Installation and User Guide

PIKE TECHNOLOGIES
Spectroscopic Creativity

MIRacle™

Single Reflection HATR

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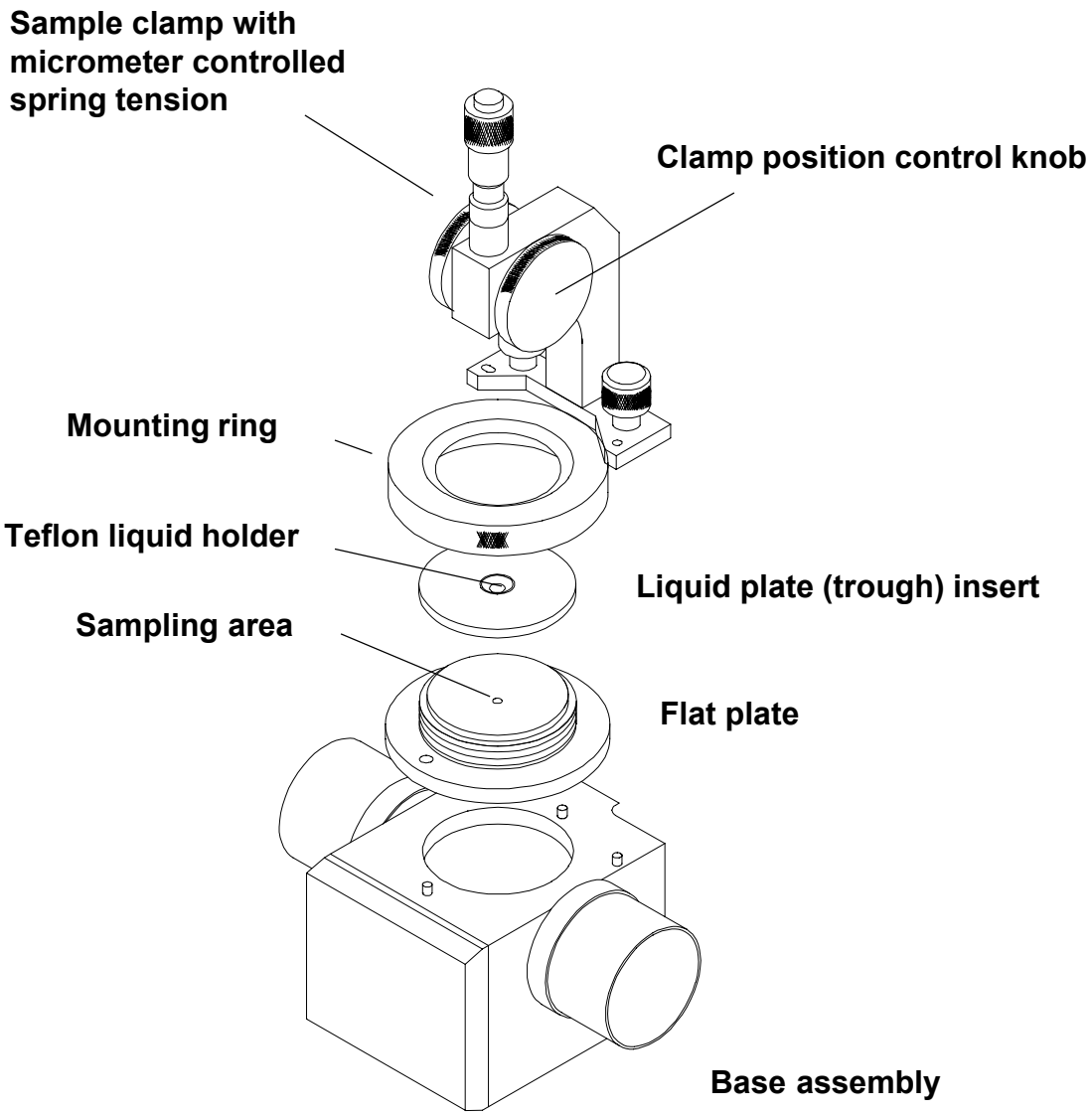
INTRODUCTION

MIRacle™ is the PIKE Technologies Single Reflection Horizontal ATR (HATR) designed for use in FTIR spectrometers (diamond version implements dual-reflection optics). The accessory features a unique optical design (patent pending) which provides exceptional sensitivity. The sampling plate of the accessory has a 2 mm round crystal allowing reliable analysis of small samples. Solid materials can be put in good physical contact with the sampling area, yielding high quality, reproducible spectra. Plates come in several configurations - ZnSe, AMTIR, Si, Ge, or diamond (dual-reflection). The first four options are suitable for analysis of liquids, semi-liquid materials and pliable solids. The diamond configuration should be used when working with reactive samples and/or solid materials which need to be pressed hard against the crystal. Single-reflection ATR works very well for the analysis of highly absorbing substances (e.g. polymers, rubber, paint chips, fibers, etc.).

The compact design of the accessory employs a transfer mirror to direct the infrared beam to one end of an IR transmitting ATR crystal. A second mirror directs the beam emitted from the other end of the ATR crystal to the spectrometer detector.

MIRacle features a universal sampling plate design which eliminates the need for two (trough and flat) plates. The accessory is equipped with a micrometer-controlled compression clamp, volatiles cover and purge attachments.



Exploded view of the MIRacle, Single Reflection Horizontal ATR Accessory

UNPACKING YOUR ACCESSORY

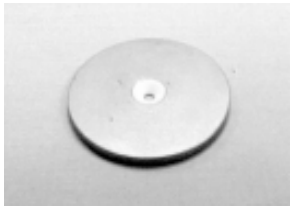
In order for you to quickly verify receipt of your accessory, we have included a packing list. Please inspect the package carefully. Call PIKE immediately if any discrepancies are found.

PACKING LIST

Single Reflection ZnSe, AMTIR, Ge or Silicon MIRacle

MIRacle Base Unit, Qty. 1

Flat Plate*, Qty. 1



Trough Insert*, Qty. 1

Mounting Ring*, Qty. 1

Clamp, Qty. 1

Hard and Soft Polymer** Press Tips, Pellet Tip; One Each

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* The flat plate, trough insert, and mounting ring are attached to the base, and shipped as a single unit.

** The Soft Polymer (swivel) Tip is attached to the Sample Clamp assembly.

Volatiles Cover, Qty. 1

Purge Tube with Connector and Clamp, Qty. 1

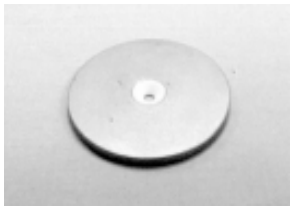
Alignment Wrenches, Set of One

PACKING LIST

Double Reflection Diamond MIRacle

MIRacle Base Unit, Qty. 1

Flat Plate*, Qty. 1



Trough Insert*, Qty. 1

Mounting Ring*, Qty. 1

Clamp, Qty. 1

Hard and Soft Polymer** Press Tips, Pellet Tip; One Each

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* The flat plate, trough insert, and mounting ring are attached to the base, and shipped as a single unit.

** The Soft Polymer (swivel) Tip is attached to the Sample Clamp assembly.

Volatiles Cover, Qty. 1

Purge Tube with Connector and Clamp, Qty. 1

Alignment Wrenches, Set of One

INSTALLATION

The accessory has been aligned and tested to ensure that it performs to specifications. There are four alignment screws provided for fine-tuning, once the accessory is installed in the spectrometer. The following is the procedure for accessory installation and final alignment.

1. Ensure that your spectrometer is performing to specifications. This should be performed by following the Spectrometer User's Manual.
2. Mount the accessory into the sample compartment using the captive screw located on the baseplate (some accessories may have two mounting screws or a mounting screw/pin combination, depending on spectrometer configuration).
3. Tighten the captive mounting screw to firmly position the accessory.

Accessory Adjustment

1. Using the thumb screw on the left side of the accessory, adjust the left mirror until the highest throughput is achieved. To do this, turn the screw slightly clockwise and check the signal. If it increases, continue until the maximum is obtained. If it decreases turn the screw counterclockwise to get the highest possible reading.
2. Repeat the same procedure with the right thumb screw.
3. Insert the enclosed allen wrench in the front adjustment screw on the top of the accessory. Adjust the screw until the highest throughput is obtained.
4. Repeat the same alignment step with the rear allen screw positioned on the top plate.
5. Repeat the entire procedure 2-3 times to fine-tune the accessory.

This is an initial (one-time) alignment procedure which optimizes the MIRacle to work with an individual optical bench. Once completed, the alignment does not have to be repeated, unless the accessory is placed in a different instrument.

PERFORMANCE VERIFICATION

- With the accessory removed from the sample compartment, collect a background spectrum.
- Place the MIRacle accessory in the instrument.
- Collect a transmission spectrum using the same collection parameters as used to collect the background spectrum.

The following are the transmission values the accessory should achieve with different crystal configurations at 1000 cm^{-1} (with the exception of the Si value which is shown at 2000 cm^{-1}).

AMTIR	DIAMOND	Ge	Si	ZnSe
20 +/- 2 %T	18 +/- 2 %T	15 +/- 2 %T	15 +/- 2 %T	20 +/- 2 %T

If your accessory does not meet this minimum transmission, please contact PIKE Technologies. On making this call, please have ready the serial number located on the rear of your accessory.

SAMPLING PROCEDURES

The spectrum of the required sample is obtained by ratioing a scan with a sample in place to a scan with no sample on the face of the crystal. The crystal mount is located on the base unit. A single crystal design is used for all types of samples (liquids, pastes, soft pliable films and solids).

Configuration for Liquid Sampling

Please note, that the accessory is shipped in a liquid sampling configuration.

The crystal plate assembly of the MIRacle HATR features a round plate design, with a 1.5 mm sampling area, located in the center. The side of the crystal plate features coarse threads provided for mounting various attachments. For liquid sampling, a trough insert is placed on the top of the plate and fastened with the knurled mounting ring. The insert forms a shallow well around the crystal for containment of liquid and finely powdered samples.

The sample must be in an intimate contact with the sampling area. For routine sampling, place a drop of your sample in the trough and collect data. Care is required when removing the sample from the trough. It is recommended that the sample be removed without scratching the surface of the crystal. Note that some crystals used in the accessory are made of fairly brittle materials. Scratches on the surface of the crystal will result in a reduction in the throughput of the accessory. Remove the sample gently with a tissue and rinse with solvent. For more thorough cleaning, unscrew the mounting ring and remove the insert. Both, the insert and the crystal plate should be cleaned with an appropriate mild solvent.

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.

Configuration for Solid Sampling

For measurements of soft pliable films and selected solid samples, the mounting ring and liquid adapter should be removed from the crystal plate assembly.

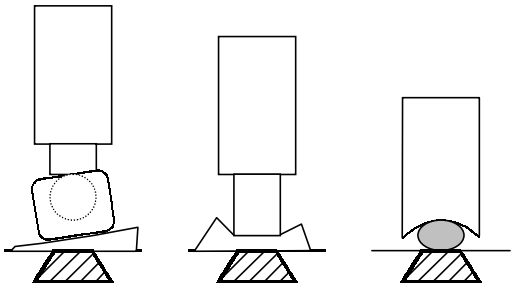
The sample is placed onto the surface of the crystal. Since the ATR effect only takes place very close to the surface of the crystal, an intimate contact has to be

made by the sample on the crystal surface. This is achieved by using the micrometer press contained in your kit. Mount the press to the side of the accessory using the two captive thumbscrews. With the sample in place on the crystal, lower the pressure point so that it is in contact with the sample. You can achieve reproducible sampling by applying the same amount of pressure to your sample. This is done by using the same settings on the micrometer screw.

Care must be used in operating the press, since the pressure device 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.

Press Attachments

The success of an ATR measurement depends mostly on the quality of the contact between the sample and the crystal. Since there is an infinite number of sample shapes and types, a single configuration of the sample press tip may not do the job. For this reason, the MIRacle sample press is designed to accept different tip attachments providing the best possible configuration for any given sample type.



PRESS TIPS: swivel straight edge concave

The accessory is shipped with the swivel tip attached to the press. The tip features a polymer cup mounted on a small ball joint. Such design allows the polymer cup to move and adjust its position to the shape of the sample and maintain the sample position parallel to the crystal surface. The relative softness of the tip has a cushioning effect and it allows for better positioning and close to perfect contact of thin materials with the crystal surface. The swivel tip is used with irregularly shaped samples, films, semi-rigid polymers (e.g. credit card like materials). It can be also used for special applications, including analysis of single fibers and combinatorial chemistry beads. When using the swivel tip, it is important to prevent its direct placement on the crystal, as its spectrum would interfere with that of the sample. This is not a problem when dealing with a majority of samples. For small samples like beads, powders or fibers, a small piece of aluminum foil should be placed between the tip and the sample to eliminate such exposure.

The second tip attachment is a straight metal barrel and it is used when analyzing rubber samples and other elastic polymers. This tip should not be used for analysis of thin films or fibers, as it may not position the sample perfectly on the crystal surface (the swivel tip described above is designed to perform such a function). Please keep in mind that the depth of penetration of an ATR crystal is only in the range of 0.5 to 2 micrometers and even a small departure from intimate contact with the crystal will affect the quality of the spectrum.

The third attachment was developed specifically to work with granules, large beads and polymer pellets. The tip features a concaved surface which does not allow the sample to escape from underneath the press. It also forces the sample to stay in the center of the crystal, assuring the best possible contact.

Sample Press

The clamp assembly consists of the base which attaches directly to the accessory top plate and the "r" shaped arm with control knobs for raising and lowering the sample press. The press itself, is a stainless steel barrel with the integrated micrometer screw at the top and the spring-loaded plunger at the bottom. A spring is located between the shaft of the micrometer screw and the plunger. The spring tension can be adjusted by changing the position of the micrometer screw. This adjustment allows application of higher or lower pressure to the sample placed on the accessory's sampling plate.

The numbers on the scale of the micrometer screw serve as reference (they do not indicate the actual pressure applied to the sample)*. The actual pressure per square inch (PSI) depends on the size of the tip attached to the press and the spring tension. Listed below are the approximate pressures calculated for the square edge stainless steel tip (diameter 0.125").

Micrometer Setting	Pressure (lbs)
3.0	408
2.0	530
1.0	693
0.0	815

The lighter pressures should be used for soft, flexible samples. The higher pressures are necessary for hard polymers, bids, granules, etc. (Please see also the note on selection of press tips). The following is a short procedure outlining proper use of the MIRacle sample press:

1. Select the appropriate tip and attach it to the press.
2. Position the sample on the accessory plate.
3. Set the micrometer screw to 2.0.

4. Lower the press barrel with the control knobs, until the edge of the sampling tip touches the lower brass end of the barrel.
5. Collect the sample spectrum.

Some FTIR spectrometers offer "real-time" data collection modes (names like MONITOR, DATA PREVIEW, etc. are used for their description). If available, you can experimentally determine the best pressure for your particular sample by observing the shape of the spectrum while adjusting the micrometer screw.

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* Please note that the spring in the press assembly is not compressed until the micrometer screw is set to 3.5. For this reason, always keep the micrometer setting between 3.5 and 0.

Volatiles Cover

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

Powder Press

With care, some powders may be analyzed with an ATR accessory. 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. Configure the MIRacle accessory for liquid sampling by installing the trough insert, holding it down with the knurled mounting ring. Mount the press using the two captive thumbscrews. Powders may now be placed in the trough and pressed into contact using the press.

Note that hard powders should be analyzed only with diamond ATR. The hard powder may even damage the surface of other crystals. Often, diffuse reflectance is the preferred technique for powder analysis.

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 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 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

must the crystals be rubbed with paper products such as “Kleenex”. Many paper products are abrasive and could cause scratching of the crystal surface.

Effects of Temperature

The PIKE Technologies MIRacle utilizes an indium gasket to seal the crystal to its mount. This sealing mechanism allows some flexibility and hot samples may be placed on the crystal without damaging the crystal or seal. However, it is recommended that the temperature difference between the sample and the crystal be not more that 30 degree Celsius. So for a crystal at room temperature, the sample may be at a temperature of up to 50 degrees Celsius. Please contact PIKE Technologies if you wish to place samples of a higher temperature on the crystal surface.

ATR SPECTRA

ATR spectra are very 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 usually a little stronger than the corresponding features in a transmission spectrum in the low wavenumber region of the spectrum. The intensity of the ATR spectrum is related to the penetration depth of the evanescent wave in the sample. This depth is dependent on the refractive index of the crystal and the sample, and on the wavenumber, increasing at lower wavenumbers. This change in penetration depth over the spectrum results in the discrepancies seen between transmission and ATR spectra.

If accurate relative band intensities are required, the ATR spectra 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 below.

ATR Correction

A spectrum collected by the ATR technique is related to a spectrum collected by transmission by the following equation:

$$S_{ATR} = k_1 * S_{CORR} * D_P$$

Where:

S_{ATR} is the ATR spectrum
k_1 is an arbitrary constant
S_{CORR} is the corrected spectrum
D_P is the ATR penetration depth

The equation for penetration depth is given in the section on useful equations. An inspection of this equation shows that, for a given experiment:

$$D_P = 1 / (k_2 * \nu)$$

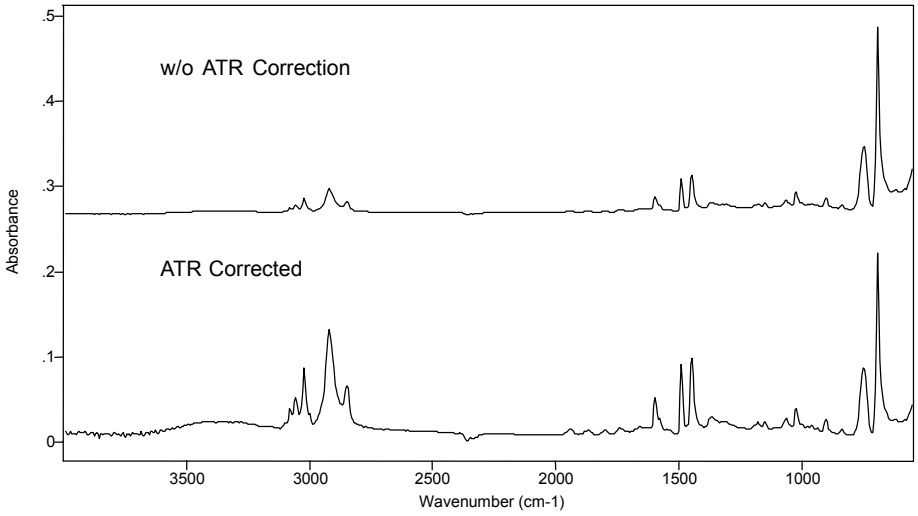
Where ν is the wavenumber and k_2 is a constant related to the angle of incidence and refractive index of the sample and ATR crystal.
In order to calculate the corrected spectrum, we have to calculate

$$S_{CORR} = S_{ATR} / (D_P * k_1)$$

or: $$S_{CORR} = S_{ATR} * \nu / k$$

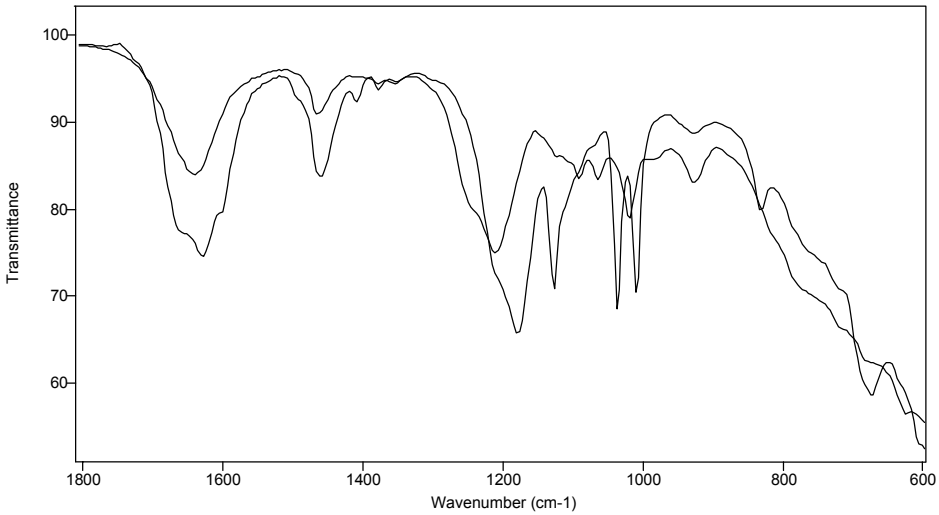
where k is an arbitrary constant.

Below are two stacked spectra of a polymer sample. The top spectrum has been processed using the ATR correction software and the bottom spectrum is the original spectrum. In using this software the ATR correction frequency was set to 4000 wavenumbers.



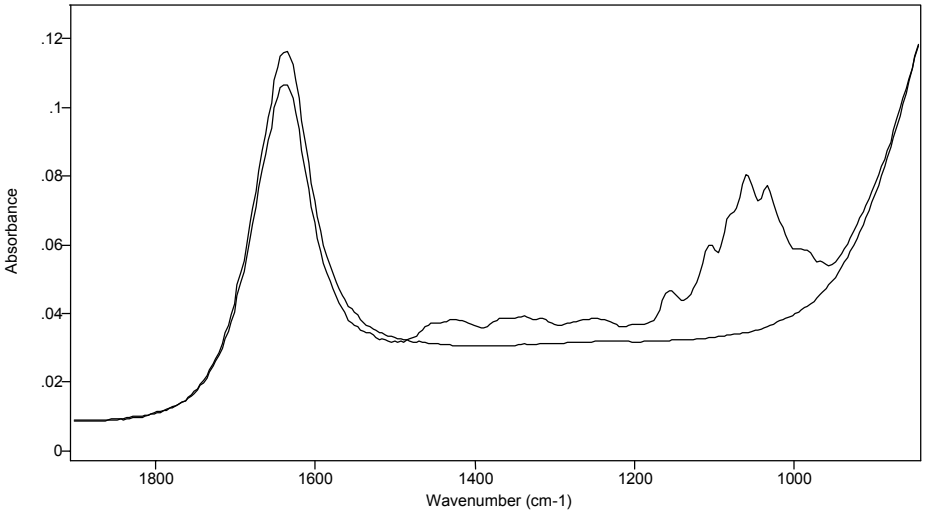
Liquids

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.



Comparison of liquid detergents

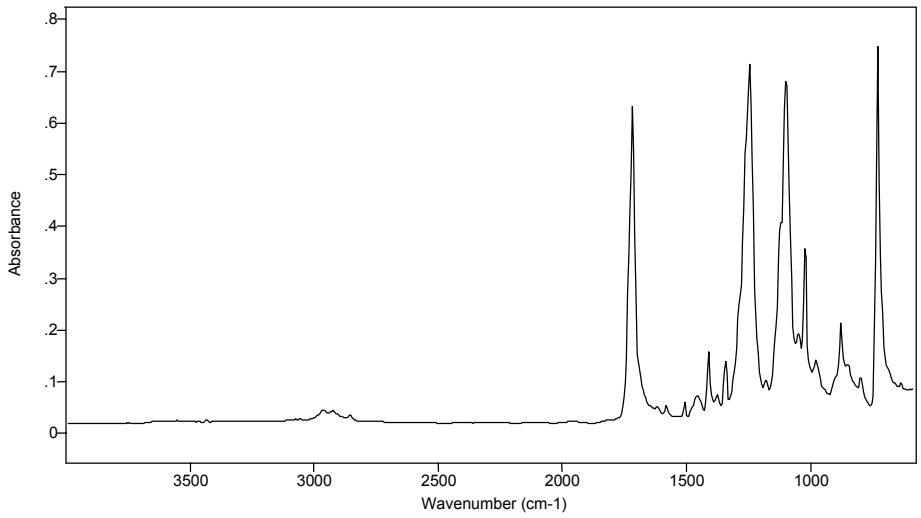
Two one minute, 4 cm^{-1} spectra were collected using a trough plate crystal. The samples were a diet and regular soft drink.



Comparison of two soft drinks

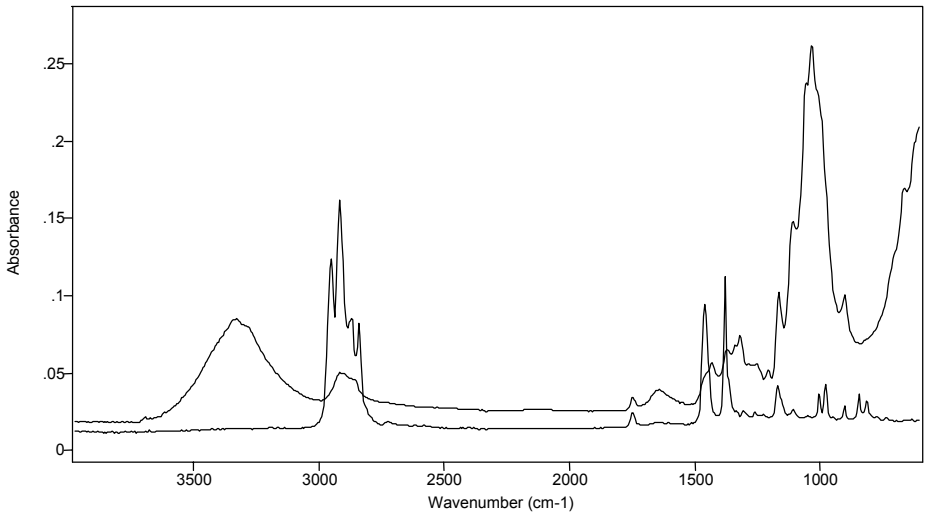
Solids

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



Spectrum of 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 clamp. The acquisition time was one minute at a resolution of four wavenumbers.



Spectra of food wrapping material

USEFUL EQUATIONS

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

$$D_p = \frac{\lambda}{2\pi\, n_c[\sin^2\Phi - (n_s/n_c)^2]^{1/2}}$$

where:

Φ = Effective angle of incidence.
n_c = Refractive index of crystal.
n_s = Refractive index of sample.
λ = Wavelength.

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}

Material	Refr. Index	45 degrees
ZnSe	2.4	1.66
AMTIR	2.5	1.46
Ge	4	0.65
KRS-5	2.37	1.73

MATERIALS

The following ATR crystal materials are available:

Material	Refr. Index at 1000 cm^{-1}	Spectral Range (cm^{-1})
Zinc Selenide	2.4	20,000-650
AMTIR (As/Se/Ge glass)	2.5	11,000-750
Germanium	4	5,500-870
Silicon	3.4	8,300-1,500/360-70
Diamond	2.4	4,500 -2,500/1,667-650

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 polycrystaline 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.

AMTIR

This material produced as a glass from selenium, germanium and arsenic, AMTIR is considered to be highly toxic during the manufacturing process. However, the brittle nature of the material and its total insolubility in water makes it safe for use as an internal reflectance element. It has a similar refractive index to zinc selenide and can be used in measurements that involve strong acids.

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 then other ATR materials. The silicon crystal is totally absorbing below 1500 cm^{-1} , therefore its usefulness in the mid-IR range is limited.

Diamond

Diamond is one of the most rugged optical materials. It can be used for analysis of a wide range of samples, including acids, bases, and oxidizing agents. Diamond is also scratch and abrasion resistant. Its disadvantage is the intrinsic absorption from approximately 2300 to 1800 cm^{-1} which limits its usefulness in this region.

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.

MAINTENANCE/REPLACEMENT PARTS LIST

The following maintenance and replacement parts are available:

Crystal Plates

025-2010	Single Reflection HATR Universal Plate, ZnSe Crystal
025-2050	Single Reflection HATR Universal Plate, Ge Crystal
025-2070	Single Reflection HATR Universal Plate, AMTIR Crystal
025-2090	Single Reflection HATR Universal Plate, Si Crystal
025-2000	Double Reflection HATR Universal Plate, Diamond

Other

025-3051	Volatiles Cover
025-3053	Press Tips Assortment