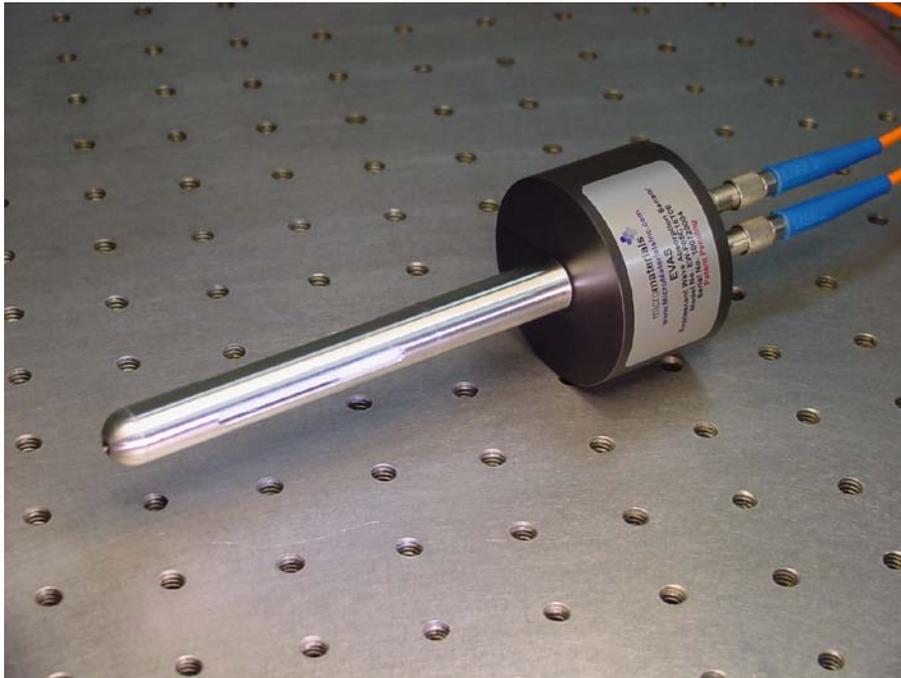


EVAS
User's Manual
Version 2



Operating Principle

We start by reviewing how lightwave is guided in an optical fiber. To simplify the discussion, we consider a ray propagating in a meridional plane of the fiber as illustrated in Fig. 1. A typical fiber consists of two regions, called the core and the cladding, with respective refractive indices n_1 and $n_2 < n_1$.

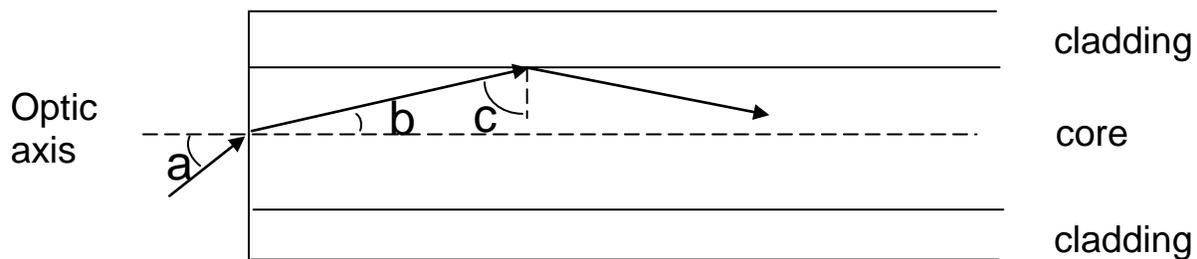


Fig. 1

The path of a representative ray launched into the optical fiber is shown in Fig. 1. The angle (a) between the ray and the optic axis of the fiber is called the launch angle, while the angle (b) between the refracted ray and the optic axis will be called the internal angle. The angle (c) between the refracted ray and the normal to the core/cladding interface will be referred to as the striking angle. Since the refractive index of the core n_1 is higher than that of the cladding n_2 , for a sufficiently small launch angle (which results in a striking angle exceeding the critical angle at the interface) the ray experiences total internal reflection. Such a ray will propagate down the fiber without loss, provided both the core and the cladding are perfectly transparent at the wavelength of the ray. Note that the smaller the launch angle is, the fewer will be the number of bounces at the core/cladding interface before exiting for a given length of the fiber.

In contrast, the fiber used for an evanescent wave absorption sensor has no cladding (i.e., it is core-only). Thus, whatever medium it is immersed in effectively becomes the cladding. Detailed analysis shows that when total internal reflection occurs, the optical field actually penetrates a short distance (on the order of a wavelength) into the cladding in the form of an evanescent field. Therefore, if the cladding is absorbing at the wavelength of the ray, the reflected field will be slightly weaker than the incident one

after each bounce. Consequently, the rays leaving the fiber will exhibit attenuation in accordance with the absorbance of the surrounding medium at their respective wavelengths. This, in essence, is the basis of how an evanescent wave absorption sensor works.

It is important to note that the extent of attenuation of the guided rays depends on the internal angle of the ray. For those rays with striking angles close to the critical angle, the evanescent field penetrates further into the surrounding medium, resulting in a larger loss per reflection at the fiber/medium interface. At the same time, they experience a larger number of reflections for a given fiber length compared to rays with smaller internal angles. Both of these effects lead to stronger attenuation for guided rays with larger internal angles.

EVAS Construction

From the above discussion it is clear that the thinner the fiber, the larger the evanescent wave absorption coefficient (i.e., fractional absorption per unit length of the fiber) will be. At the same time, to maximize the evanescent wave absorption effect, the launch numerical aperture ($\sin a$) should be as large as possible, so that a large range of internal angles will result. However, in practice the launch NA is determined by the NA of the patch cable connecting the probe to the light source, which is typically about 0.2. One way to increase the range of internal angles is to incorporate a taper in the fiber. When the diameter of the fiber changes, the internal angle changes in an approximately inverse manner. Therefore, the input end of the probe should have a larger diameter than the sensing part of the fiber. This also helps in coupling light into the probe. By the same token, since the fiber-coupled spectrometer used to analyze the transmitted signal has a relatively small acceptance NA, the output end of the probe should also be tapered up to a large diameter.

The EVAS evanescent wave absorption probe is made from a thin sapphire fiber with up-tapered ends. Sapphire was chosen because of its strong resistance to chemical attacks. This is a very important consideration, since evanescent wave absorption is highly sensitive to the surface characteristics of the fiber. The use of sapphire fiber ensures the stability of the probe over long periods of time. The small diameter of the sensing part of the probe permits the rendering of the probe in a reasonably compact

package in the form of a coil. Two models of the EVAS are being offered at present. Their specifications are given in Table 1.

Table 1

<u>Model</u>	<u>Probe Diameter</u>	<u>Probe Length</u>	<u>Active Fiber Length</u>
F65C16T06	1.0"	5.25"	12"
F50C08T07	0.5"	4.5"	7"

Absorption Measurement Procedure

A typical arrangement for making absorption measurements with the EVAS is shown in Fig. 2. One end of the probe is connected to a light source via an SMA patch cable (with the use of an SMA mating sleeve). The other end is similarly connected to a fiber optic spectrometer. The probe is to be used in a vertical position. For reproducible measurements, the fluid should always be even with the scribed line on the probe, which is indicated in Fig. 3.

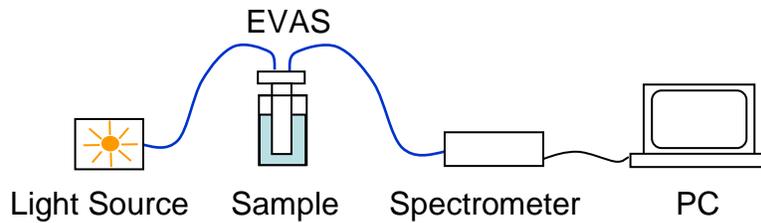


Fig. 2

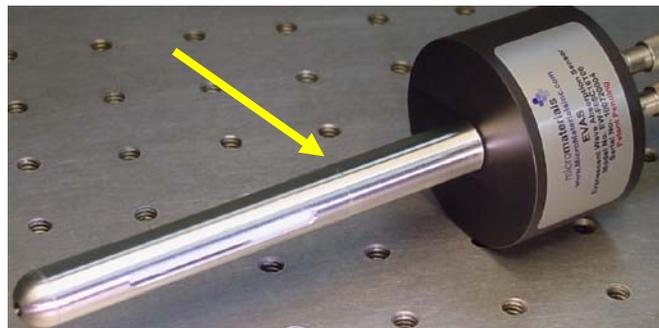


Fig. 3

To find the absorption spectrum of an unknown fluid, first record the transmitted spectrum with the probe in air. If the probe has not been cleaned after a previous use (which is not good practice), immerse it in a volatile solvent which would remove any possible residue adhered to the fiber up to the scribed line and sonicate for several minutes. Then allow it to dry completely before taking the transmitted spectrum in air. Next, place the probe in the sample of interest and allow the transmitted spectrum to stabilize (usually several minutes) before recording it. Because the transmission of the fiber could be significantly different when immersed in a fluid compared to that in air, the absorption spectrum is to be found by subtracting the sample spectrum from a multiple of the air spectrum. The correct multiplier is the smallest positive number which gives positive values for the difference within the entire spectral range. Finally, division of the difference spectrum by the adjusted air spectrum gives the percentage absorption due to the sample. From this description, one sees that, in the case of a completely unknown sample, absorption measurements with the EVAS can only be semi-quantitative.

If the sample has a known solvent, however, then highly accurate quantitative absorption spectra can be obtained. In this case, one simply takes a transmitted spectrum with the probe in the pure solvent first. Then subtracting the spectrum obtained with the probe in the sample and dividing the difference by the pure solvent spectrum gives the desired evanescent wave absorption spectrum. That is, the need to find a multiplier in order to produce an adjusted reference spectrum is obviated.

Examples

Two examples are given here to illustrate some of the finer aspects with the operation of the EVAS and point to situations where it offers some very unique advantages. In both examples an Ocean Optics NIRQuest spectrometer was used, along with its HL-2000 light source and QP400-2-VIS/NIR patch cables. Absorption spectra were taken with the Absorbance Measurement function of the SpectraSuite software. For the Reference Spectrum, the transmitted spectrum with the probe in the pure solvent was used. The Dark Spectrum was generated by disconnecting the input patch cable from the light source. Finally, the EVAS-F50C08T07 probe was held fixed throughout a series of measurements (i.e., the sample was moved into and out of position) to ensure the same coupling of light into and out of the probe.

A. Water in ethanol

The sorption of water vapor from the atmosphere by solvents in contact with open air is a ubiquitous problem in chemistry. This example shows that water concentration as low as 0.25% V/V can be easily measured with the EVAS. While this can also be done with conventional open-path probes, the much lower cost of the EVAS makes it an attractive alternative. Also illustrated by this example is the saturation phenomenon in evanescent wave absorption. The origin of this effect will be explained.

The parameter settings of the NIRQuest used in these measurements were Integration Time = 10 ms, Scans to Average = 10, and Boxcar Width = 3. To correct for fluctuations in the light source, OD readings at two wavelengths were made. They were 1,928 nm and 1,799 nm, corresponding to the peak of an absorption band in H₂O and a wavelength where absorptions in both ethanol and water are relatively weak. The true OD at 1,928 nm was then taken to be the difference between the two. For reference, nominally 99.5% pure absolute ethyl alcohol was used. After each change of the sample, 2 min. were allowed for the new solution to come to equilibrium with the fiber surface.

The measured OD at 1,928 nm vs. the % V/V of water added to the reference ethanol is shown in Fig. 4. Two features here are worth noting. First, a linear relationship holds between the measured OD and added water concentration up to an OD of about 0.15, corresponding to an absorption of approximately 30%. Beyond that, however, a sub-linear dependence sets in. The explanation lies in the fact that the observed absorption is the weighted average of absorptions undergone by all guided rays, with internal angles ranging from nearly zero to the maximum determined by the NA of the input patch cable. As the absorber concentration is increased, more and more of the larger-angle rays are almost completely removed from the transmitted signal, leading to a smaller angle-weighted effective evanescent wave absorption coefficient. The coiling of the fiber alleviates the problem somewhat by changing the internal angle of the ray as it propagates down the fiber, but does not eliminate it in most situations.

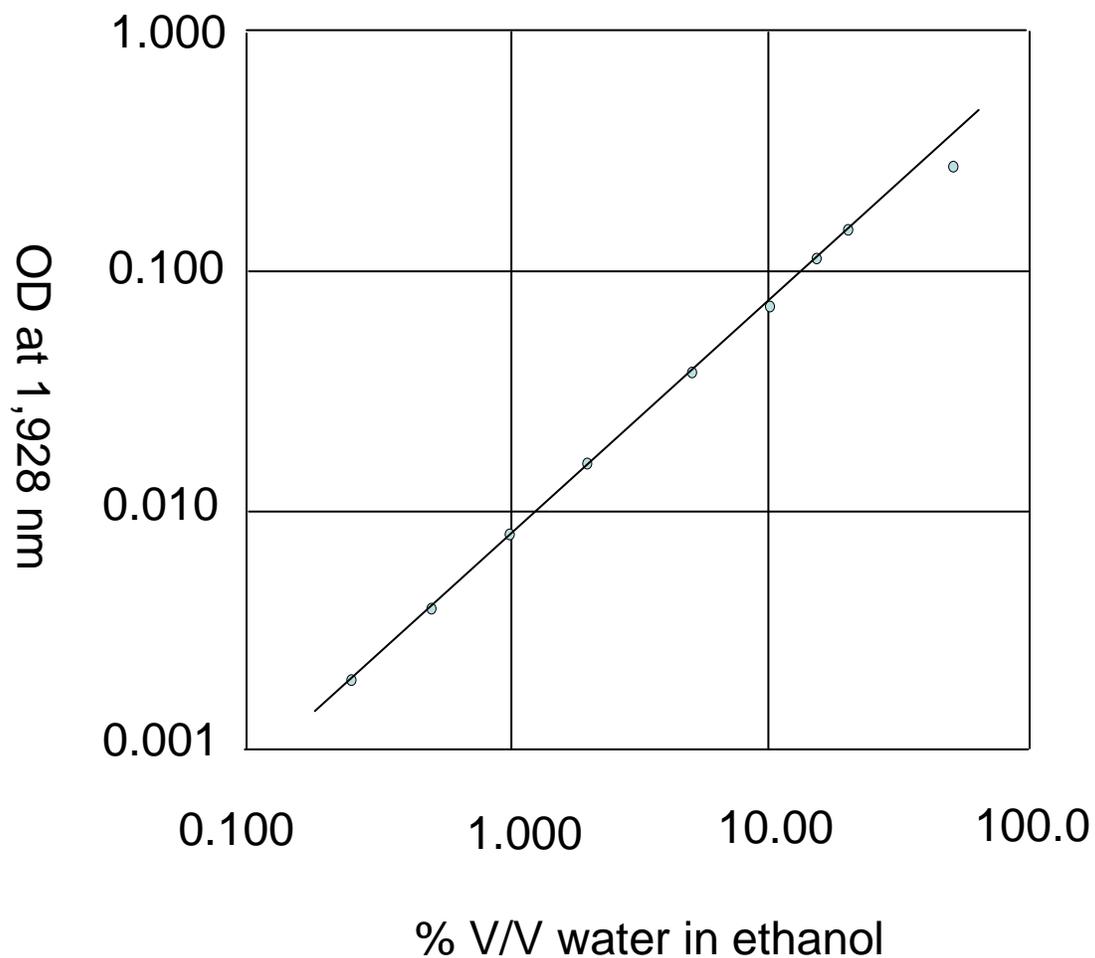


Fig. 4

This saturation of measured absorbance as the absorber concentration is increased is inherent to evanescent wave absorption, and is an effect EVAS users should be aware of. The point of its onset varies with the physical parameters of the probe, the wavelength of the measurement, as well as the refractive index of the sample fluid. However, it does not prevent one from making quantitative measurement of high concentration solutions. All it means is that the probe must be calibrated beforehand for the entire range of concentrations of interest, which is something one has to do in any event even in the linear response region.

B. Filtered and unfiltered nigori sake

Perhaps the most interesting application of the EVAS is in absorption measurements on turbid media, which complicates analysis when open-path probes are used. The EVAS, on the other hand, is largely insensitive to turbidity produced by gas bubbles or solid particles. In this example, the absorption spectrum of cloudy nigori sake (due to residues of fermented rice) is compared to that of the same sake after filtering. The appearances of the unfiltered and filtered sake are shown in Figs. 5a and 5b.

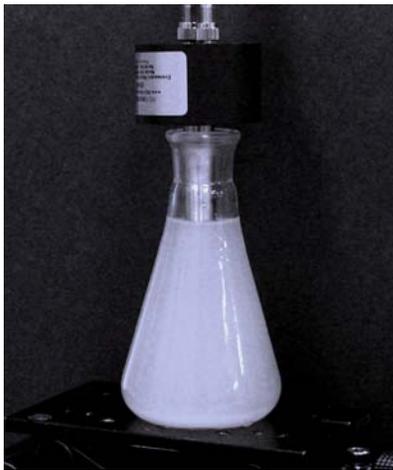


Fig.. 5a

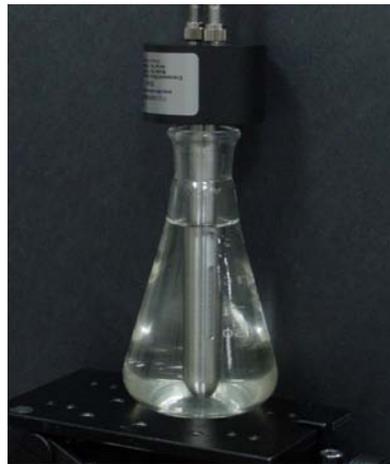


Fig. 5b

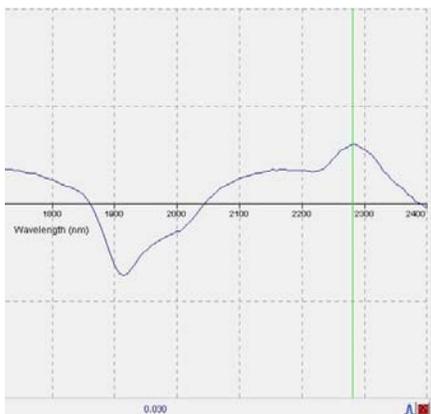


Fig. 6a

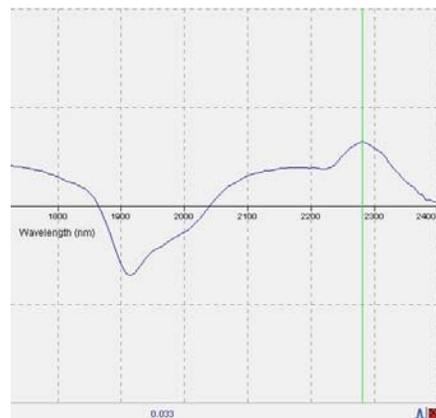


Fig. 6b

The NIR quest settings for these measurements were the same as those used in the first example. Filtered deionized water served as the reference. The absorbance spectra for the unfiltered and filtered samples are shown in Figs. 6a and 6b. The peak near 2,300 nm is due to the alcohol in the sake, while the dip near 1,900 nm is the result of reduced water content (compared to the reference). The only noticeable change from one to the other is a slight upward shift attributable to fluctuations in the light source. The difference between the peak and the dip was identical for the two, indicating that the presence of solids in the unfiltered sake had no effect on the measurement.

Care of EVAS Probe

The EVAS probe should be handled with the same care as one would exercise with glassware. The body of the probe which supports the coiled sapphire fiber is made from PTFE, and the protective cover is made from stainless steel. Therefore, it is suitable for use in most chemicals. The sapphire fiber, while chemically resistant, is mechanically fragile. One should never attempt to touch it by inserting objects through the openings of the protective cover, which itself should never be removed or adjusted. Once a set of measurements is completed, the probe can be placed in storage as is after drying if it has only been in contact with completely volatile liquids. However, if the sample contains any condensable material (e.g., tap water), it should be placed in the pure solvent (e.g., distilled water) and sonicated for several minutes before storage.