Fiber-optic Probes for Mid-infrared Spectrometry

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1 INTRODUCTION

Chemical composition sensors in the form of systems incorporating mid-infrared fiber-optic probes are commercially available from multiple sources and they provide a wide range of capability. Basically if a technique can be used in the sample compartment there is a fiber-optic equivalent available. Fiber-optic techniques are quantitative and can almost always be calibrated. This, combined with the flexibility and ability to measure in situations where taking a sample is not possible, means that fiber-optics provide a very powerful technique to analytical chemists. The mid-infrared region of the spectrum as defined by chemists is $4000\,\mathrm{cm}^{-1}$ to $400\,\mathrm{cm}^{-1}$ ($2.5\,\mu\mathrm{m}$ to $25\,\mu\mathrm{m}$). In that range occur most of the fundamental molecular vibrations and many of the first overtones and combinations. The bands in the mid-infrared tend to be sharp and have very high absorptivities, with both characteristics being desirable. Because the bands are sharp, most small molecules have distinctive spectral "fingerprints" that can be readily identified in mixtures. Also, because individual peaks can often be associated with individual functional groups, it is possible to see changes in the spectrum of an individual reagent due to a specific chemical reaction.

None of the fibers now available covers the full mid-infrared range. However chalcogenide glasses in the As−Se−Te system and chalcohalide glasses in the so-called TeX[1] system cover most of the fingerprint region ($>4000\,\mathrm{cm}^{-1}$ to $900\,\mathrm{cm}^{-1}$) and so can be used in chemical sensing systems. If it is acceptable to use just the O–H or N–H stretching region or the C–H region then it is possible to consider the glasses in the As–S system such as As_2S_3 or the heavy metal fluoride glasses.

Chemical sensing is arguably the first truly commercial application of mid-infrared transmitting optical fibers. The availability at an economic cost of chalcogenide glass optical fiber with losses of less than $1\,\mathrm{dB\,m}^{-1}$ over most of the spectral range has made possible the development of commercially viable sensor systems using mid-infrared fiber-optics. Infrared (IR) fibers provide the capability of "taking the spectrometer to the sample" instead of the traditional method of taking the sample to the spectrometer. This ability to place probes in reaction flasks or reactors has created a whole new paradigm for molecular spectroscopy. Systems based on IR fibers are being used on a daily basis in university laboratories, for industrial process development, and in industrial quality control laboratories. They are being used because they conveniently provide important information that is not readily available by any other method.

Sensors can be constructed using any of five basic sensing schemes: transmission, reflection, grazing angle reflection, attenuated total reflection (ATR), and a variant on the ATR effect known as the fiber evanescent wave sensor.[2]

2 OPTICAL DESIGN ISSUES

Two major factors underlie the design of a mid-infrared fiber-optic system: overall optical signal level and the magnitude of the chemical signature (i.e. the strength of IR absorption by the sample). All other questions come back to these two fundamental issues.

The problem we have when working in the mid-infrared is that the sources are weak, the detectors are not very sensitive, and the fiber is not low-loss. The output of a mid-infrared source is fundamentally limited by the black body curve, which in turn limits the amount of improvement that can be made to sources. Because IR photons are low in

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energy, it is usually necessary to use liquid nitrogen-cooled detectors to get high sensitivity or D^* (and hence a high signal-to-noise ratio, S/N). In a typical commercial system a liquid nitrogen-cooled mercury cadmium telluride (MCT) detector where the frequency cutoff has been matched to the fiber cutoff to give the maximum possible D^* is used. Typical commercial fiber for broad-band applications has losses in the range of a few tenths to $1\,\mathrm{dB\,m^{-1}}$, with a 6 to $10\,\mathrm{dB\,m^{-1}}$ spike at the hydrogen selenium vibration (arising from residual hydrogen bonded to the selenium in the glass). While this is usable, losses of less than $0.1\,\mathrm{dB\,m^{-1}}$ over the whole range would enable the design of much more capable systems.

The S/N of a spectrometer is typically defined as the signal level of a blank "100% line" divided by the noise level. While that may give an indication of the performance of the electronics and optics within a spectrometer, what the user is really interested in is the signal-to-noise performance when the absorbance of the analyte is compared to the noise level of the system. In this definition of S/N, the design of the probe becomes important as it can define the signal to noise performance of the system. A probe design that gives three times the signal of another probe has three times the sensitivity of that other probe at a given noise level.

All IR spectrometers use a finite source and the collimated beam emitted from most commercial interferometers typically has a beam divergence of about 2°. Chalcogenide fibers typically have a refractive index for the core of 2.4–2.8 and a numerical aperture between 0.3 and 0.6. When the IR beam is focused into a fiber it is important not to exceed the numerical aperture of the fiber (see Figure 1); beyond the numerical aperture, the beam simply reflects off the front surface of the fiber and is lost. The problem is that the minimum spot size that can be obtained without exceeding the numerical aperture of the fiber is typically a few millimeters in diameter. This means that either large diameter fibers (flexible glass rods) or fiber bundles must be used to obtain acceptable levels of optical throughput. Fresnel (reflection) losses are also an issue, but at the present time the volume of systems being produced does not justify the routine use of antireflective coatings. Chromatic aberration can be a concern if lenses are used in the coupling optics, as the refractive index of some IR materials changes across the mid-infrared region. For that reason reflective optics should be used where possible.

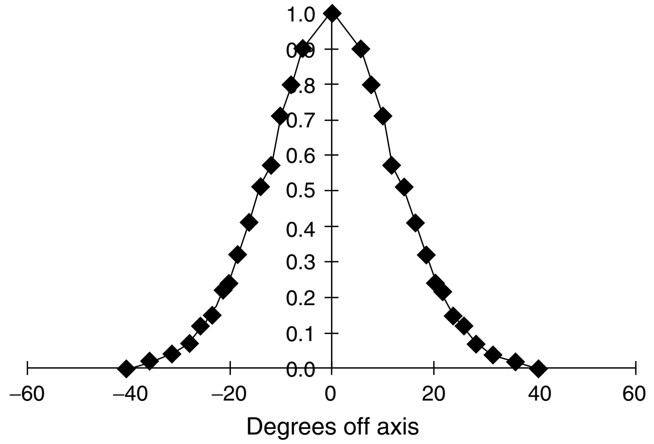

Figure 1. Far field numerical aperture of a 300 µm chalcogenide glass optical fiber.

The only area where the system designer has any real choice is in the configuration of the fiber and in the optical coupling methods used. Given the optical requirements, two basic approaches have been taken. One is to use large diameter fibers to construct a single-fiber system and the other is to use fiber bundles to provide superior throughput and flexibility.

2.1 Commercial single-fiber designs

The first reported IR fiber-optic probe was an ATR probe built by Ciba Geigy (Basel, Switzerland) for monitoring dye synthesis reactions.[3] The first commercially available IR fiber-optic probe was produced by Specac Ltd (Orpington, UK) and has been available since the early 1990s;[4] however, regular commercial production has now been discontinued. The Specac probe designs use large diameter single fibers to carry the signal via a series of lenses either to an ATR crystal or to a transmission head. Thermo Spectra-Tech Inc. (Shelton, CT, USA) is also producing single-fiber probes for ATR and specular reflection measurement[5,6] but their performance is limited by the low throughput of single-fiber designs and the fragility of large diameter fibers. The use of adhesive to retain an optical window that is in solution contact also limits the application of their bent fiber ATR design.

2.2 Commercial bundle designs

Remspec Corporation (Sturbridge, MA, USA) has been marketing mid-infrared probes using bundle technology since early 1993.[7] These probes consist of two bundles that are intermingled at the probe end and are separated into a spectrometer cable and a detector cable. For a standard probe, they use 500 µm core As–Se–Te fiber with 50 µm thick glass cladding from Amorphous Materials Inc. (Garland, TX, USA). The input cable has seven fibers and the common end is 19 fibers (the next hexagonal pack) leaving 12 for the return or detector cable. The common bundle is housed in a 6 mm diameter stainless steel shaft that is polished at one end and mated to a splitter assembly at the other end. Flexible armored cables are then used for the remainder of the length. The use of such large bundles makes the probes more expensive to fabricate than single-fiber probes but there are two major advantages: increased signal throughput that results in lower noise levels in the system and the ability to use smaller diameter fibers which have superior mechanical properties. The configuration used also allows a uniquely flexible choice of sampling heads for the probe (Figure 2) including ATR, transmission, and reflection.[8]

A grazing angle specular fiber-optic reflection probe has also been developed[9] which comprises a 19-fiber cable to bring the signal from the spectrometer to the probe head and either another 19-fiber cable to return the signal to a remote detector or a detector is mounted directly on the probe (Figure 3). In this probe the signal exiting the fiber cable is collimated using an off-axis parabola, and directed towards the sample at 80° from normal. It is then refocused by another off-axis parabola into the return fiber cable or a detector element.

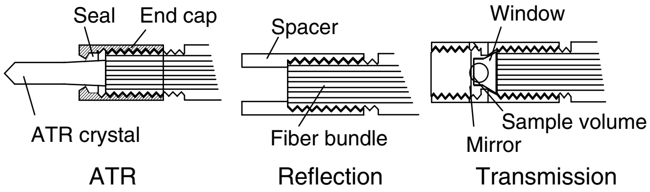

Figure 2. Alternative interchangeable heads for a bundle fiber-optic probe.

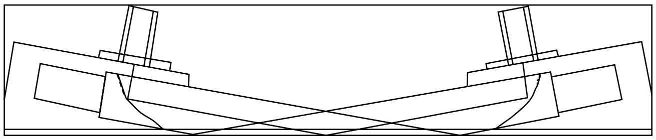

Figure 3. Schematic of the optics for grazing angle reflection measurements.

2.3 Spectroscopic issues

For those interested in metal carbonyls or the isocyanate or thiocyanate linkage the strong absorbtion by the H–Se bond at around 2300 cm^{-1} can be a problem. For a dedicated system it is always possible to use a different fiber such as As_2S_3 but then you lose much of the fingerprint region from the shorter wavelength cut-off of the sulfide fiber. If bundles are used, however, it is possible to mix two types of fiber;[10] this combines the maximum coverage of using a selenide/telluride glass with the elimination of the H–Se blind spot (Figure 4).

2.4 ATR tip designs

ATR is a technique that is used in mid-infrared spectroscopy because extinction coefficients are very high and the required path lengths of transmission cells can become too short for practical use. In the ATR technique a signal beam is introduced into an IR-transparent crystal in such a way that it is incident on the internal surface at an angle which is below the critical angle, leading to total internal reflection. The geometry may be set up so that many such reflections or "bounces" occur before the beam exits the crystal at a predetermined face. At each bounce an evanescent wave penetrates the medium surrounding the crystal and so samples the spectrum of that medium. An approximate indication of the penetration depth at each bounce is given by:[11]

$$d_\mathrm{p} = \frac{\lambda}{2\pi n_\mathrm{p}(\sin^2\theta - n_\mathrm{sp}^2)^{1/2}} \tag{1}$$

where λ is the wavelength of the radiation, n_p is the refractive index of the crystal, θ is the angle of incidence of the light beam, and n_sp is the ratio of the refractive indices of the sample and the crystal.

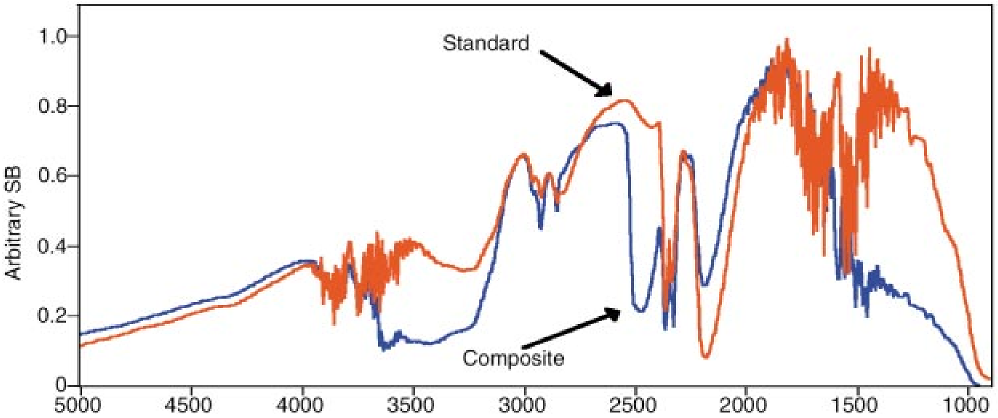

Figure 4. Comparison of the single beam spectra of a standard and a composite fiber-optic probe.

Two ATR tip designs are in use with bundle probes: a two-bounce 90° conical tip which behaves like a corner cube reflector; and a three-bounce, flat-ended tip for use with soft solids such as biological tissue, rubbers, and many plastics. When observing the performance of a ZnSe or ZnS conical tip it is evident that the measured absorbance is greater than would be expected from two 45° bounces. To understand this it is necessary to consider the numerical aperture of the fiber, and hence the contribution of "off-axis" rays and the shape of the curve generated by equation (1) (Figure 5b).

In the case of high refractive index materials, such as silicon or germanium, there is no enhancement but in the case of ZnSe or ZnS the reduction in penetration of the high angle bounce is more than offset by the increase in penetration of the low angle bounce (Table 1).

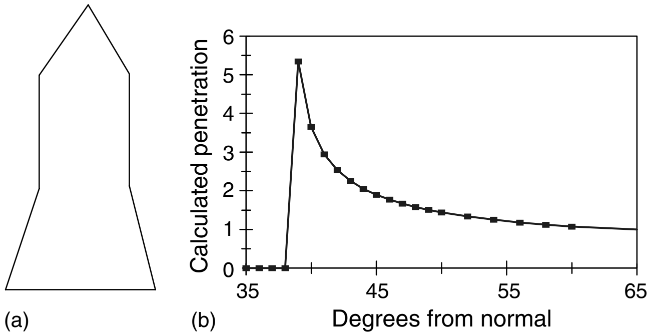

Figure 5. (a) Conical crystal design. (b) Penetration depth plot for ZnSe.

This distribution of angles should not be regarded as introducing any noise or randomness into the system; it does not. The net absorbance of any analyte is governed only by the extinction coefficient and the coupling of the crystal to the fiber bundle (which defines the optical path in the crystal). Despite the inclusion of low angle bounces this probe design gives very good linear calibrations over wide concentration ranges as can be seen from a typical calibration curve (Figure 6a). Moving the fiber cables does not affect this coupling and so it does not affect any calibration that may have been developed with a given probe. Provided the optical coupling between the ATR tip and the fiber bundle is kept constant then it should be possible to transfer calibrations from probe to probe, and indeed there are some data to suggest that this is possible (Figure 6b).

Table 1. Penetration depth versus angle for ATR material.

Initial incident angle (deg)	ZnSe		ZnS		Ge		Si		Diamond	
	P[a]	R[b]	P	R	P	R	P	R	P	R
45	4.01	1.00	7.72	1.00	1.33	1.00	1.69	1.00	3.80	1.00
44	4.05	1.01	8.60	1.11	1.33	1.00	1.70	1.00	3.83	1.01
43	4.18	1.04	48.88	6.33	1.33	1.00	1.70	1.00	3.93	1.03
42	4.42	1.10			1.34	1.01	1.71	1.01	4.12	1.08
41	4.89	1.22			1.35	1.01	1.73	1.02	4.46	1.17
40	5.91	1.47			1.36	1.02	1.75	1.03	5.10	1.34
38					1.39	1.05	1.81	1.07		
36					1.43	1.08	1.90	1.12		
34					1.50	1.13	2.03	1.20		
32					1.59	1.19	2.24	1.32		

[a] Penetration depth for two bounces (in micrometers).
[b] Ratio to penetration depth at 45°.

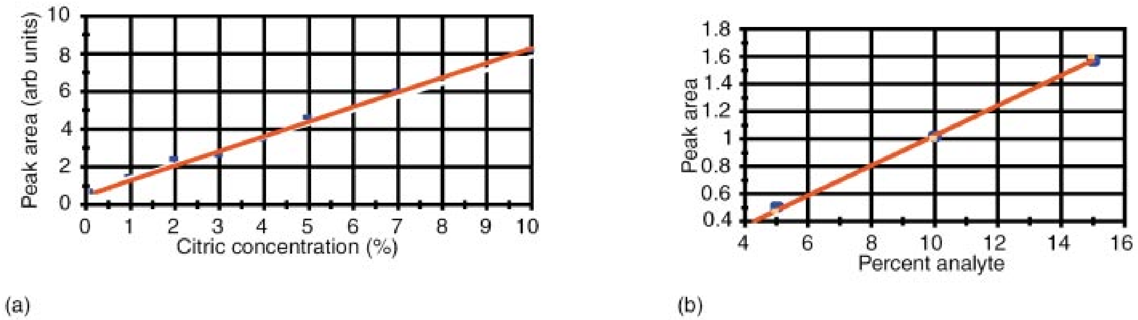

Figure 6. (a) Typical ATR probe calibration plot, in this case for an aqueous solution of citric acid. (b) Measurement of the same solutions by two different probes: solid points from standard probe; shaded points from enhanced probe.

3 EXTREME CONDITIONS

The mid-infrared optical fibers used in fiber-optic probes are suitable for use in standard conditions of temperature and pressure. However, when extremely high or low temperatures are involved, measures have to be taken to protect the fibers from the effects of heat and of thermally induced stress associated with temperature cycling. The As–Te–Se fibers used in standard probes can be safely used up to about 60 °C. Above 80 °C, the glass in the optical cladding begins to be subject to softening and flow. In addition, the nylon protective coating that is applied to the fibers during manufacture may begin to flow, exposing the fibers to increased risk of breakage from bending or pulling. Aggressive chemical environments can also affect fiber-optic probes. Strong acids such as fuming nitric or fuming sulfuric acid will not affect the fiber but they will attack the epoxies used to hold the fiber in place. Strong bases will dissolve chalcogenide glass fiber, as will halogenating environments. The preferred ATR crystal materials such as ZnSe and ZnS are also affected by aggressive chemical environments. For conditions where standard ATR materials would be corroded, diamond can be used as the crystal material. It has the disadvantage that the C–C vibration from the tetrahedral diamond structure occurs around 2000 cm^{-1}, obscuring a large part of the sample spectrum, but it can still be used for monitoring reactions in many cases.

3.1 High temperature

Since optical throughput is the dominating design issue in mid-infrared fiber-optic devices, the design of probes for use at elevated temperature must combine thermal isolation of the fibers from the heated sample medium with the best possible optical coupling. An approach which has been used very successfully is to interpose a rod crystal between the end of the ATR crystal and the end of the fiber bundle.[12] Fortunately, the materials that are best suited to optical transmission in the mid-infrared, such as zinc selenide and zinc sulfide, are also good thermal insulators for this purpose. Heat transfer to the fibers is further decreased by actively cooling the insulating crystal using a stream of room temperature air or nitrogen directed through a cooling structure built into the body of the probe. Insulating and cooling measures such as these result in mid-infrared probes that can be used at temperatures over 200 °C. For example, a cooled probe was used to obtain the spectra of peanut oil shown in Figure 7. As expected, the oil shows little sign of molecular change up to 175 °C. The changes in spectral intensity across the temperature range arise from several factors such as changes in the refractive indices of both the oil and the ATR crystal (which was zinc selenide in this case), and variations in the baseline population of the vibrational excited states in the sample.

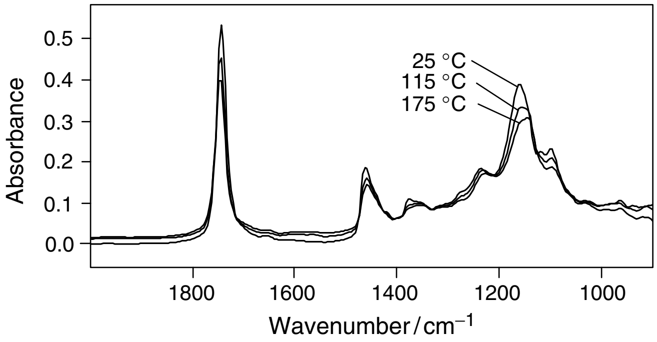

Figure 7. Comparison of spectra of peanut oil measured at different temperatures.

3.2 High pressure

With a recent surge in interest in supercritical fluid technology for chemical synthesis and the expected construction of the first manufacturing facility[13] there is a need for IR probes that will operate at very high pressures, in some cases over 300 bar. Because of the serious hazards present when working at such pressures the probe must be made as small as possible, to minimize the structural weakening caused by the entry port, and the IR crystal/window must be very thick compared to its diameter. By using tapered crystals and tapered seals (Figure 8) coupled to fiber optics it is possible to build probe heads that will operate under extreme conditions (hundreds of bars and hundreds of degrees Celsius) and to measure spectra under those conditions (Figure 9).

3.3 Low temperature

At low temperatures active heating has proved to be unnecessary provided the fibers are kept above the liquid level. Both ATR and transmission low temperature heads may be constructed by using a long (typically 75 mm)

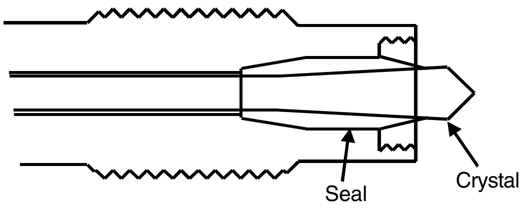

Figure 8. Typical high pressure head seal design.

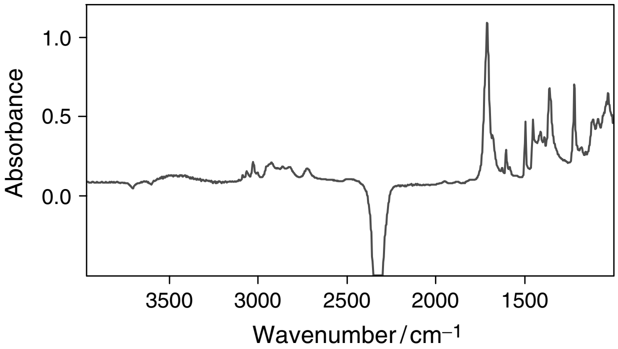

Figure 9. Spectrum of cinnimaldehyde in CO_2 measured at 120 bar with liquid CO_2 as the background.[14]

Figure 10. Low temperature transmission head.

ZnS or ZnSe crystal and an extension body made of a thermally insulating high performance chemically resistant engineering plastic (Figure 10). With such a probe head the heat flow down the shaft holding the fiber bundle is sufficient to keep the fibers warm enough and spectra may routinely be collected at temperatures below −100 °C.

4 EXAMPLE APPLICATIONS

4.1 Coatings and surface contamination analysis

Grazing angle spectroscopy is a powerful technique that is extremely sensitive to low levels of material on metallic surfaces and when coupled with fiber optics can be used for a wide variety of cleaning validation and coating measurement tasks. Using the system shown in Figure 11 which has a room temperature deuterated L-alanine doped triglycine sulfate pyroelectric detector mounted directly on the probe head it is possible to measure layers as thin as the 1.9-nm-thick fluorocarbon lubricant layer on a hard disk drive platter (Figure 12). Workers at the University of Puerto Rico[15] have obtained good results when measuring pharmaceutical residues on reactor surfaces, and other workers[16] have demonstrated linear concentration vs peak height correlations for silicone and hydrocarbon contamination on aluminum surfaces.

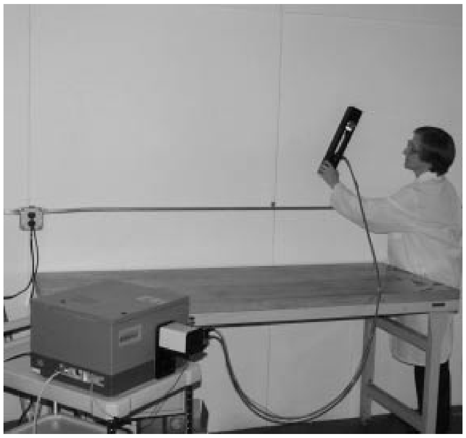

Figure 11. Room temperature fiber-optic grazing angle system.

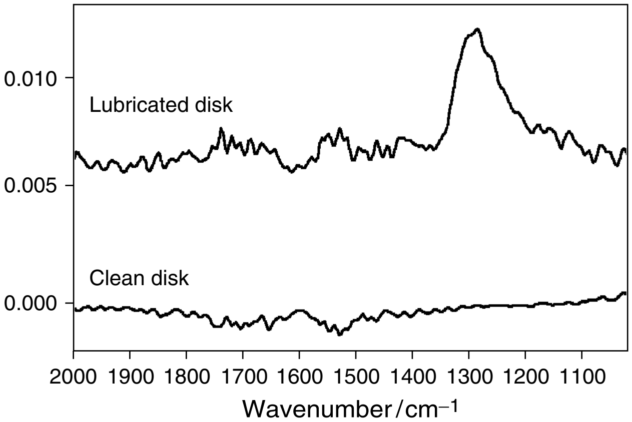

Figure 12. Fluorocabon layer (1.9 nm thick) on a hard disk platter (8 cm^{-1}, 1 min scan time).

4.2 Urethane curing

A simulated rocket fuel, comprising a urethane-based binder of undisclosed composition, was provided in uncured form. The sample was held at a temperature of 55 °C for ∼27 h and mid-infrared spectra were collected by placing a fiber-optic probe with a zinc selenide ATR head in contact with the curing mass (in industrial practice, this type of cure can take over a week). The characteristic isocyanate peak at 2250 cm^{-1} (arising from the asymmetrical stretch of the C=N=O group) was monitored by collecting the mid-infrared spectrum every 2 min. After the data collection was complete, the peak area at 2250 cm^{-1} was calculated for each spectrum and a graph was drawn of peak area versus reaction time. Selected spectra and the final graph are shown in Figures 13 and 14, respectively. It is clear

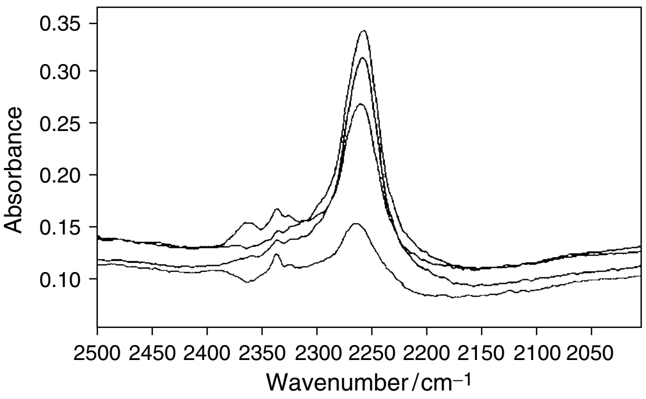

Figure 13. Isocyanate band at different times during a reaction.

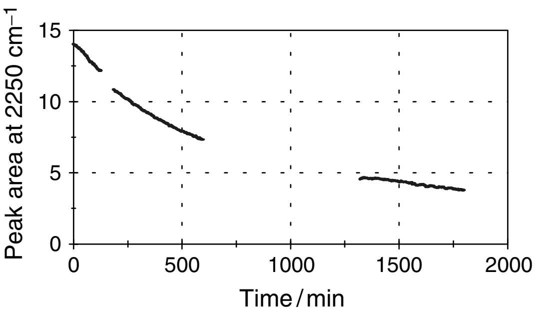

Figure 14. Time evolution of the isocyanate band during polymer curing.

that the disappearance of the isocyanate peak provides a valuable spectroscopic marker for the progress of the reaction. In cases like this, mid-infrared spectral features are sufficiently strong and isolated to be interpreted using simple peak-fitting and graphing techniques.

4.3 Air-free and low-temperature studies

Starting with the work of Shaw and Geiger[17] who used a transmission probe to study electrochemical reactions in an air-free environment there have been a variety of studies under air-free and low-temperature air free conditions where the ability to collect IR spectra of unstable species has led to a better understanding of the chemistry of the complexes under study.

In their 1996 paper, Shaw and Geiger demonstrated that the use of a fiber-optic probe eliminates the need for specially designed electrochemical reaction cells to accommodate a spectroscopic sampling method. In their study of the redox chemistry of cyclopentadienyl manganese and iron compounds, they carried out all the reactions in a standard electrolytic "H" cell, without any cell design compromises to diminish the accuracy of the electrochemical data. Oxygen had to be rigorously excluded from the reaction, which was carried out under argon using Schlenk procedures and the mid-infrared fiber-optic transmission probe was inserted into the cell using an entry port similar to those used for the electrodes. The electrochemical reaction was followed in situ by collecting spectra at regular intervals during the course of the reaction. For example, in the oxidation of acetylferrocene in CH_2Cl_2/[NBu_4][PF_6] at 273 K, it was possible to show that the carbonyl peak at 1700 cm^{-1} (from the cationic form) was directly proportional to the amount of charge passed, while the peak at 1660 cm^{-1} (from the neutral form) was inversely proportional to the charge passed, confirming that the mechanism of the oxidation does not vary during the electrolysis. Although this is a simple example, it demonstrates the power of true in situ spectroscopy. The work has been extended to include detailed mechanistic studies of electrochemical reactions, and spectroscopic identification of a range of electrochemically generated species.[18,19]

The Schauer group at the University of North Carolina has also demonstrated the role of fiber-optic spectroscopy in elucidating the detailed chemistry of electrochemically active species,[20] while Li *et al.* at Brown University have used a fiber-optic mid-infrared probe at low temperatures to follow the reactions of model compounds for hydrodesulfurization catalysts.[21]

Puskas and co-workers[22,23] have been very successful using both ATR and transmission to study polymerization reactions at low temperatures (−80 °C) in the air-free environment of a glove box. Under these conditions the taking of a sample is just not possible and fiber optics hold substantial advantages over light-pipe systems in the cramped and difficult environment of a glove box. One of the advantages of working in the mid-infrared region of the spectrum is that comparatively simple spectral interpretation methods can often be used due to the sharp, well separated absorption bands that characterize the mid-infrared. For example, straightforward conversion–time plots for the consumption of a monomer 1,5-cyclooctadiene were used to monitor the ring-opening polymerization of the compound.[22] The method was based on the assumption that monomer concentration is proportional to the area of the associated mid-infrared bands – in this case the C–C deformation of the CH_2 groups at 1486 cm^{-1} was used. The results were in good agreement with final conversion data obtained by gravimetry. Similarly, a fiber-optic Fourier transform infrared (FT-IR) probe was used to track the disappearance of the C=C stretching frequencies from isobutylene (1655 and 1780 cm^{-1}) and p-t-Bu-styrene (1630 cm^{-1}) during a block copolymerization reaction.[23] In both of these examples, the fiber-optic probe provided an effective spectroscopic "window" into the progress of reactions carried out under air-free conditions at low temperature, without making major changes to the established experimental equipment and methods.

4.4 Human skin

A fiber-optic probe with an ATR crystal provides a completely noninvasive method for obtaining spectroscopic information in vivo. An example is the spectroscopic examination of the surface layers of human skin.[24] This study took advantage of the sensitivity of mid-infrared spectroscopy in determining molecular composition and conformational order as well as the capacity of probing the surface to a depth of less than 1 μm to obtain data on the lipid composition in two superficial components of human skin – the stratum corneum and the sebum. It was possible to distinguish between the contributions of the molecular components from the two layers. The presence of spectral "signatures" of the sebaceous lipids allowed for improved interpretation of some mid-infrared bands from the sebum. In addition, the fiber-optic probe provided a convenient way to study the recovery of superficial lipids after the removal of sebum. With calibration, a method was developed to quantify the relative amount of fatty acids in sebum. It was observed that the sebaceous fatty acids that reach the surface of the skin recover at a lower rate than other sebaceous lipids. Fiber-optic based ATR methods in the mid-infrared were established as a promising tool for the study of epithelial surfaces and surface skin contaminants in vivo.

4.5 Fermentation

Fermentation is fundamental to a number of important industries, including the ancient arts of winemaking and brewing as well as emerging biotechnology processes. Fiber-optic FT-IR spectroscopy lends itself well to the important task of monitoring fermentation processes for progress and completeness. A very simple example illustrates this: the fermentation of a sucrose substrate using common baker's yeast, *Saccharomyces cerevisiae*. This reaction has been successfully used for centuries, and the determination of the desired end-point is largely a matter of art and experience. Fiber-optic spectroscopy offers the opportunity to observe and monitor the chemistry of fermentation in real time. In this case, the sucrose substrate and the fermentation products, fructose, glucose and ultimately ethanol, have mid-infrared spectra that overlap considerably (Figure 15). This means that partial-least-squares analysis is required to give quantitative results. However, the combination of a fiber-optic probe directly inserted into the fermentation reactor with the powerful capabilities of modern spectroscopic software makes it possible to "open a window" into the fermentation reaction. When a mid-infrared probe with a zinc selenide ATR crystal was placed in a fermentation reactor, and spectra were collected every minute for almost 36 h. The time–concentration profile shown in Figure 16 was obtained.[25]

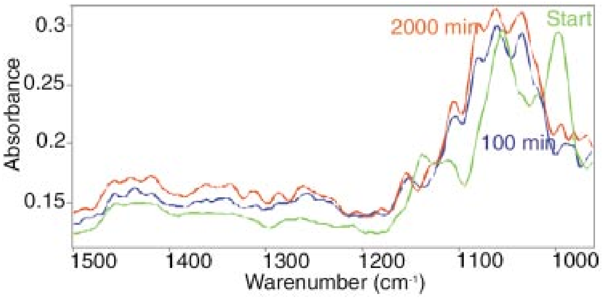

Figure 15. Comparison of spectra during a fermentation reaction.

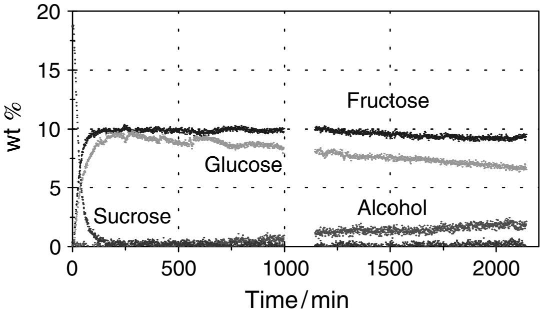

Figure 16. Time profile of the constituents in a sucrose fermentation.

5 CONCLUSIONS

Mid-infrared fiber-optic probes are gaining acceptance as convenient and useful tools for chemical sensing in a wide variety of applications. Fiber optics make possible many measurements that would otherwise be impractical and the technology has matured to the point where it is in routine use in laboratory environments by nonspectroscopists. If it is not possible to take a sample or if there is an advantage in speed, flexibility or safety, then almost any technique which will work in the sample compartment of a spectrometer can be made available at the end of a fiber-optic cable.

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