INSTALLATION AND USER GUIDE

HATR

Horizontal ATR Accessory

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Introduction

The PIKE Technologies Horizontal ATR (HATR) is a low cost, high throughput ATR accessory designed for use in your FTIR spectrometer. The compact design employs a pair of transfer optics to direct the infrared beam to one end of an IR transmitting ATR crystal. A similar pair of optics directs the beam emitted from the other end of the ATR crystal to the spectrometer detector.

The accessory is available with two basic types of mounted crystals, the **trough plate** for the analysis of liquids and pastes, and the **flat plate** for the analysis of pliable solid films. The most common material used for the ATR prism is Zinc Selenide. This material is relatively hard and durable and has high mid-infrared throughput and a wide spectral range. However, it can be damaged by strong acids and bases. Other materials are available and are described later in this manual.

The ATR crystal for the liquid flow-through cell is of a trapezoid shape and is 80 mm long, 10 mm wide and 4 mm thick. In order to produce optimum performance from the accessory, the thickness of the crystal has been carefully chosen. A thicker crystal would result in less bounces of the infrared energy in the crystal, resulting in lower absorbances in the resulting spectrum. A thinner crystal would give more bounces in the crystal, resulting in a greater absorbance in the spectrum, but the overall throughput of the device would be reduced. The standard crystal dimensions have been chosen to maximize the ***signal to noise*** in the resulting spectra; although, 2 mm thick Ge and ZnSe are available for applications requiring more reflections.

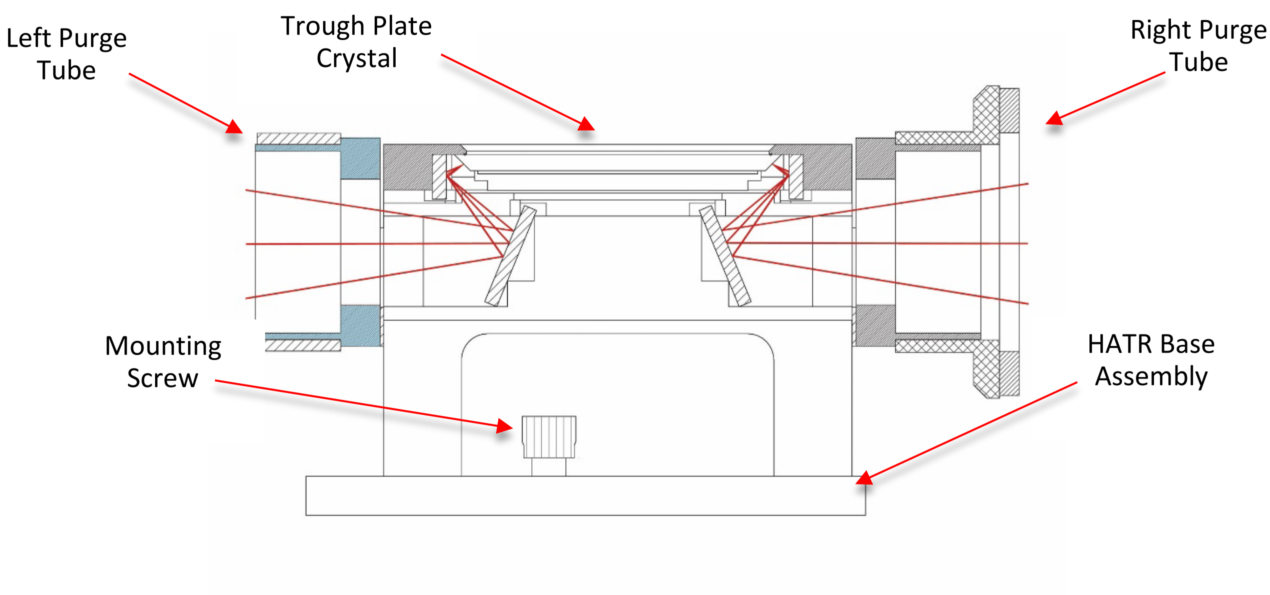


Figure 1. HATR optical diagram.

Note: The final configuration is spectrometer dependent and may be slightly different from the picture above.

Unpacking Your Accessory

In order for you to quickly verify receipt of your accessory, we have included a packing list. Please inspect the package carefully.

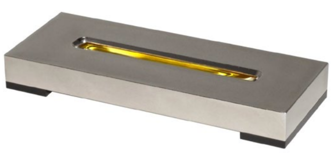
Packing List

HATR Manual
PN 350-002200
Quantity 1

HATR Base Assembly
PN 022-19XX
Quantity 1

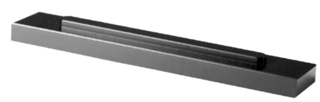
HATR Pressure Clamp*
PN 022-3050
Quantity 1

Trough Plate**
PN 022-2010-45
Quantity 1



Flat Plate*
PN 022-2020-45
Quantity 1

Powder Press**
PN 022-3052
Quantity 1



Purge Tubes
Quantity 1-2 (system dependent)

Purge Kit
Quantity 1 (system dependent)

Volatiles Cover**
PN 022-3051
Quantity 1

** Included with Flat Plate systems (022-11xx)*
*** Included with Trough Plate Systems (022-10xx)*
Note: Some base optics assemblies may appear different depending on specific FTIR model.

Installation

The accessory has been aligned and tested to ensure that it performs to specification. There are no customer alignments necessary to use the accessory.

1. Peak up the energy of your spectrometer by adjusting the interferometer. This procedure should be performed by following the manufacturer's instructions.

2. Mount your accessory into the sample compartment using the captive hardware provided on the baseplate.

3. In alignment mode, check the signal throughput of the spectrometer with the accessory in place.

Figure 2. Typical HATR with volatiles cover, pivot pressure clamp, trough plate and flat plate.

Performance Verification

1. With the accessory removed from the sample compartment, collect a background spectrum.

2. Place the HATR accessory in the instrument.

3. Collect a transmission spectrum using the same collection parameters as used to collect the background spectrum.

The transmission value for this accessory is shown in Table 1. If your accessory does not meet this minimum transmission value when installed, please contact PIKE. Please have ready the serial number of the accessory which is located on the rear of your accessory.

Table 1. Transmission value for HATR accessory.

Crystal Type	Crystal Thickness (mm)	Crystal Angle (°)	Plate Type	Energy Throughput (%) @ 1000 cm^{-1}
ZnSe or Ge	4	45	Flat or Trough	≥ 13
ZnSe or Ge	2	45	Flat or Trough	≥ 8
ZnSe or Ge	4	45	Sealed Flat	≥ 7
ZnSe or Ge	4	60	Flat or Trough	≥ 8

Sampling Procedures

The spectrum of the required sample is obtained by ratioing a sample scan collected with a sample placed on the face of the crystal to a background scan collected with no sample on the face of the crystal. The ATR crystal is mounted into a flat or trough plate configuration. The crystal plate is located on the base unit by means of two dowel location pins. The trough crystal plate is used for the analysis of liquids and pastes, while the flat crystal plate is used to analyze soft, pliable films.

Trough Crystal Plate

The trough crystal plate may be removed from the accessory base for convenient filling and emptying of the trough. When filling the trough, ensure that the sample completely covers the exposed surface of the crystal.

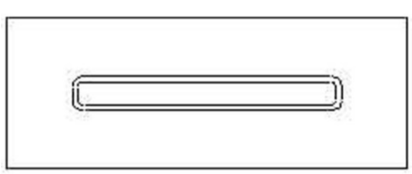


Figure 3A. Top view of trough crystal plate.

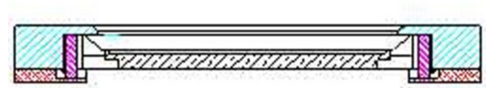


Figure 3B. Side sectional view of trough crystal plate.

Care is required when removing the sample from the trough. It is required that the sample be removed without scratching the surface of the crystal. Note that the crystal used in the accessory can be made from a variety of materials, many of which are soft and brittle. Scratches on the surface of the crystal will result in a reduction in the throughput of the accessory. A solvent (see the section below on crystal cleaning) and a "Q-tip" or microfiber swab should be used to remove traces of a previous sample when using a Ge, AMTIR or ZnSe ATR element. KRS-5 element is extremely soft and should be rinsed with solvent only as rubbing with a q-tip (cotton swab) will scratch the surface of the element.

Sometimes "carry over" may occur from one sample to another due to incomplete cleaning of a prior sample from the face of the crystal. This effect may be minimized by "washing" the trough with the new sample, cleaning the crystal and then running a background scan. The sample is then placed on the crystal again and a sample spectrum collected. Samples should never be left in contact with the crystal for an extended period of time since some samples may degrade the crystal material. Once the measurement has been made, remove the sample from the crystal and clean the surface of the crystal with a suitable solvent.

Flat Crystal Plate

The flat plate crystal assembly is used for measuring soft pliable films. The crystal is positioned so that the top surface of the crystal is slightly higher than the mount.

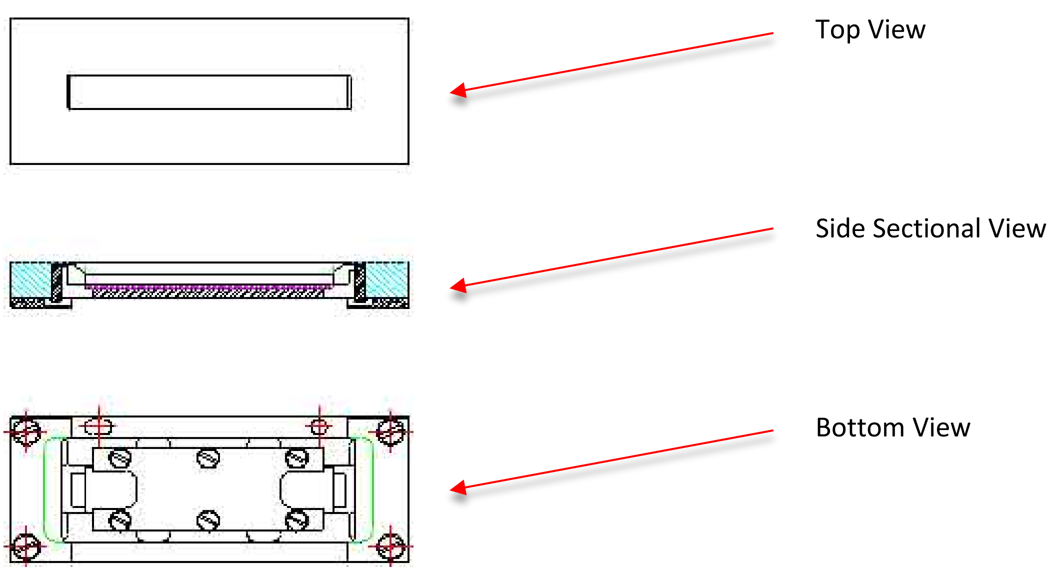


Figure 4. Flat plate cut-away view.

The sample is placed onto the surface of the crystal. Since the ATR effect only takes place at the surface of the crystal, intimate contact has to be made by the sample on the crystal surface. This is achieved by using the pressure clamp contained in your kit. Mount the clamp to the rear of the accessory using the two captive thumbscrews. With the sample in place on the crystal, lower the pressure plate so that it is in contact with the sample. The press will lock into position. You may now vary the amount of pressure placed onto the sample. The amount of pressure depends on the pliability of the sample.

Care must be used in operating the press, since the pressure plate may slide the sample over the crystal. If the sample contains grit or abrasive materials, the surface of the crystal may be damaged. Ensure that the sample remains stationary while loading the press.

Volatiles Cover

A cover is provided to place over the sample when volatile liquids are being analyzed on the trough plate crystal. This reduces the amount of evaporation of the sample on the surface of the trough plate crystal.

Powder Press

With care, some powders may be analyzed with the trough crystal plate. Note that since the ATR effect requires the sample to be in intimate contact with the crystal, this method is only effective when analyzing soft powders. Place the powder on the surface of the crystal. Using the powder press, lightly tap the surface of the sample to press it into contact with the crystal. Note that hard powders could damage the ATR. It will be difficult to have a hard powder make good contact with the crystal. For these samples diffuse reflection or a single reflection is the preferred technique.

Crystal Cleaning

The solvent used for cleaning your crystal is dependent on the sample that has been analyzed. In all cases it is best to attempt to clean the crystal with the mildest solvent possible. For most cases the preferred solvent is 70% isopropyl alcohol. If a more vigorous solvent is required, acetone may be used. In very stubborn cases dimethylformamide may be used. In all cases when using solvents, inspect the materials safety data sheet associated with the solvent you are using and comply with any recommended handling procedures. Apply the solvent to the crystal with a Q-tip or microfiber swab and gently remove using a Q-tip or non-abrasive wipe. Repeat this procedure until all traces of the sample have been removed.

Under no circumstances should the softer crystals (such as ZnSe, AMTIR or KRS-5) be rubbed with paper products such as “Kleenex”. Many paper products are abrasive and could cause scratching of the crystal surface. <u>KRS-5 element is extremely soft and should be rinsed with solvent only</u>.

Effects of Temperature

It is recommended that the temperature difference between the sample and the crystal not be more than 30 °C. So for a crystal at room temperature, the sample may be at a temperature of up to 50 °C. Please contact PIKE Technologies if you wish to place samples of a higher temperature on the crystal surface. Heated HATR plates are also available and can be heated up to 120 °C.

ATR Spectra

ATR spectra are similar to transmission spectra. A careful comparison of ATR spectra and transmission spectra reveals that the intensities of the spectral features in an ATR spectrum are of lower absorbance than the corresponding features in a transmission spectrum and especially in the high wavenumber (short wavelength) region of the spectrum. The intensity of the ATR spectrum is related to the penetration depth of the evanescent wave into the sample. This depth is dependent on the refractive index of the crystal and the sample, and upon the wavelength of the IR radiation.

The relatively thin depth of penetration of the IR beam into the sample creates the main benefit of ATR sampling. This is in contrast to traditional FT-IR sampling by transmission where the sample must be diluted with IR transparent salt, pressed into a pellet or pressed to a thin film, prior to analysis to prevent totally absorbing IR bands.

A comparison of transmission vs. ATR sampling result for a thick polymer sample is shown below where the sample is too thick for high quality transmission analysis (shown in the lower spectrum). In transmission spectroscopy, the IR beam passes through the sample and the effective path length is determined by the thickness of the sample and its orientation to the directional plane of the IR beam. Clearly in the example below the sample is too thick for transmission analysis because most of the IR bands are totally absorbing.

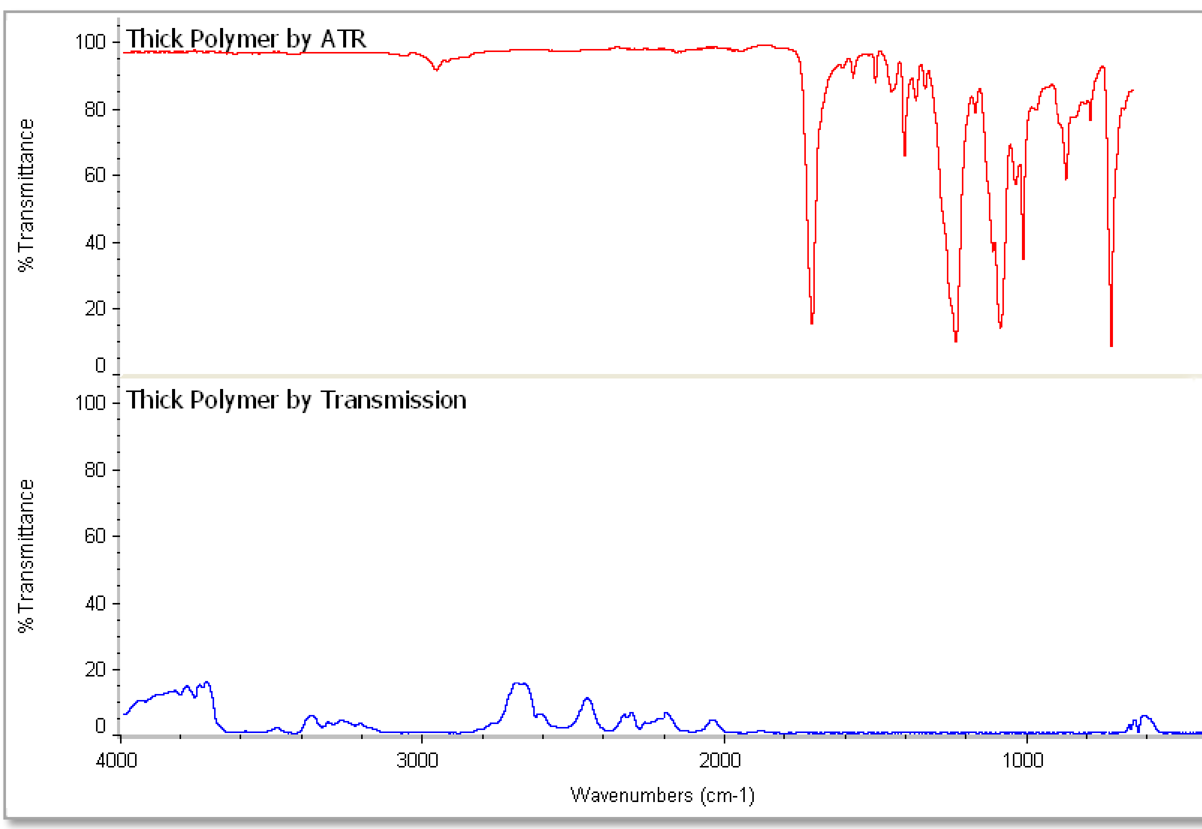


Figure 5. Comparison of ATR and transmission spectrum.

However, simply placing the thick sample on the ATR crystal and applying pressure generates a high quality spectral result (upper red spectrum) - identified by library search as a polybutylene terephthalate. The total analysis time for the thick polymer by ATR was less than 1 minute.

ATR Correction

If an ATR spectrum representative of a transmission spectrum is desired, the ATR spectrum must be processed with the ATR correction program available on your instrument. An example of the effect of this correction on a spectrum is shown in the following example for polystyrene. The lower spectrum is the original ATR spectrum of polystyrene. The middle, blue spectrum is the transmission spectrum of polystyrene. Clearly the IR bands around 3000 cm^{-1} in the ATR spectrum are weaker relative to the IR bands at longer wavelength.

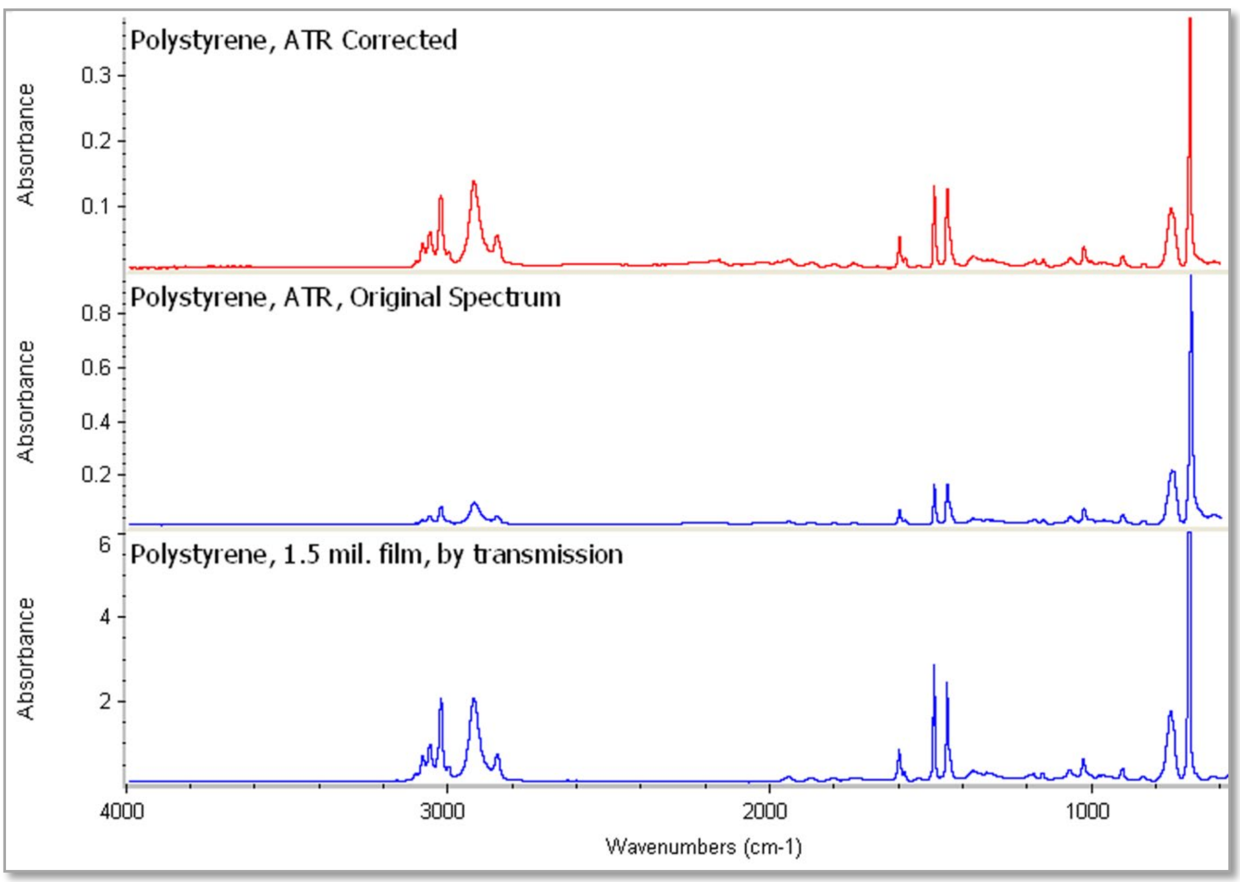


Figure 6. Original and corrected spectra.

However, in the upper red spectrum after ATR correction, we see relative IR band intensities very similar to those from the polystyrene run by transmission.

Liquids

Two, one minute, 4 cm^{-1} resolution spectra of dishwashing liquids were collected using a trough plate configuration. There is an apparent difference between the purely water based and alcohol containing detergents.

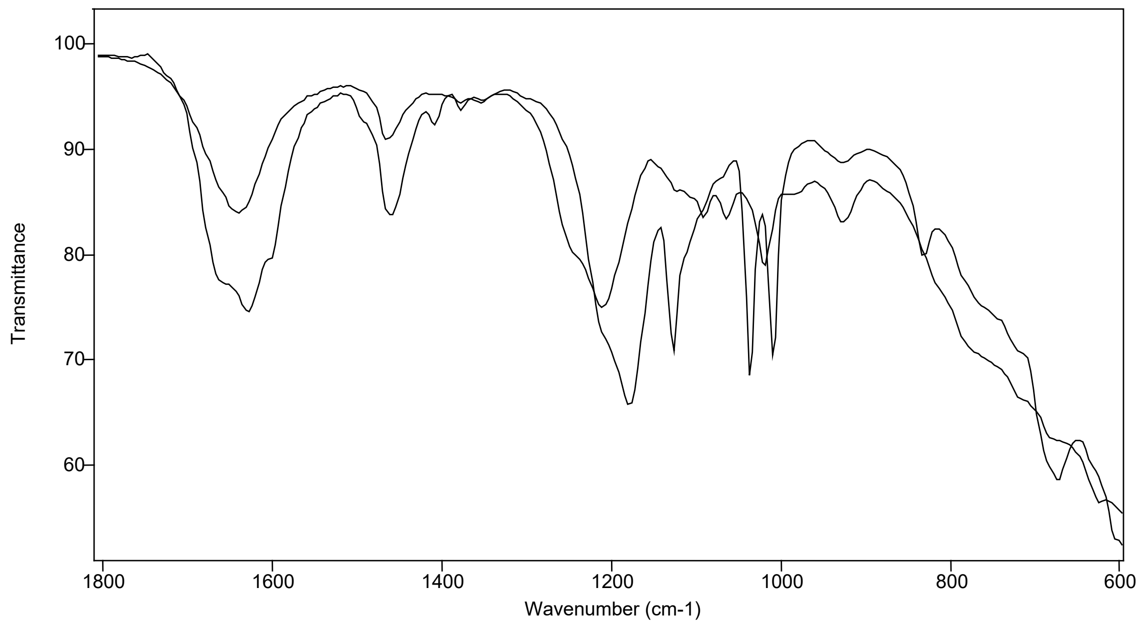


Figure 7. Comparison of liquid detergents.

Two, one minute, 4 cm^{-1} spectra were collected using a trough plate crystal. The samples were a diet and regular soft drink.

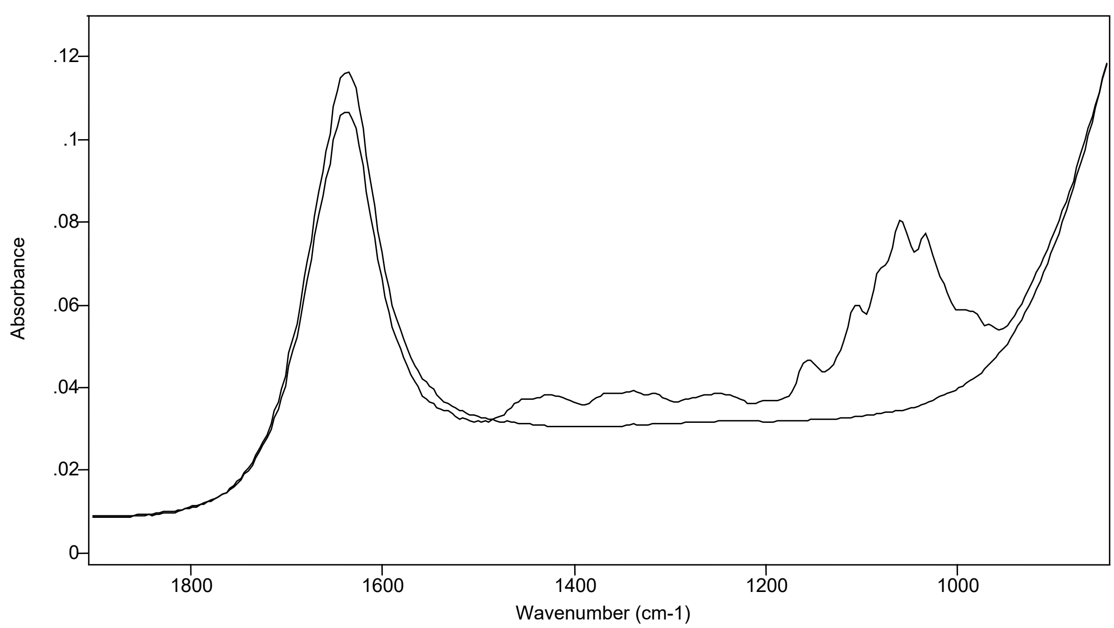


Figure 8. Comparison of two soft drinks.

Solids

The spectrum below is of a plastic bottle. A section was cut out of the bottle and analyzed using a flat plate configuration. The sample was kept in contact with the ATR crystal using the pressure clamp. The acquisition time was one minute at a resolution of four wavenumber.

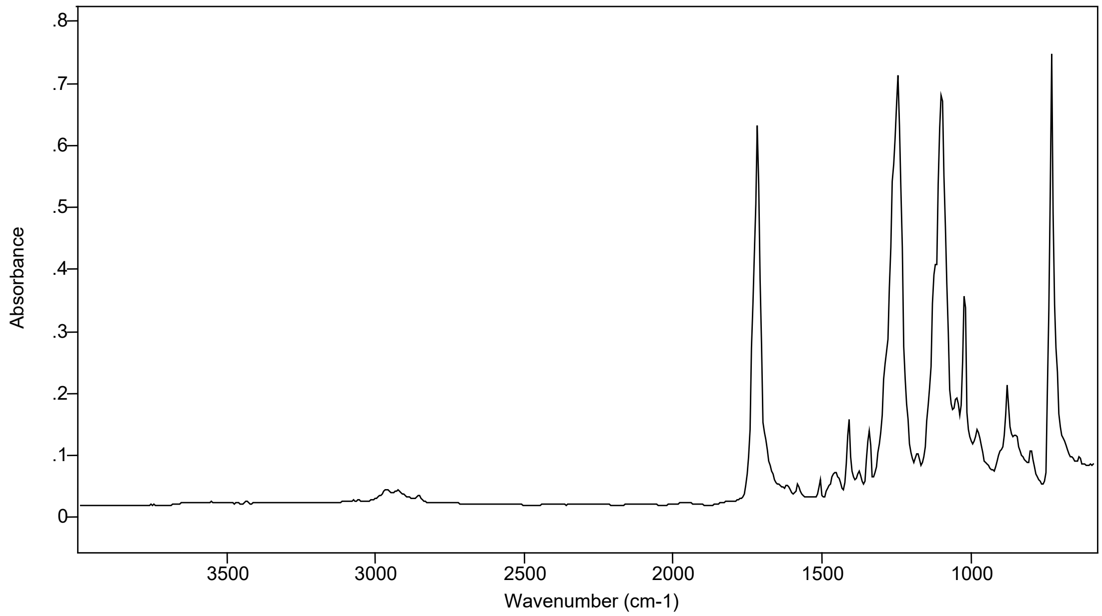


Figure 9. Spectrum of a plastic bottle.

The following are two overlaid spectra showing each side of a multilayer plastic food wrapping material. The sample was kept in contact with the ATR crystal using the pressure clamp. The acquisition time was one minute at a resolution of four wavenumber.

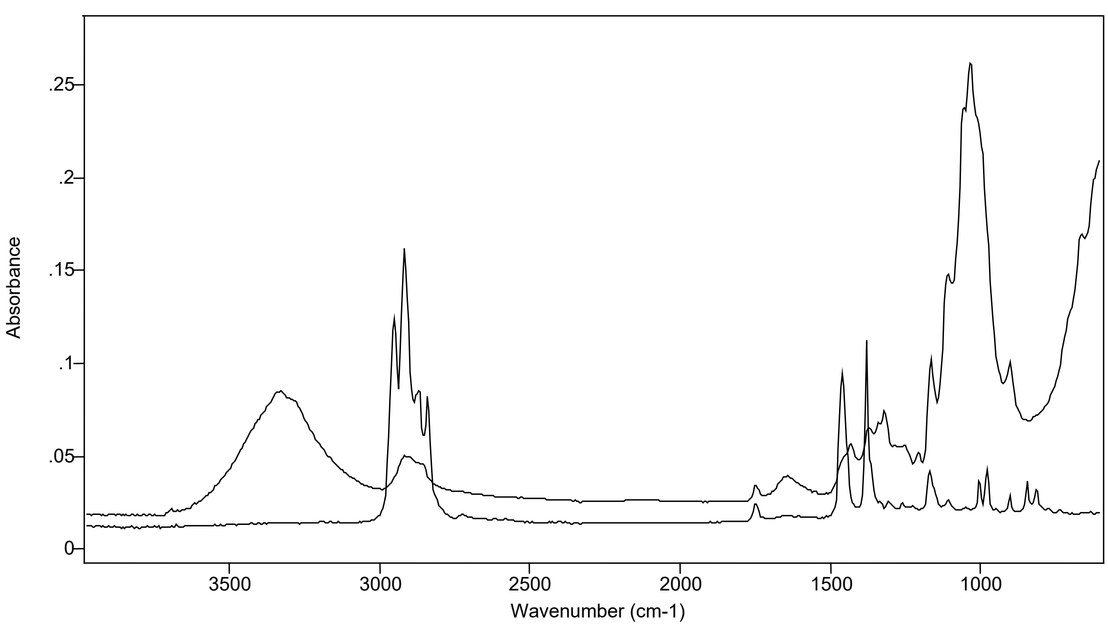
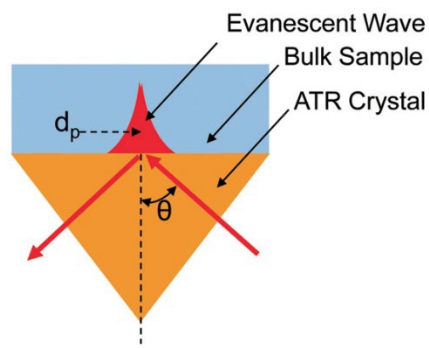


Figure 10. Spectra of food wrapping material.

Theory

How ATR Works

With ATR sampling we direct the IR beam into a crystal of relatively higher refractive index. The IR beam reflects from the internal surface of the crystal and creates an evanescent wave, which projects orthogonally into the sample in intimate contact with the ATR crystal. Some of the energy of the evanescent wave is absorbed by the sample and the reflected radiation (some now absorbed by the sample) is returned to the detector. This ATR phenomenon is shown graphically in the following representation of a single reflection ATR.



Graphical Representation of a Single Reflection ATR

Depth of Penetration

The depth of penetration gives us a relative measure of the intensity of the resulting spectrum and is expressed by the following equation:

$$d_p = \frac{\lambda}{2\pi\left(n_1^2 \sin^2\theta_1 - n_2^2\right)^{\frac{1}{2}}}$$

where:

λ	=	Wavelength of light
θ	=	Angle of incidence of the IR beam
n_1	=	Refractive index of the crystal
n_2	=	Refractive index of the sample

Below is a table giving depth of penetration in microns as a function of crystal material. The penetration depth is calculated for a sample with a refractive index of 1.40 at 1000 cm^{-1} with a 45° angle of incidence.

Material	Refr. Index	Depth of Penetration (µ)
ZnSe	2.4	1.66
AMTIR	2.5	1.46
Ge	4.0	0.65
Si	3.4	0.84
KRS-5	2.37	1.73

Number of Reflections

The number of reflections in the crystal gives a measure of the intensity of the resulting spectrum. This number is a function of the effective angle of incidence, and the length and thickness of the crystal. For this accessory, the crystal is 4 mm thick and 80 mm long. The angle of incidence is typically 45°.

Substituting these values in the equation:

$$N = \frac{l}{2t*\tan\theta}$$

Nomenclature

θ = Effective angle of incidence.

l = Length of crystal.

t = Thickness of crystal.

Gives a value of 10 for the number of reflections on the sample.

Materials

The following HATR crystal materials are available:

Material	Refractive Index at 1000 cm^{-1}	Spectral Range (cm^{-1})	Safe pH
Zinc Selenide	2.4	20000-630	5-9
AMTIR (As/Se/Ge)	2.5	11000-630	1-9
Germanium	4.0	5500-780	1-14
Silicon	3.4	8300-1500	1-12
KRS-5	2.37	17900-400	5-8

Zinc Selenide

ZnSe is the preferred replacement for KRS-5 for all routine applications. Its useful spectral range is less at the low frequency end than that of KRS-5, but the mechanical strength of this rigid, hard crystalline material is superior. Although a general purpose material, it has limited use with strong acids and alkalies. The surface becomes etched during prolonged exposure to extremes of pH. Note that complexing agents, such as ammonia and EDTA, will also erode its surface because of the formation of complexes with the zinc. It is one of the most affordable ATR materials.

Germanium

Germanium has been used extensively in the past as a higher refractive index material for samples that produce strong absorptions such as rubber O-rings. The crystal is also used when analyzing samples that have a high refractive index, such as in passivation studies on silicon.

Silicon

Silicon is hard and brittle. It is chemically inert and it is affected only by strong oxidizers. Silicon is well suited for applications requiring temperature changes as it withstands thermal shocks better than other ATR materials. It also is the hardest crystal material offered except for Diamond, which makes it well suited for abrasive samples that might otherwise scratch softer crystal materials. Typically, Silicon crystal is totally absorbing below 1500 cm^{-1} making its usefulness in the mid-IR range limited with multi-reflection HATR applications.

KRS-5

KRS-5 is one of the most traditional mid infrared optical materials. It can be used for analysis of a wide range of samples similar to Zinc Selenide and has a wider spectral range going down to below 400 cm^{-1}. It is toxic and should be handled with gloves or finger cots. KRS-5 is one of the softest materials and can be easily scratched. It cold flows and can deform under pressure and high temperature. This is its main disadvantage. It can be attacked by complexing agents and is slightly soluble in water.

Precautions

Mirrors

In order to provide the maximum transmission in the infrared, with the minimum spectral interferences, the mirrors used in this device are uncoated (bare) aluminum on a glass substrate. Since the coatings are soft, care must be taken to avoid damage. Normally, these mirrors will not need cleaning, since they are contained within the housing of the accessory. If they do need cleaning, they may be gently wiped with a lint free, abrasive free cloth, such as lens tissue, or with a camel hair brush.

Under no circumstances must the mirrors be rubbed with paper products such as "Kleenex" since this will produce scratching of the mirror coating.

SAFETY

Caution should be used when handling and using ATR crystals since some of the materials can be hazardous. Specifically, zinc selenide is a heavy metal material and should be handled with this in mind. If the crystal is broken or pulverized, the dust may be harmful by inhalation, ingestion or skin absorption.

HATR Plate Options

All HATR ATR plates are pin-mounted to the HATR base with no alignment required. Crystal plate changeover is rapid, allowing a wide range of samples to be analyzed with maximum convenience. The HATRs have been optimized for maximum optical throughput and excellent quality spectra can be obtained from demanding samples. Several high-quality crystal materials covering a full spectrum of applications are available. Trough and sealed flat crystal plates are sealed using metallic gaskets, eliminating premature failure and the risk of cross-contamination associated with inferior, epoxy-bonded systems.

Flat Plate

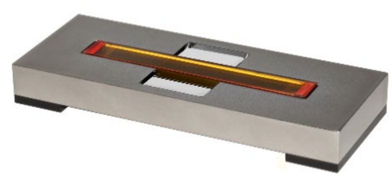
The flat plate is used for the analysis of solid materials – including polymer and film samples. The crystal is mounted slightly above the surface of the metal plate, which helps to achieve good crystal/sample contact when the flat plate press is used. The ZnSe and Ge 45-degree flat plates are available in a sealed version, which is ideal for sampling of oils and other types of low surface tension, non-volatile liquids.

Trough Plate

The trough plate is designed for easy sampling, with a large, recessed crystal to accommodate the sample – generally a liquid, powder, or paste. Typically, only a thin layer of the sample needs to be applied onto the crystal surface. For fast evaporating samples, a volatiles cover should be used to cover the sampling area. By using the optional powder press, soft powders often produce quality spectra when analyzed by HATR, assuming that they can be put in intimate contact with the crystal.

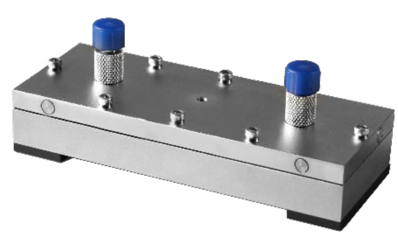
RCPLATE™

For special applications where you need to look at coatings on an HATR crystal, consider the RCPlate option. It is designed to enable easy removal and reinsertion of the HATR crystal. Applications include analysis of coatings, mono-molecular layers, or bio-films deposited directly upon the HATR crystal.



Flow-Through Cell

Flow-through cells are a versatile option for the dynamic laboratory. The ATR crystal is sealed in with O-rings, which allows for user-changeable crystals. The sample may be introduced by syringe or through tubing connected to a 1/16-inch compression fitting. Flow-through cells may be configured for temperature control and with PTFE coating.



Replacement Parts and Options

The following parts and options may be ordered for the HATR accessory:

Part Number	Description
022-19xx	HATR, Base Assembly (w/o crystal plate)
022-3050	HATR Pressure Clamp
022-3051	HATR Volatiles Cover
022-3052	HATR Powder Press
022-3054	HATR High Pressure Clamp
022-4010	500µ HATR Flow Cell, ZnSe 45°
022-5110	HATR Heated Trough Plate, ZnSe 45°, Single RTD
022-5210	HATR Heated Flow-Through Cell, ZnSe 45°
022-5310	HATR Liquid Jacketed Trough Plate, ZnSe 45°

Refurbished Crystal Plate Assemblies

Part Number	Description
022-2110-45	Refurbished HATR Trough Plate ZnSe 45°
022-2120-45	Refurbished HATR Flat Plate ZnSe 45°
022-2130-45	Refurbished HATR Trough Plate KRS-5 45°
022-2140-45	Refurbished HATR Flat Plate KRS-5 45°
022-2150-45	Refurbished HATR Trough Plate Ge 45°
022-2160-45	Refurbished HATR Flat Plate Ge 45°
022-2170-45	Refurbished HATR Trough Plate AMTIR 45°
022-2180-45	Refurbished HATR Flat Plate AMTIR 45°
022-2190-45	Refurbished HATR Trough Plate Si 45°
022-2200-45	Refurbished HATR Flat Plate Si 45°

Contact us for options not shown here.

Regulatory Compliance

We hereby declare that this product conforms to the following standards:

Safety Requirements For Electrical Equipment For Measurement, Control, And Laboratory Use – Part 1: General Requirements [IEC 61010-1:2010 Ed.3+A1]

Safety Requirements For Electrical Equipment For Measurement, Control, And Laboratory Use Part 2-010: Particular Requirements For Laboratory Equipment For The Heating Of Materials [IEC 61010-2-010:2003 Ed.2]

Safety Requirements For Electrical Equipment For Measurement, Control, And Laboratory Use – Part 1: General Requirements [UL 61010-1:2012 Ed.3+R:29Apr2016]

Safety Requirements For Electrical Equipment For Measurement, Control, And Laboratory Use – Part 1: General Requirements (R2017) [CSA C22.2#61010-1-12:2012 Ed.3+U1;U2]

Safety Requirements For Electrical Equipment For Measurement, Control And Laboratory Use - Part 2-010: Particular Requirements For Laboratory Equipment For The Heating Of Materials [UL 61010-2-010:2015 Ed.3]

Safety Requirements For Electrical Equipment For Measurement, Control And Laboratory Use - Part 2-010: Particular Requirements For Laboratory Equipment For The Heating Of Materials [CSA C22.2#61010-2-010:2015 Ed.3]

RoHS 2.0: 2011/65/EU

	The crossed out wheeled bin is a clear reminder that the product must NOT be disposed with household waste. It is the responsibility of the buyer to discard the product in accordance with Federal, regional and local environmental regulations.	This label is located outside the accessory, on the back cover.