MOLECULAR SPECTROSCOPY



Introduction to Sample Handling

Analyze • Detect • Measure • Control™

Thermo
ELECTRON CORPORATION

Introduction

Why is it important to know about different methods of sample handling?

Certain techniques of sample handling are more effective than others for specific sample types. In order to obtain the best quality spectra from your sample, it is important to know which sampling technique works best for your sample type. Acquiring the best spectral data possible will give you more confidence in your results.

Sampling Techniques

Transmission

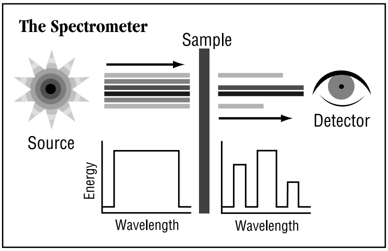
How does it work?

The transmission technique for sample handling does not require a separate accessory. The user simply places a sample within the sample compartment of an infrared (IR) spectrometer. The infrared beam is then passed through the sample, the energy that transmits through the sample is measured and a spectrum is generated. However, the analyst must often prepare the sample into a pellet, mull, film, etc. before the transmission measurement can be made. This requires expertise and can be time consuming.

What types of samples can you analyze?

Excellent quality spectra can be obtained for many types of samples using transmission. The transmission technique can be used alone or in conjunction with accessories such as microscopes and liquid or gas cells to analyze:

- Organic powders in pellet or mull form
- Thermoplastic powders
- Soluble polymers
- Thin polymer films
- Regular-shaped polymers (with preparation)
- Irregular-shaped polymers (with preparation)
- Dark polymer films (not carbon-filled)
- Liquids (free-flowing or viscous)
- Gases (high concentrations to trace amounts)

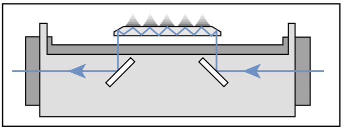


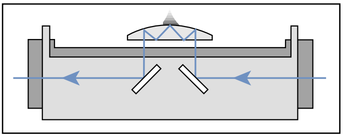
Conceptual diagram of the beam path through a transmission sample

What are the advantages of transmission?

- **Inexpensive** – does not require an additional accessory
- **Well established** – most traditional form of sample measurement
- **Excellent spectral information** – ideal for qualitative measurements

Attenuated Total Reflection (ATR)


Beam path for a multi-bounce horizontal ATR


Beam path for a single bounce horizontal ATR

How does it work?

An attenuated total reflection accessory operates by measuring the changes that occur in an internally reflected infrared beam when the beam comes into contact with a sample. 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. In regions of the infrared spectrum where the sample absorbs energy, the evanescent wave will be attenuated. The altered (attenuated) energy from each evanescent wave is passed back to the IR beam, which then exits the opposite end of the crystal and is directed to the detector in the IR spectrometer. The detector records the attenuated IR beam as an interferogram signal, which can then be used to generate an infrared spectrum.

What types of samples can you analyze?

ATR is ideal for strongly absorbing or thick samples which often produce intense peaks when measured by infrared transmission. ATR works well for these samples because the intensity of the evanescent waves decays exponentially with distance from the surface of the ATR crystal, making the technique generally insensitive to sample thickness.

Other solids that are a good fit for ATR include homogeneous solid samples, the surface layer of a multi-layered solid or the coating on a solid. Even irregular-shaped, hard solids can be analyzed using a hard ATR crystal material such as diamond. Ideal solids include:

- Laminates
- Plastics
- Coatings
- Solids that can be ground into powder
- Paints
- Rubbers
- Natural powders

In addition, ATR is often the preferred method for liquid analysis because analysis simply requires a drop of liquid to be placed on the crystal. ATR can be used to analyze these liquids:

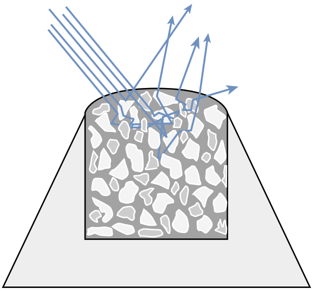
- Free-flowing aqueous solutions
- Viscous liquids
- Coatings
- Biological materials

What are the advantages of ATR?

- **Minimal sample preparation**
- **Fast and easy clean-up** – simply remove the sample and clean the surface of the crystal
- **Analysis of samples in their natural states** – unlike the transmission technique, which often requires the sample to be heated, pressed or ground in order to collect a spectrum
- **Excellent for thick or strongly absorbing samples** – ideal for samples that cannot be easily analyzed through transmission

Diffuse Reflectance (DR)

How does it work?



The IR beam interacting with a sample in a diffuse reflectance experiment

When an infrared beam is focused onto a fine particulate material, the incident beam can react with the particle in one of several ways. First, radiation can be reflected off the top surface of the particle without penetrating the particle. Second, the light can undergo multiple reflections off particle surfaces without penetrating into the particle. True diffuse reflectance results from the penetration of the incident radiation into one or more sample particles and subsequent scatter from the sample matrix.

A diffuse reflectance accessory operates by directing the infrared energy into a sample cup filled with a mixture of the sample and an infrared transparent matrix (such as KBr). The infrared radiation interacts with the particles and then reflects off their surfaces, causing the light to diffuse, or scatter, as it moves throughout the sample. The output mirror then directs this scattered energy to the detector in the spectrometer. The detector records the altered IR beam as an interferogram signal, which can then be used to generate a spectrum. Typically, a background is collected with the diffuse reflectance accessory in place and the cup filled with just the IR matrix. Excellent quantitative and qualitative data can be collected with proper sample preparation. However, transmission and ATR techniques are preferable to diffuse reflectance for quantitative data due to pathlength.

What types of samples can you analyze?

Diffuse reflectance is commonly used for the analysis of both organic and inorganic samples that can be ground into a fine powder (less than 10 microns) and mixed in a powder matrix such as potassium bromide (KBr). Typical sample types include:

- Soft powders and powder mixtures
- Hard polymers
- Rigid polymers

The diffuse reflectance technique can also be used with silicon carbide paper for the analysis of large intractable surfaces. Silicon carbide paper can be used to rub off a small amount of a variety of samples for analysis. This technique is a viable alternative to traditional sampling techniques for:

- Paint and varnish surfaces
- Tablets
- Rigid polymers

What are the advantages of diffuse reflectance?

- **Little to no sample preparation**
- **Fast and easy clean up**
- **No need for pressed KBr pellets or messy mulls** – samples can be run neat or diluted with KBr powder

True Specular Reflectance / Reflection-Absorption

How does it work?

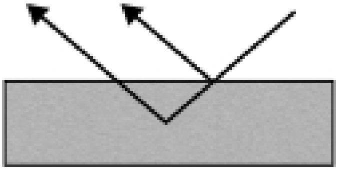


Diagram of the interaction of the beam using true specular reflectance

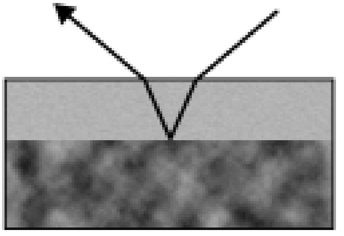


Diagram of the interaction of the beam using reflection-absorption

True specular reflectance is a surface measurement technique that works on the principle of reflective efficiencies. This principle states that every sample has a refractive index that varies with the frequency of light to which it is exposed. Instead of examining the energy that passes through the sample, true specular reflectance measures the energy that is reflected off the surface of a sample, or its refractive index. By examining the frequency bands in which the rate of change in the refractive index is high, users can make assumptions regarding the absorbency of the sample. The true specular reflectance technique provides excellent qualitative data.

Reflection-absorption works on the same principle, but due to sample properties, some of the energy passes through the surface layer, is absorbed into the bulk of the sample and then reflects off a substrate below the surface layer. A combination of true specular reflectance and reflection-absorption can occur when criteria for both techniques are met. If a qualitative comparison to transmission spectra is desired, users can apply the Kramers-Kronig correction to the data to remove the effects of dispersion.

What types of samples can you analyze?

Specular reflectance is commonly used for the analysis of both organic and inorganic samples having large, flat, reflective surfaces. Reflection-absorption can occur when one of the above criteria is compromised and the sample has a reflective substrate present just below the surface. This type of analysis is commonly used for:

- Metallic surfaces
- Silicon wafers
- Thin films on reflective substrates
- Laminated materials on metals

What are the advantages of specular reflectance?

- **Sensitivity to monolayer samples** – can detect Angstrom thick coatings on metal substrates
- **Little to no sample preparation**
- **Wide range of accessories available** – can utilize main spectrometer and microscope accessories depending on the size of the sample and the thickness of surface layer

RATINGS

- Excellent
- Good
- Adequate

KEY

- * capable of being ground
- † incapable of being ground

		Transmission	Transmission – IR microscope	Diffuse Reflectance	Diffuse Reflectance – Si Carb Sampler	Diffuse Reflectance – IR microscope	ATR	ATR – IR microscope	Specular Reflectance	Specular Reflectance – IR microscope
Solids	Thermoplastic Polymers (can be melted)	Excellent	Excellent		Adequate		Good	Good		
Solids	Thermoplastic Polymers (can't be melted)				Adequate		Good	Good		
Solids	Soluble Polymers	Excellent					Good			
Solids	Thin Polymer Films	Excellent	Excellent		Adequate		Good	Good		
Solids	Thick Polymer Films				Adequate		Excellent		Adequate	
Solids	Flat, Smooth Polymers *	Excellent	Excellent		Adequate		Good	Good	Adequate	Adequate
Solids	Flat, Smooth Polymers †				Adequate		Good	Good	Adequate	Adequate
Solids	Irregularly Shaped Polymers *	Good	Excellent		Adequate		Excellent	Excellent		
Solids	Irregularly Shaped Polymers †				Adequate		Good	Good		
Solids	Thin, Dark Polymer Films	Good	Excellent		Adequate		Excellent	Excellent		
Solids	Thick, Dark Polymer Films		Excellent		Adequate		Excellent	Excellent		
Solids	Layered Polymer Films		Excellent				Adequate	Adequate		
Solids	Thin Polymer Film on Reflective Substrates				Adequate		Good		Excellent	Excellent
Solids	Thick Polymer Film on Reflective Substrates				Adequate		Good		Excellent	
Solids	Organic Powders	Excellent	Excellent	Good		Good	Good			
Solids	Adhesives	Adequate	Good				Excellent	Excellent		
Solids	Rubber		Good		Adequate		Excellent	Excellent		
Solids	Thin Fibers	Adequate	Excellent				Good	Excellent		
Solids	Thick Fibers	Adequate	Excellent				Good	Excellent		
Solids	Surface Analysis	Adequate		Good			Excellent	Excellent	Good	Good
Liquids	Free-Flowing Aqueous Solutions	Excellent					Excellent			
Liquids	Other Free-Flowing Liquids	Excellent					Excellent			
Liquids	Viscous Liquids	Excellent					Excellent			
Gas	Gases (ppb to 100% concentration)	Excellent								
Gas	Environmental Studies									

Index of Sample Types

Powders – organic and inorganic solids that can be ground into a powder (2-5 micron particle size); Examples: chemicals, pharmaceuticals, crystalline materials, pigments, fibers, polymers and powders

Thermoplastic Polymers – polymers that can be pressed into free-standing thin films

Soluble Polymers – polymers that can be dissolved in a solvent or cast as a thin film

Thin Polymer Films – free-standing polymer films that are not thermoplastic or soluble and are less than 50 microns thick

Thick Polymer Films – free-standing polymer films that are not thermoplastic or soluble and are more than 50 microns thick

Regularly Shaped Polymers* – polymers, films and plaques that are hard or soft with a smooth surface, capable of being ground, not thermoplastic or soluble and regularly shaped

Regularly Shaped Polymers † – polymers, films and plaques that are hard or soft with a smooth surface, incapable of being ground, not thermoplastic or soluble and regularly shaped

Irregularly Shaped Polymers* – polymers that are hard or soft with a rough or uneven surface, capable of being ground, not thermoplastic or soluble and irregularly shaped; Examples: formed polymers, polymer beads and pellets

Irregularly Shaped Polymers † – polymers that are hard or soft with a rough or uneven surface, incapable of being ground, not thermoplastic or soluble and irregularly shaped

Thin, Dark Polymers – carbon-filled polymers high in inorganic content that are not thermoplastic or soluble and less than 10 microns thick, such as carbon black

Thick, Dark Polymers – carbon-filled polymers high in inorganic content that are not thermoplastic or soluble and more than 10 microns thick

Layered Polymer Films – polymers that contain two or more layers or thin or thick films; Examples: layered paints and packaging materials

Thin Polymer Film on Reflective Substrate – polymer film on any kind of surface that reflects IR energy (usually metal) that is less than 15 microns thick; Examples: lubricants on hard disk media and layers on silicon wafers

Thick Polymer Film on Reflective Substrate – polymer film on any kind of surface that reflects IR energy (usually metal) that is more than 15 microns thick; Examples: coatings on containers (such as soda cans)

Adhesives – solid adhesives like tapes and solid glues

Rubbers – irregular-shaped rubber items that are not thermoplastic or soluble; Examples: o-rings, gaskets and fittings

Thin Fibers – thin and bundled fibers

Thick Fibers – thick and bundled fibers

Surface Analysis – for qualitative analysis of the outermost layer of any solid or film

Free-Flowing Aqueous Solutions – liquids that contain any amount of water; Examples: inks, dyes, solvents and paints

Other Free-Flowing Liquids – liquids that do not contain water

Viscous liquids – thick liquids, pastes and emulsions; Examples: polyols, greases and heavy oils

Gases (ppb to 100% concentration) – any sample that is a gas at room temperature or slightly above room temperature

Smart Accessories™

Design elements to consider when choosing an accessory:

Thermo Electron Corporation appreciates the need for efficiency and reproducibility in today's lab. We conducted extensive research regarding the features and benefits our users desire in their sampling accessories. This exhaustive process led to the development of unique Smart Accessories. These accessories offer the following value-added features:

- **Permanently aligned optics** – needs no optical adjustment, so results are reproducible and quantifiable
- **Rugged design** – protects optics from daily use and dust
- **Automatic and fast purge** – achieves purge up to three times faster than a standard accessory
- **Accessory recognition** – automatically identifies the accessory as soon as it is snapped in place and records its serial number in a non-editable history file
- **Experiment setup** – automatically sets up your experiment parameters so you can start sampling immediately
- **Accessory performance checks** – tests the accessory to ensure that it is performing optimally
- **Spectral quality checks** – examines data as it is collected and rates the quality of the spectra you have collected, offering suggested improvements when necessary
- **Multi-media tutorials and on-line help** – answers any questions you may have while conducting your analysis

Thermo Electron offers a comprehensive line of both Smart Accessories and standard sampling accessories to meet the needs of your laboratory. In addition, We offer a selection of microscope objectives to facilitate in the analysis of small samples.

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