

## Performance and Application Comparisons for Single and Three Reflection Diamond Crystals for the MIRacle ATR Accessory

### Introduction

Single reflection attenuated total reflection (ATR) accessories have become a leading sampling tool for Fourier transform infrared (FTIR) spectroscopy due to the ease and speed of sampling by this method. Solid, liquid or polymer samples are placed in intimate contact with the ATR crystal, generally with no sample preparation, and the infrared (IR) spectrum is collected. Analysis times of less than 1 minute are typical. The key sampling phenomenon of ATR which enables its ease of analysis is the minimal depth of penetration of the IR beam into the sample.

Further advancement in ATR sampling comes from the optimization of the ATR crystal choice and optical features. Of all ATR crystal materials, diamond provides a unique, long lasting and chemically inert sampling medium and its use grows as users discover the benefits of this material. To optimize the IR absorption by the sample for high concentration and low concentration components, one can make adjustments for angle of incidence of the IR beam, the refractive index of the ATR crystal and the number of reflections of the IR beam at the ATR sampling surface<sup>1</sup>.

The ability to perform a rapid, high quality analysis by FTIR using an ATR accessory is enhanced as a function of the performance of the ATR accessory. This note characterizes the performance of single and three reflection diamond ATR crystal plates using the MIRacle™ ATR accessory. Example applications will also be shown to demonstrate the sampling flexibility of the single and three reflection diamond crystal plates.

### Instrumentation

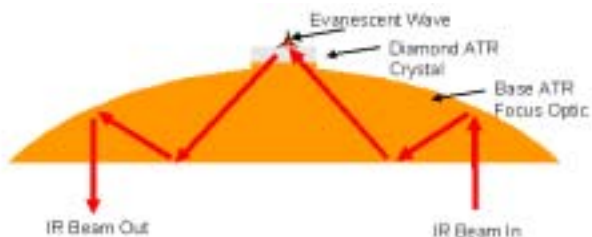
The ATR accessory used for these evaluations is the PIKE Technologies MIRacle, previously described<sup>2</sup>.

Single or three reflection diamond ATR crystal plates (shown in Figure 1) are placed onto the pinned position of the MIRacle ATR accessory.



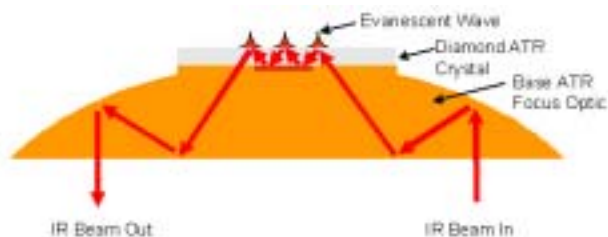
**Figure 1.** Single (right side) and Three Reflection (foreground) Diamond Crystal Plates for the MIRacle ATR Accessory.

Alignment of the MIRacle base optics provides maximum throughput for the specific crystal plate. The MIRacle utilizes a patented optical design where the ATR crystal both focuses the IR beam and also provides the interface for ATR sampling<sup>3</sup>. A graphical representation of the beam path for the single reflection MIRacle ATR is shown in Figure 2. The orange colored sphere represents the zinc selenide base focus optic and the red arrows show the IR beam path. The IR beam is first directed upward from the base accessory optical housing and into the base optic. The IR beam is internally reflected and focused as it passes to the 1.8 mm diameter diamond ATR sampling area at the top and center of the plate. The diamond MIRacle ATR crystals utilize a 0.5 mm thick Type 2A diamond window with IR transparent contact onto the base crystal. With a sample in intimate contact with the diamond ATR crystal, an evanescent wave projects into the sample. Absorption of quanta of the IR beam provides an infrared spectrum.



**Figure 2.** Optical Graphic Showing the IR Beam Path within the MIRacle Single Reflection Diamond ATR Crystal.

The optical beam path of the three reflection diamond ATR crystal plate is similar, except that a narrow reflective strip is placed between the base focus optic and the 6.0 mm diameter diamond sampling plate to provide the additional internal reflections. This optical beam path is shown in Figure 3.



**Figure 3.** Optical Graphic Showing the IR Beam Path within the MIRacle Three Reflection Diamond ATR Crystal.

The three reflections at the surface of the ATR crystal would provide a theoretical multiple of 3 times increase in sample absorbance relative to the single reflection ATR crystal if all other optical dimensions are the same.

### Measurement Parameters

All spectra were collected at 4 cm<sup>-1</sup> spectral resolution using a 1 minute data collection time. Liquid samples were applied onto the full diameter of the diamond ATR crystal. Solid samples were placed onto the diamond ATR crystal and the high pressure clamp was turned to its slip-clutch limit to achieve maximum pressure. The extent of solid sample pressure is related to the crystal and pres

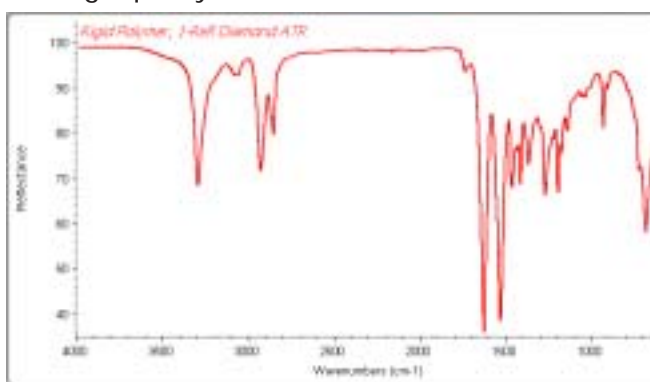
	Lbs Pressure	Crystal Diameter, mm	PSI
High Pressure Clamps	40	1.8	10,141
		6.0	913
Micrometer Pressure Clamp	8	1.8	2,028
		6.0	183

**Table 1.** ATR Solid Sample Pressure for Single and Three-Reflection ATR Crystals.

sure tip diameters. Sample pressure using the high pressure and micrometer pressure clamp choices for the MIRacle is as shown in Table 1.

For samples with an irregular surface, high pressure is critical to deform the sample into intimate contact with the full surface of the ATR crystal. Sufficient pressure necessary to deform a rigid sample is only possible with the single reflection ATR due to its high pressure per square inch.

Figure 4 shows the ATR spectrum for a rigid polymer collected using the single reflection diamond ATR crystal of the MIRacle accessory and over 10,000 psi. Full and intimate contact of the sample onto onto the ATR crystal is essential to achieve this high quality result.

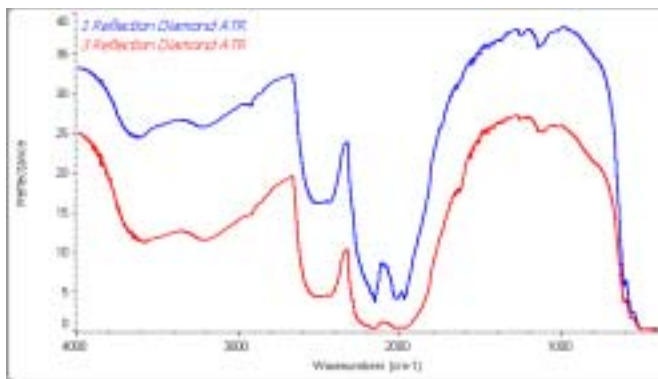


**Figure 4.** Spectrum of Rigid Polymer Sample using High Pressure.

### Performance Comparisons

One of the most important performance features of a FTIR accessory is its optical throughput. High optical throughput provides the highest signal-to-noise ratio (SNR) in the final spectrum and also minimizes required sampling time. Optical throughput can be measured from the ratio of the IR beam energy through the accessory relative to the IR beam energy without the accessory installed. The PIKE MIRacle ATR accessory with diamond single reflection crystal is a high throughput design – typically 40% or greater (shown in Figure 5). The three reflection version of the plate has a somewhat lower throughput compared to the single reflection crystal plate due to required optical masking of the IR beam into the ATR crystal, however, it still offers the highest throughput in the industry for a multi-reflection ATR.

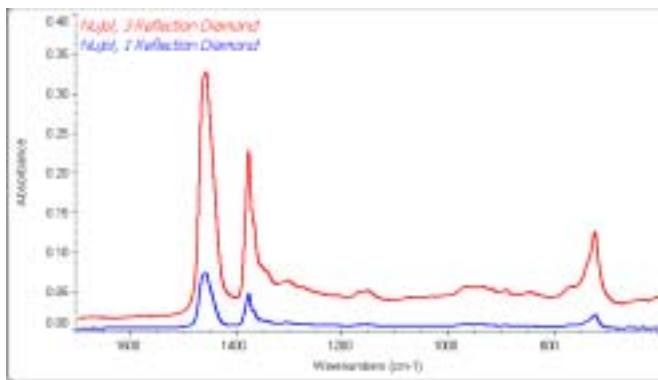
The three reflection crystal plate provides benefit for measurement of low concentration components of a liquid or solid samples.



**Figure 5.** Throughput Comparison for Single and Three Reflection Diamond Crystal Plates for the MIRacle.

The theoretical increase in sample absorbance (with all other ATR sampling parameters equivalent) is equal to the multiple of the effective pathlength and the number of reflections of the IR beam from the ATR sampling surface.

Figure 6 shows the results for the measurement of Nujol® (mineral oil) liquid using the single and three reflection diamond ATR crystal plates. The use of a liquid sample for this comparison ensures complete sample – ATR crystal contact, thus eliminating any sampling pressure effects.



**Figure 6.** Sample Absorbance Comparison Using Single (lower, blue) and Three Reflection (upper, red) Diamond ATR Crystal Plates for MIRacle.

The three reflection spectrum of Nujol clearly demonstrates stronger absorbance than the single reflection spectrum. Corrected peak heights for the 1458 cm<sup>-1</sup> band of Nujol for these 2 spectra are shown in Table 2.

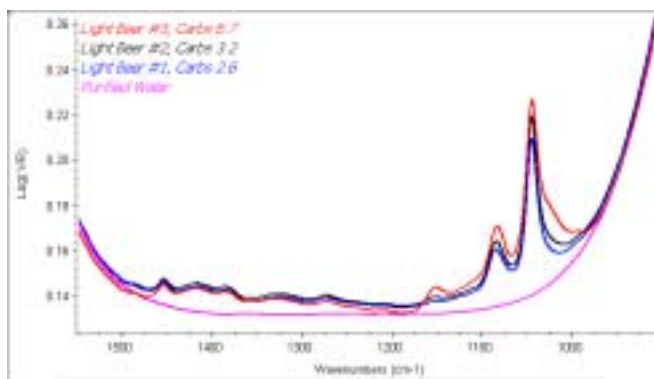
The factor increase of the three reflection crystal plate vs. the single reflection crystal plate is 4.48 – well above the expected factor of 3.0. This difference between observed and expected factors is

	Peak Height, abs. units
3 Reflection Crystal	0.309
1 Reflection Crystal	0.069

**Table 2.** Sample Absorbance for Three Reflection and Single Reflection Diamond ATR crystals.

due to the lower angle of incidence of the IR beam in the three reflection crystal plate required by the wider ATR crystal diameter. This lower angle of incidence provides a greater depth of penetration and thus higher than predicted absorbance.

The higher absorbance provided by the three reflection diamond ATR crystal is useful for many applications, including liquid samples with low concentration components. A good example of this is the analysis of carbohydrate content of light beer samples. Carbohydrate content of these samples is typically at weight concentrations of about 1% and less. Light beer samples from 3 different manufacturers and purified, bottled drinking water (shown in Figure 7) were analyzed using the three reflection diamond crystal plate on the MIRacle ATR accessory. All samples were analyzed by placing about 500 microliters of the liquid onto the ATR crystal. This sample volume is sufficient to cover the full diameter of the ATR crystal and ensure a constant pathlength.



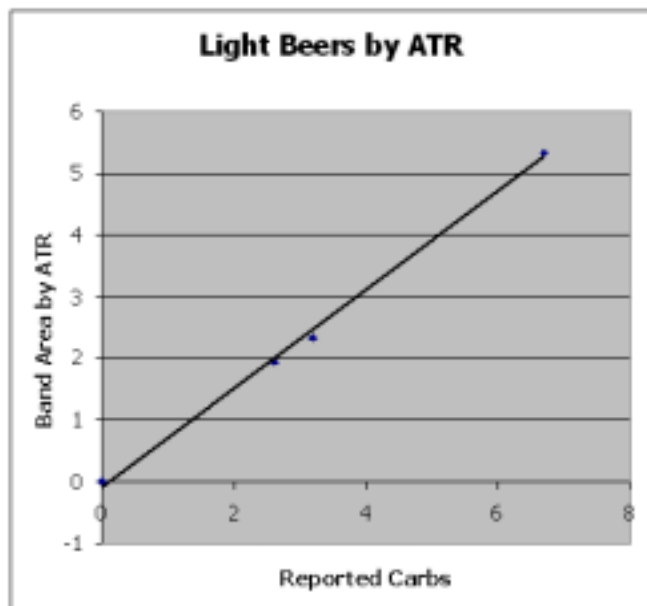
**Figure 7.** ATR spectra for Light Beers and Purified Water.

Band area calculations were made for each of the samples within the region of 1218 – 817 cm<sup>-1</sup> after performing a subtraction of the water reference spectrum. The calculated results are shown in Table 3 and a plot of band area vs. reported carbohydrate content is shown in Figure 8.

	Reported Carbs	Area, 1218 - 817 cm-1
Light Beer #2	3.2	2.34
Light Beer #1	2.6	1.95
Light Beer #3	6.7	5.32
Purified Water	0	0

**Table 3.** Band Area Results for Light Beer Samples and Purified Water.

This analysis demonstrates a linear relationship for band area vs. carbohydrate content of light beers and suggests the possibilities of using a three reflection diamond ATR accessory for analysis of carbohydrate content in liquid samples.



**Figure 8.** Band Area vs. Reported Carbohydrate Content of Light Beer Samples.

### Summary

The single and three reflection diamond crystal plates for the MIRacle ATR are both high performance products with their unique high throughput, focusing optical design and provide high quality spectra within a minimal sampling time. The three reflection diamond crystal for the MIRacle demonstrates greater than 3 fold increase in IR absorbance compared to the single reflection diamond crystal. The higher absorbance provided by the three reflection diamond crystal plate is useful for the measurement of low concentration components in liquid and pliable samples.

It is important to select the appropriate crystal configuration and composition to maximize spectral quality and minimize sampling time. The single reflection diamond crystal plate is recommended for rigid and irregular samples and for general sample

identification. The three reflection diamond ATR crystal plate is recommended for analysis of liquid or pliable samples with minor components at less than 1% by weight composition.

### References:

1. ATR Theory and Applications. Applications Note - 0401, PIKE Technologies, 2004.
2. MIRacle ATR, Product Data Sheet, PIKE Technologies, 2003.
3. United States Patents; 5,965,889 & 6,128,075. Philip R. Brierley, PIKE Technologies, 1999, 2000.