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Aperture Design for Near Critical Angle FTIR ATR Spectroscopy

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Figure 1. Diaphragm aperture installed in the entrance beam side of the Seagull™.

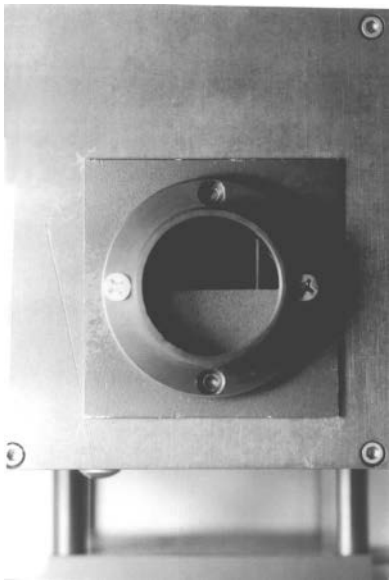

Figure 2. Half-moon aperture installed in the exit beam side of the Seagull™.

OBJECTIVE

The objective of this study is to investigate the effects of geometry changes of apertures on the sensitivity, baseline, and throughput of ATR data acquired near the critical angle.

ABSTRACT

In a previous report,[1] experimental equipment and techniques were discussed that empirically demonstrated the effects of approaching the critical angle in FTIR ATR spectroscopy. Using a variable angle ATR accessory in a modern FTIR spectrometer, it was shown that sensitivity does increase as the critical angle is approached. Contrary to a first order theoretical prediction, however, the increase is limited. Although spectral distortion with certain intense peaks plays a part in this limitation, the chief cause for the apparent discrepancy is the beam spread of the FTIR instrument. This spread is exacerbated by refraction in the ATR element of the accessory. For example, with the reflection angle of the accessory set slightly above the critical angle, almost half of the actual optical rays are below the critical angle. These rays exit the optical system, resulting in an overall increase in the absorbance baseline with no contribution to increased sensitivity. Furthermore, with the same setting, absorbance contributions from rays that are at significantly greater angles than the setting will attenuate those at or near the setting. For this study, a variable aperture in the ATR accessory is used to reduce the beam spread. The effect of decreasing the aperture diameter on sensitivity and throughput will be studied. Similarly, a new "half-moon" aperture, designed to eliminate rays at angles lower than the setting, will be investigated for effects on the baseline and throughput.

EXPERIMENTAL

All spectra were taken with a Thermo/Nicolet Nexus™ 670 FTIR spectrometer equipped with a DTGS detector and a standard mid-IR beamsplitter and using Thermo/Nicolet Omnic™ Version 6.1a software. All spectra were run at 4000cm^{-1} to 400cm^{-1}, 4 cm^{-1} resolution, and a gain equal to 1. Spectra were derived from 64 co-added scans, except where indicated. The spectrometer aperture was set to 100. A background spectrum (air) was taken prior to each sample spectrum, with the exception of the throughput scans taken for all aperture configurations. For these, only

applications note

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one background spectrum (the open beam sample compartment) was used for all sample scans. The purge inputs of the spectrometer and the installed accessory were connected to filtered air (water and CO_2 removed) produced by a Parker Balston Model 75-62 FT-IR Purge Gas Generator at 30 SCFH.

The Harrick Seagull™ variable angle reflection accessory was installed in the sample compartment of the FTIR spectrometer, except where noted. The Seagull™ accessory allows the angle of incidence to be changed continuously from 5° to 85°. The ATR kit was installed in the accessory along with a Luer-compatible liquid cell. All runs were taken using a hemispherical ZnSe ATR element. A Hamilton Model 1002 2.5ml Luer-tipped syringe was used to inject samples into the liquid cell.

All angles were set in the Seagull™ by first moving the angle several degrees lower than the desired angle and then carefully moving the adjustment continuously higher until the desired angle was reached. This was to assure the consistent removal of any backlash.

Spectrophotometric grade Toluene (Alpha Aesar Stock No. 19376) was used as the sample in all tests, except where noted.

Transmission spectra were converted to absorbance spectra using the Omnic™ "Absorb" function. Baseline corrections on the absorbance spectra, where required, were performed using the Omnic™ "Aut Bsln" function. Absorbance peak maxima and associated wavelengths were found using the Omnic™ "Analyze Find Peaks" function. The Harrick CristalCalc™ software was used to calculate some depths of penetration used for the Discussion section.

Two custom apertures were installed in the Seagull™ accessory. An iris diaphragm aperture (Part No. NT41-973; Edmund Optics Inc.; Barrington, NJ) was installed in the entrance beam side of the accessory. See Figure 1. Five precision metal shafts were used to adjust this aperture to exact diameter positions. For the three smaller sizes (4.95mm, 9.93mm, and 14.9mm), the shank ends of three metric drills were used (Part No.'s 029050, 029100, and 016150 Series 2AB Jobber Length Drills; Precision Twist Drill Co.; Crystal Lake, IL). For the two larger sizes (20.0mm and 25.0mm), 7/8" and 1" aluminum rods were machined to the desired sizes. The largest aperture size, with the iris diaphragm fully open, is actually formed by the purge input fitting at 33.0mm.

A half-moon aperture was installed in the exit beam side of the accessory. See Figure 2. The plate used in the half-moon aperture was painted with Sherwin Williams Krylon Semi-Flat Black No. 1613.

RESULTS

In the first experiment, the diaphragm aperture was fully opened (33.0mm diameter). The angle on the Seagull™ was set to 38°. This is the critical angle calculated using 2.4295 as the refractive index of zinc selenide at 2000cm^{-1} and 1.4961 as the refractive index of toluene.[2] Spectra were then taken with and without the half-moon aperture. The results are presented in Figure 3. The spectrum taken with the unapertured equipment has an overall elevation in its baseline of over 0.2 absorbance units. Perhaps more seriously, the same spectrum has a negative distortion preceding the intense peak at 725 cm^{-1} and a positive distortion following the adjacent intense peak at 692 cm^{-1}. These types of distortion are attributed to dispersion. The negative distortion makes baseline correction difficult. Both the negative distortion and the elevated baseline were removed by using the half-moon aperture.

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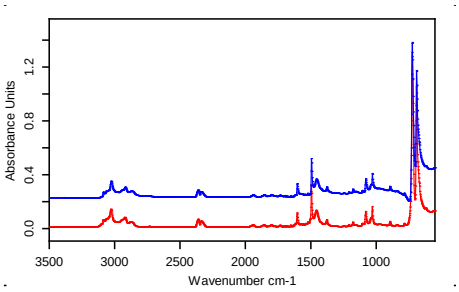

Figure 3. Comparison of toluene spectra at 38° with (red) and without (blue) half-moon aperture.

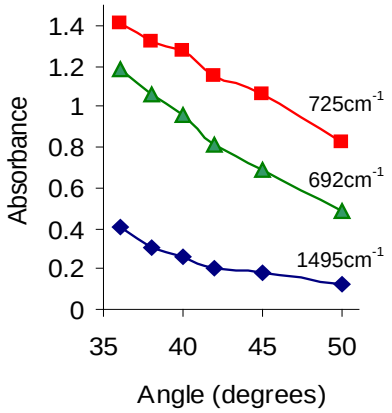

Figure 4. Determination of optimum angle for highest sensitivity.

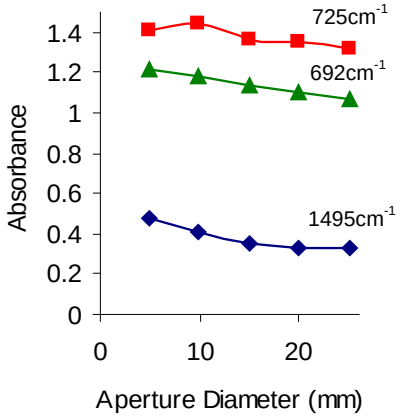

Figure 5. Determination of the optimum aperture for highest sensitivity.

In the second experiment, the half-moon aperture was left in place, the diaphragm aperture was left fully open, and the absorbances at the peaks located at 1495, 725, and 692 cm^{-1} were monitored as the angle was decreased from 50° to 36° (50, 45, 42, 40, 38, and 36 degrees). A summary of the data is presented in Figure 4. A significant increase in sensitivity is observed as the angle is decreased. The spectrum at 36° exhibited negative distortion preceding the 725 cm^{-1} peak, calling the associated baseline corrected absorbance data in question. For this reason, 38° was chosen as the angle for the next experiment.

In the third experiment, the half-moon aperture was left in place, the angle was set to 38°, and the same three peak absorbances were monitored as the diaphragm aperture was decreased from 25.0mm to 4.95mm (25.0, 20.0, 14.9, 9.93, and 4.95mm). Since the noise increased significantly with the 4.95mm aperture, the number of co-added scans was increased from 64 to 256. Figure 5 summarizes the data. A modest increase in sensitivity is observed as the aperture is decreased. The 9.93mm aperture was chosen as the smallest practical size.

DISCUSSION

In ATR spectroscopy, as the angle of incidence is decreased, an increase in sensitivity is expected. However, the beam spread in modern FTIR spectrometers causes some problems as the critical angle is approached and this beam spread is exacerbated by refraction in the high refractive index ATR element material. First, those rays lower than the selected angle that are also lower than the critical angle are lost. This causes an overall decrease in the energy that reaches the detector, resulting in an elevated absorbance baseline. Second, rays higher than the selected angle contribute to a decrease in sensitivity.

Use of the half-moon aperture to eliminate rays lower than the selected angle minimizes absorbance baseline shifts as the selected angle is decreased towards the critical angle. This type of aperture also greatly reduces dispersive negative shifts preceding intense absorbance peaks.

Use of the diaphragm aperture reduces rays higher than the selected angle which contribute to lowered sensitivity. The smaller the diameter of this diaphragm, the higher the sensitivity.

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Lowering the angle, as seen in Figure 4, had a significant effect in increasing the sensitivity. Reducing the aperture had a more modest effect. See Figure 5. The most sensitive, practical configuration was with the half-moon aperture in place, the angle set at 38°, and the diaphragm set at 9.93mm. A comparison of the spectrum obtained with these parameters set in the Seagull™ and one obtained using the fixed 45° angle ZnSe ATR Harrick AccessATR™ is given in Figure 6. Table 1 compares the absorbances of peaks obtained with the two setups. The apertured 38° Seagull™ results are 1.3 to 2.9 times higher than those obtained from the 45° AccessATR™ results. Different peaks have different sensitivity increases, probably due to different localized differences in the refractive indices of the sample near the peak maxima. It can be shown that a greater sensitivity increase will take place at any given wavelength for samples of higher refractive indices. In general, the absorbances of weaker peaks were increased more than those of stronger peaks. No correlation can be seen between sensitivity increases and wavelength. Additional work with alternate samples would be required before making further generalizations. Also of interest, three of the peaks detected by the FTIR software for the 38° results were not found by the same software in the 45° results.

One disadvantage of using apertures to increase sensitivity is that the throughput is simultaneously lowered. Figure 7 plots the throughput at 2600 cm^{-1} versus the aperture area for different diaphragm settings with and without the half-moon aperture. (This wavelength was chosen since it lies in an area that is relatively free of spectral artifacts. The open beam sample compartment was run for the background. The sample was the Seagull™ accessory set at 45° with the ZnSe ATR kit and air as the sample.) From aperture openings of 33 to 25mm, there is essentially no change in throughput, indicating that the FTIR beam diameter is smaller than 25mm. Between 25 and 15mm, there is a nonlinear drop in throughput, indicating that the beam is not uniform. Between 15 and 5mm, there is a

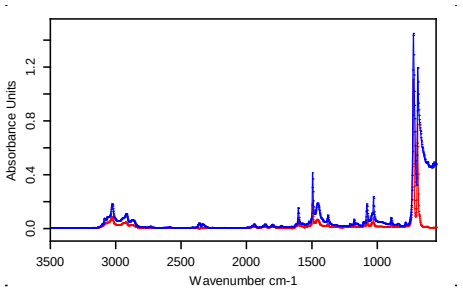

Figure 6. Comparison of toluene ATR spectra taken with a standard 45° accessory (red) and the experimentally apertured Seagull™ at 38° (blue).

Table 1. Comparison of sensitivity of fixed 45° ATR accessory vs. apertured variable angle ATR accessory at 38°.

Peak Wavelength (cm^{-1})	Absorbance		Sensitivity Increase
	45°	38°	
3028	0.0850	0.179	2.11x
2919	------	0.107	------
1604	0.0612	0.149	2.43x
1495	0.187	0.407	2.18x
1457	------	0.179	------
1378	------	0.0891	------
1080	0.0620	0.169	2.73x
1030	0.0781(5)	0.227	2.91x
725	1.103	1.444	1.31x
692	0.768	1.185	1.54x

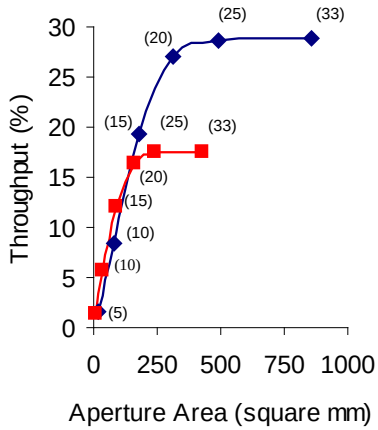

Figure 7. Throughput at 2600cm^{-1} vs. aperture area for configurations with (red) and without (blue) the half-moon aperture. Numbers in parentheses are diaphragm aperture diameters in mm.

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steep linear drop in throughput, indicating that the beam is strong and uniform. It is in this latter area, where the most precipitous drop in throughput occurs, that one would expect the best increases in sensitivity to be derived over unapertured equipment. Loss of throughput, of course, will decrease Signal/Noise, so that eventually any benefits of increased sensitivity will be lost. This did in fact occur during the course of this work, at least at the 64 coadded scan level.

Although further work with alternate samples is clearly indicated, one can propose a possible direct method of obtaining the highest possible sensitivity with the equipment here described. First, the critical angle is calculated based on the bulk refractive index of the sample. Then, the Seagull™ is set to this angle. The half-moon and diaphragm apertures are installed with the latter set to 10mm.

REFERENCES

1. J. P. Lucania and S. L. Berets, "Near Critical Angle FTIR ATR Spectroscopy with a Variable Angle Reflection Accessory," Poster Paper No. 1870-9P, Session 1870; 2006 Pittsburgh Conference; Orlando, Florida; March 15, 2006.

2. N.J. Harrick, *Internal Reflection Spectroscopy*, Harrick Scientific Corporation, Ossining (1987).