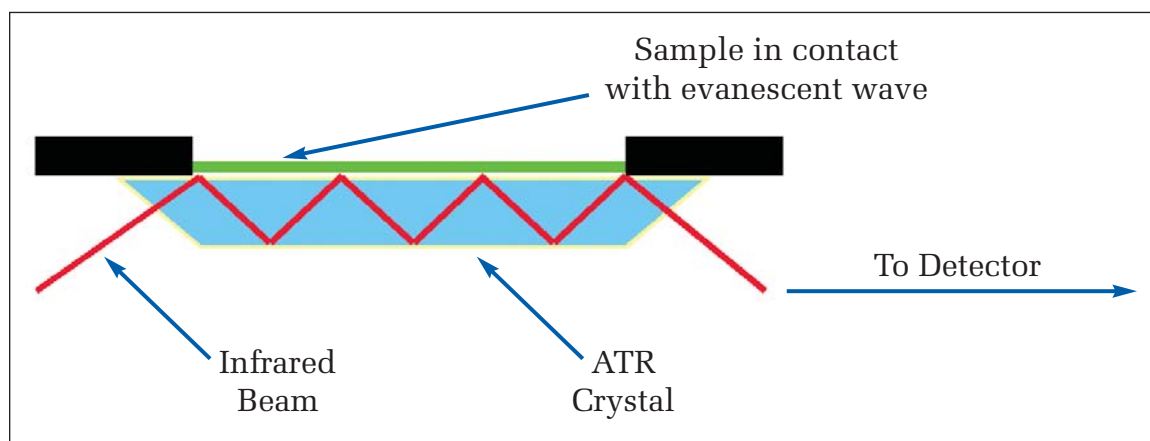


FT-IR Spectroscopy

Attenuated Total Reflectance (ATR)



Introduction

Mid-Infrared (IR) spectroscopy is an extremely reliable and well recognized fingerprinting method. Many substances can be characterized, identified and also quantified.

One of the strengths of IR spectroscopy is its ability as an analytical technique to obtain spectra from a very wide range of solids, liquids and gases. However, in

many cases some form of sample preparation is required in order to obtain a good quality spectrum. Traditionally IR spectrometers have been used to analyze solids, liquids and gases by means of transmitting the infrared radiation directly through the sample. Where the sample is in a liquid or solid form the intensity of the spectral features is determined by the thickness of the sample and typically this sample thickness

Key Features

- ▶ Faster sampling
- ▶ Improving sample-to-sample reproducibility
- ▶ Minimizing user-to-user spectral variation
- ▶ Higher quality spectral databases for more precise material verification and identification

cannot be more than a few tens of microns. Figure 1 displays a typical IR transmission spectrum.

The technique of Attenuated Total Reflectance (ATR) has in recent years revolutionized solid and liquid sample analyses because it combats the most challenging aspects of infrared analyses, namely sample preparation and spectral reproducibility.

Issues surrounding traditional transmission sample preparation

The two most common forms of sample preparation for solids both involve grinding the material to a fine powder and dispersing it in a matrix. The ground material can be dispersed in a liquid to form a mull. The most commonly used liquid is mineral oil (nujol). Typically no more than 20 mg of solid is ground and then one or two drops of nujol are used to create a paste which is then spread between two Mid-Infrared transparent windows e.g. NaCl, KBr, CaF₂. The sample is now ready to be placed in the spectrometer for analysis by transmission.

Potassium bromide (KBr) is probably the most widely used matrix material. Between 1 and 3 mg of ground material needs to be mixed

thoroughly with about 350 mg of ground KBr. The mixture is now transferred to a die that has a barrel diameter of 13 mm (Figure 2). This is then placed in a suitable press and pressed (evacuation is optional) at around 12,000 psi for one to two minutes. Re-crystallization of the KBr results in a clear glassy disk about 1 mm thick. This disk is now ready to be analyzed by transmission.



Figure 2. Potassium bromide 13 mm die.

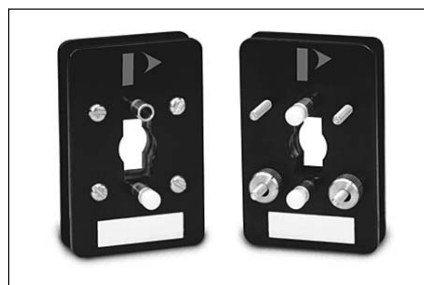


Figure 3. Sealed (l) and demountable (r) liquid cells.

Liquids are traditionally analyzed as thin films in cells (Figure 3), a cell consists of two IR transparent windows. A Teflon[®] spacer is generally used to produce a film of the desired

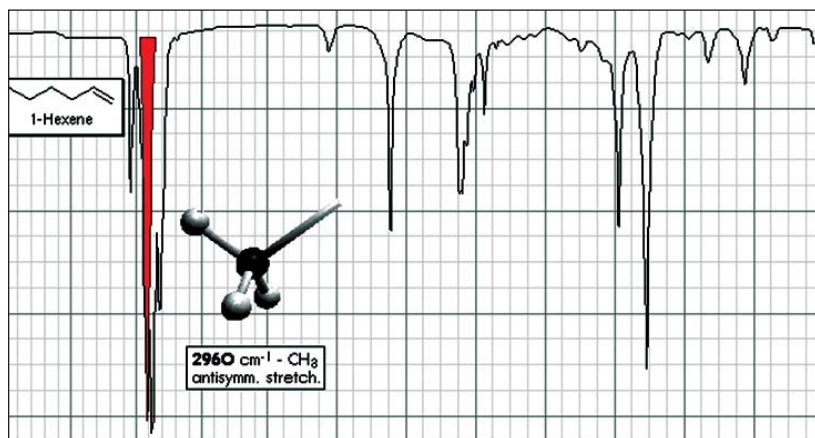


Figure 1. A Mid-Infrared spectrum of Hexene.

thickness or pathlength. A constant pathlength is highly desirable when performing quantitative analyses.

Overall, sample preparation is easier for liquid transmission studies when compared to solid transmission sampling but both suffer from inevitable reproducibility issues given the complexity of the sample preparation methods. In addition, preparation can be very messy and time consuming and is further complicated by difficulties in getting sample to matrix ratios correct and homogenous throughout the sample. The materials involved are fragile and hygroscopic and the quality of measurements can be adversely affected if handled or stored incorrectly. The technique of Attenuated Total Reflectance addresses these issues.

Principles of ATR

An attenuated total reflection accessory operates by measuring the changes that occur in a totally internally reflected infrared beam when the beam comes into contact with a sample (indicated in Figure 4). An infrared beam is directed onto an optically dense crystal with a high refractive index at a certain angle. This internal reflectance creates an evanescent wave that extends beyond the surface of the crystal into the sample held in contact with the crystal. It can be easier to think of this evanescent wave as a bubble of infrared that sits on the surface of the crystal. This evanescent wave protrudes only a few microns (0.5 μ - 5 μ) beyond the crystal surface and into the sample. Consequently, there must be good contact between the sample and the crystal surface. In regions of the infrared spectrum where the sample absorbs energy, the evanescent wave will be attenuated or altered. The attenuated energy from each evanescent wave

is passed back to the IR beam, which then exits the opposite end of the crystal and is passed to the detector in the IR spectrometer. The system then generates an infrared spectrum.

For the technique to be successful, the following two requirements must be met:

- The sample must be in direct contact with the ATR crystal, because the evanescent wave or bubble only extends beyond the crystal $0.5\ \mu - 5\ \mu$.
- The refractive index of the crystal must be significantly greater than that of the sample or else internal reflectance will not occur – the light will be transmitted rather than internally reflected in the crystal. Typically, ATR crystals have refractive index values between 2.38 and 4.01 at $2000\ \text{cm}^{-1}$. It is safe to assume that the majority of solids and liquids have much lower refractive indices.

ATR accessories

The traditional ATR design in which a thin sample was clamped against the vertical face of the crystal has been now replaced by a horizontal design. In horizontal ATR (HATR) units, the crystal is a parallel-sided plate, typically about 5 cm by 1 cm, with the upper surface exposed (Figure 4). The number of reflections at each surface of the crystal is usually between five and ten, depending on the length and thickness of the crystal and the angle of incidence.

When measuring solids by ATR, it is essential to ensure good optical contact between the sample and the crystal. The accessories have devices that clamp the sample to the crystal surface and apply pressure. This works well with elastomers and other

deformable materials, and also with fine powders but many solids give very weak spectra because the contact is confined to small areas. The effects of poor contact are greatest at shorter wavelengths where the depth of penetration is lowest.

The issue of solid sample/crystal contact has been overcome to a great extent by the introduction of ATR accessories with very small crystals, typically about 2 mm across. The most frequently used small crystal ATR material is diamond because it has the best durability and chemical inertness. These small area ATR crystal top-plates generally provide only a single reflection but this is sufficient, given the very low noise levels of PerkinElmer's modern FT-IR spectrometers. Much higher pressure with limited force can now be generated onto these small areas. A much smaller area of contact is now required in comparison to the HATR units. As a result, spectra can be obtained from a wide variety of solid materials including minerals.

Crystal materials and cleaning

There are a number of crystal materials available for ATR. Zinc Selenide (ZnSe) and Germanium are by far the most common used for HATR sampling. Zinc Selenide is a relatively low cost ATR crystal material and is ideal for analyzing liquids and non-abrasive pastes and gels but it is not particularly robust with a working pH range of 5-9. ZnSe scratches quite easily and so care must be taken when cleaning the crystal. It is recommended that lint free tissue is used.

Germanium has a much better working pH range and can be used to analyze weak acids and alkalis. Germanium has by far the highest refractive index of all the ATR materials available which means that the effective depth of penetration is approximately 1 micron. For most samples this will result in a weak spectrum being produced, however, this is an advantage when analyzing highly absorbing materials; carbon black filled rubbers are typically analyzed using Germanium ATR accessories.

Diamond is by far the best ATR crystal material because of its robustness and durability. The original purchase cost is obviously higher than that of other crystal materials available, but over the instrument's lifetime replacement costs should be minimal. The same cannot be said of Zinc Selenide or Germanium, both of which can scratch and break with improper use.

As with all FT-IR measurements, an infrared background is collected, in this case, from the clean ATR crystal. The crystals are usually cleaned by using a solvent soaked piece of tissue. Typically water, methanol or isopropanol are used to clean ATR crystals. The ATR crystal must be checked for contamination and carry over before sample presentation, this is true for all liquids and solids.

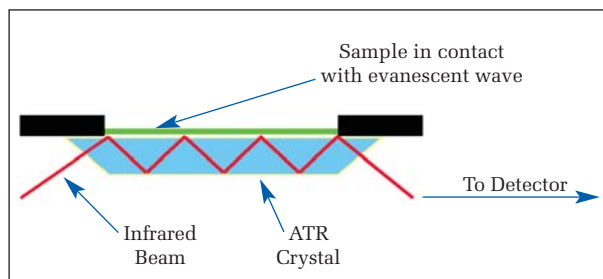


Figure 4. A multiple reflection ATR system.

Analyzing liquids

After the crystal has been cleaned and an infrared background has been collected, the liquid is simply poured onto the crystal (Figure 5). The whole crystal must be covered if performing a quantitative or qualitative analysis. The crystal is recessed into the metal plate to retain the sample. Pastes and other semi-solid samples are readily measured by spreading them on the crystal. Horizontal ATR units are often used for quantitative work in preference to transmission cells because they are easier to clean and maintain.

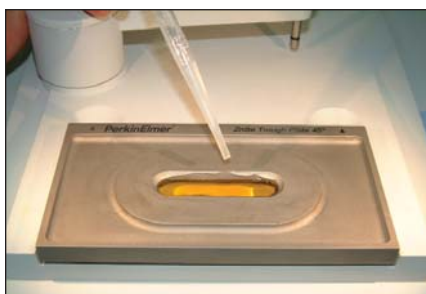


Figure 5. Using a pipette to add a liquid sample to a ZnSe HATR trough plate.

Analyzing solids

Solids are generally best analyzed on the single reflection ATR accessories; diamond being the preferred choice for most applications because of its robustness and durability.



Figure 6. Placing a powder sample onto the Universal diamond ATR top-plate.

After the crystal area has been cleaned and the background collected, the solid material is placed onto the small crystal area (Figure 6). Experience has shown that ideal results from powder samples have been achieved by placing just enough sample to cover the crystal area. The sample height should not be more than a few millimeters.

Once the solid has been placed on the crystal area, the pressure arm should be positioned over the crystal/sample area. When using the Spectrum 100 Series' Universal ATR accessory, the pressure arm locks into a precise position above the diamond crystal (Figure 7). Force is applied to the sample, pushing it onto the diamond surface.



Figure 7. Applying pressure to a solid sample on the Universal diamond ATR top-plate.

PerkinElmer's revolutionary Spectrum™ FT-IR software utilizes a 'Preview Mode' which allows the quality of the spectrum to be monitored in real-time while fine tuning the exerted force. It is good practice to apply pressure until the strongest spectral bands have an intensity which extends beyond 70% T, namely from a baseline at 100% T down to 70% T. Good sample/crystal interface contact has been achieved once this rule has been satisfied. This is very easy to achieve with soft samples and fine powders, this is shown in Figure 8.

The strongest bands here extend beyond 20% T with relatively little force applied; the force gauge is registering 80 N. A lot more pressure would need to be applied when analyzing high density polymers and coatings on metal surfaces. Once the user is satisfied with the spectrum shown in this 'Preview Mode', the data is then collected in the normal manner. The force should not be adjusted when co-adding the final spectrum. Unlike transmission measurements, ATR sampling does not produce totally absorbing spectral bands because the effective path-length is controlled by the crystal properties thereby minimizing sample re-preparation time.

After the spectrum has been collected, which should typically take no more than 32 seconds, the user must return to the 'Preview Mode'. This mode is now used to check that the crystal area is clean before placing the next sample on the crystal. A 100% T line with no spectral features (Figure 9) should be seen if the crystal is clean, if spectral features are seen, the crystal should be cleaned again using a solvent soaked tissue. The next sample can be placed on the crystal area once the 100% T line has been displayed and the sampling steps are repeated.

Conclusion

ATR is an IR sampling technique that provides excellent quality data in conjunction with the best possible reproducibility of any IR sampling technique. It has revolutionized IR solid and liquid sampling through:

- Faster sampling
- Improving sample-to-sample reproducibility
- Minimizing user to user spectral variation

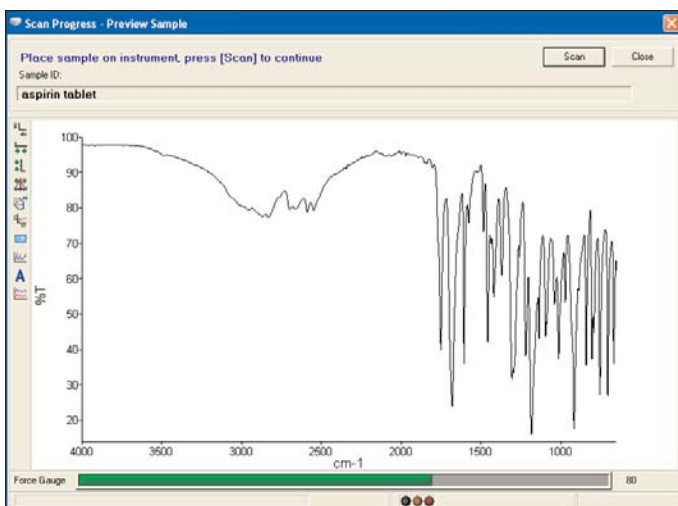


Figure 8: 'Preview Mode' screenshot taken from PerkinElmer's Spectrum v6 FT-IR software.

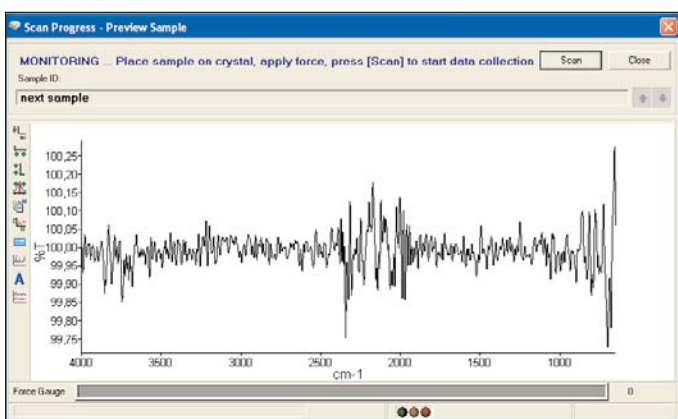


Figure 9: 'Preview Mode' displaying a 100%T line, namely a spectrum of a clean diamond ATR crystal.

Most importantly, the improved spectral acquisition and reproducibility associated with this technique leads to better quality database building for more precise material verification and identification. ATR is clearly an extremely robust and reliable technique for quantitative studies involving liquids.

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