USING FIBER OPTICS FOR MID-INFRARED SPECTROSCOPY WITH A DTGS DETECTOR

Figure 1. The FiberMate.
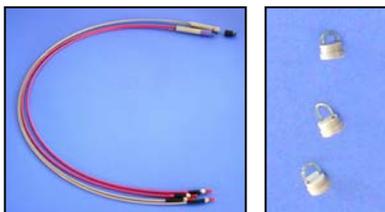

Figure 2. The MultiLoop-MIR fiber o probes (left) and sampling tips (right).

Figure 3. AccessATR single reflection ATR accessory.

INTRODUCTION

Mid-infrared fiber optics systems have been commercially available since the early 1990s[1] and are becoming a valuable tool for remote sampling and in-situ studies[2]. Unlike visible and near-IR fiber optic systems, however, these systems are not in common use. The low throughput of the fibers typically required a nitrogen-cooled detector and the fragile nature of the appropriate fibers limit their potential applications.

A new mid-infrared fiber optic system has been recently developed to surmount these limitations. This system includes a high-efficiency FT-IR fiber optic coupler and an ATR fiber optic probe with disposable sampling tips for use over the entire mid-IR.

The paper examines the sensitivity of this new fiber optic system in an FT-IR spectrometer with a DTGS detector. Specifically, the number of reflections for the fiber loop tip will be determined and differences between the tips explored. The sensitivity of the system will also be examined by looking at several samples, including liquids and pastes.

EXPERIMENTAL

All spectra were recorded using a Thermo Nexus 670 spectrometer with a DTGS detector configured for data collection at 8 cm^{-1} resolution.

For the fiber optic measurements, the spectrometer was equipped with Harrick Scientific Products' FiberMate™ fiber optic coupler (Figure 1) and the MultiLoop-MIR™[3] infrared fiber optic probes (Figure 2). The MultiLoop-MIR™ system consists of two fiber optic probe extensions and disposable loop ATR sampling tips covering the mid-infrared. One of the probes is made from chalogenide (CIR) designed for use from 4000 cm^{-1} to 1700 cm^{-1} and the other is a silver halide composite (PIR) for operation from 2000 cm^{-1} to 600 cm^{-1}. The tips are also made of silver halides. Data collected with the FiberMate™ and MultiLoop-MIR™ installed in the FTIR spectrometer were signal averaged over 64 scans.

For comparison, traditional ATR measurements were recorded using the Harrick AccessATR™, a 45° single reflection ATR accessory with a ZnSe triangular prism ATR crystal (Figure 3). Infrared spectral data collected with the AccessATR™ were averaged over 32 scans.

Background spectra were collected from the clean fiber loop or ATR crystal. Then the samples were brought into intimate contact with the sample. Solid samples were compressed gently against the fiber optic

USING FIBER OPTICS FOR MID-INFRARED SPECTROSCOPY WITH A DTGS DETECTOR

loop. The data collected with the loop were then baseline corrected and joined together to show the full spectral range.

Several different samples were examined: paraffin oil, red grape products and toothpaste. The red grape products included Carlo Rossi Paisano red wine, Progresso Red Wine Vinegar, and Kedem Grape Juice. The toothpastes were Procter & Gamble's Crest® Kid's Sparkle Fun Flavor and Cinnamon Rush Whitening Expressions, Colgate-Palmolive's Colgate® Regular, and Glaxo-SmithKline's Sensodyne®.

THEORETICAL DISCUSSION

In ATR spectroscopy, a material is brought into intimate contact with the optical element, where light is totally internally reflected and the sample interacts with the evanescent wave. This interaction is completely described by the Fresnel equations[4,5]. These equations are complex and not particularly intuitive. Most importantly, they relate the reflectance to the incident angle, the incident polarization, and the complex refractive indices of the sample and ATR element.

For ATR, the reflectivity, R, of a bulk material can be expressed as:

$$R = 1 - \alpha\, d_e \qquad (1)$$

where α is the absorption coefficient. The d_e term is defined as the effective thickness, analogous to the thickness parameter for transmittance.

For N multiple reflections, the reflectivity becomes:

$$R^N = (1 - \alpha\, d_e)^N \qquad (1)$$

For weakly absorbing materials, $\alpha\, d_e \ll 1$ and:

$$R^N = 1 - N\, \alpha\, d_e \qquad (2)$$

The expression for the effective thickness can be derived from the Fresnel equations. For weakly absorbing isotropic materials, the effective pathlengths[2] for perpendicular and parallel polarizations are:

$$\frac{d_{e\perp}}{\lambda_1} = \frac{n_{21}\cos\theta}{\pi(1 - n_{21}^2)(\sin^2\theta - n_{21}^2)^{1/2}} \qquad (3)$$

$$\frac{d_{e\parallel}}{\lambda_1} = \frac{n_{21}\cos\theta(2\sin^2\theta - n_{21}^2)}{\pi(1 - n_{21}^2)[(1 + n_{21}^2)\sin^2\theta - n_{21}^2](\sin^2\theta - n_{21}^2)^{1/2}} \qquad (4)$$

where λ_1 is the wavelength, θ is the incident angle, and n_{21} is the refractive index of the sample relative to that of the ATR element.

RESULTS AND DISCUSSION

Traditional ATR crystals have well-defined geometries that result in one or more reflections from the sample. A triangular prism, such as used by the AccessATR™ provides a single reflection. Multiple reflection ATR crystals are typically parallelepipeds or trapezoids in which the number of reflections can be easily calculated the length and thickness of the crystal, in addition to the incident angle. For the fiber loop probe used herein, it is extremely difficult to ascertain the effective incident angle and the number of reflections from geometrical considerations. However, the number of reflections can be determined experimentally.

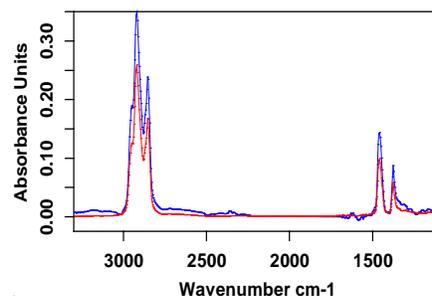Spectra were recorded from paraffin oil using four different

Figure 4. ATR Spectra of parafin oil, recorded by single reflection ATR (red) and fiber optic loop 3 (blue).

| Loop ID | Effective Number of Reflections | |
	CIR Probe 3100-2850 cm⁻¹	PIR Probe 1530-1230 cm⁻¹
1	2.2	1.8
2	2.1	1.6
3	2.0	1.8
4	2.0	1.7

Table 1. Effective number of reflections for the fiber loop probe as compared to 45° single reflection ATR on ZnSe.

USING FIBER OPTICS FOR MID-INFRARED SPECTROSCOPY WITH A DTGS DETECTOR

sampling tips and the two fiber probes. These spectra were then compared to the single reflection ATR spectrum (see Figure 4). For all eight combinations, the differences between these spectra were calculated to determine the effective number of reflections, which are presented in Table 1.

With respect to band intensities, the fiber loop sampling tips provides the sensitivities equivalent to slightly less than two ATR reflections when compared to ATR with a 45° incident angle on a ZnSe triangular prism. Note that the effective number of reflections appears to be a function of wavelength. This is due to the fact that the infrared bands around 3000 cm^{-1} technically do not meet the criteria for a weak absorption and thus eq. 3 does not pertain.

The measured number of reflections is not surprising. The 'incident angle' for the fiber loop is not well defined and is likely to be much higher than 45°, since it is the grazing or high angle rays that propagate down the length of the fiber.

Note that there are also slight differences among the fiber loops. This most likely results from the small differences in the overall length and curvature of the loop. These slight differences indicate that for quantitative measurements it

would be advisable to either use an internal standard or calibrate each loop prior to use.

Figures 5 through 9 show spectra of several liquids and pastes recorded using this fiber optic system. The first three figures show spectra recorded from different liquids, all derived from red grapes. Figure 5 shows the spectrum of grape juice, where distinct characteristics of the organic component of the grapes are clearly visible over the water bands. Figure 6 shows the spectrum of wine. There are distinct bands at 2984 cm^{-1} and 1046 cm^{-1} that are not present in juice. These are the C-H and C-O bands respectively from the alcohol in the wine. Figure 7 shows the spectrum of red wine vinegar. Bands are present in the 1712 cm^{-1} and around 1300 cm^{-1} that are characteristic of the carboxylic acids in vinegar.

Figure 8 shows spectra from two gel-like toothpastes. These spectra are very similar, indicating that their composition is nearly identical. This is confirmed by the package, which indicates very similar primary ingredients (see Table 2).

In Figure 9, two additional spectra of white toothpastes are shown. The spectrum of Sensodyne has some similarities to that of glycerin[6] and it has distinct bands around 830 cm^{-1},
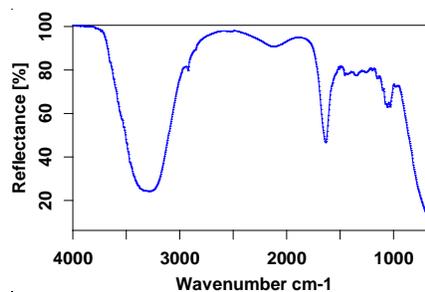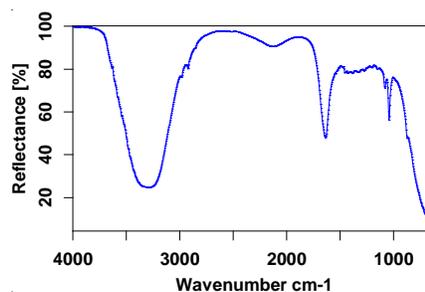
Figure 5. ATR spectrum of red grape juice.

Figure 6. ATR spectrum of red wine.
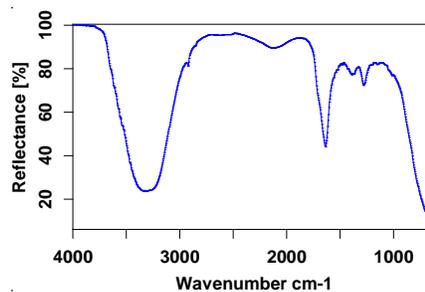
Figure 7. ATR Spectrum of red wine vinegar.

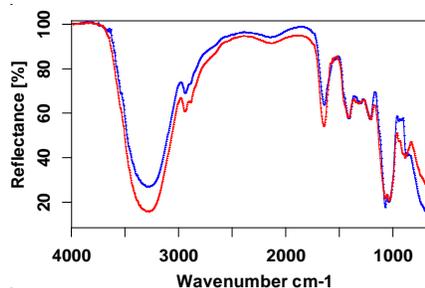Figure 8. ATR spectra of colored toothpastes: Cinnamon Rush (red) and Kid's Crest (blue).

USING FIBER OPTICS FOR MID-INFRARED SPECTROSCOPY WITH A DTGS DETECTOR

indicating the presence of a peroxide. From the spectra, the Colgate paste appears to have a lower concentration of glycerin and somewhat more water.
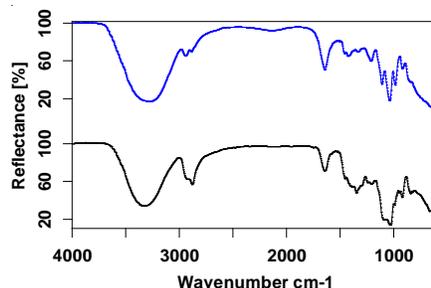
CONCLUSION

This mid-infrared fiber optic system, consisting of the FiberMate coupler and MultiLoop-MIR, has sufficiently high sensitivity for use with commercial FTIR spectrometers and their DTGS detectors. These fiber optic probes provide approximately two reflections from the sample compared to single reflection 45° ATR on ZnSe. As demonstrated here, this system is suitable for use in qualitative studies and has sufficient performance for quantitative work. Additional work is in progress to determine the limits of this system for quantitative studies.

Figure 9. ATR spectra of white tooth-pastes: Colgate Regular (blue) and Sensodyne (black).

Toothpaste	Primary Ingredients Listed
Crest Cinnamon Rush	sodium fluoride, sorbitol, water, hydrated silica, glycerin, Tetrasodium pyrophosphate
Kid's Crest	sodium fluoride, sorbitol, water, hydrated silica, trisodium phosphate, xanthan gum
Sensodyne	potassium nitrate, sodium monofluorophosphate, calcium peroxide, flavor, glycerin, hydrated silica, PEG-12
Colgate Regular	sodium monofluorophos-phate, dicalcium phosphate dehydrate, water, glycerine, sodium lauryl sulfate, cellulose gum

Table 2. Primary ingredients of the toothpastes examined.

[1] John M. Chalmers and Peter R. Griffiths, ed., *Handbook of Vibrational Spectroscopy* (John Wiley and Sons, 2002).

[2] Mary A. Thomson, Peter J. Melling, and Anne M. Slepski, Polymer Preprints 42(1), 310 (2001).

[3] J. T. Ingram, 316 Harlequin Ct, Oviedo, FL 32765

[4] N.J. Harrick, *Internal Reflection Spectroscopy* (John Wiley and Sons, Inc., 1967).

[5] M. Milosevic and S. L. Berets, *Appl. Spectros.* 47 (5), 566 (1993) and references therein.

[6] See www.chemexper.com