Technical Note

T5

Multiple Reflection versus Single Reflection ATR Accessories

by Cindy F. Baulsir

Spectra-Tech, Inc. Shelton, CT. 06484

Attenuated total reflectance (ATR) is an ideal technique to study the surface phenomena of a large variety of samples. A number of different ATR accessories are available today. Most are affordable, can accommodate a variety of skill levels, and can analyze samples with different sizes, morphologies, and chemical states. To narrow the choice of accessories, one of the first questions asked should be "do I need a multiple reflection crystal", as in the Baseline Horizontal ATR (HATR), or "do I need a single reflection crystal" as in the Single Bounce accessory? To correctly answer that question, a number of factors must be considered: the volume, area, hardness, pH and the infrared absorbance of the sample.

For liquid samples, an accessory with the optimum effective pathlength will need to be chosen. The depth of penetration, or $dp = \lambda / 2\pi n_1 (\sin^2\theta - n_{21}^2)^{1/2}$, where λ is the wavelength of infrared radiation, n_1 is the refractive index of the ATR crystal, θ is the angle of incidence of the crystal, and n_{21} is the ratio of the refractive indices of the sample and the ATR crystal. The effective pathlength (EP) of an ATRcrystal is approximately equal to the depth of penetration (dp) multiplied by the number of reflections within the ATRcrystal. As you can see, the number of reflections is critical in the calculation of effective pathlength. For all calculations, the Spectra-Tech Baseline HATR has ten reflections, and the Single Bounce has one reflection. So, for a sample with a refractive index of 1.5, and a crystal with a refractive index of 2.4, at 2000 cm-1 (5 micrometers) the effective pathlength would be 9.4 micrometers and 0.94 micrometers, respectively. A shorter pathlength is often desired for strong infrared absorbers (such as aqueous solutions), and when spectral subtractions are performed. With the correct accessory, it is easy to obtain the best quality spectral subtractions and quantitative results. It is highly desired that all quantitative measurements follow Beer's Law, with typical absorbance values between 0.3 and 0.7.

The water spectra obtained with both a Baseline HATR and a Single Bounce accessory can be seen in *Figure 1.* The -OH band centered around 3305 cm-1 for the Single Bounce is approximately 0.32 absorbance units, and 2.57 absorbance units with the Baseline HATR.

The spectrum of another strong infrared absorber, isopropanol, can be seen in *Figure 2.* This spectrum was obtained from a single drop of isopropanol with the Single Bounce accessory. A volatile liquid cover was used to eliminate evaporation.

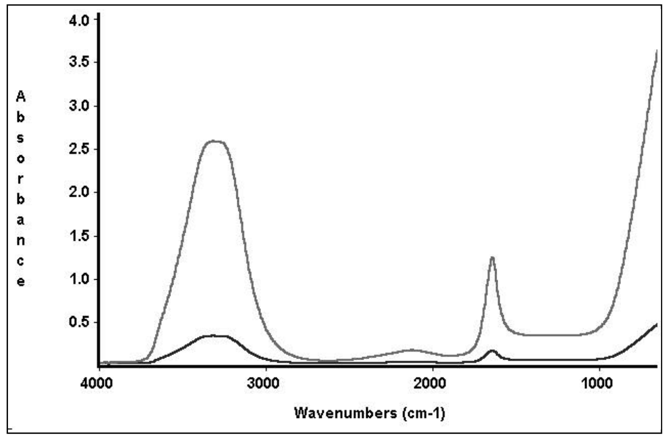

Figure 1: Spectrum of water spectra obtained with both a Baseline HATR and Single Bounce accessories. The -OH band centered around 3305 cm-1 for the Single Bounce is approximately 0.32 absorbance units, and 2.57 absorbance units with the Baseline HATR.

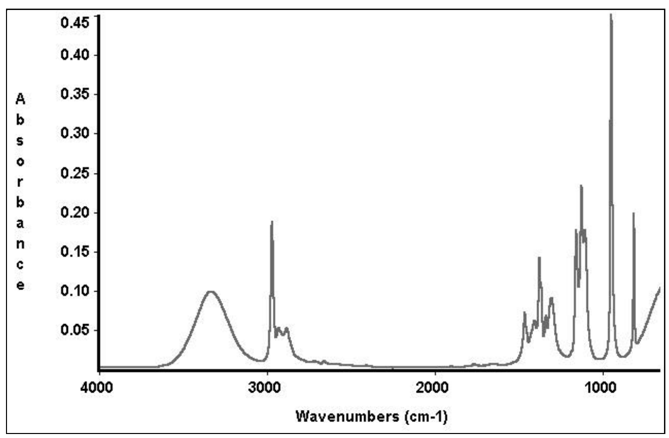

Figure 2: Spectrum of isopropanol obtained from a single drop using the Single-Bounce accessory equipped with the volatile liquid cover.

Higher sensitivity can be achieved with the multiple reflection crystal than with a single reflection crystal, due to the larger effective pathlength of the multiple reflection crystal. There is approximately one order of magnitude difference in sensitivity between the two ATR crystal types. Assuming that the sample is a strong absorber in water (such as acetone in water), the typical detection limit for a multiple reflection crystal is 0.1%, and 1.0% for a single reflection crystal. For low concentration samples, such as additives in solution, either the Baseline HATR or the ARK HATR accessory would be the optimum accessory.

Significantly more liquid is required to cover a multiple reflection crystal than a single reflection crystal. One milliliter of water is needed to cover the surface of a Baseline HATR crystal. Alternatively, only 1-3 drops of water are necessary to cover the active surface of a Single Bounce HATR. Therefore, when you are sample limited, the single reflection ATR would be the better choice. However, even when the sample volume is limited, the multiple reflection crystal can still be used. To analyze small volumes of liquid on a Baseline HATR crystal, it is acceptable to cover the part of the crystal that is closest to the source of the instrument (if the infrared beam is coming from right to left, detector on the left, then you would place your liquid on the right side of the HATR crystal).

For hard, solid samples it is easier to make physical contact with a single reflection ATR crystal. A single reflection crystal has less surface area and the risk of crystal damage is reduced. With hard samples, the greatest risk to a single reflection crystal would be chipping the edges. This occurs when the sample is not placed flat on the crystal and heavy pressure is applied.

There are a number of applications where the risk of crystal damage must be minimized. Germanium is a harder material than the other alternatives such as ZnSe and is less susceptible to chipping and scratching that can result from contacting hard samples. Also, Germanium has a high refractive index and a relatively shallow penetration depth. A shallow penetration depth is useful and in many cases is required for the measurement of highly absorbing or highly scattering samples, for example, carbon-filled rubbers.

The spectra of a carbon filled rubber can be seen in *Figure 3.* The top spectrum was obtained with a 45 degree germanium crystal and a pressure device, with the ARK HATR (which has 12 reflections), the bottom spectrum was obtained with a germanium crystal on the Single Bounce HATR. The spectral features of the rubber obtained with the ARK are very easily discerned. The band intensities are weaker in data collected with the Single Bounce *(Figure 3)*, due to the shorter effective pathlength.

The standard crystal material for the Single Bounce, the ARK, and Baseline HATR is zinc selenide. This material is suitable for samples that have a pH from 5-9. Zinc Selenide has a broad spectral range (4000-650 cm-1) and can be scratched easily with hard samples. Germanium is harder and useful for samples that have a pH from 1-14, but suffers reflection losses due to a high refractive index, and has a short spectral range (4000-800 cm-1). The choice of crystal materials is limited to zinc selenide and germanium for both the Single Bounce and the Baseline HATR, while there are eight choices of materials when using the ARK. With its diverse selection of crystal materials, the ARK would be the choice for hard or soft samples, high or low pHs, and strong or weak absorbers.

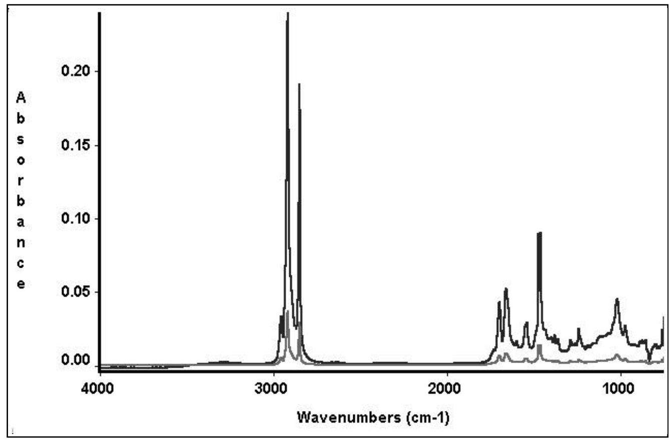

Figure 3: Spectrum of a a carbon filled rubber obtained with a 45 degree germanium crystal, and a pressure device, with the ARK HATR is displayed on top, and the bottom spectrum was obtained with a germanium crystal on the Single Bounce.

Table I summarizes the differences between single reflection and multiple reflection HATR accessories.

Table 1 Single Reflection Versus Multiple Reflection ATR Accessories

Sample/Accessory Characteristic	**Single Reflection**	**Multiple Reflection**
IR Absorber	Strong	Weak
Detection Limit	~1.0% in solution	~0.1% in solution
Sample Volume	1-3 drops	1 milliliter
Effective Pathlength	0.6-2 µm	0.6-45 µm
No. of Crystal Materials	2	8

3/98

Representative Offices in Europe, Asia and Latin America
For the name of the representative in your local area, please contact Spectra-Tech.

A subsidiary of Thermo Optek Corporation;
a Thermo Instrument Systems Company

website: www.spectra-tech.com
e-mail: masterwebber@spectra-tech.com

In USA
Spectra-Tech Inc.
2 Research Drive
P.O. Box 869
Shelton, CT 06484-0869
Tel: 203-926-8998
Toll-free 800-243-9186
FAX: 203-926-8909

In Japan
ST Japan
1-14-10 Kakigara-cho
Nihonbashi, Chuo-ku
Tokyo, 103 Japan
Tel: (033) (666) 2561
FAX: (033) (666) 2658