
Installation and User Guide



HATR

Horizontal Attenuated Total
Reflectance Accessory

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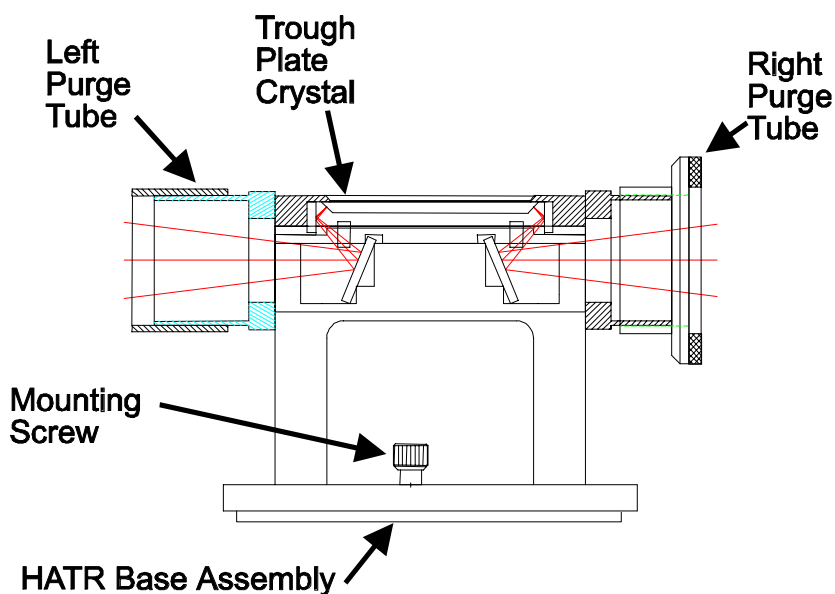
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INTRODUCTION

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 crystal, 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 prism is zinc selenide. This material is hard and durable and has a wide spectral range. Other materials are available and are described later in this manual.

The ATR crystal for both the flat plate and trough plate crystals is of a trapezoid shape and is 80mm long, 10mm wide and 4mm 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 crystal dimensions have been chosen to maximize the *signal to noise* in the resulting spectra.



Sectional view of the HATR Accessory (please note that 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. Call PIKE immediately if any discrepancies are found.

PACKING LIST

Combination Trough and Flat Plate System

HATR Base Unit
Quantity 1



Trough Plate Crystal
Quantity 1



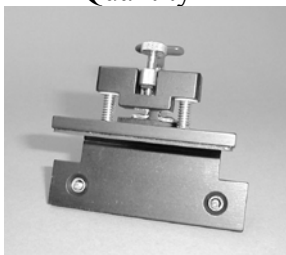
Flat Plate Crystal
Quantity 1



Volatiles Cover and
Powder Press
Quantity 1



Flat Plate Press
Quantity 1



Purge Tube with
Connector and Clamp
Quantity 1



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.

PERFORMANCE VERIFICATION

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

The transmission value of this accessory should be at least 18 % at 1000 cm^{-1} for both ZnSe prism plates. (When using optional Germanium prism, the minimum transmission value is 14% for Trough plate and 15% for Flat plate at 1000 cm^{-1} .)

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

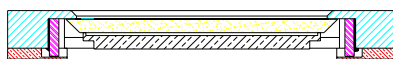
SAMPLING PROCEDURES

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 crystal is located on the base unit by means of two dowel location pins. Two types of mounted crystals are available. The trough plate crystal is used for the analysis of liquids and pastes, while the flat plate crystal is used to analyze soft, pliable films.

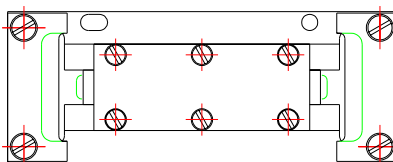
Trough Plate Crystal



Top View



Side Sectional View



Bottom View

The trough 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.

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 the crystal used in the accessory is made from zinc selenide, a fairly brittle material. 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" should be used to remove traces of a previous sample.

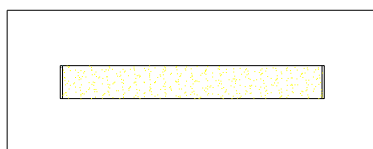
Sometimes "carry over" may occur from one sample to another due to incomplete cleaning of a prior sample from the face of the crystal. This effect may be minimized by "washing" the trough with the new sample, cleaning the crystal and then running a background scan. The sample is then placed on the crystal 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

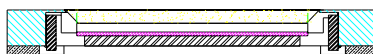
has been made, remove the sample from the crystal and clean the surface of the crystal with a suitable solvent.

Flat Plate Crystal

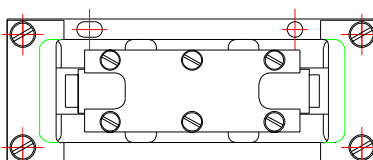
The flat plate crystal assembly is used for measuring soft pliable films. The crystal is positioned so that the top surface of the crystal is slightly higher than the mount.



Top View



Side Sectional View



Bottom View

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, intimate contact has to be made by the sample on the crystal surface. This is achieved by using the flat plate press contained in your kit. Mount the press 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 plate crystal. 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 tamp the surface of the sample to press it into contact with the crystal.

Note that hard powders should never be analyzed by ATR. The hard powder will not make a good contact with the crystal, and may even damage the surface of the crystal. For these samples diffuse reflectance 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 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 HATR trough plate utilizes an indium gasket to seal the crystal to its mount. This sealing mechanism allows some flexibility in this seal 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 than 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 intensity 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.

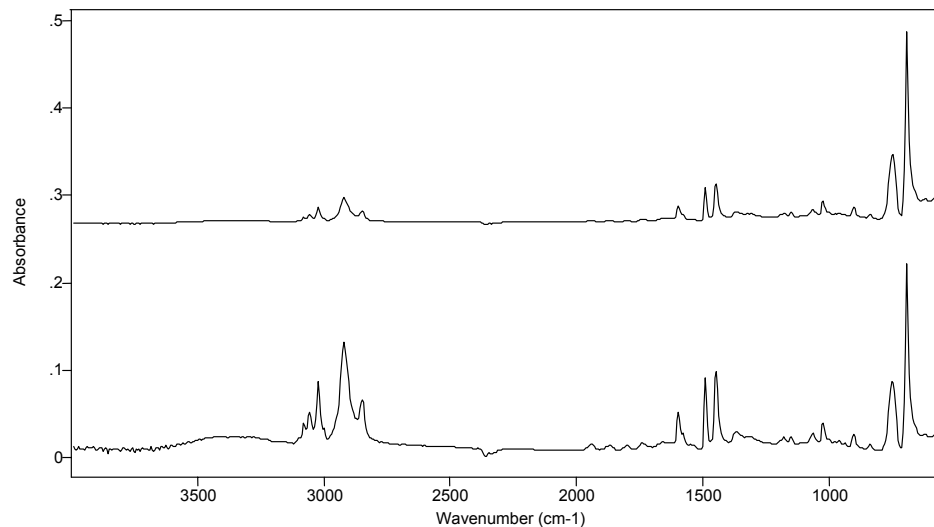
In order to calculate the corrected spectrum, we have to calculate

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

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

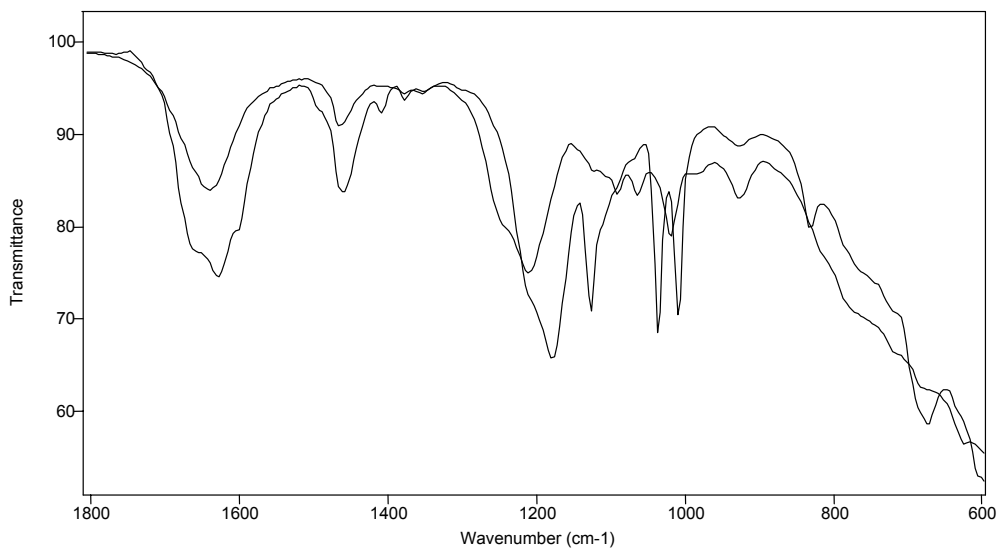
where k is an arbitrary constant.

Below are two stacked spectra of a polymer sample. The bottom spectrum has been processed using the ATR correction software and the top spectrum is the original spectrum.



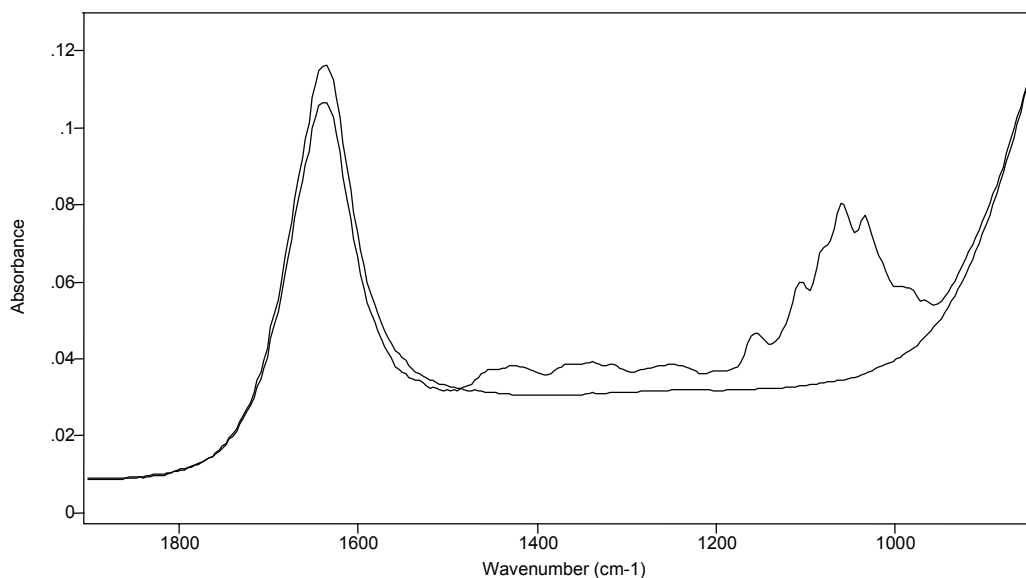
LIQUIDS

Two one minute, four wavenumber resolution spectra were collected using a trough plate crystal. The spectra of dishwashing liquids are overlaid. One of the liquids is alcohol free while the other uses ethyl alcohol as a dispensing aid.



Comparison of liquid detergents

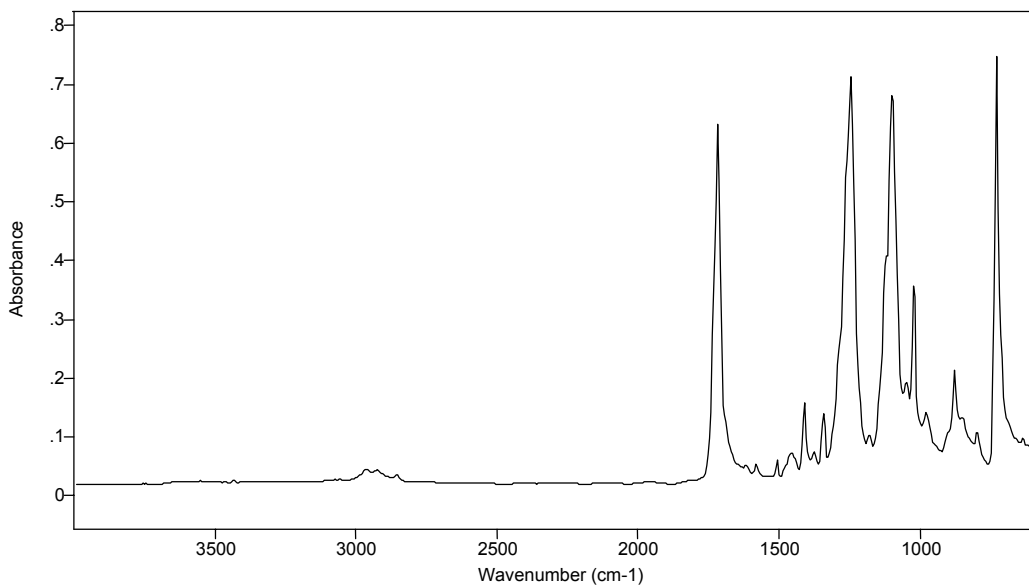
Two one minute, four wavenumber resolution spectra were collected using a trough plate crystal. The samples were a diet and regular soft drink. Differences are readily apparent in the two overlaid spectra shown below.



Comparison of two soft drinks

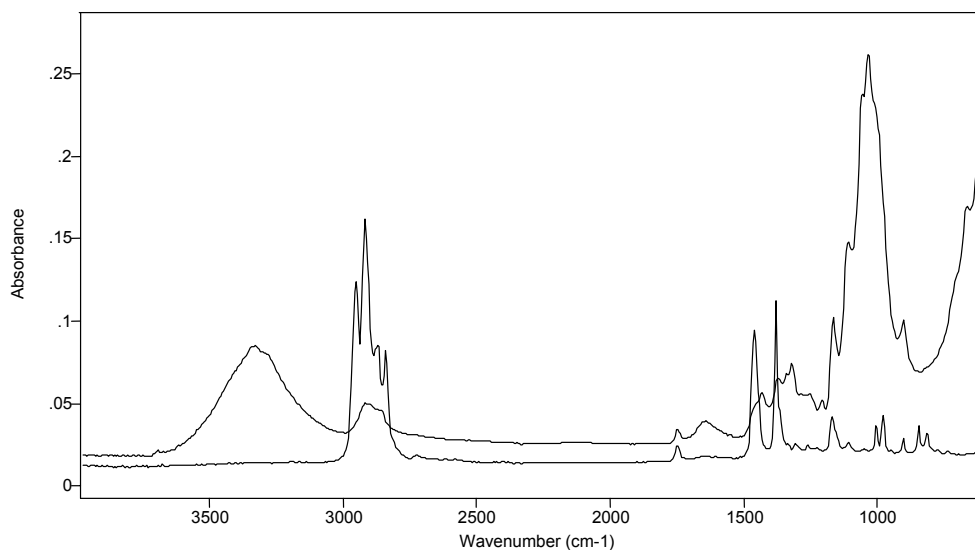
SOLIDS

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



Spectra of food wrapping material

USEFUL EQUATIONS

The angle of incidence is equal to the angle of the beam in the crystal when the incident beam strikes the crystal at normal incidence. At other angles, the effective angle of incidence in the crystal can be calculated. The following formulae may be used to calculate the number of reflections, penetration depth in the sample and effective pathlength.

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 4mm thick and 80mm long. The angle of incidence is 45 degrees.

Substituting these values in the equation:

$$N = \frac{l \cot \Phi}{2t}$$

gives a value of 10 for the number of reflections.

Depth of Penetration

This gives a measure of the intensity of the resulting spectrum.

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

Below is a table giving depth of penetration in microns as a function of material and angle of incidence. The penetration depth is calculated for a sample with a refractive index of 1.40 at 1000 cm⁻¹

MATERIAL	REFRACTIVE INDEX	30 DEGREES	45 DEGREES	60 DEGREES
ZnSe	2.4		1.66	1.04
Ge	4.0	1.11	0.65	0.50

Effective Pathlength

This is the product of the number of reflections and the depth of penetration.

Nomenclature

Φ	= Effective angle of incidence.
n_c	= Refractive index of crystal.
n_s	= Refractive angle of sample.
l	= Length of crystal.
t	= Thickness of crystal.
λ	= Wavelength.

MATERIALS

The following materials are available. Others are available to special order.

MATERIAL	REFRACTIVE INDEX AT 1000 CM ⁻¹	SPECTRAL RANGE (CM ⁻¹)
Zinc Selenide	2.4	20,000-650
Germanium	4.0	5,500-870

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 polycrystalline material is superior.

Although a general purpose material, it has limited use with strong acids and alkalis: 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.

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.

SAFETY

Caution

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 PARTS LIST

The following maintenance parts are available:

Refurbished Crystal Plate Assemblies

PART NUMBER	Description
022-2110-45	HATR Trough Plate ZnSe 45°
022-2120-45	HATR Flat Plate ZnSe 45°
022-2150-45	HATR Trough Plate Ge 45°
022-2160-45	HATR Flat Plate Ge 45°

Other Items

022-1915	HATR, Base Assembly (w/o crystal plate)
022-3050	HATR Flat Plate Press
022-3051	HATR Volatiles Cover
022-3052	HATR Powder Press