PIKE TECHNOLOGIES
Spectroscopic Creativity

Installation and User Guide

VeeMAX™ III Variable Angle Specular Reflectance Accessory

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VeeMAX™ III Variable Angle Specular Reflectance Accessory

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Introduction

The PIKE Technologies VeeMAX™ III is a high throughput, variable angle specular reflectance accessory designed for use in FTIR spectrometers. The VeeMAX III employs a unique optical design (US Patent 5,106,196) which enables samples to be analyzed in the specular reflectance sampling mode over a range of incident angles from 30° to 80°. The angle of incidence is conveniently selected by rotating the positioning wheel on the accessory or with the optional automation version, via PIKE AutoPRO™ software. The VeeMAX III may also be fitted with optional single reflection ATR crystals – ideal for depth profiling studies or monolayer analysis.

The optical diagram of the VeeMAX III is shown below in Figure 1. The infrared beam from the spectrometer is reflected from two beam steering mirrors to a parabolic optic which collimates the beam and sends it upwards to the vertical adjustable mirror. The beam is then directed to the large parabolic mirror. Since this beam is collimated, the parabola produces a focused spot at the sample position. As the sliding mirror assembly is moved, the angle of incidence of the beam is varied at the sample. The reflected beam is passed through an identical set of optics to the instrument detector.

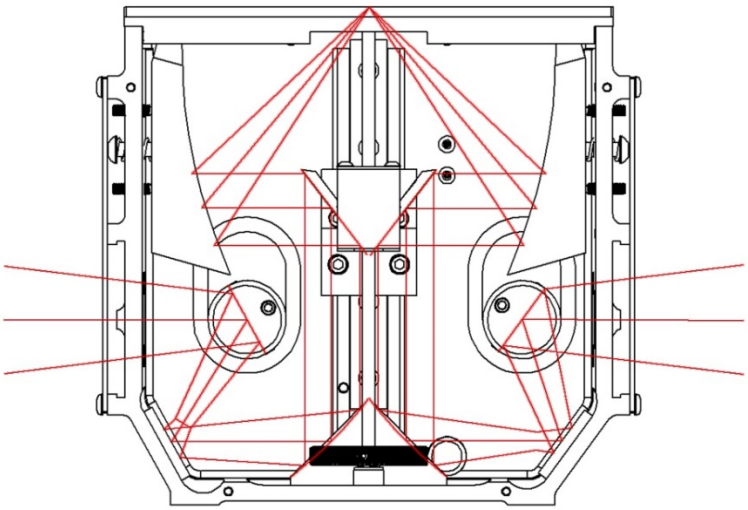


Figure 1. VeeMAX III optical diagram

In the specular reflectance sampling mode a sample is placed face downwards on the sample platform for analysis. Since the sample position is external to the accessory, large and bulky samples may be analyzed easily. A set of sample masks is included with the VeeMAX III to define smaller sampling dimensions. Internal polarizer mounts (left and right side) are provided to obtain enhanced results when performing the analysis of thin films at grazing angles or when it is necessary to collect polarized spectral data.

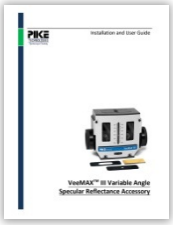
When used with the optional VeeMAX ATR crystals, the accessory provides the ability to do single-reflection, variable-angle ATR spectroscopy. The effective angle of incidence may be calculated from the set angle, the refractive index of the crystal and the face angle of the crystal. Detail of this is further discussed in subsequent pages of this manual.

Unpacking Your Accessory

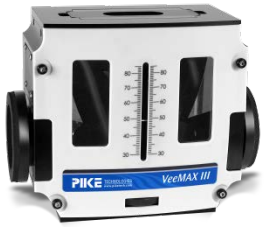
In order for you to quickly verify receipt of your accessory, we have included a packing list. Please inspect the package carefully. Call PIKE Technologies immediately if any discrepancies are found.

Packing List

VeeMAX III Manual
PN 350-001311
Quantity 1



VeeMAX III Base Unit
PN 013-11XX
Quantity 1



Mask Set
PN 013-3010
Quantity 1

Wrench Set
Quantity 1

Sooting Candles
PN 198-1002
Quantity 2

Alignment Mirror
PN 300-0002
Quantity 1

Purge Sponge Rings

Specular Insert
Quantity 1

Purge Tube Kit
Quantity 1

Installation

The accessory fits into the sample compartment of the spectrometer. Depending upon the model of your FTIR, the VeeMAX III will either be pin-mounted into the baseplate in the FTIR, or it will mount onto a removable baseplate which then fits into your FTIR. Either a baseplate will already be attached to the VeeMAX III or you will attach the VeeMAX III to the baseplate included with your new accessory. In all cases there will be pin locators or screw locators to position the VeeMAX III precisely on the baseplate of your FTIR.

The baseplate may be attached to the VeeMAX III prior to shipping. If your accessory has the Baseplate Position Screw located at the back of the accessory, push down and tighten it into the tapped hole in the baseplate of the instrument sample compartment or onto the FTIR baseplate included with your VeeMAX III accessory.

The accessory includes purge tubes which fit against the sample compartment walls of the spectrometer. It may be necessary to adjust the purge tubes on the accessory so that they touch the sample compartment walls in order to ensure a good seal. A barb-type purge fitting located on the back of the accessory is provided on the accessory to further purge the accessory if required.

Alignment of the VeeMAX III for Specular Reflectance

The accessory has been aligned and tested at the PIKE Technologies factory to ensure that it performs to specification. It is recommended that you optimize the alignment further on your instrument upon receipt of the accessory.

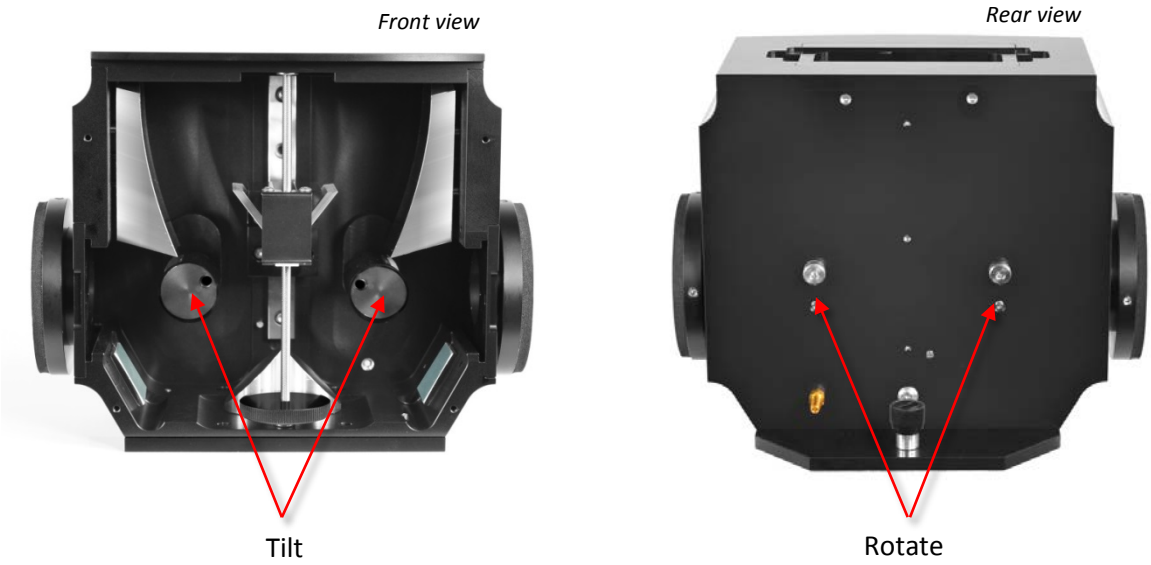


Figure 2. Location of alignment mirrors on the VeeMAX III

Once it has been aligned to your instrument, it will remain stable and usable without further adjustment. The input and output mirrors on the VeeMAX III are adjusted to maximize performance in your spectrometer – do not adjust any other mirrors within the accessory. Depending upon your FTIR spectrometer model and whether the IR beam travels from right to left or left to right within the sample compartment, the input mirror shown in Figure 2 may be the output mirror on your instrument.

The alignment procedure is identical regardless of the direction of travel of the IR beam and is as follows:

1. Set the reflectance angle of the VeeMAX III accessory to 50°.

2. Mount the accessory into the sample compartment. Remove the molded cover from the front of the accessory.

3. Compare your accessory with Figure 2 on the previous page and locate the tilt and rotation adjustments. The tilt adjustment located on the front side needs a 3/32 hex wrench while the rotation adjustment located on the back side requires a 1/8 hex wrench.

4. Install the 5/8" sample mask into the specular insert on the upper surface of the VeeMAX III accessory and place the alignment mirror on the sample surface of the accessory.

5. In the FTIR software alignment mode, check the signal throughput of the spectrometer with the accessory in place. The spectrometer should be set for 4 cm^{-1} spectral resolution and have its J-stop (aperture) set for this spectral resolution. Set the electronic gain to a fixed value of 1 for sample and background spectrum. For testing purposes, we recommend a one minute data collection time using the DLaTGS detector.

6. Using the wrenches provided, adjust the rotation of the input mirror to maximize the signal.

7. Adjust the rotation of the output mirror to maximize the signal.

8. Adjust the tilt of the input mirror to maximize the signal.

9. Adjust the tilt of the output mirror to maximize the signal.

10. Repeat the above four steps until the signal no longer increases. Replace the front cover.

11. Remove the VeeMAX III from the sample compartment of the FTIR and collect an open beam background spectrum.

12. Re-install the VeeMAX III accessory set at 50° angle of incidence with the 2” sample mask and gold alignment mirror on top of the mask and collect a sample spectrum. The ratioed spectrum will appear similar to the spectrum shown in Figure 3. Place the spectrum cursor over the spectrum at 1000 cm^{-1}. The measured value at this position should be greater than 40%. In the spectrum shown in Figure 3 the value is 58%.

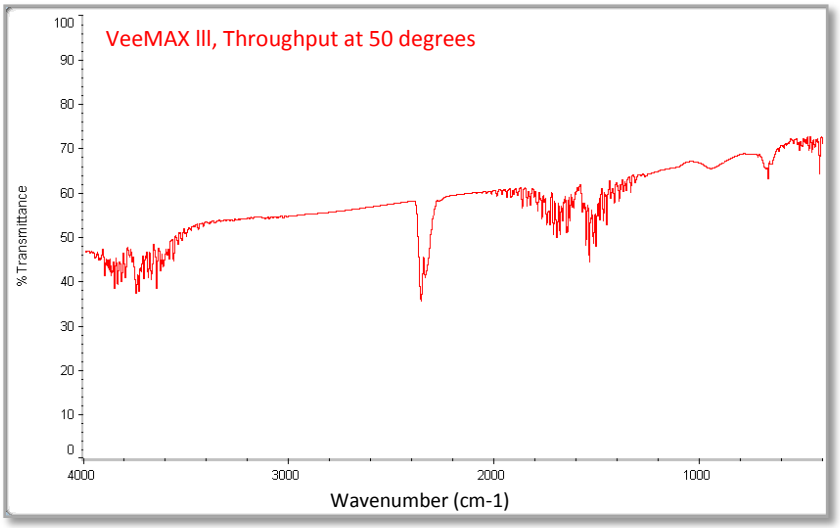


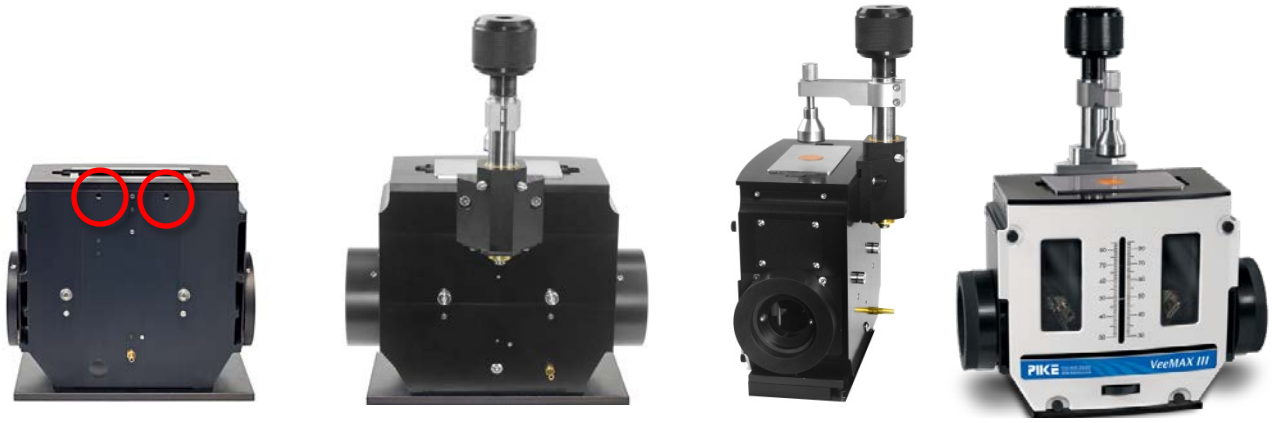
Figure 3. Throughput spectrum for VeeMAX III at 50° angle of incidence

13. Install the optional polarizer into the polarizer slot (left or right side) on the body if required for your application. Use a coin to pry off the polarizer cover to access the slot. Set the polarizer to the desired angle of polarization; from 0° to 360°. For a PIKE Technologies polarizer, when the polarizer is set to 0° the grid lines run parallel to the width of the polarizer mount and the transmitted IR radiation will be perpendicular to this (s polarization relative to the sample measured on the VeeMAX III). When the PIKE Technologies polarizer is set to 90° the grid lines run parallel to the length of the polarizer mount and the transmitted IR radiation will be perpendicular to this (p polarization relative to the sample measured on the VeeMAX III).

Note: Installation of the Manual Polarizer is illustrated below. Refer to separate manual for Automated Polarizer installation.

Polarizer Slot Polarizer Slot

14. To install the optional clamp for ATR applications, secure the clamp to the back side of the accessory using two (2) 10-32 x 1/2” socket screws.



Notes about the alignment of the VeeMAX III for specular reflectance: Throughput will vary depending upon the set angle of incidence. For general information, the maximum throughput of the VeeMAX III will occur at a set angle of incidence of about 45° to 50° and declines to less than 15% throughput at extreme set angles of 30° and 80°. The theoretical beam dimensions at higher angles of incidence become increasingly elliptical in shape (see Table 1).

VeeMAX lll Beam Size on Sample

Table 1. Theoretical beam sizes for VeeMAX III at various set angles of incidence

Angle of Incidence	X Width inches	X Width mm	Y Width inches	Y Width mm
30°	0.542	13.8	0.631	16.1
35°	0.508	12.9	0.626	15.9
40°	0.479	12.2	0.632	16.1
45°	0.454	11.6	0.649	16.5
50°	0.432	11.0	0.681	17.3
55°	0.414	10.5	0.732	18.6
60°	0.398	10.1	0.810	20.6
65°	0.383	9.8	0.931	23.7
70°	0.371	9.4	1.132	28.8
75°	0.359	9.1	1.520	38.7
80°	0.347	8.8	2.606	66.3

Assumptions:

- J-Stop set for 4 cm^{-1} spectral resolution
- Theoretical values, affected by alignment

Alignment of the VeeMAX III for Optional ATR Crystals

1. Align the VeeMAX III for specular reflectance measurements as previously described.

2. Set the reflectance angle of the VeeMAX III to match the face angle of the ATR crystal. For example if the face angle of the ATR crystal is 45°, set the reflectance angle of the VeeMAX III to 45°.

3. For ATR measurements replace the specular insert with the ATR crystal plate.

4. Adjust the rotation of the input mirror to maximize the signal throughput of the FTIR. Assuming that you have previously aligned the VeeMAX III for specular reflectance, this is the only adjustment required.

5. Remove the VeeMAX III accessory from the FTIR and collect an open beam background spectrum.

6. Reinstall the accessory with the ATR crystal and collect a sample spectrum. The throughput spectrum will appear similar to the data shown in Figure 4.

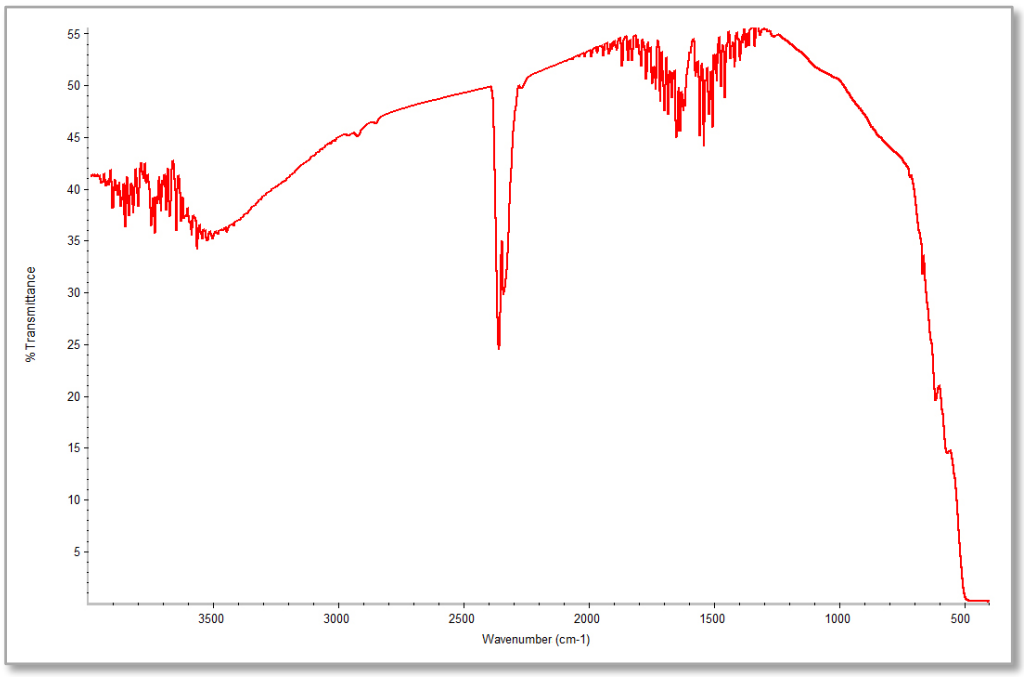


Figure 4. Throughput of VeeMAX III at set angle of 45° with 45° ZnSe crystal

Notes about the alignment of the VeeMAX III for optional ATR crystals: Throughput for ATR crystals will vary depending upon the set angle of incidence and the face angle of the ATR crystal. Generally speaking the throughput of the ATR crystal will be at its maximum and will decrease as we change the set angle to larger differences between the ATR face angle and VeeMAX III set angle. Typical throughputs range from 20% to 40% of the open beam of the FTIR.

Sampling Procedures

For specular reflectance, a set of three masks is available to limit the size of the beam striking the sample. The elongated mask also included optimizes throughput and sampling area when operating high angles of incidence or at grazing angles. To use masks, put the specular insert on the VeeMAX III top and place the mask on the insert. Background and sample spectra are collected at each set angle of incidence and with the chosen mask. Background spectra are collected using the gold-coated slide included with this accessory.

The masks include three different sized apertures: 3/8”, 5/8”, and 2”. The masks have a machined surface on the underneath side, which should be placed downward for sampling. When testing at a high angle of incidence, the beam may reflect off of the bottom of the mask creating a sinusoidal feature in the spectrum especially when using the smaller aperture masks. To eliminate mask reflections, a candle is provided for producing a non-reflective coating on the underneath side of the mask if required. To coat the mask, hold the mask with pliers and wave a lit candle across the underneath side. A sooty non-reflecting material will materialize. If your instrument has an adjustable aperture, reducing the size of the aperture to match the mask will reduce stray reflections.

Measuring Thin Films on Reflective Surfaces

These measurements are generally done within the range of 30° to 60° angle of incidence and are relatively straightforward. A sample mask is selected appropriate for the sample and then background and sample spectra are collected at each angle of incidence.

With the VeeMAX III you can optimize specular reflectance measurements by selecting optimal angle of incidence and making these measurements with or without polarization. In Figure 5 we show the spectral data for the measurement of a multi-layered coating on metal at various angles of incidence.

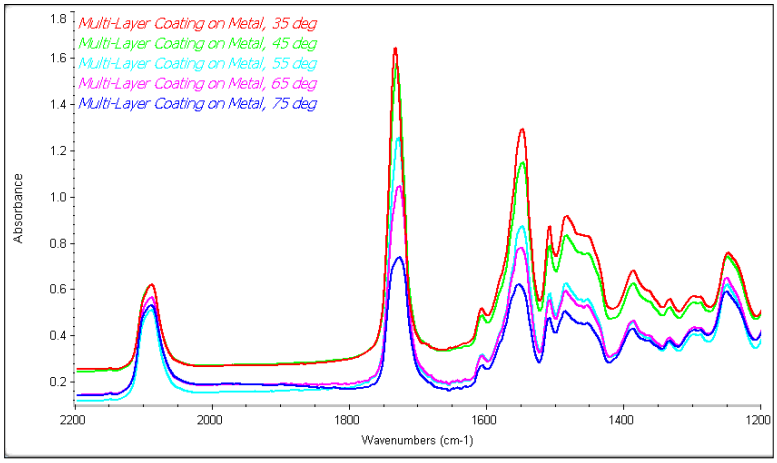


Figure 5. Analysis of Multi-Layered Coating on Metal using the VeeMAX III

Analysis of Monomolecular Layers on Reflective Surfaces

Advantage can be taken of the enhanced absorbance of infrared energy at a large angle of incidence - a grazing angle. The theory of the grazing angle effect was explained by R.G.Greenler in his paper titled "Infrared Study of Adsorbed Molecules on Metal Surfaces by Reflection Techniques" (J. Chem. Phys., 44, 10 (1966)). In this paper Greenler discusses the interaction of infrared energy at a metal surface. If this energy is polarized so that the electric vector is perpendicular to the surface of the sample (p polarization), and strikes the sample at a grazing incidence, the interaction of this energy with the metal surface (and any thin surface film deposited on this surface) is greatly enhanced. The enhancement is a function of the angle of incidence of the impinging IR energy, being greatest at incidence angles close to 90°. This effect is illustrated in Figure 6 which shows two spectra of an identical thin film measured at an 80° angle of incidence, with and without a polarizer.

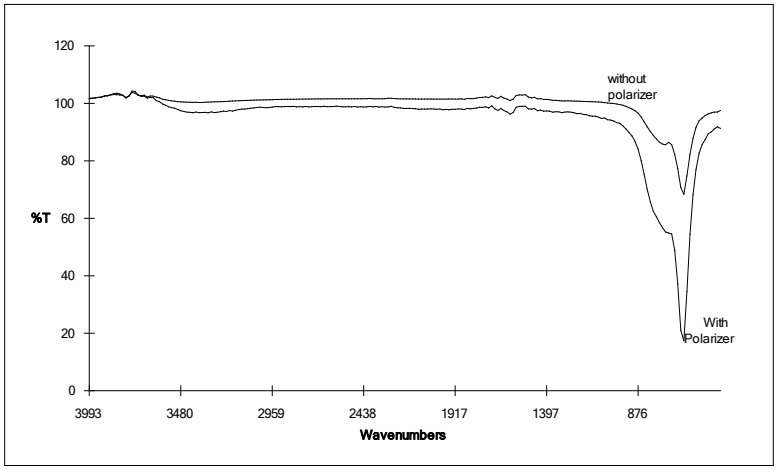


Figure 6. Effect of using a polarizer when measuring a thin film on a metallic substrate

Analysis of Relatively Thick Samples by Specular Reflectance

For relatively thick samples, the specular reflectance experiment produces results which require additional considerations as the specular component of the total reflected radiation is relatively high. At wavelengths where the sample exhibits a strong IR absorption, the reflectivity of the sample increases. The superposition of the extinction coefficient spectrum with the refractive index dispersion results in a spectrum with derivative shaped bands. This specular reflection spectrum can be transformed using a Kramers-Kronig conversion to a transmission-like spectrum as shown in Figure 7.

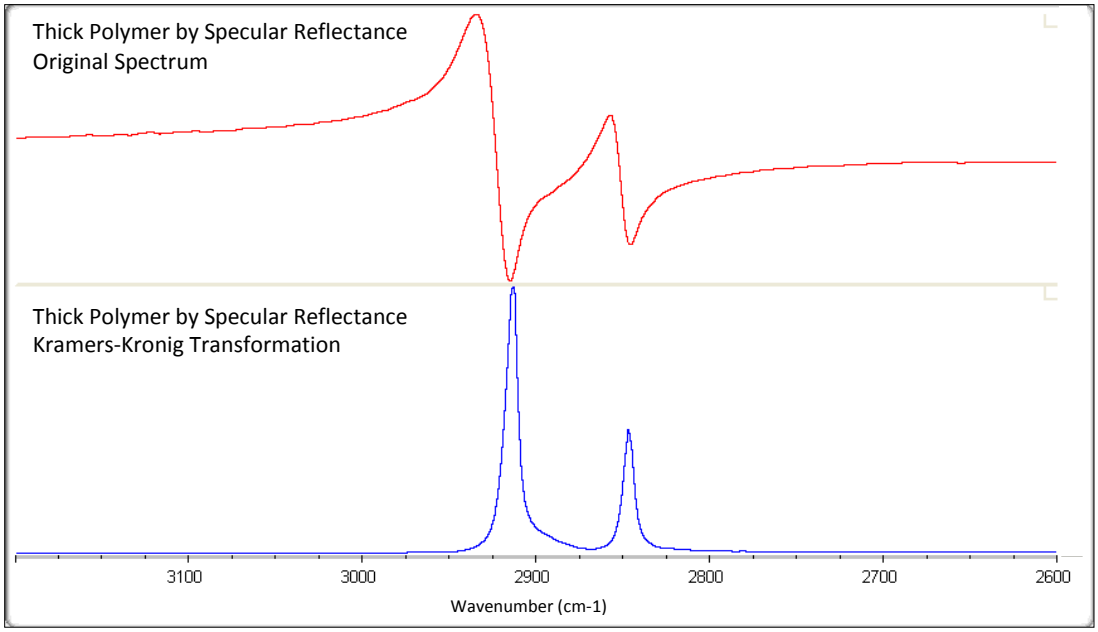


Figure 7. Spectrum (upper – original) of a thick polymer sample measured at 30° angle of incidence using the VeeMAX III. The lower spectrum has been transformed using the Kramers-Kronig software algorithm and is very similar to a transmission spectrum of the polymer – polyethylene.

Analysis of Relatively Thick Samples at Brewster's Angle

At Brewster's angle p polarized light is not reflected except where an IR absorbance occurs. Brewster's angle in specular reflectance may be represented by the following equation:

$\theta_B = \tan^{-1}(n)$

In this equation, θ_B is known as the Brewster's angle and n is the refractive index of the sample. For the typical polymer sample, the Brewster's angle will be about 58°.

The reflection spectrum from the Brewster's angle measurement is relatively weak; however, it does not exhibit the dispersion of a simple specular reflectance measurement. The Brewster's Angle measurement is done conveniently using the VeeMAX III with an IR polarizer.

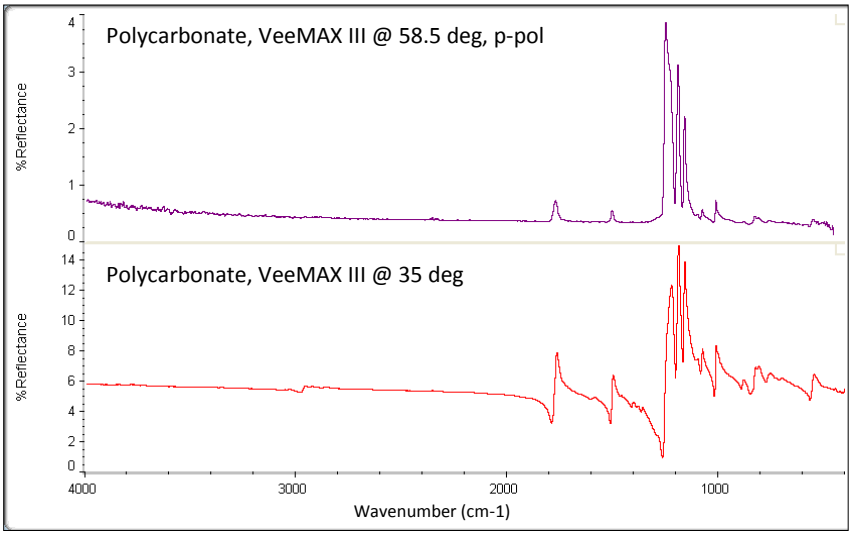


Figure 8. Upper spectrum is Brewster's Angle Spectrum of Polycarbonate. Lower spectrum is specular reflectance spectrum of the same sample.

The results of an analysis of a sheet of 2.8 mm thick polycarbonate using the VeeMAX III are shown in Figure 8. The top spectrum is measured at Brewster's angle; 58.5° angle of incidence and p polarization and shows well-defined reflection bands with no spectral distortions. The lower spectrum is measured at 35° and without polarization. This spectrum exhibits dispersion at all absorbance bands as expected.

Variable Angle ATR Sampling with the VeeMAX III

The VeeMAX III with optional ATR crystals is designed for depth profiling studies. By selecting an appropriate ATR crystal material and adjusting the set angle of the VeeMAX III you can control depth of penetration of the IR beam into the samples. Typical applications for this include analysis of skin layers, determination of the thickness of surface layers on polymer films and the study of coatings on materials. The VeeMAX III ATR crystals are available in different crystal face angles to provide a wide range in effective angles of incidence for the depth profiling experiment.

The effective angle of incidence for the measurement may be calculated as follows:

$$\theta_e = \theta_f + \sin^{-1}(\sin(\theta_s - \theta_f) / n_1)$$

Where θ_e is the effective angle of incidence, θ_f is the face angle of the crystal, θ_s is the set angle of the VeeMAX III and n_1 is the refractive index of the crystal. Effective angle of incidence is conveniently calculated by using PIKECalc software (PN 007-0300). As a point of reference, Table 2 shows calculated values of effective angle of incidence for ZnSe and Ge crystals with 45° face angles.

Table 2. Calculated values of effective angle of incidence for ZnSe and Ge crystals with 45° face angles.

ZnSe Crystal, 45°	
Set Angle	**Effective Angle**
35°	40.9
40°	42.9
45°	45.0
50°	47.1
55°	49.2

Ge Crystal, 45°	
Set Angle	**Effective Angle**
35°	42.5
40°	43.8
45°	45.0
50°	46.3
55°	47.5

Running samples with the VeeMAX III with optional ATR crystals is relatively straightforward. The sample is placed face down onto the ATR crystal and pressure is applied via the high pressure clamp for the VeeMAX III. As the set angle is adjusted to lower angles, the IR beam penetrates more deeply into the sample. Depth of penetration in ATR may be calculated via the following equation:

$$d_p = \frac{\lambda}{2\pi(n_1^2 \sin^2\theta - n_2^2)^{1/2}}$$

where λ is the wavelength of light, n_1 is the refractive index of the crystal, n_2 is the refractive index of the sample and θ is the effective angle of incidence.

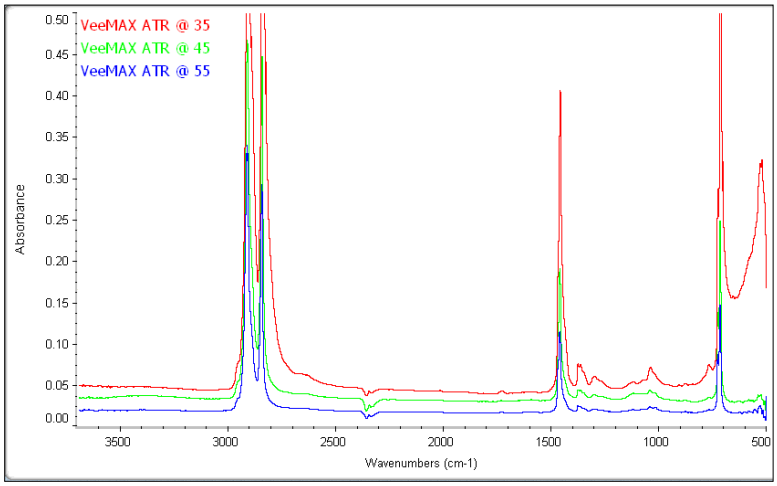


Figure 9. Depth profiling spectral data for a multi-layered polymer sample measured using the VeeMAX III with 45° ZnSe crystal and p-polarization.

This phenomenon is demonstrated in Figure 9 for the analysis of a multilayered polymer material. It is readily apparent from these data that the absorbance of the surface layer of the sample increases as we decrease the angle of incidence of the experiment. It is also readily apparent that at 35° set angle; new IR absorbance bands appear between 1500 and 500 cm^{-1} presumably from a base layer of the sample.

Precautions

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 swept with a 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.

Replacement Parts and Options

The following parts and options may be ordered for the VeeMAX III accessory.

Part Number	Description
013-4010	VeeMAX III Sample Masks (2”, 5/8”and 3/8”)
300-0002	Gold Substrate Alignment Mirror (1.25” x 3.0”)
013-4021	Flat Plate, ZnSe, 45°
013-4031	Flat Plate, ZnSe, 60°
013-4041	Flat Plate, Ge, 45°
013-4051	Flat Plate, Ge, 60°
013-4061	Flat Plate, Ge, 65°
013-3401	Liquid Retainer for VeeMAX III ATR Crystals
013-3101	VeeMAX III ATR Pressure Clamp
090-1000	Manual Polarizer, ZnSe
090-1200	Manual Polarizer, KRS-5

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