# Principles and Applications of Fourier Transform Infrared (FTIR) Process Analysis

Walter M. Doyle

The past few years have seen rapid growth in the use of infrared spectroscopy for at-line, on-line, and even in-line analysis. This progress has been made possible by developments in the design of both FTIR instruments and equipment to interface these instruments to chemical processes. It has been driven by the need for real-time monitoring of the chemistry underlying various processes and by infrared's ability to provide a wealth of information about chemical structure. The present paper reviews some of the more important developments, with emphasis on the optical and mechanical hardware available for interfacing the FTIR to the process. Finally, it reviews a number of representative applications areas in which process FTIR is currently being used.

## 1. Introduction

In many ways, mid-infrared spectroscopy would appear to be the ideal technology for on-line chemicals analysis. After all, IR spectroscopy is the only analytical method which provides both ambient temperature operation and the ability to directly monitor the vibrations of the functional groups which characterize molecular structure and govern the course of chemical reactions. In principle, IR also offers the advantages of continuous (near real-time) operation and low maintenance compared to gas chromatography and low cost and structural specificity compared to mass spectroscopy.

The term "infrared" generally refers to any electro-magnetic radiation falling in the region from 0.7 μm to 1000 μm. However, the region between 2.5 μm and 25 μm (4000 to 400 cm$^1$ ) is the most attractive for chemical analysis. This "mid-IR" region includes the frequencies corresponding to the fundamental vibrations of virtually all of the functional groups of organic molecules. These spectral lines are typically narrow and distinct, making it possible to identify and monitor a band corresponding to the specific structural feature that is to be modified by a reaction. As a result, quantitative calibrations performed in the mid-IR are usually straightforward and robust, being largely immune to the effects of spurious artifacts.

The author is with Hellma Axiom, 1451-A Edinger Ave, Tustin, California 92780. W.M. Doyle's e-mail address is michael.doyle@hellma.com.

Despite its obvious attractiveness, mid-IR did not find widespread use in process analysis until quite recently. Instead, for the past several years, much more attention has been directed toward the use of near-IR for on-line spectral analysis (1). This may seem somewhat surprising in view of the fact that in the near-IR one is often dealing with combination frequencies and harmonics of mid-IR functional group frequencies. These near IR bands tend to be weak and broadly overlapping making it impossible to single out distinct bands for analysis. This necessitates the use of fairly sophisticated statistical methods to correlate observed spectra with the process variables of interest (2, 3). These methods are very powerful but are also quite capable of producing spurious results, particularly when they encounter a condition that was not anticipated during calibration. This is the infamous "false sample" problem endemic to near-IR (4).

In contrast, the mid-IR region is a spectroscopist's dream, with meaningful, well understood absorption bands often adjacent to weakly absorbing regions, making calibrations largely independent of effects such as source variations, changes in overall sample transmission, or scattering. Despite these advantages, the widespread application of mid-IR on the process line had to await technological advances in three general areas:

- FTIR spectrometers capable of reliable operation in the process environment;

- Methods for transmitting the IR radiation to and from the measurement location;

- Robust sample interfacing equipment capable of providing consistent results in the process environment and of dealing with the very strong absorptions generally encountered in the mid-IR

The particular need for these advances has to do with some specific fundamental differences between mid- and near-IR. For example, the radiation source power available in the mid-IR is much lower due to the nature of the black body radiation curve. At the same time, mid-IR detectors capable of operating at room temperature are less sensitive than their near-IR counterparts. These two factors together necessitate the use of the Fourier transform infrared (FTIR) approach rather than the far less sensitive dispersive approach commonly used in the near-IR.

The transmission of radiation to and from the measurement site is more problematic in the mid-IR due to the need for high throughput combined with the limited selection of optical materials which transmit in this region. Ironically, this latter problem arises from the very fact that most molecular vibrations fall in the mid-IR region.

Sample interfacing in the mid-IR is often complicated by the fact that the absorptions corresponding to the fundamental molecular vibrations are orders of magnitude stronger than their near-IR overtones. As a result, the simple transmission cells which can be used for near-IR liquid analysis are usually not suitable for use in the mid-IR.

Despite the considerable challenges, mid-IR does offer attractive benefits in the form of distinct and meaningful bands, robust and straightforward calibrations, proven diagnostic methods, and insensitivity to spectral artifacts. Fortunately, the final obstacles to the widespread implementation of process mid-IR have been now been surmounted, and as a result, the field is starting to experience accelerated growth. The following sections will outline some of the advances that have made this possible as well as some of the previously available technology now being applied in process FTIR. The final sections will give some specific examples of process FTIR hardware and the types of applications to which it is being applied.

## PROCESS FTIR SPECTROMETERS

Infrared instrumentation has been used in chemical process control for approximately fifty years, making it one of the first analytical techniques to be put on-line. However, until recently, on-line infrared instruments were generally restricted to one and two wavelengths nondispersive (NDIR) analyzers. Dispersive IR lab instruments, the only full spectrum IR spectrometers available prior to 1970, were simply too slow and insensitive to find widespread use in process applications.

The advent of commercial FTIR instruments in 1970 represented a major advance in IR spectroscopy in terms of both raw performance and data manipulation capability. However, the early FTIR's were strictly laboratory instruments, being highly sensitive to ambient temperature variations, vibration, and acoustic disturbances, all of which are typical of the pro-
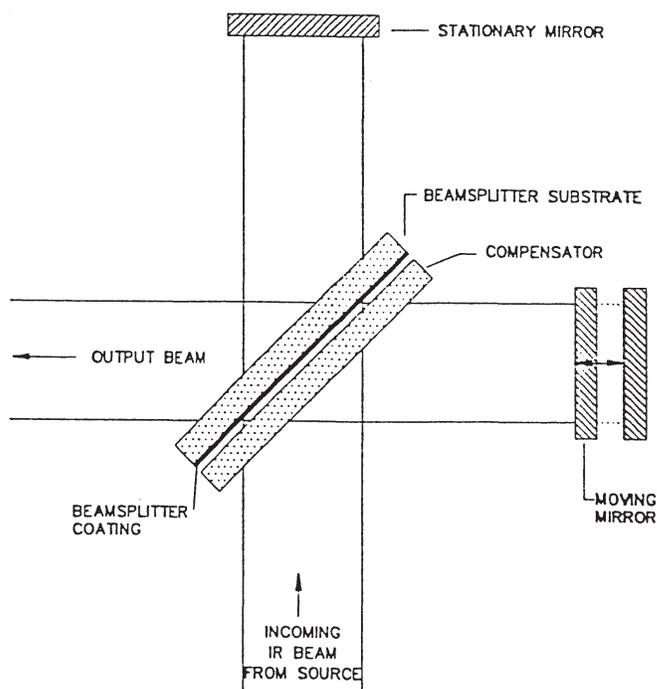


**Fig 1. Conventional Michelson interferometer.**

cess environment. To understand the reasons for this sensitivity, we need to briefly review the operation of an FTIR spectrometer.

The heart of any FTIR spectrometer is an amplitude division interferometer. The original Michelson design - still employed in the majority of laboratory FTIR's - consists of a beamsplitter, a compensating plate, and a pair of mirrors (see Fig. 1). The difference in path length between the two arms is varied by mechanically scanning the position of one of the mirrors. This gives rise to a time dependent variation in transmitted optical intensity, called the interferogram. When the inteferometer is illuminated by a monochromatic source such as a single frequency laser, the interferogram will be a sine wave of intensity versus mirror position. On the other hand, if the source is characterized by a broad infrared spectrum, the interferogram will correspond to the superposition of an infinite number of since waves having different periods but a common zero phase point (or central maximum) which occurs when the lengths of the two interferometer arms are equal.

In principle, the intensity of a given spectral point could be determined by simply passing the electrical signal obtained from the IR detector through a narrow band electronic filter. And the complete spectrum could be measured by varying the filter frequency. A much more rapid approach is to use a digital computer to perform a Fourier transformation of the interferogram, thereby directly yielding the composite spectrum of the source, the instrument, and any sample interposed in the optical path. This is the basis of all modern rapid-scan FTIR spectrometers.

Over the past several years, FTIR spectrometers have almost completely supplanted the older dispersive instruments for laboratory IR analysis. The reasons for this include the
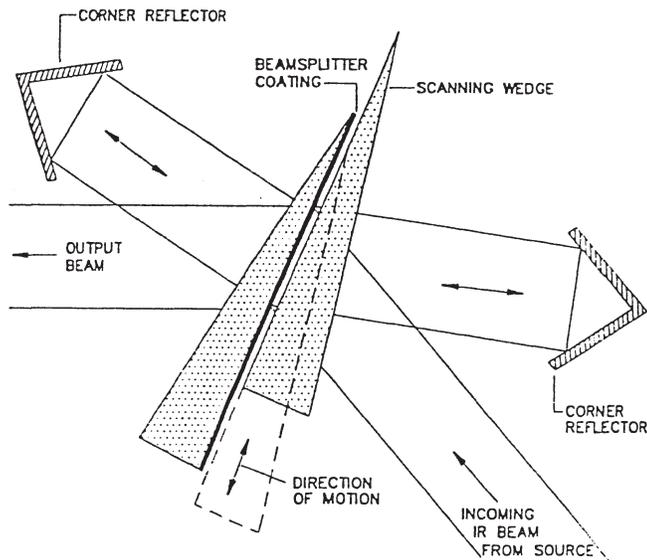
Fig. 2. The refractively scanned Transept™ interferometer (trademark KVB/Analect).

"multiplex advantage", the "throughput advantage", greater frequency accuracy, and the suppression of stray light (5). The most generally important of these is the multiplex advantage. This is derived from the fact that the FTIR measures all wavelengths simultaneously instead of sequentially stepping from wavelength to wavelength. In principle, this means that the time required to obtain a spectrum having a given signal-to-noise ratio can be reduced in proportion to the number of data points in the spectrum. This greatly increased speed is not only valuable in the laboratory, but it is also the key factor that makes process FTIR possible.

If the multiplex advantage made process FTIR possible, the key to making it practical lay in reducing its sensitivity to ambient temperature and vibration effects. These effects arise from the fact that the proper operation of the Michelson interferometer requires continuous alignment of the moving mirror as well as both tracking and control of its motion to within a small fraction of a wavelength.

There are two possible approaches to solving the problem of interferometer ambient sensitivity. The first involves the combination of a massive structure with vibration and thermal isolation to decouple the interferometer from the environment. The second involves the use of an alternative interferometer design which is inherently less sensitive to its environment. Both of these approaches are currently being employed in process FTIR instruments with considerable success.

The refractively scanned "Transept®" interferometer, which is employed in a substantial number of current process FTIR installations, is illustrated in Fig. 2 (6). This design differs from the standard Michelson interferometer in that path length scanning is accomplished by moving one of a pair of matched wedges of transparent material across one arm of the interferometer so as to effectively change the thickness of a

uniform layer of this material. This leads to an optical path length change, $\Delta p$, equal to

$$\Delta p = \Delta y (n - 1) \sin \alpha \qquad (1)$$

where $\Delta y$ is an increment of wedge translation, $n$ is the refractive index of the wedge, and $\alpha$ is its apex or wedge angle.

Refractive scanning produces two benefits. First, it amplifies the optical path length change by typically an order of magnitude, thereby substantially reducing the effect of errors in scanning position, including those caused by vibration. Second, the effect of any inadvertent wedge tilt will be simply a lateral displacement of the beam rather than a change in angular alignment. Compared to the conventional moving mirror design, this distinction corresponds to more than a two order of magnitude reduction in the required angular stability during scanning (7). In operation, the refractively scanned interferometers have proven to be largely immune both to the effects of vibration and to changes in ambient temperature (7). They do not require thermal of vibrational isolation other than that provided by mounting the interferometer in a standard NEMA-4 enclosure.

A second novel interferometer that has found considerable application in process FTIR is the dual moving corner reflector design employed in the Bomem Michelson Series instruments and illustrated in Fig. 3 (8). Like the refractively scanned interferometer, this design can be essentially permanently aligned. This is made possible by taking advantage of two characteristics of corner reflectors. First their alignment is inherently unaffected by tilt. Second, by suitably coupling the motions of the two corner reflectors, the effects of lateral displacement (i.e. shear) can be minimized (9). In the design illustrated in Fig. 3, each optical ray traveling along either arm of the interferometer will be effectively reflected from the corner reflector in a plane where it is at a right angle to a line through the pivot point. As a result, the lateral displacements of the corner reflectors relative to the light path will be proportional to the cosine of the angle of rotation (i.e. no first order term). Shear effects are thus negligible for the resolutions employed in process FTIR.

Vibration sensitivity of this interferometer is minimized by supporting the moving mechanism on a laterally stiff flexible pivot and by accurately balancing it so that lateral impulses are not translated into rotational motion. Thermal stability is insured by taking advantage of the high thermal conductivity of aluminum in constructing both the rotating assembly and the interferometer beamsplitter support.

Process FTIR systems employing both refractively scanned interferometers and dual moving corner reflector interferometers are now operating in a wide variety of rather hostile environments - ranging from a number of outdoor locations on the Gulf coast to a catwalk two thirds of the way up a smokestack. The success of these systems, as well as systems employing more conventional environmentally isolated interferometers, is strong evidence for the fact that the most fundamental
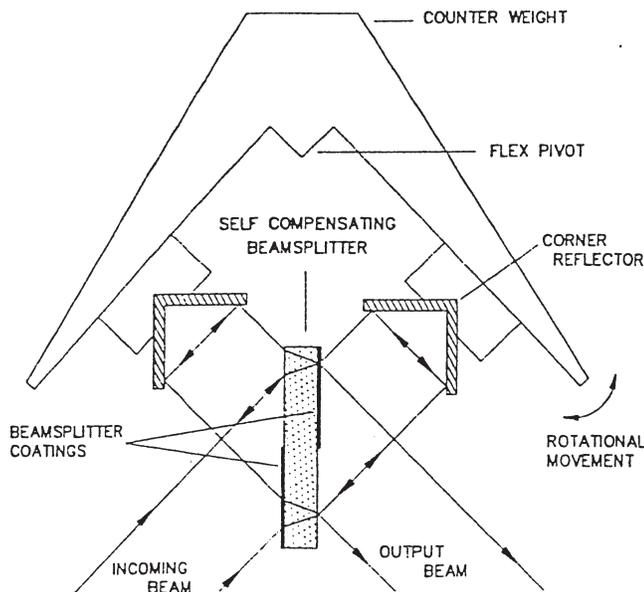
Fig. 3. The dual moving corner reflector design used in the Bomem Michelson™ Series interferometers (trademark, Bomem/Hartmann and Braun)

obstacle to the success of process FTIR has been surmounted, opening the way for the application of this technology to a wide variety of challenging tasks.

## COMMUNICATING WITH THE SAMPLING SITE

Fiber optics is potentially the most attractive means for communicating between an optical instrument and a remote sampling site. Indeed, fiber optics links are commonly used with visible and near-IR instruments, allowing an instrument to be located in an air conditioned control room while the actual sample interfacing takes place on the factory floor. The availability of near-IR fibers is one of the primary reasons for the attractiveness of near-IR instruments for use in manufacturing environments (10,11).

Unfortunately, the performance of optical fibers decrease rapidly as one moves out into the mid-IR. Fluoride glass fibers are available for operations at the high frequency end of the mid-IR spectrum and have been used at frequencies down to about 2000 cm$^{-1}$, although with relatively limited overall system transmission due to the low throughout of the fiber optics subsystem (12). In the fingerprint region (frequencies below 2000 cm$^{-1}$), where most of the interesting bands occur, the problems become both severe ad fundamental.

The problems with the IR fibers are two-fold. First, since the great majority of materials have fundamental absorptions in the fingerprint region, there simply are not very many candidate materials for consideration as mid-IR fibers. Chalcogenide glass fibers have received considerable attention of late, but their inherent mid-IR absorptions limit their use to very specialized applications involving distances of one or two meters at most (13, 14).

The materials that offer the greatest possibility of transmitting mid-IR radiation over a significant distance are the alkali halides. But these are soft, water soluble, and thermally unstable. Heo et al. have recently investigated the possibility of modifying chalcogenide glasses by the addition of alkali halides (15). Such "chalcohalide" glasses have properties intermediate between the chalcogenides and the alkali halides. These authors concluded that concentrations of halogen elements above 30 at. % will lead to phase separations. This suggests that there is little hope of this approach producing glasses with sufficiently low absorptions to be useful for remote instrument operation.

The second obstacle to the use of fiber optics in the mid-IR results from the relative insensitivity of mid-IR detectors and the inherently low source emittance in this region. These factors necessitate the use of the highest possible throughput in the optical transmission system. To understand the significance of this, we will review the all important concept of throughput.

Throughput (also known as etendue) is a measure of the ability of an optical system to transmit power obtained from an incoherent source. A throughput value can be calculated at any element of the system - such as at a lens, detector surface, or interferometer aperture - where the radiation is uniformly distributed over an area and a range of angles (16).

The throughput at a given optical element is usually defined as the area of the element times the solid angle subtended by the radiation passing through or striking it i.e.:

$$TP = 2\pi A (1 - \cos\theta) \qquad (2)$$

where $A$ is the area of the element, and $\theta$ is the half-angle field of view (see Fig. 4)

A more precise definition of throughput takes into account the fact that the effective are of the aperture, as viewed from a given ray direction, is reduced in proportion to the cosine of the angle between the ray direction and the system axis (17), i.e.;
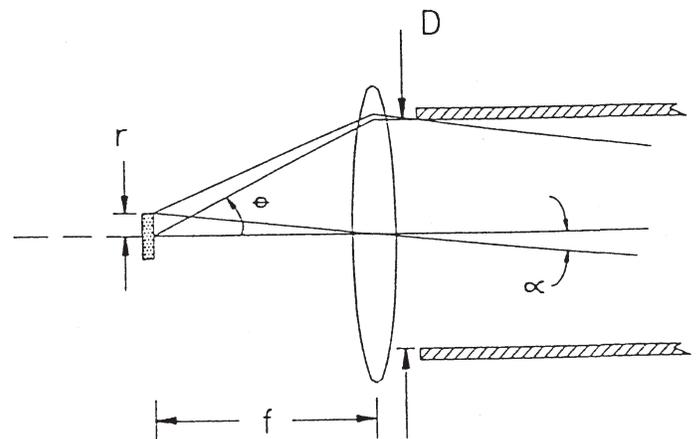


Fig. 4. Idealized detector optical geometry.

$$TP = \int_0^{\theta} \cos\theta \; d\Omega \; dA$$

where $d\Omega = \sin\theta \; d\theta \; d\phi$ \hfill (3)

For a cone of radiation centered on the system axis, this becomes

$$TP = \pi A \, (NA)^2 \hfill (4)$$

where $NA = \sin\theta$ is defined as the numerical aperture of the cone of radiation.

Note that throughput is geometric quantity and should not be confused with transmission. Assuming an extended radiation source, the total power reaching the detector will be approximately proportional to the limiting throughput times the optical transmission for radiation traveling along the system's axis. The limiting throughput of the overall optical system will be equal to the lowest throughput at any element of the system.
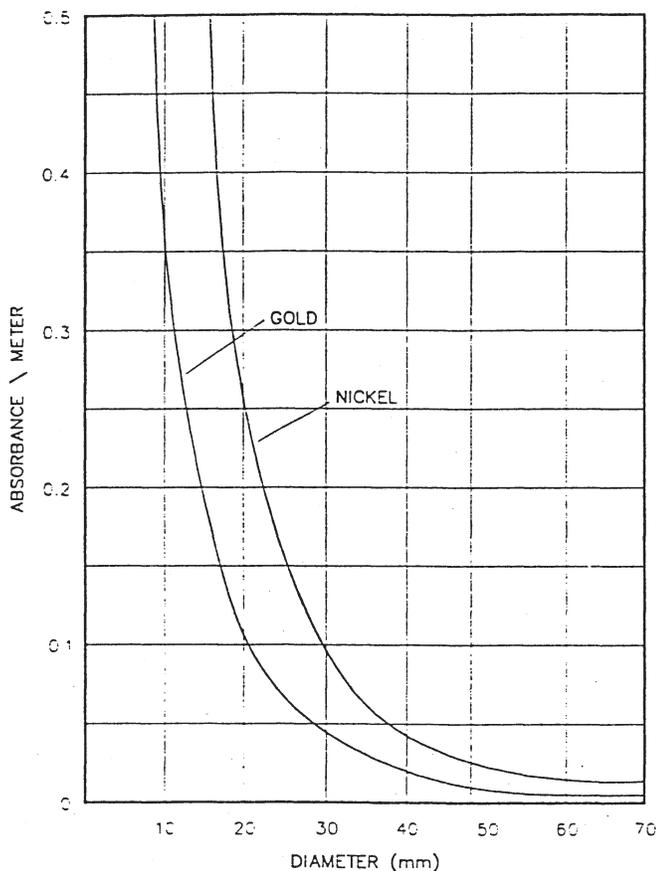


Fig. 5. Absorbance per unit length as a function of light guide diameter for the median ray of a nominally collimated IR beam. The two curves correspond to gold and nickel coated light guides. This figure assumes a 1 mm diameter IR detector and an $f$: 0.8 collecting optics matched to the diameter of the light guide.

In most industrial FTIR spectrometers, the limiting throughput will be that of the detector and its associated optics. Typically, this will involve a detector with a diameter of at least 1 mm and a 60° cone of radiation (NA = 0.5). This is close to a practical limit for a system using reflecting optics. Since the problems of coupling light to a fiber and to detector are essentially the same, it is reasonable to assume that the same practical maximum numerical aperture would apply in each case. Thus, matching the throughput of an optimized detection system would require an optical fiber with a core diameter of at least 1 mm. While this is theoretically possible, a large diameter such as this would substantially compound the mechanical problems associated with the rather brittle materials being considered for use in the mid-IR.

From the considerations discussed above, it does not seem likely that we can expect the early development of mid-IR fibers with the low absorbance and geometrical throughput required to communicate between a remote sampling location and an instrument located in a control room. Fortunately, this lack is not a real impediment to the implementation of process FTIR. Modern process FTIR interferometers have been hardened to the point where they will function reliably in almost any manufacturing environment - tolerating severe vibration and acoustic disturbances and the outdoor temperatures experienced in tropical climates. Some examples of specific installations will be given in a later section.

A typical process FTIR installation involves a NEMA enclosed, environmentally hardened FTIR interferometer at a convenient location within ten or twenty feet (3-6 m) of the process sampling site and a PC data system located in the control room. Communication between the interferometer and the data system is via either a fiber optic or a coaxial cable local area network link.

Communication between the FTIR interometer and the sample interfacing equipment can be accomplished by using either an image transfer optical system (18) or a series of hollow metallic light guides (19). The image approach is most often used when the sampling system is located immediately adjacent to the spectrometer. For greater separations, the light guide approach is easier to implement and more economical as well as being completely adjustment free. The following discussion will give an idea of the performance that can be obtained with this type of system.

The transmittance of a light guide for a given optical ray depends on the number of reflections that the ray makes with the wall and on the reflectance of the coating material used. This, in turn, can be highly dependent on the angle of incidence of the ray as it strikes the wall. In general, the highest transmission will be obtained when the radiation is as nearly collimated as possible. If we assume that this is the case, the maximum divergence angle of the rays actually being used will be determined by the limiting throughput of the FTIR optical system.

In the absence of a sampling system, the limiting through-

put of an FTIR spectrometer can be either the interferometer throughput depends on resolution, optical beam diameter, and the scanning method employed (20). When operating at the modest resolutions employed in most process applications, the interferometer throughput will generally be greater than that of the detector optics.

For sake of illustrations, we will assume here that the usable field of view in the system is determined by the detector optics, as illustrated by Fig. 4. For simplicity, this illustration uses a simple lens to focus the IR radiation emerging from the light guide onto an IR detector. In most practical mid-IR applications, the focussing element would be a 90° off-axis reflecting paraboloid. As the figure illustrates, the maximum divergence angle of a ray that can strike the detector is given by $\propto$ = arctant $(r/f)$ where "$r$" is the radius of the detector and "$f$" is the focal length of the detector collecting optics. Assuming that the end of the light guide is the limiting aperture, the above expression can be written in terms of the diameter of the light guide, D, and the F# of the detector optics, i.e.:

$$\propto = \text{arctan } (r/FD), \text{ where F = F\# = } f/D \qquad (5)$$

In a light guide of length $L$ the number of reflections experienced by a ray in an axial plane, having a grazing angle of a $\propto$ is given by

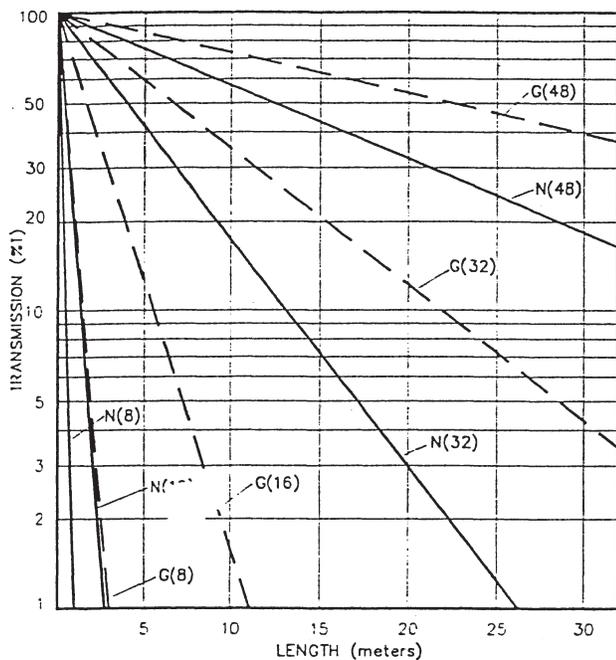$$N = (L/D) \text{ tan } \propto = rL/FD^2 \qquad (6)$$



Fig. 6. Transmission versus length for various diameter light guides under the same assumption as Fig. 5 "G" and "N" refer to gold and nickel respectively, and the numbers in parentheses are the light guide inner diameters (mm).

For a single reflection, the absorbance experienced by a ray at an angle $\propto$ is, by definition $a(\propto)$ = -log $R(\propto)$. Thus, for $N$ reflections, the total absorbance will be $A(\propto)$ = $-N$ log $R(\propto)$. Combining these expressions, we have

$$A(\propto) = -(rL/FD^2) \log R(\propto) \qquad (7)$$

This can be converted to transmission $T$ by using $T = 10^{-A}$.

The results of the above analysis are plotted in Figs. 5 and 6 for median ray ($\propto_m = \propto / \sqrt{2}$) and two coating materials. The reflectance values were obtained by using a computer program to calculate reflectance as a function of angle for radiation polarized parallel and perpendicular to the plane of incidence. The two values for a given angle were then averaged since the plane of incidence changes as a given ray passes through the light guide.

## Sample Interfacing Equipment

In this paper, we have been using the term "process FTIR" rather broadly to refer to both process and environmental monitoring installations. This is reasonable in view of the fact that the demands placed on the equipment are similar in both of these areas. Continuing this generalization, we can safely state that the largest number of installations to date have involved gas sampling. This is due to the large number of applications for ambient air monitoring and the availability of practical long path gas cells for use in these applications as well as to the availability of simple short path cells for process gas analysis.

Liquid analysis clearly is the largest area of potential application in chemical processing. Indeed, most reactions take place in the liquid state. However, this area has only recently started to see steady growth as the appropriate sample interfacing equipment has become available.

The analysis of solids is the most difficult of the three general area of application. However, even in this area there have been some successful applications, and new techniques now being developed promise to open up additional possibilities.

The sample interfacing equipment available for use in each of the three general areas is described below. A later section will outline a number of current and planned applications using the various equipment described.

## Gas Sampling

Gas sampling applications generally fall into two categories; short path and long path. A typical on-line short path application would involve high concentration gasses flowing through a process pipe. In this case, sample

interfacing can be as simple as directing the IR radiation through a pair of windows mounted on opposite sides of the pipe.

Long path applications generally require a sample interfacing system (commonly called a gas cell) to confine the gas while providing a relatively long radiation path through it. One exception is ambient air monitoring along an open path.

The most widely used type of long path gas cell is the White cell (21-23). As Fig. 7 illustrates. this design uses a set of three mirrors to reflect the light back and forth through a fixed volume of gas. A very high ratio of path length to cell volume is achieved by creating a series of images of the input aperture on a mirror between the input and output apertures. The beam simply steps back and forth across this mirror taking one step on each successive round trip and eventually leaving through the exit aperture.

The important features of the White cell include a high ratio of path length to volume and of path length to manufacturing cost as well as the availability of very long paths in a compact package. Its limitations include a dependence of transmission on ambient temperature, at elevated temperatures, and a relatively slow response



Fig. 8. A linear flow gas cell employing four parallel light guides to conduct both the gas and the IR radiation. This cell achieves essentially plug flow conditions, assuring very rapid sample exchange.

to changes in gas composition - due in part to the lack of uniform overlap between the gas volume and optical path and in part to turbulent mixing in the large diameter cell. This latter factor leads to exponential decay when a sample is purged from the cell.

White cells are widely used in such applications as ambient air monitoring and auto exhaust analysis, applications in which the combination of long pathlength and low cost are especially important.

Figure 8 illustrates a new type of "linearity flow" gas cell based on the use of light guides of the type discussed in the previous section. With this design, the gas and the IR radiation both uniformly fill the cell volume. As a result, the response to the introduction of a new sample can be quite fast, requiring only the time that it takes for the gas sample to diffuse across the diameter of the cell (see Fig. 9). The depletion time will also be very fast since the gas travels through the cell in a linear, plug flow fashion (24).

The primary advantages of the linear flow design are fast response time, the absence of optical adjustments, a high degree of environmental tolerance, and compatibility with high temperature and high pressure opera-
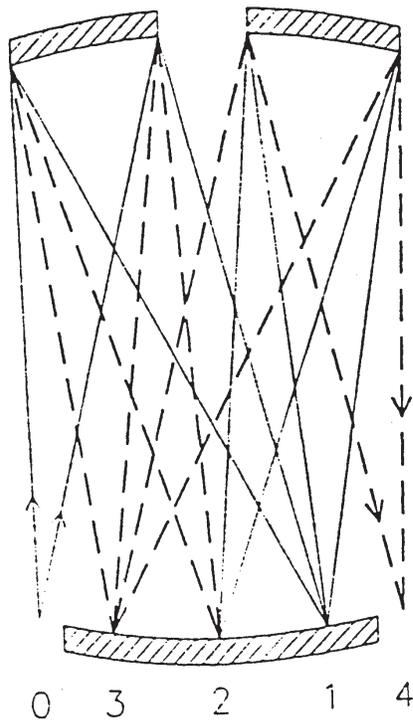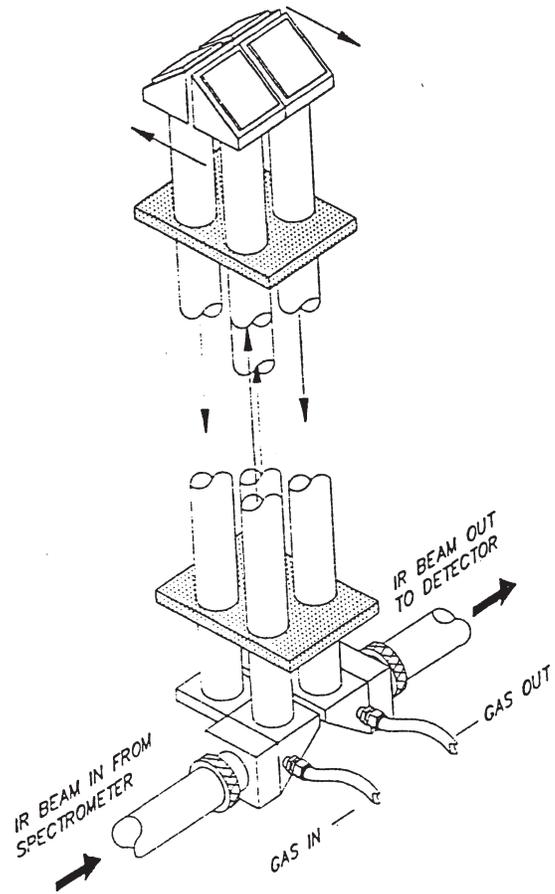


Fig. 7. An example of an eight-pass White cell design. The centers of curvature of the two smaller mirrors fall on the surface of the larger mirror. Light enters at "0" and eventually leaves at "4" after sequentially being reflected at positions "1", "2", and "3". For clarity, the first four passes are shown as solid lines and the last four as dashed lines. This cell features a high path length to volume ratio and low manufacturing cost.
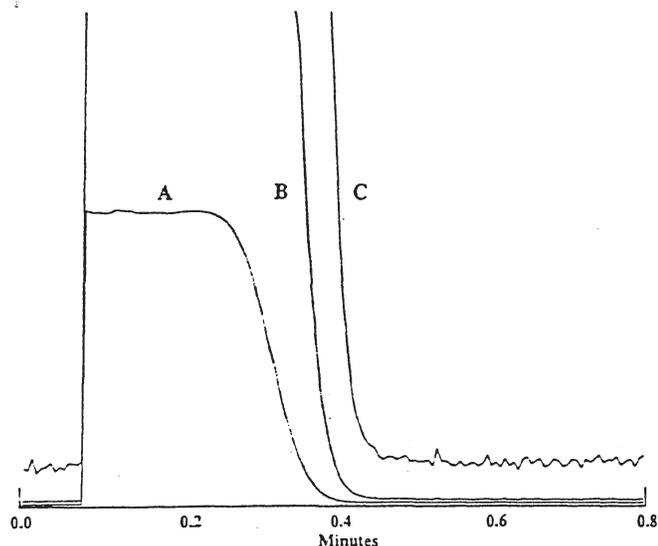
Fig. 9. The time response of a four meter linear flow gas cell to the injection of a short plug of acetone vapor in the presence of a constant 8 liter /minute flow of nitrogen. Traces B and C are a ten-fold and hundred-fold vertical expansions of trace A. The measured acetone level had fallen to less than 0.05% of its initial value after a total purge of less than 1.5 cell volumes.

tion. The primary disadvantages are relatively high cost and large size. To date, these cells are finding their main use in demanding applications such as hazardous waste incinerator monitoring and process gas analysis. Their rapid response has also proven valuable in a commercial system for sparging-infrared waste water analysis.

The analysis of solids is particularly difficult area for mid-IR spectroscopy. In contrast, near-IR has been ap-

plied extensively in this area, especially in the analysis of agricultural products and other materials in powder form (25,26). The reason for this is based on the fact that powders and many other materials are highly scattering and weakly absorbing in the near-IR. As a result, they exhibit a substantial level of diffuse reflectance, characterized by measurable absorption bands.

In the mid-IR, most solid samples exhibit very weak diffuse reflectance. This is due to the fact that scattering decreases rapidly with increased wavelength while mid-IR absorptions are orders of magnitude stronger than those in the near-IR. Thus, diffuse reflectance is generally only usable for quantitative measurements when the sample is ground up and mixed with a transparent scattering matrix (27). Clearly this approach is not appropriate for continuous on-line analysis.

Attenuated total reflectance (to be discussed in greater detail with respect to liquids in a later section) can be applied to the analysis of powders and pliable solids (28). Although the use of this contact method with solids has been limited to laboratory applications, to date, one can envision its eventual use for near-line and perhaps on-line powder analysis. Figure 10, a spectrum obtained by dipping a two reflection ATR probe into a container of powdered aspirin, illustrates this potential.

Specular reflectance is another approach to solid sampling which has not been applied on-line yet. This method is based on the spectral analysis of the dielectric reflection which occurs at the front surface of a sample. After recording a spectrum of a sample's reflectance, we can calculate a corresponding spectrum of its refractive index
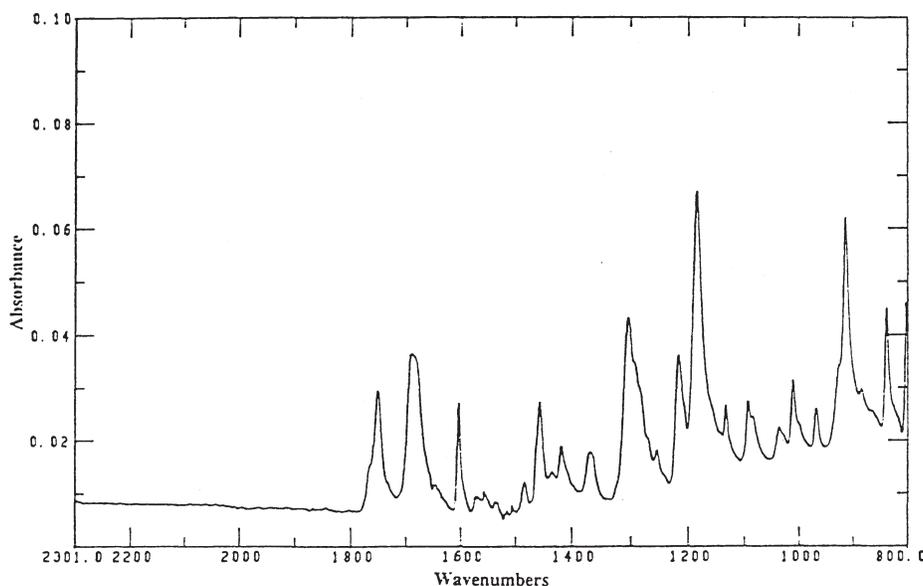


Fig. 10. A spectrum obtained by dipping a two reflection conical ATR probe into a container of powdered aspirin. Although the band shapes are somewhat distorted by the dispersion of acetone's refractive index, this approach would clearly be usable as a means of identifying powdered raw materials.
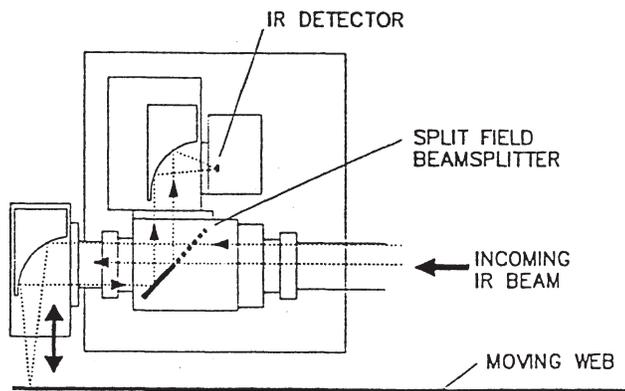
Fig. 11. Isotropic specular reflectance measurement geometry. This design employs a three bladed, split field beamsplitter to separate the incoming and reflected beams while providing essentially normal incidence operation (34).

by using the laws of reflectance (29). This in turn can be used to calculate an absorbance spectrum by means of a mathematical process called the Kramers-Kronig transform (30-32).

The specular reflectance technique is applicable to any sample having a reasonably smooth (i.e. specular) surface and an adequate combination of thickness and absorbance to eliminate contributions from scattering or rear surface reflection. However, in using this technique, it is important to measure the reflectance spectrum under conditions that closely approximate normal incidence (see. Fig. 11). This isotropic situation is only case in which the refractive index spectrum can be conveniently

calculated from the measured reflectance spectrum (33, 34). Some data obtained with this technique will be given in the following section.

*Solid sampling - Web Processes*

Over the years, there has been considerable interest in the use of both near-IR and mid-IR to monitor web processes, i.e. processes in which the product is in sheet form. In these processes, the samples are often thin enough to allow measurement in transmission or, in the case of coatings on metals, reflection/absorption. But even in this area, applications have been limited and sometimes problematic. The difficulties fall into two broad categories, problems characteristic of transmission measurements in general (35) and problems associated with sample motion (36). The first category includes the problem of interference fringes (i.e. optical interference between the light reflected from the front and back surfaces of the film). These fringes cannot simply be subtracted out of the spectrum since they do not depend monotonically on thickness. They can lead to quite large measurement errors - for both thin free sanding films and coatings on reflecting substrates. On the other hand, if the sample is thick enough so that fringes are not a problem, the mid-IR absorbances are likely to be too strong to be useful. Measurement may still be possible at shorter wavelengths, but with much less precision and specificity.

The primary difficulty with sample motion has to do with the high speed of many web processes combined with variations in sample transmission which may or may not effect the quality of the product. Any variation
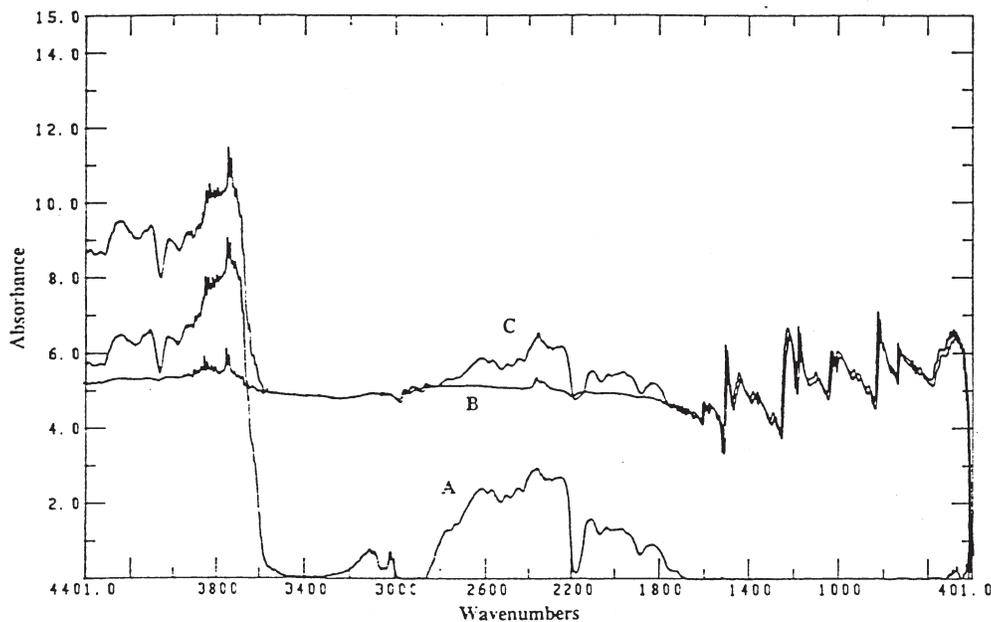


Fig. 12. Spectra of a printed circuit board obtained by three different methods: (A) transmission, (B) isotropic specular reflection and (C) reflection with a mirror behind the sample. The spectral characteristics seen in the low frequency region of the reflectance spectra are the result of dispersion of the samples refractive index in the vicinity of absorption bands. These bands are strong enough to render the sample opaque in transmission.
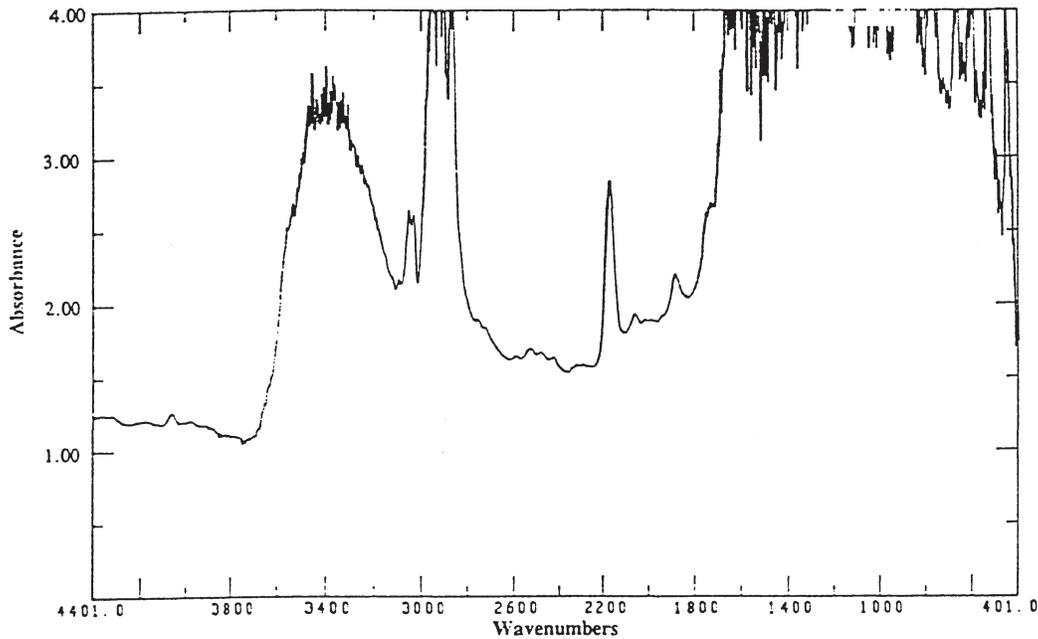
Fig. 13.  Absorbance spectrum calculated from the transmission spectrum given in Fig. 12A.  Few distinct lines are available in this spectrum for use in quantitative analysis.

in transmission which takes place on a time scale shorter than the scanning time of the FTIR interferometer can give rise to excessive noise and measurement error (36). a second problem area is sheet flutter, which can be particularly troublesome in the reflection/absorption analysis of coatings on metals.

As a result of the above difficulties, inplant web process applications to date have been limited to either static or slowly moving samples.  An approach being pursued by one large scale manufacturer of films, for example, is to use near-IR for high speed on-line monitoring combines with FTIR for highly accurate near-line profiling of tear sheets (37).

Within the limits imposed by sample motion problems, there are a variety of techniques available which offer the promise of improved FTIR web analysis (38).  For example, with thick web samples, one has the options of working at shorter wavelength or using the specular reflectance technique.  The tradeoffs between these two choices are illustrated by Figs. 12, 13, and 14.  Figure 12
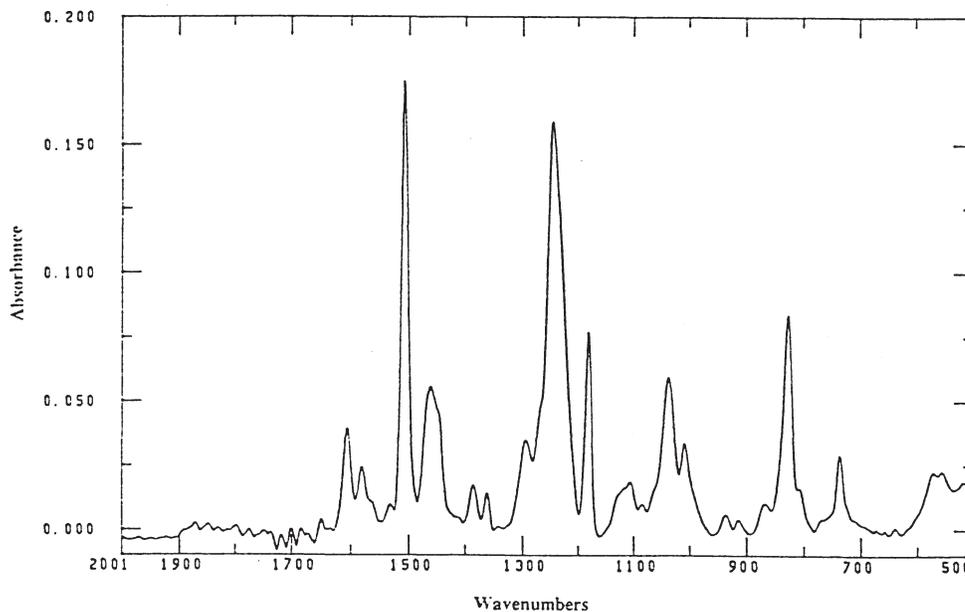


Fig. 14.  Fingerprint region absorbance spectrum calculated from the reflectance spectrum of Fig. 12B by using the Kramers-Kronig transform.  Note the comparative wealth of spectral information available.
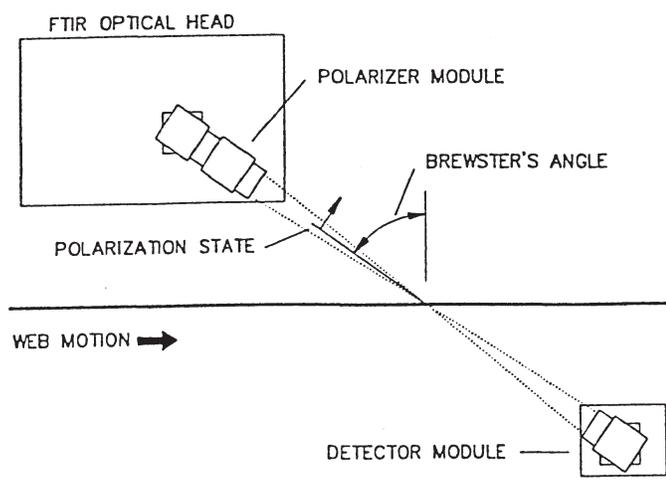
Fig. 15. Measurement geometry for web transmission measurement using polarized radiation.

sions in these two regions are only about 3% and 9% respectively.

In contrast to the transmission spectrum, both the pure reflection spectrum and the reflection/absorption spectrum of Figure 12 reveal a wealth of detail in the fingerprint region. This is the dielectric reflectance spectrum of the sample. As has been discussed by several authors, a dielectric reflectance spectrum can be converted into an absorbance spectrum by use of a mathematical process called the Kramers - Kronig transform (30 - 32). Applying this process to the spectrum of Figure 12B yields an absorbance spectrum (Fig. 14) having a number of distinct bands which could be used to provide detailed chemical structure information for on-line analysis. For this example, the information content of the reflectance spectrum is clearly much greater than that of the transmission spectrum.

With rapidly moving targets, the specular reflectance method might experience sample variation problems similar to those encountered in transmission analysis. However, since this technique only monitors the characteristic of the surface layer, it would not be effected by thickness variation or internal defects.

Another example of a technique currently being considered for near-line and on-line analysis is the use of polarized radiation to eliminate the fringing problem that occurs with thin samples (38). The measurement geometry is illustrated in Fig. 15. In this approach, the radiation is incident at Brewster's angle and is polarized with its

includes three different types of spectra obtained from the same printed circuit board, a transmission spectrum, a first surface reflectance spectrum, and a composit spectrum obtained by placing a mirror behind the sample. The latter two of these obtained by using the isotropic specular reflectance geometry illustrated in Fig. 11 (39).

Figure 13 is an absorbance spectrum calculated from the transmission spectrum (Fig. 12A). Clearly, the sample is too strongly absorbing for transmission analysis in the fingerprint region. There are a few overtone bands in the 1800 to 2800 cm$^{-1}$ that might be of use as well as one band at 3930 cm$^{-1}$. However, the overall transmis-
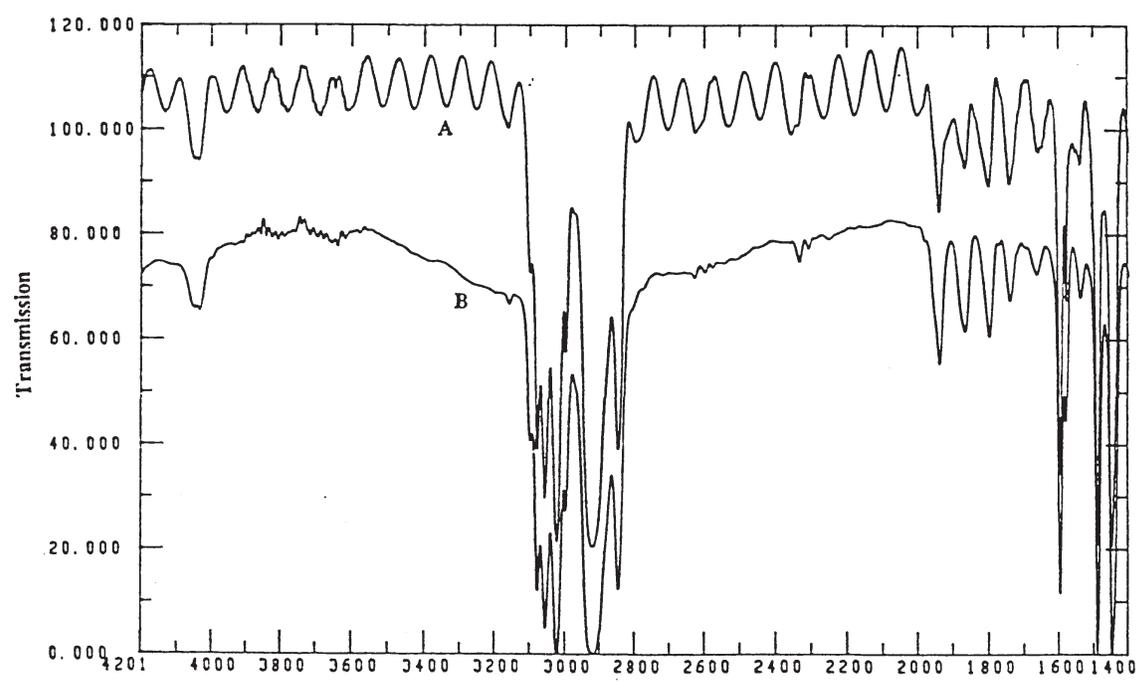


Fig. 16. (A) A portion of a polystyrene spectrum obtained at normal incidence. (B) A spectrum of the same sample obtained with the geometry shown in Fig. 15. A has been offset 20% for clarity.
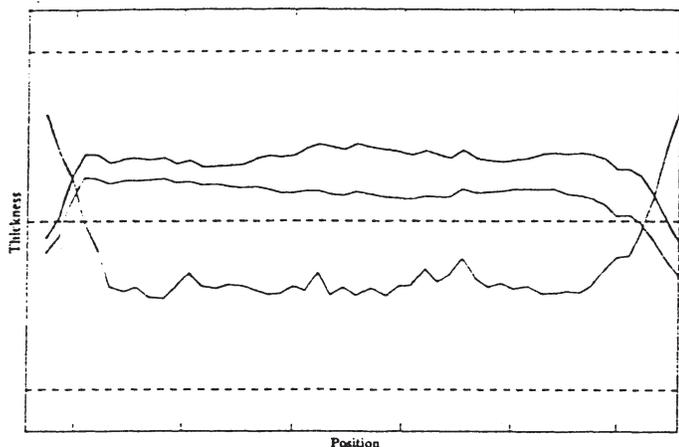
Fig. 17. Thickness profiles of the three layers of a coextruded film obtained by using the Brewster angle measurement geometry in Fig. 15. (Courtesy of KVB/Analect.)

electric field parallel to its plane of incidence. Note that Brewster's angle is the angle at which parallel polarization is not reflected at a dielectric surface. In the absence of reflection, there are no interference fringes, as illustrated in Fig. 16. Figure 17 illustrates the use of this approach, along with "**P**" matrix software to profile the thicknesses of three different polymer layers in a coextruded film.

It is interesting to note that the use of polarized radiation at Brewster's angle to eliminate fringing effects predates the field of process FTIR by several years, having been used as early as 1976 in a filter spectrometer for monitoring the thickness of coatings on aluminum (40).

### Liquid sampling

Liquid analysis obviously encompasses the largest number of potential applications for process FTIR. However, it is only quite recently that sample interfacing equipment suitable for most of these applications has become commercially available.

The difficulty of liquid analysis is related to the strengths of the fundamental functional group absorbances encountered in the mid-IR. Transmission cells for use in this region are necessarily very thin (typically 25 to 100 $\mu$m thick) and, as a result, tend to be plagued by such problems as interference fringes, wedged cell effects, excessive flow resistance, and sample buildup and clogging.

One area in which thin transmission cells have proven quite effective is in the analysis of hot polymer melts (41). Here, cells specifically designed for highly temperature and pressure are used to directly monitor a polymer during extrusion. In this case, the problems of flow resistance and sample build up are minimized by the high temperature and pressure operation. One cell uses either ZnSe or diamond windows with their separation adjust-

able from 30 $\mu$m to 2 mm. This cell can be operated at pressures to 300 bar and temperatures to 400°C (42).

A fairly general solution to the problem of high mid-IR absorbance is the use of the attenuated total reflectance (ATR) technique. The theory of this technique has been treated in detail in the excellent book by Harrick (43). The basics will be briefly reviewed.

Consider a trapezoidal block of transparent material (the internal reflectance element), having a relatively high index of refraction (e.g.: $n_1$ = 2.4), in contact with a material having a lower index (e.g.: $n_2$ = 1.4), as illustrated in Fig. 18. Now let us assume that the IR beam from an FTIR spectrometer is directed into this element so that it strikes the longitudinal surface of the element at an angle of incidence of $\theta_c$, measured from the normal to the surface. The reflection characteristics of this system are illustrated in Fig. 19.

If the lower index material is nonabsorbing, the IR beam will be largely transmitted for angles near normal incidence. As the angle if incidence is increased, a point will eventually be reached where the beam is fully reflected. This is the critical angle, $\theta_c = n_2/n_1$). This behavior is illustrated by the solid curves of Fig. 19 for two orthogonal polarization states. On the other hand, if the lower index material is absorbing, the beam will actually penetrate slightly into the medium on reflection, even if the angle of incidence is greater than the critical angle. The effect of this penetration is to give rise to a partial absorption of the beam at each reflection, the total absorption will be adequate to provide an IR spectrum corresponding to an equivalent pathlength of typically 10 to 100 $\mu$m, an ideal range for most liquid chemicals.

Some of the characteristics of ATR are illustrated in Fig. 20, a plot of penetration depth versus refractive index ratio for the most common angle of incidence, 45° (44). As indicated by the ordinate units, the penetration depth, $d$, is proportional to wavelength, $\lambda$.
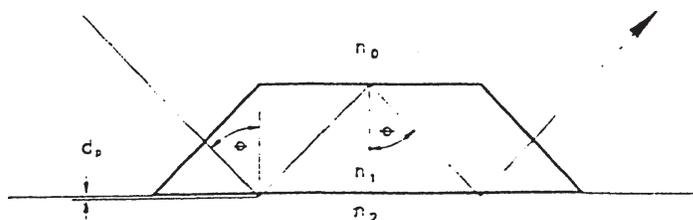


Fig. 18. Attenuated total reflectance (ATR) measurement geometry in which a trapezoidal element with a refractive index. $n_1$ is in contact with a sample having a lower index, $n_2$. In spectral regions where the sample is absorbing, a portion of the radiation will penetrate into the sample a distance represented by $d_p$, giving rise to an IR spectrum analogous to a transmission spectrum.
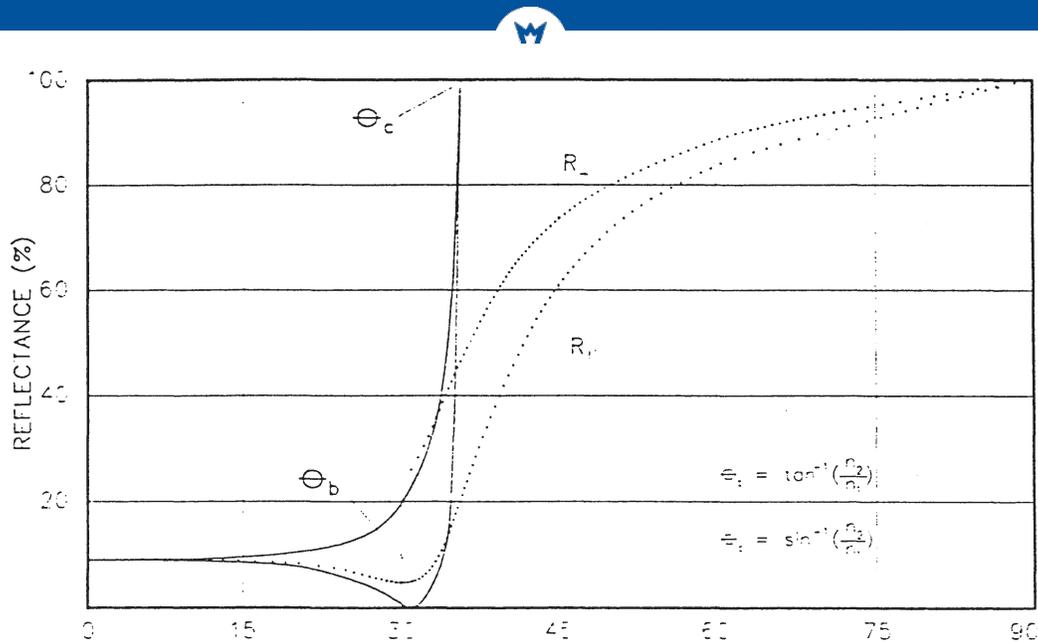
Fig. 19. Dependence of reflectance on angle of incidence for radiation incident on a surface from the direction of the higher index material. $R_\parallel$ and $R_\perp$ represent radiation polarized parallel and perpendicular to the plane of incidence, respectively. For this example, $n_2 = 1.44$ and $n_1 = 2.4$. The solid curves correspond to pure dielectric reflection (no absorption). The dotted curves correspond to a situation in which the second medium is absorbing.

ATR has been used in laboratory analysis for at least thirty years. However, its application to routine process monitoring had to await the development of robust ATR devices capable of providing the required long term stability and reliability. An early advance in this regard was the development at Dow Chemical and E.I. du Pont of one and two reflection process compatible ATR cells for use with dispersive and filter instruments (45, 46). More recently, a series of commercial multiple reflection ATR sampling devices has been developed specifically for process applications (44). These employ, circular cross section ATR elements with "O" ring seals and stainless steel construction. They are available in two forms, self contained cells for flowing liquid analysis and immersion probes for insertion into a volume of chemicals (47). Both of these use the "Tunnel" ( trade mark, Axiom Analytical, Inc.) optical design illustrated in Fig. 21.

The Tunnel design employs a polished rod of high refractive index material such as ZnSe or Amtir-1 with 90° conical surfaces at each end. The radiation is not focussed on the ends of the rod. Instead the IR beam is redirected by a conical reflector so that each ray strikes the end of the rod at approximately normal incidence. As a result, the distribution of incidence angles at the interface between the rod and the surrounding liquid is very narrow, typically less than $\pm 1°$ for nominally collimated input radiation. This narrow range of angles is necessary to eliminate the "wedged cell" effect which occurs with focussed radiation. As is well known from transmission measurements, this effect leads to a nonlinear dependence of absorbance on concentration (35).
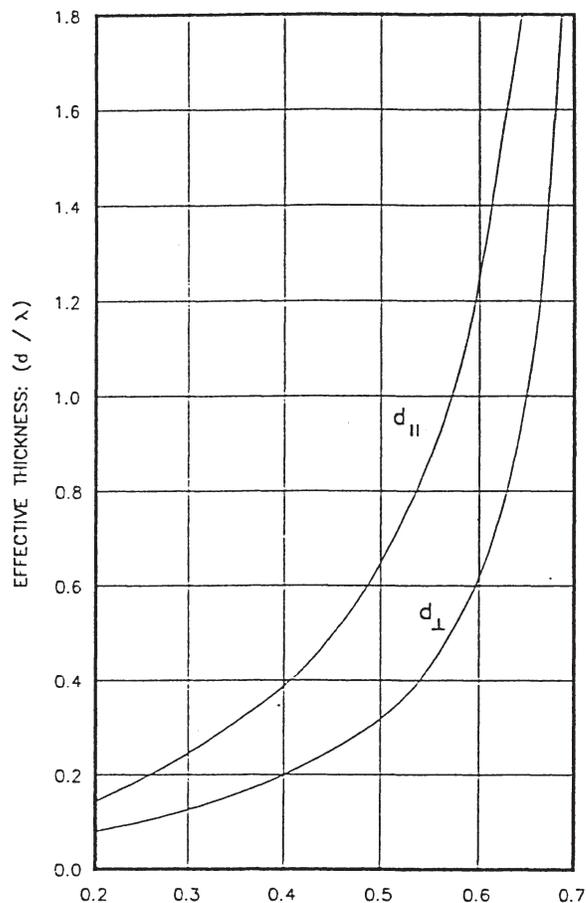


Fig. 20. Dependence of penetration depth on refractive index ration $(n_2 / n_1)$ for radiation incident at 45°. Note that the penetration depth is proportional to wavelength.
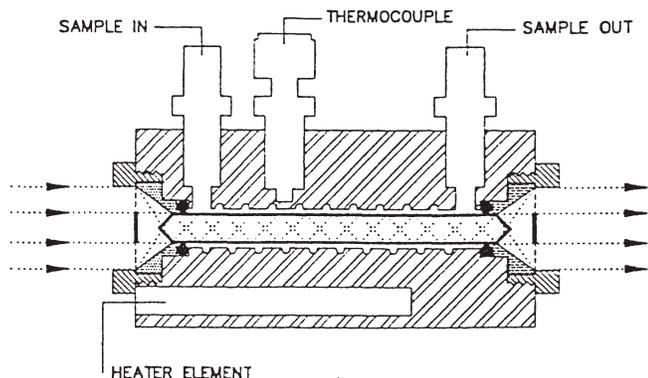
Fig. 21. An Adjustment-free ATR flow cell designed for process applications. The design utilizes solid stainless steel construction with all optical elements solidly mounted within the cell body.

The optical elements of the Tunnel Cell are clamped in place by the mechanical structure, eliminating the need for adjustments as well as the possibility of alignment variations with time. The solid stainless steel construction insures the robustness required for process application. Tunnel flow cells are routinely constructed with rod diameters ranging rom 1/8 inch to 1/2 inch and flow cross sections ranging from 0.012 cm² to 163 cm². They are being used in a wide variety of laboratory and on-line applications.

The use of the Tunnel optical design in an immersion probe configuration is illustrated in Fig. 22 (48). This design uses hollow metallic light guides to communicate between the ATR element immersed in the chemical process and the FTIR interferometer and IR detector. Large scale process immersion probes are 3.5" in diameter, use a 1/2" diameter, 6.5" long ATR element and have been constructed in lengths up to eight feet. Small scale laboratory probes are 1" in diameter and typically 16" long and use a 1/8" diameter, 1.55" long element. The number of reflections is approximately the same for each size probe. Thus, a calibration done in the lab using a small probe can be applied directly on line using the large process scale probe (49).

## Process FTIR Calibration Methods

The present paper is primarily devoted to the hardware developments that have made the widescale use of process FTIR possible. In parallel with these developments, the past few years have seen the development of mathematical methods which enable quantitative measurements to be made under a very wide range of conditions. Since these methods have been treated extensively in the literature (50-52), we will restrict our comments to those needed to understand the applications example of the following section.

Process FTIR spectroscopy often involves the simultaneous monitoring of several chemical species present in a reacting mixture. A number of mathematical methods are available for use in performing this analysis, including the various chemometric techniques commonly employed in the near-infrared (53). As noted above, however, the distinct and meaningful absorption bands available in the mid-IR greatly simplify the analysis. Rather than using full spectrum correlation techniques, it is often possible to select bands which bear a well understood relationship to the chemical bonds involved in the reaction and to make use of a relatively simple and transparent method such as the inverse least squares or "**P**" matrix approach. This method was used for the example to be treated in the following section.

In the "**P**" matrix method, the concentrations of the various species are expressed as a set of simultaneous equations involving all of the absorbances, i.e.: **C = PA**. Here **C** represents the set (or vector) of concentrations of the various species present, $A$ is the set of IR absorbances at selected frequencies, and **P** is the matrix of coefficients which relate concentrations to absorbances. The usual calibration approach involves the preparation of a set of samples having known concentrations of each of the various species to be analyzed. A spectrum of each of the samples is obtained and a set of frequencies are chosen for the analysis. The analytical frequencies can be selected by using purely mathematical techniques or by making use of a knowledge of the chemical structures of
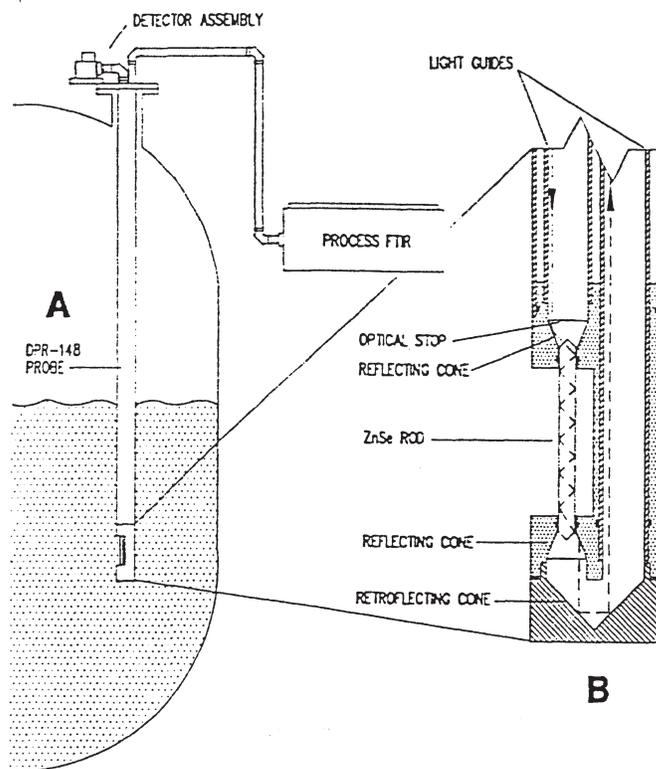


Fig. 22. (A): A process scale ATR immersion probe mounted in a batch reaction vessel. (B): Detail of the probe sensing head.
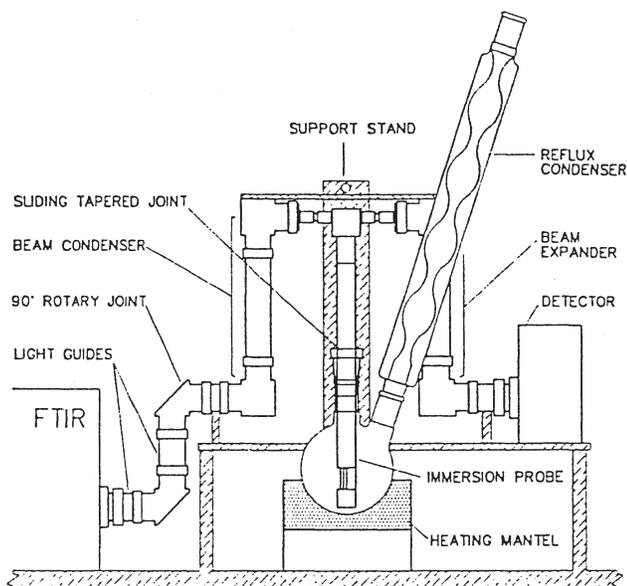
Fig. 23. Experimental arrangements using a laboratory scale immersion probe.

the constituents present. (This latter approach was used for the example given below.) Finally, the measured spectral absorbances are used in conjunction with the know concentrations to determine the values of the coefficients of the **P** matrix. When a spectrum of a new unknown mixture is obtained, all that is necessary is to perform a matrix multiplication of the **P** matrix times the new set of absorbances to determine the concentrations in the new mixture.

## An Applications Example - Copolymerization of Polystyrene and Polymethyl-Methacrylate

This section will illustrate some of the techniques involved in FTIR process monitoring by describing a set of experiments carried out in the laboratory. In this example, we used the "**P**" matrix approach to monitor the concentrations of monomers and polymers in various polymerization processes. These experiments have been reported in detail elsewhere (49) so the present discussion will be somewhat condensed. Although this data was obtained in the laboratory using a small scale immersion probe, the methods used and data obtained were very similar to those encountered in on-line full scale process applications.

The apparatus used for our experiments is shown schematically in Fig. 23. This is a typical laboratory configuration, with the small scale probe inserted into a round bottom flask through a 29/42 ground glass tapered joint and locked in place by a sliding tapered joint. A pair of beam condenser/ expanders is used to match the IR beam to the diameter of the small light guides in the probe.

The experiments involved the polymerization of styrene and methylmethacyrlate both individually and as a copolymer. Spectra corresponding to the starting point of the acid catalyzed styrene polymerization are shown in Fig. 24. The bands used to monitor the concentrations of styrene and toluene are indicated by the letters "S" and "T". Fig. 25, which includes ten-fold and hundred fold expansions of a portion of the lower trace of Fig. 24, gives an idea of the wealth of bands available for analysis and the high sensitivity of this technique.

Fig. 26 is the spectrum of the final reactions mixture as observed and after subtracting first a toluene spectrum and then a styrene spectrum. The result is a spectrum of polystyrene. The band used for polystyrene quantification is indicated by the letter "P". In Fig. 27, an expanded portion of the final difference spectrum of Fig. 26 is compared to a spectrum of a pure polystyrene film deposited on the ATR rod. The good match obtained testifies to the quality of the ATR data obtained, even after performing a double subtraction.

In this discussion, the subtraction method ws used only for the sake of illustration. In performing the actual analysis of concentration versus time, we employed the **P** matrix approach outlined in the previous section. Even though the band chosen for polystyrene measurement overlaps bands of both toluene and styrene , the **P** matrix calculations can still provide accurate concentrations measurements.

The results of the acid catalyzed styrene polymerization experiments are shown in Fig. 28. As the figure indicates, the process has a long initiation period followed by a short reaction time. This is an example of a type of reaction in which the FTIR monitoring technique would be valuable in accurately determining the end point.

We subsequently carried out experiments involving the free radical polymerization of both styrene and methylmethacrylate as well as their copolymerization. Since these reactions occur under diffusion controlled conditions, they are much more gradual than the acid catalyzed reaction. The results of the copolymerization experiment are shown in Fig. 29.

An interesting aspect of this data is the nonuniform rate at which polystyrene and PMMA units were formed. Polystyrene was formed preferentially during the early stages of the process with PMMA formation accelerating after 15 or 20 minutes. Spectroscopic analysis of the final product, however, indicated that it was indeed a true copolymer rather than just a mixture of polystyrene and PMMA. This experiment demonstrates the ability of FTIR not only to elucidate the dynamics of a process but also to analyze the results. This capability constitutes an extremely valuable tool for diagnosing any problems or other unexpected readings that occur during on-line
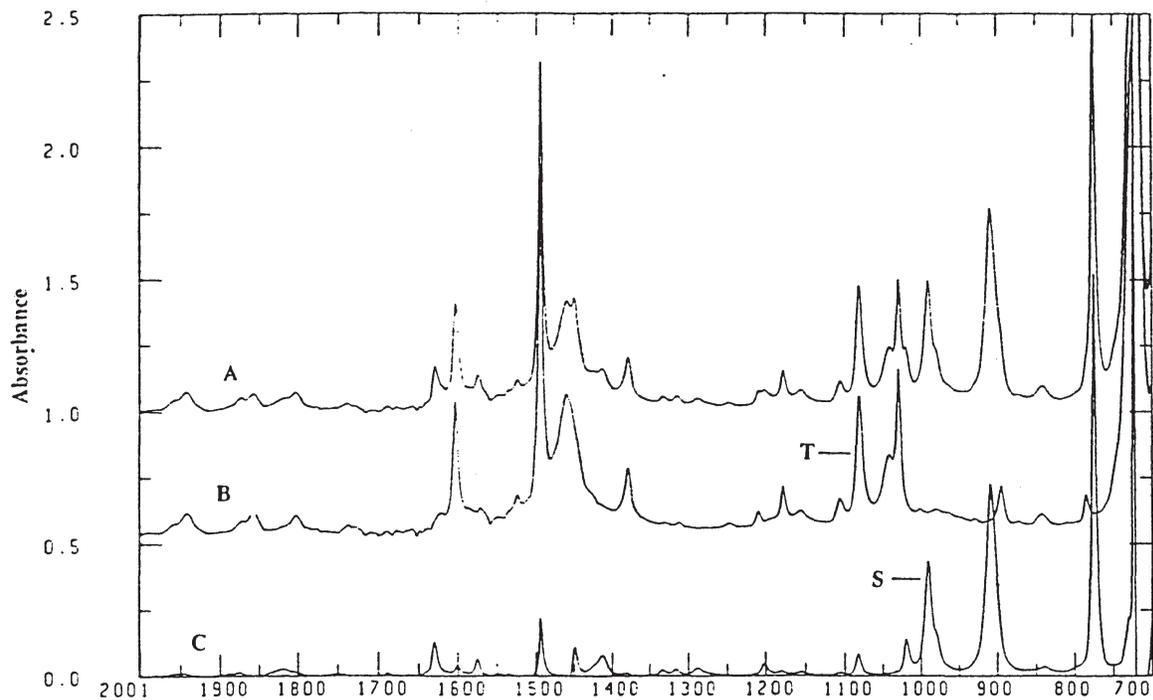
Fig. 24. (A): Spectrum of 20% solution of styrene monomer in toluene. (B): Toluene spectrum. (C): Spectrum (A) minus spectrum (B). This is the spectrum of styrene, "S" and "T" indicate the bands used for styrene and toluene quantitation, respectively.

operation.

### Process FTIR In The Real World

This section will briefly review several representative applications areas of process FTIR. In most of these areas, installations are planned for the near future.

Historically, the greatest number of applications have involved transmission measurements; including various forms of gas monitoring, mid-IR measurements involv-
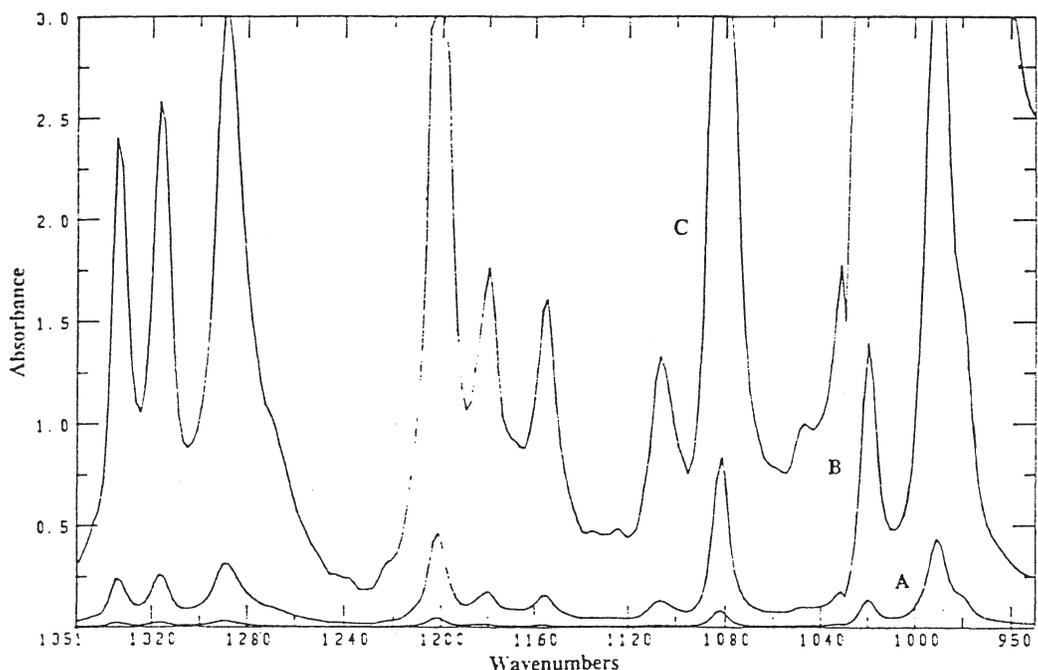


Fig. 24. (A): A portion of the difference spectrum shown in Fig. 24(C). (B) and (C): The same spectrum expanded 10 x and 100 x.
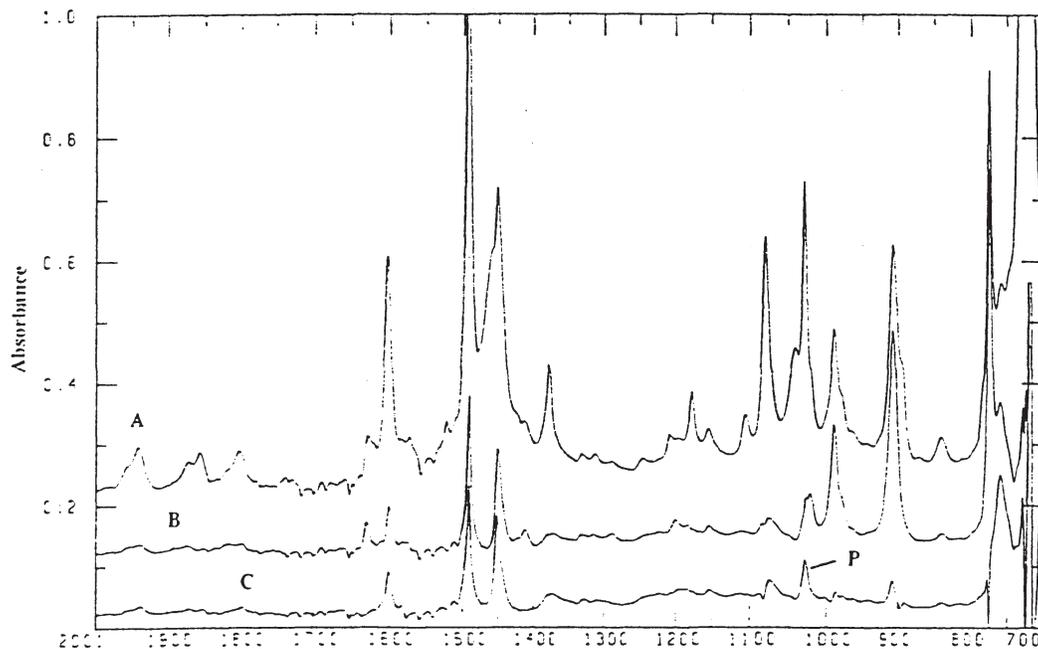
Fig. 26. (A): Acid catalyzed reaction mixture on completion. (B): Spectrum (A) less toluene. (C): Spectrum (B) less the styrene spectrum of Fig. 24(C). This is a spectrum of polystyrene. "P" indicates the band used for polystyrene quantitation.

ing highly transparent (usually inorganic) liquids, and measurements of overtone bands in organic liquids. The earliest organic mid-IR installations employed ATR cells built in-house at Du Pont. It is only within the past three years, with the availability of commercial process compatible ATR devices, that the door has been opened to the widescale application of process FTIR to the monitoring of the fundamental functional group bands of organic liquids (54).

The sampling techniques listed for each applications area discussed below include only those which are currently in industrial operation or are scheduled for installation in the near future.

*Ambient air monitoring*

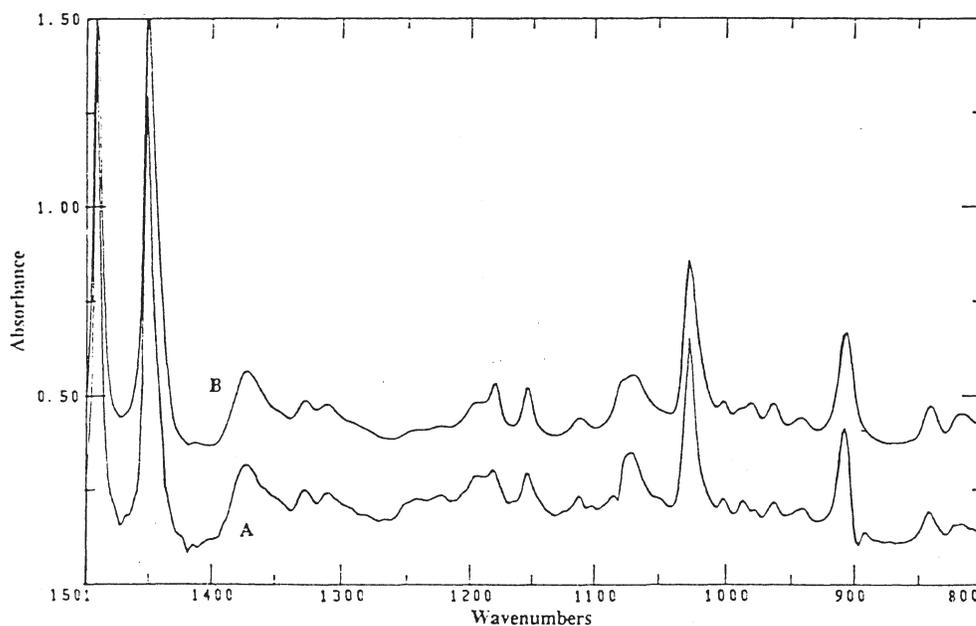*Sampling techniques: White cell/open path transmission*



Fig. 27. (A): An expanded portion of the product spectrum (Fig. 26C), compared to (B) a spectrum of a polystyrene film deposited on the ATR element.
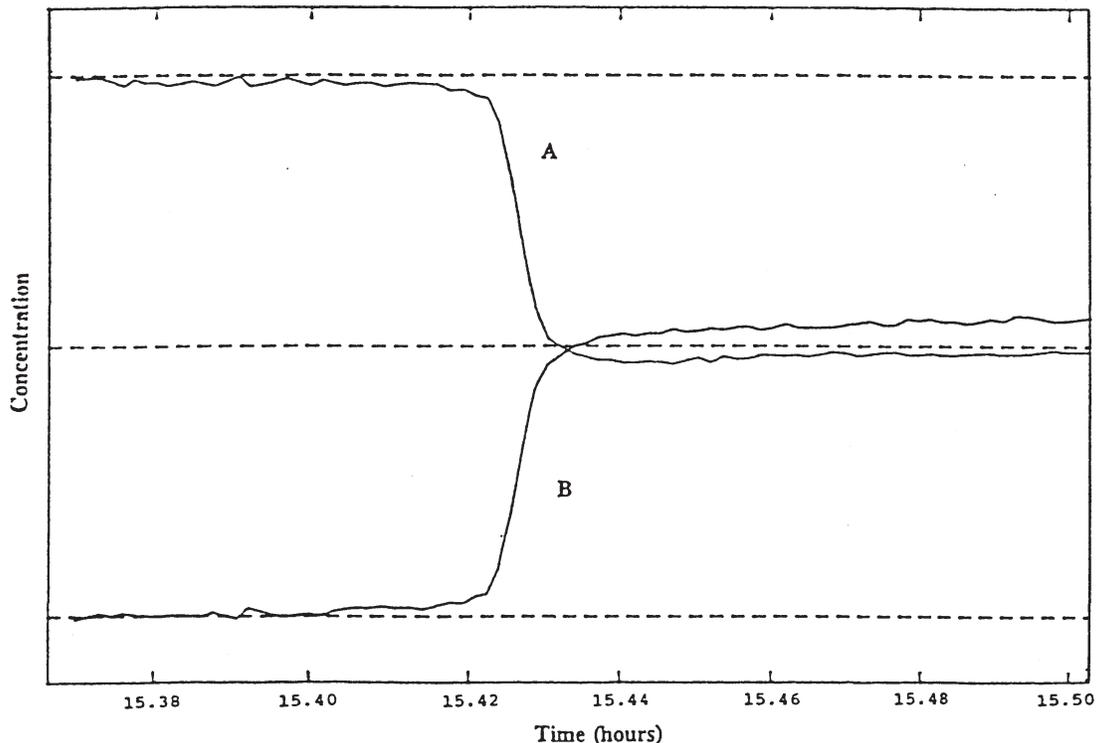
Fig. 28.  Concentration versus time of (A) styrene and (B) polystyrene in the acid catalyzed polymerization process.

This area has seen a number of highly successful applications starting with one of the first successful industrial FTIR installations at Dow Corning in 1982.  A typical workplace safety monitoring application may involve pumping air from 30 sequentially sampled points in the workplace and monitoring 20 or 30 species simultaneously.

Another approach to ambient air monitoring involves the use of an open path spanning the area to be monitored.  This type of system can use either a separate transmitter and receiver at opposite ends of the path or a large retroreflector to return the modulated beam back across the path to the spectrometer site.



Fig. 29.  Indicated concentration versus time of (A) styrene, (B) methylmethacrylate, (C) polystyrene, and (D) PMMA during the free radical copolymerization process.

## Stack gas monitoring

### Sampling techniques: Linear flow gas cell (LFG)/White cell

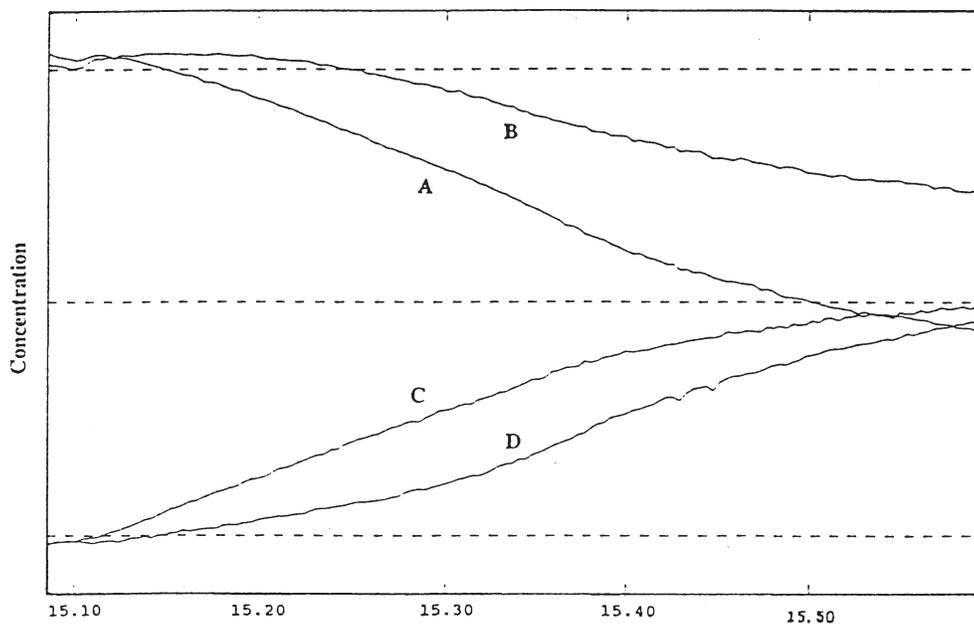This is a relatively new area of activity for FTIR, with much of the current interest being in the field of stationary source monitoring for hazardous waste incinerators. The success of the early installations is viewed as crucial to the widespread acceptance of FTIR in this field (55). The potentially wide range of environmental conditions, corrosive nature of the flue gas, and need for extreme reliability place high demands on the performance of both the spectrometer and the sampling system.

In monitoring combustion gases, it is important to guard against condensation of any of the components of the effluent stream in either the transfer lines or the gas cell. This can be accomplished either by heating the transfer lines a cell above the dew points to below ambient temperature. Typically dilution ratios are between 10:1 and 30:1. The advantage of the dilution approach is lower transfer lines cost. The disadvantage is the need for a much greater gas cell path length for a given sensitivity.

### Motorcar emissions analysis

### Sampling technique: White cell

One manufacturer has developed a turnkey instrument for the on-line analysis of exhaust from either automobiles or free standing engines. This system can monitor up to twenty-five components with response times of between 1 and 30 seconds depending on the level of difficulty of a particular component and the precision required.

### Detection of trace impurities in inorganic gases

### Sampling techniques: White cell/LFG cell

A wide variety of applications require the detection of trace contaminants in IR clear gases. For many of these, the compact and inexpensive White cells prove to be the optimum sampling system. Other applications, particularly those involving corrosive gases require the use of the linear flow gas cells. One version of this cell is provided with all internal surfaces either solid nickel or nickel plated for maximum chemical resistance.

One example of this use is the monitoring of impurities such as HCl and freon in gaseous chlorine, a substance which, by itself, does not absorb in the IR. In this case, it is important to use a window material such as HCl, NaCl, or AgCl, which is not attacked by chlorine.

## Process gas monitoring

### Sampling techniques: Short path gas cell/White cell/LFG cell

Process gas applications are similar to trace impurity applications with the exception that the concentrations of the gases being measured are generally much higher. As a result, the required path length will usually be shorter. In several installations, where it is necessary to make the measurement at the process temperature, the IR radiation is simply directed across the process pipe through a pair of IR windows on either side.

In some commercial processes, gases evolve during the reaction. In such cases FTIR can be used to accurately determine the reaction's end point by monitoring the disappearance of the gaseous species.

### Reaction end point monitoring

### Sampling technique: ATR (flow cell or immersion probe)

By selecting one or more IR bands corresponding to functional groups that will be altered in a reaction, highly accurate endpoint determinations can be made - essentially in real time. For example, a common type of reaction in polymer chemistry as well as other fields is one which an isocyanate molecule is combined with another molecule by attachment at the C-N-O group. When this happens, the strong 2250 cm$^{-1}$ absorption, characteristic of this group, will vanish. The amplitude of this band can thus be used as an accurate measure of the degree of completion of the reaction.

The advent of process compatible ATR sampling systems, both probes and flow cells, has paved the way for the application of process FTIR to a wide variety of reaction monitoring tasks. The first installation involving a large scale (eight foot long) probe in a process batch reactor took place in the summer of 1990. This installation has been essentially continuous operation ever since.

### Precision blending

### Sampling technique: ATR (flow cell or immersion probe)

Many processes require the price control of solution concentrations prior to blending. Process FTIR systems employing ATR flow cells are already proving invaluable in a number of such applications including the blending of high value components, controlling the input streams to a polymerization process, and the monitoring of multiple input streams to an aqueous based process.

### Petrochemical manufacturing and feedstock control

#### Sampling technique: ATR flow cell

Although still at an early stage of application in this field, FTIR can provide substantial benefits at various stages in the manufacture of petrochemical products. For example, the ATR technique is currently being used to monitor such properties as unsaturation, degree of branching, and other factors that relate to octane.

One specific example, in this field, is the use of FTIR to determine the concentrations of the various isomers of xylene in petrochemical feedback without the need for prior separation. This is made possible by the fact that, although geometric isomers have the same mass and chemical functional groups, they have distinct infrared spectra. This particular application involves the use of an ATR flow cell with a periodic wash cycle to remove heavier wax type materials which gradually build up on the surface.

### Fermentation monitoring

#### Sampling technique: ATR flow cell

Fermentation processes have traditionally been monitored by periodically removing a sample for laboratory analysis by a technique such as HPLC. This approach is both labor intensive and slow, a problem which becomes increasingly important as the process accelerates near its end point. Process FTIR is now being used to monitor both the creation and the consumption of components in such processes. This approach allows unattended 24 hour a day operation with automatic decanting of the product at the end.

### Aerosol measurement in ambient air

#### Sampling technique: ATR

Ultrafine aerosol particles (typically 0.3 $\mu$m in diameter) have been monitored by impacting them onto an ATR crystal and measuring the corresponding absorptions. Components containing functional groups such as $SO_4^{2-}$, $NO_3^-$, $NH_4^+$, and C-H have sufficient infrared absorptions to be measured in real time. This system is mounted in a mobile laboratory.

### Waste oil BTU measurements

#### Sampling technique: Near-IR transmission

Optimization of waste (spent) oil incineration requires a knowledge of BTU (calorific) content. FTIR operating in the near-IR region has been applied to this task by using chemometric techniques to correlate near-IR absorption with BTU content measured by calorimetry. This demonstrates the feasibility of calibrating an FTIR system to measure physical parameters as well as chemical concentrations.

### Detection of trace organics in waste water

#### Sampling technique: Sparging/IR using a long path gas cell (White/LFG)

This is a new field of application for process FTIR involving the use of counter current sparging to transfer contaminants from a waste water stream to an intermediate path gas cell for rapid IR analysis. Pioneered a E.I. du Pont (56) the sparging-FTIR technique has now become the basis of a commercial waste water analysis system (57, 58).

### Analysis of polymer melts

#### Sampling technique: High pressure transmission cell

The high pressures and temperatures encountered in the manufacture and extrusion of molten polymers present a unique sample interfacing challenge. Nevertheless, narrow gap transmission cells have been developed which function quite well with most polymer systems and one company has developed a complete turnkey FTIR process control system around such a cell (41). This cell is rated for temperatures to 400°C and pressures to 300 bar. Its path length is variable from 30 $\mu$m to 2 mm.

### Polymer cure monitoring

#### Sampling technique: Reflection absorption/transmission/specular reflectance/fiber-optic ATR

This is one of the few fields in which FTIR is currently being applied to the analysis of bulk solids either on line or at line. Sample types being monitored or under consideration include coating on metal foils, thick polymer sheets, and thick coatings on nonreflective substrates. The sampling technique being used in these three cases are reflection absorption, short wavelength transmission, and first surface specular reflection, respectively.

In another application, FTIR is being used to monitor the curing of resin materials in an autoclave. The IR radiation is brought into the autoclave by means of fiber

optics. A short length of unclad sapphire fiber connected to the main fiber is embedded in the resin material. This acts as an ATR sensor to monitor chemical changes during the cure process.

*Web monitoring*

*Sampling technique: Transmission*

As mentioned earlier, the monitoring of rapidly moving webs with FTIR can be problematic due to the occurrence of sample variations on a time scale fast compared to the scanning time of the interferometer. One major manufacturer of polymer films has opted to use near-IR for on-line monitoring along with an at-line FTIR system to periodically obtain more accurate data static samples (37).

FTIR is also starting to be applied in moving web situations in which the motion is sufficiently slow or the uniformity of the film adequate so that the noise is generated by sample variations is minimal.

## Getting Started in Process FTIR

Process FTIR is an exciting new field with potentially dramatic impact on a variety of industries in the form of more efficient material and energy resources utilization, reduction of waste, improvement of product quality, and reduction of environmental pollution. Nevertheless, it is a complex field with each new application introducing a new set of questions concerning such subjects as material compatibility, operating environment, sample access, appropriate spectral bands for analysis, and optimum quantification methods.

The first step in determining whether process FTIR is right for your applications is to contact the various manufacturing companies active in this field so as to learn as much as possible from their experience with similar applications. The Appendix to this article includes a list of such companies with a general indication of their areas of activity.

If these initial discussions indicate a reasonable chance of success, the next step is to involve as wide a range of individuals in your company as possible in analyzing the potential payoff and the internal level of support required for your process FTIR application. At this stage, it is especially important to involve the individuals who will have responsibility for operating and maintaining the equipment. Experience has proven that including the maintenance and instrument engineering groups in the equipment selection process and applications development effort has led to a very high level of commitment

as well as significant contribution to fostering the success of the project.

In most cases, it will be necessary to prepare a set of samples for use in developing and testing the system calibration. A preliminary calibration can often be developed by the instrument or system vendor. However, it is often very desirable for the customer to have his own method development system for use both in developing the initial calibration and for ongoing system support. This becomes especially important whenever there is a change in the manufacturing process that may require developing a new calibration.

For some applications it will be possible to simply purchase a turnkey system to be delivered precalibrated and ready for use by relatively unskilled personnel. However, in most cases the complexity of the applications as well as well as the power of the analytical methods will require a much higher level of involvement on the part of the customer. This is, in fact, one of the long range advantages of FTIR. The wealth of data available and the extensive computational power of the FTIR system will make it possible to continuously fine tune your analysis to keep up with changes in your manufacturing process. Thus, process FTIR can be thought of as a whole new way of dealing with and controlling the manufacturing process - an instrumentation approach that can continuously evolve as your manufacturing capabilities expand.

## Acknowledgements

## Appendix

The following is a list of manufacturing companies and their phone numbers currently active in the market for process FTIR systems.

*Manufacturing of process FTIR spectrometers and systems*

• Bomem/Hartmann and Braun, Quebec, Que., Canada (418) 877-2944

• KVB/Analect, Irvine, CA (714) 660-8801

• Midac, Inc., Costa Mesa, CA (714) 645-4096

• Nicolet Instruments, Inc. Madison WI, (608) 271-3333

• Automatic Machinery Corp. Charlotte, NC (704)523-7921 and Automatik Apparate-Maschinenbau GmbH, Grossestheim, Germany 0 06 26-5030 (Polymer process control systems).

• Infrared Analysis, Inc., Anaheim, CA (714) 535-7667 (Environmental gas analyzers).

• MDA Scientific, Inc., Lincolnshire, IL (800) 433-6076 (Open path area monitoring systems).

• Rosemount Analytical, Inc., Orrville, OH (800) 433-6076 (Stack gas monitoring systems).

• Telos Labs, Inc., Freemont, CA (415) 490-2087 (Point source industrial hygiene monitors).

*Manufacturers of process FTIR sample interfacing equipment*

• Axiom Analytical, Inc., Irvine, CA (714) 757-9300

• Harrick Scientific Corp., Ossinging, NY (914) 762-0020

• Infrared Analysis, Inc., Anaheim, CA (714) 535-7667

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