Installation and User Guide

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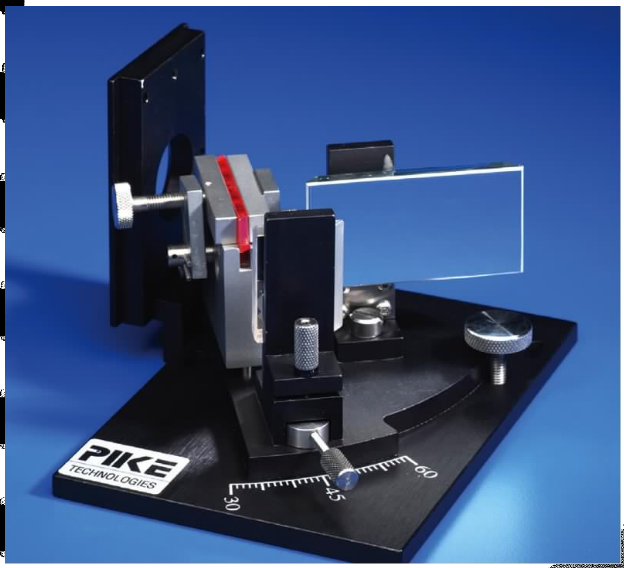

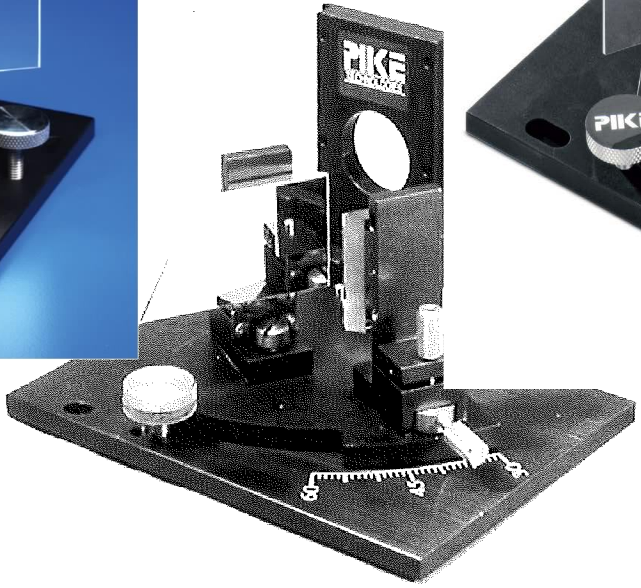

VATR

Variable Angle ATR Accessory

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CONTENTS

Introduction

The Vertical Variable Angle ATR Accessory is based on the classic design by Gilby (Applied Optics **13**, 2479 (1974)). The major feature of this design is that the angle of incidence of the incoming beam striking the ATR crystal may be varied from between thirty and sixty degrees in a continuous manner. This is achieved while keeping the optical pathlength through the accessory constant at all angles and equal to the distance traveled by the Infra Red beam without the accessory in place. This means that there are no defocusing effects due to the accessory, resulting in the optimum accessory throughput at all angles.

This design offers several unique features which enable precision alignment and enhanced throughput. The accessory features a specially developed mirror adjustment system which allows for more precise alignment. In addition, unique mirror placement and pivoting makes changing angle to adjust the infrared depth of penetration simple and reproducible.

Unpacking Instructions

The accessory is supplied in a protective box. The contents of this box are:

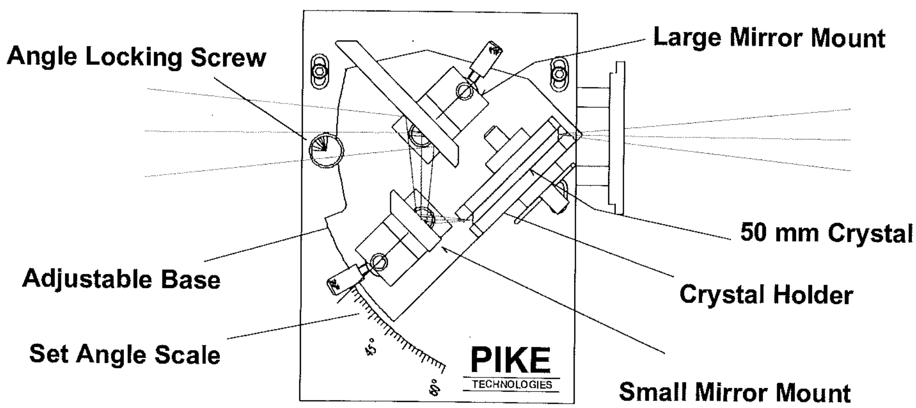
Variable ATR Accessory
25mm Adapter Mirror
KRS-5 Crystal (or Crystal of choice), 50mm long
User Manual

Please check that this package is complete and undamaged. In case of problems, please call PIKE Technologies.

Accessory Description

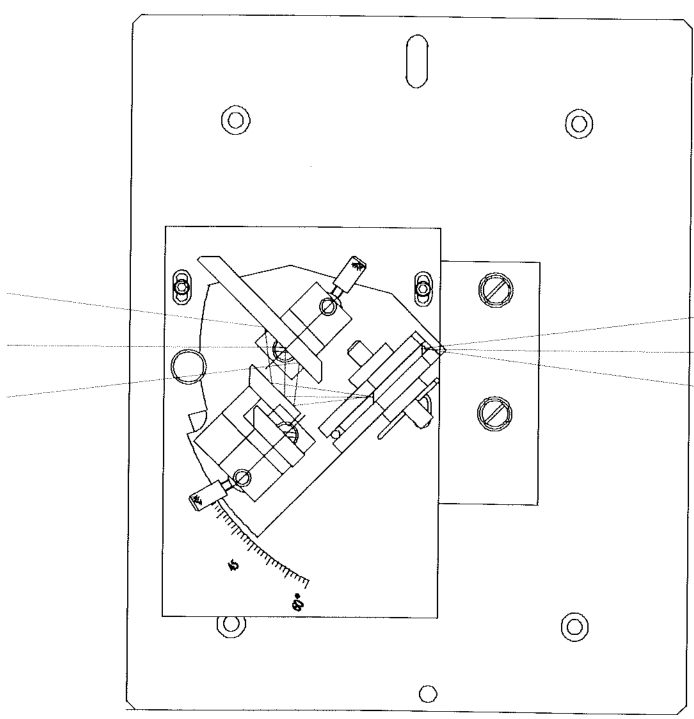
The accessory is shown in figure 1 below. Two diagrams are shown, one for the accessory with a 50mm crystal and one with a 25mm crystal.

Variable ATR
Optical Layout at 45 Degrees



Slide Mount Version

Figure 1



Base Mounted Version (Optional)

The Crystal Mount and Anvils

This assembly is shown in detail in figure 2. The crystal mount is made of stainless steel which has been chosen for its corrosion resistance. The mount will hold two different lengths of crystals, the standard 50mm and a shorter 25mm crystal. The clamping plate thumb screw should be turned counter-clockwise to allow the clamp bar to open enough so that the edge of the crystal may be inserted into the holder. Using finger cots, the crystal should be inserted and the thumb screw tightened. One of the ends of the crystal should be positioned to be half over the hole in the end of the block, prior to clamping in place, to ensure that the crystal face is at the correct position. The holder with its mounted prism may now be placed in position on the ATR baseplate for alignment or the collection of data.

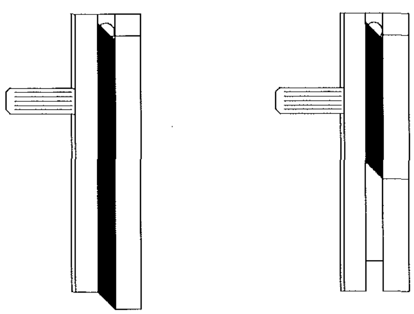
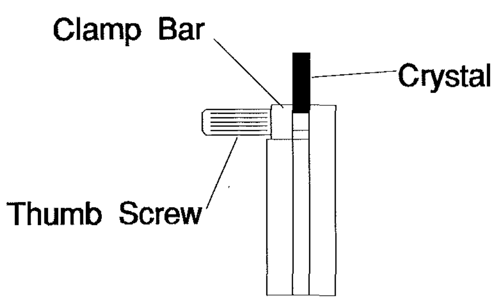
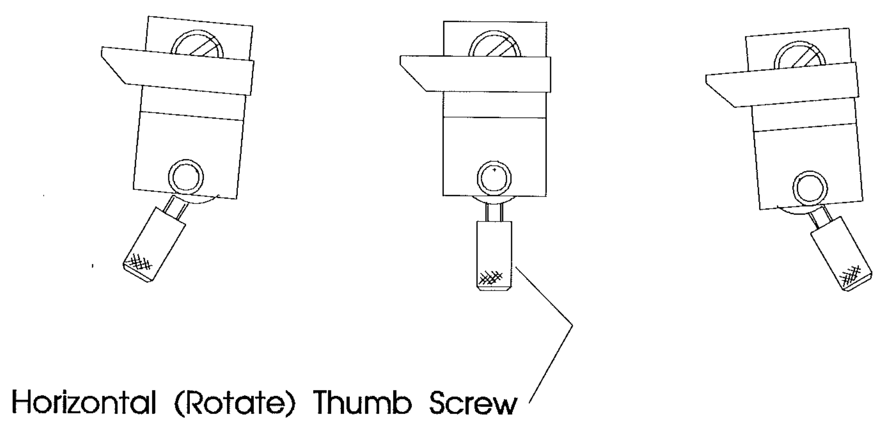


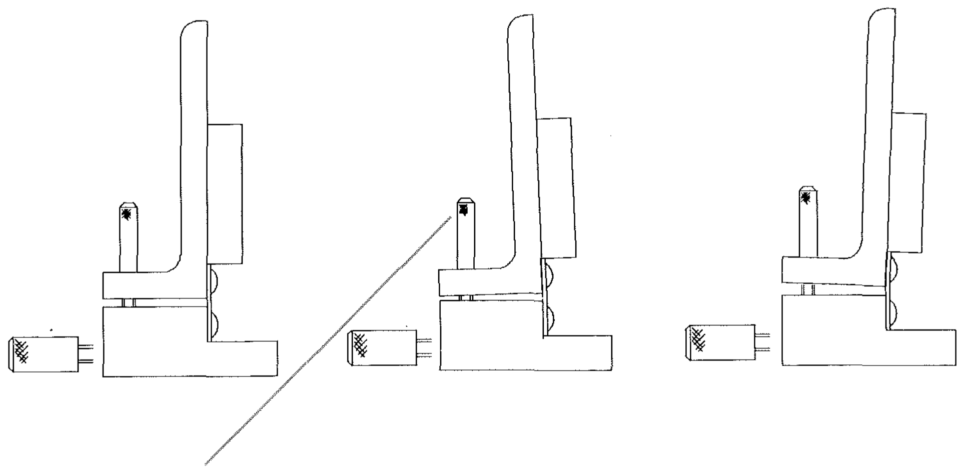
figure 2



Small and Large Mirror Mounts

The two transfer mirrors are mounted on mirror mounts which allow the orientation of the mirror to be set precisely and with ease. The rotation adjustment of these mirrors is performed using the horizontal adjustment knob. When this knob is turned the mirror may easily be may be adjusted through a range of five degrees by rotating the adjustment knob through approximately ninety degrees. This unique cam action allows the mirror to be adjusted easily and with great accuracy. Once adjusted, the mirror may be locked in place by tightening the knob. The mirrors may be tilted by using the vertical adjustment knob. Tightening or loosening this knob will tilt the mirrors through a five degree range.





Vertical (Tilt) Thumb Screw

Adjustable Base

The adjustable base of the accessory is clamped in position by a single locking screw and is able of being rotated about a dowel pin which also locates the position of the crystal mount. The base may be rotated from its mean position of 45 degrees to as low as 30 degrees and as high as 60 degrees, the angle being set on the angle scale. After a desired angle has been set, this plate should be locked in position using the locking screw provided.

Support and Mounting Plate

The accessory is provided on a standard slide mount which can be fitted to most FTIR instruments. The baseplate option is located in the sample compartment using the two dowels and is clamped in position using the four thumbscrews provided.

25mm Mirror

The 25mm mirror is a separate mirror that should be used when a 25mm crystal is in use. This mirror attaches to the side of the small mirror mount. It is located on the side of this mirror mount using the dowel pins and locked in place using the thumbscrew.

Aligning the Vertical Variable ATR Accessory

The accessory has been pre-aligned and tested prior to shipment. Minor alignment may be needed to maximize throughput. This involves fitting the crystal in the holder and aligning the mirrors. These procedures are shown below in the description of the complete optical alignment of the accessory

1. Place the accessory into the sample compartment.
2. Ensure that the angle is set to forty five degrees.
3. Refer to Figure 1. Remove the crystal holder. Loosen and anvil clamp screw and place the crystal in the holder. Ensure that the crystal is located so that the end of the crystal is positioned over the hole in the base of the crystal holder. Carefully tighten the crystal clamp screw to secure the crystal. Do not over tighten this screw as the crystal may be deformed or broken if too much pressure is applied.
4. Locate the crystal holder with its crystal over the two dowel pins in the adjustable base.
5. The main support on the baseplate mounted accessory has an adjustment that may be used to locate the crystal at the center of the infrared beam. The three screws holding down the main support may be loosened and the main support moved so that the Infra Red beam strikes the crystal at the center of the end face. When this adjustment has been done the three screws should be tightened to secure the main support.
6. Adjust the tilt screws on the two mirror mounts so that the mirrors are positioned to be vertical.
7. Loosen and turn the rotation adjustment of the two mirror mounts so that they are in the middle of their travel.
8. Adjust the tilt of the two mirror mounts to maximize the throughput of the accessory. Again, this should be done by cycling back and forth between the two mirror mounts.
9. Finally, the mirrors should be rotated using the rotation adjustment to ensure that the accessory is aligned at the maximum throughput. If the throughput is increased at this stage then the tilt adjustment should be repeated, followed by a further rotation adjustment.
10. At this point, the accessory should be aligned, with the transmission through the accessory being at a maximum. The accessory is now ready for use.

Using the Variable ATR Accessory

There are multiple reflections along the sample holder where the infra red beam interacts with the sample to produce a spectrum. The sample should fill the crystal to take advantage of all these interactions. Also since the penetration depth of the infrared beam into the sample is very small, it is important that the sample is in intimate contact with the crystal. This, however must be achieved without exerting too much force on the sample anvils, since distortion or breakage of the crystal may occur. Too much force can also result in the surface of the crystal being damaged. Rubber pads are provided to minimize crystal deformation, aid in producing an intimate contact between sample and crystal and increase the life of the crystal. If the sample is smaller than the crystal, then there may be some spectral interference from these rubber pads. To minimize this effect, the rubber may be coated with Calcium Fluoride powder.

Samples that have a low absorption coefficient may not produce very intense spectra. Although applying more pressure to the sample anvils may increase the size of the spectral features due to a better contact with the crystal, this procedure should be avoided. A better solution is to decrease the angle of incidence of the crystal, thus increasing the penetration depth or use a thinner crystal, increasing the number of reflections of the infrared beam at the sample. Conversely samples having a high absorption coefficient will produce spectral features in the spectrum that are too intense. In this case, the angle of the crystal should be increased, lowering the penetration depth or a thicker crystal should be used, reducing the number of reflections.

1. Mounting the crystal.
2. Aligning the accessory
3. Mounting the sample
4. Not too much pressure.
5. Changing the angle

Sample Preparation

It is important that there be intimate contact between the sample and the ATR crystal, in order that good spectra are obtained. Because of this it is important that solid samples are flat. Irregular samples will result in intermittent contact with the crystal and poor spectra will result. Attempting to improve the quality of the spectra by tightening the anvils can distort or destroy the crystal. Before mounting solid samples, make sure that the surface to be in contact with the crystal is flat. This can be done by cutting or grinding the sample. If this is not possible the crystal may be coated with mineral oil prior to mounting the sample. This will promote good contact, but the oil will exhibit it's own particular spectrum.

Powdered samples should first be ground and pressed in a pellet press to produce a sample suitable for mounting in the holder.

In order to aid contact of solid samples to the crystal, rubber gaskets are provided. These are useful if the solid sample is thin and of approximately constant thickness. The rubber will take up any minor irregularities in the sample and will minimize crystal deformation. Note that very thin transparent samples or samples that are smaller than the ATR crystal may exhibit spectra with a contribution from the rubber gasket, especially if the rubber is contaminated with a prior sample. If spectral interferences due to the rubber gaskets are undesirable, the rubber may be coated with CaF_2 powder to eliminate these.

The ATR Spectrum

The ATR spectrum differs from a transmission spectrum. The ratio of the intensity of spectral features at lower wavenumbers compared to high wavenumbers is different for ATR spectra than for transmission spectra. This is because the penetration depth for an ATR measurement varies over the wavelength range measured. If the angle of the crystal is made high or the sample has a high refractive index, these differences are magnified. Another effect that comes into play is due to refractive index changes. The index of the material varies in the region of an absorption band and this can give rise to anomalous band shapes, where the band has a steep slope on the long wavenumber side of the band but a gentle slope on the high wavenumber side of the band. This effect is not very noticeable if the refractive index is low, which is try for most organic compounds. If this effect is severe then it is necessary to go to a higher angle of incidence, or use a crystal having a higher refractive index.

Effective Angle of Incidence

The angle of incidence as measured using the angle scale of the accessory is only equal to the angle in the crystal when the incident beam is striking the crystal at normal incidence i.e when the angle as measured with the scale is equal to the crystal angle. At other angles, the effective angle of incidence in the crystal can be calculated. The following formulae may be used to calculate the effective angle of incidence, as well as number of reflections, penetration depth in the sample and effective pathlength.

$$\Phi = \Phi_{scale} - \sin^{-1}\left[\frac{\sin(\Phi_{scale} - \Phi_{face})}{n_c}\right]$$

The following tables may be used to determine the effective angle of incidence for different material.

KRS-5, refractive index = 2.38

		Scale Angle		
		30^{o}	45^{o}	60^{o}
Crystal	30^{o}	30^{o}	38.8^{o}	47.9^{o}
Face	45^{o}	36.2^{o}	45^{o}	53.8^{o}
Angle	60^{o}	42.1^{o}	51.2^{o}	60^{o}

ZnSe, refactive index = 2.40

		Scale Angle 30^{o}	45^{o}	60^{o}
Crystal	30^{o}	30^{o}	38.8^{o}	48.0^{o}
Face	45^{o}	36.2^{o}	45^{o}	53.8^{o}
Angle	60^{o}	42.0^{o}	51.2^{o}	60^{o}

Ge, refractive index = 4.02

		Scale Angle 30^{o}	45^{o}	60^{o}
Crystal	30^{o}	30^{o}	41.3^{o}	52.9^{o}
Face	45^{o}	33.7^{o}	45^{o}	56.3^{o}
Angle	60^{o}	37.1^{o}	48.7^{o}	60^{o}

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:

$$D_P = 1 / (k_2 * n)$$

Where n 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: $$S_{CORR} = S_{ATR} * n / k$$

where k is an arbitrary constant.

Depth Of Penetration

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 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	4.02	0.65
KRS-5	2.38	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	4.02	5,500-870
KRS-5	2.38	20,000-350

KRS-5

KRS-5 was the most widely used material for ATR elements prior to the common availability of zinc selenide. Although it has a wide spectral range, KRS-5 is very soft and is easily damaged. Like the zinc based compounds, the thallium in KRS-5 is readily complexed by ammonium compounds and amino-based chelates. The only advantage of KRS-5 is its wide spectral range.

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 the 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.

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.

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.

Safety

Caution should be used when handling and using ATR Crystals since some of the materials can be hazardous.

KRS-5 Thallous Bromide-Iodide
This is a heavy metal material and should be handled with this in mind. KRS-5 Crystals should be handled only with forceps of using finger cots. The material should not be allowed to come into direct contact with skin, especially if the skin is broken. If the crystal is broken, or pulverized, the dust is particularly dangerous and should not be inhaled

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