

Potential of Fourier Transform Infrared Spectroscopy and Fiber Optics for Process Control

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Fourier transform infrared (FT-IR) spectroscopy is well-established as an off-line analytical technique. In this work, the spectrometer is adapted through the addition of an optical fiber system to provide a powerful tool for on-line analysis and control. A multiplexed fiber interface has been constructed, enabling rapid sequential analysis of up to six different samples. Novel fiber optic sampling cells developed for the system include a transmission cell for use in the near-infrared (near-IR) and an attenuated total reflectance (ATR) cell for the mid-infrared (mid-IR). A number of commercially available optical fibers with varying transmission properties have been investigated. High-quality spectra have been acquired from a variety of food samples and calibrations obtained for components such as carbohydrates and ethanol in soft and alcoholic drinks. A prototype process control system uses the calibration data to control simple processes such as additions and dilutions.

1. INTRODUCTION

There is currently much demand from the food industries for sensor instrumentation that can be used for the on-line monitoring and analysis of food production processes. Fourier transform infrared (FT-IR) spectroscopy is a highly promising technique for this type of sensing, as it is rapid and nondestructive (Wilson, 1990; Belton et al., 1988a,b). Furthermore, the high information content of the infrared spectrum can allow the simultaneous analysis of many components, in contrast to the limited capabilities of single-wavelength devices commonly used. Near-infrared (near-IR, 10 000–4000 cm^{-1}) and mid-infrared (mid-IR, 4000–400 cm^{-1}) spectra can yield information useful for the evaluation of product quality or the optimization of processing. However, the off-line nature of many of these measurements, requiring sample preparation and batch analysis, has hindered the wider uptake of the technique. On-line FT-IR aims to overcome these limitations by analyzing the sample directly during the course of the production process.

There are two distinct approaches that may be taken to achieve on-line FT-IR: dedicated sensing, in which analysis takes place within the sample chamber of the instrument, and remote sensing, in which the infrared beam is directed out of the instrument through light pipes or optical fibers to a remote sample. For the FT-IR spectrometer to be used as a dedicated on-line instrument, specially adapted sampling cells must bring the sample from the production line to the instrument for analysis. This method has been employed in the past to monitor a variety of processes (Alberti et al., 1985). However, there are disadvantages to using FT-IR in this way: the low cost-effectiveness of dedicating a relatively expensive machine to a single analysis and the inherent risk involved in exposing what remains essentially a laboratory instrument to the rigors of a production line environment. In fiber optic FT-IR, the infrared light is carried to and from the sample by lengths of infrared-transmitting optical fibers. The spectrometer itself may therefore be situated at some distance from the sampling point, safe from accidental spillage and harsh vibrations. Furthermore, by using an appropriate spectrometer-to-fiber interface, a multichannel system can be realized, which will allow sequential monitoring of more than one process using a single FT-IR spectrometer. Multiplexing a number of sampling points to a single expensive spectrometer can

offer considerable cost benefits and is likely to accelerate the establishment of the technique in the process field.

Fiber optic spectroscopy is well-established in the near-IR (Schirmer and Foulk, 1988). However, many systems use multicore or bundled fibers, which are relatively expensive. Furthermore, as the silica fibers commonly employed are unable to operate at wavenumbers below 4500 cm^{-1} , the technology is not suitable for use in the mid-IR, for which alternative fiber interfaces are required (Saggese et al., 1988; Driver et al., 1990).

An automated, six-channel fiber optic FT-IR system for on-line process control has been designed and constructed, including fiber interfaces, sampling cells, and devices such as valves and switches. The full details of the optical design will be published elsewhere, but sufficient information will be given for comprehension. Single-core fibers have been used throughout, with the aim of developing a system at a realistic cost. In addition to silica, fluoride glass fibers (Katsuyama and Matsumura, 1989) have been investigated, which have a broader transmission window, covering the whole of the near-IR to around 2000 cm^{-1} in the mid-IR. Spectroscopic work has been carried out using the fiber system throughout the available spectral range. Effort has been concentrated on the development of calibrations for a range of food products, such as soft and alcoholic drinks, cooking oils, and dairy produce and on the subsequent use of the calibration information for the monitoring or control of processes. Two analyses are described in detail.

2. PROCEDURE

2.1. Instrumentation. All work was carried out on a Digilab FTS-60 FT-IR spectrometer. This instrument, fitted with the appropriate source and beamsplitter, can operate across a wide wavelength range. A tungsten halogen bulb together with a silicon beamsplitter was employed for the near-IR and a silicon carbide source and germanium-on-potassium bromide beamsplitter for the mid-IR. A liquid nitrogen-cooled indium antimonide (InSb) detector was used throughout, as it can operate across most of the near-IR as well as the part of the mid-IR accessible with the fiber system.

Two interfaces between the fibers and the spectrometer were constructed: one where the IR beam is condensed into the fibers; the other at the detector, where the light emerging from the fibers is directed onto the detector element. Up to six fiber channels can be accommodated. Each interface includes a stepper motor, to enable fully automated channel switching and align-

Table I. Calibration Set for Carbohydrate Content of Fruit Juice Concentrate

sample	carbohydrate, g/100 mL	height of 4391-cm ⁻¹ peak relative to baseline 4500–4550 cm ⁻¹
diluted sample 1	14.4	0.0782
diluted sample 2	23.0	0.1302
diluted sample 3	30.3	0.1676
diluted sample 4	41.8	0.2275
diluted sample 5	50.2	0.2722
fruit concentrate	75.0	0.4047

ment. The motors are controlled by the computer attached to the spectrometer.

Two different classes of optical fiber were used: plastic clad silica (PCS) and zirconium fluoride fibers. The PCS fibers were obtained from Fibredata, Redruth, Cornwall, England, with 200- and 400- μm core diameters. Zirconium fluoride fibers were supplied with 250- μm core by Iris Fiber Optics Inc., Acton, MA, and with 400- μm core by Le Verre Fluore (LeVF), Verne-sur-Seiche, France. Fiber transmission characteristics were evaluated from single-beam spectra, obtained by connecting the fibers in closed loops to the interfaces.

Two types of sampling accessory were built: a variable path length transmission cell, for liquid sampling in the near-IR, and an attenuated total reflectance (ATR) probe, for analysis of liquids and semisolids in the mid-IR (Belton and Wilson, 1990). In both cases, the interferometer output is carried from the external beam port interface by a first length of fiber to the sampling cell and then returned to the detector interface by a second length of fiber. The transmission cell is plumbed into a pipeline and sample pumped through it for analysis. The ATR cell is suitable for immersion in a sample reservoir.

The computer was also interfaced to various external devices. Three components were used to construct a process control system: a solenoid valve and two reed relay switches used to control the mains power reaching a trailing socket to which other appliances may be connected.

All experimental work was carried out in an air-conditioned room, with the temperature maintained between 20 and 22 °C. No investigations were carried out into the effect on spectral quality of temperature variation of sample, fibers, or spectrometer.

2.2. Calibrations. 2.2.1. Fruit Juice Concentrate. A fruit juice concentrate is commercially available which contains 75 g of carbohydrate/100 mL, as a mixture of fructose and sucrose. It is normally diluted before consumption. Five diluted samples were prepared, with carbohydrate contents in the range 14–50 g/100 mL (Table I). The path length of the transmission cell was set to 1 mm, and near-IR single-beam spectra of each sample and of the undiluted concentrate were obtained. Five-meter LeVF fluoride fibers were connected to the cell to form a 10-m fiber-cell-fiber circuit. Sixty-four scans were co-added before Fourier transformation, at a resolution of 16 cm⁻¹. The cell was pumped with water and then an amount of sample running to waste between acquisitions. A water background spectrum was also obtained, to which all sample spectra were ratioed, presenting the spectra in absorbance units. A calibration for the carbohydrate content was performed.

2.2.2. Alcohol Content of Liqueurs. Typical fruit liqueurs have a total sugar content of around 300 g/L and an alcohol content of 27–30% by volume. A fruit syrup was obtained which contained a total sugar content of 395 g/L, as a mixture of sucrose, glucose, and fructose. Five samples were prepared from the syrup, each containing a different amount of ethanol, to a maximum of 36% by volume (Table II). The ATR probe was used to obtain mid-IR single-beam spectra of each mixture and of the pure syrup. Sampling was carried out by immersion of the probe in the sample reservoir. Optical fiber and acquisition conditions were the same as in section 2.2.1. The ATR crystal was flushed with water and dried between acquisitions. A water background spectrum was also obtained, to which all spectra were ratioed, again presenting the spectra in absorbance units. A calibration for the alcohol content was performed.

2.3. Process Control Systems. A system was devised to demonstrate the control of two processes: the dilution with water of fruit juice concentrate to a predetermined strength and the

Table II. Calibration Set for Ethanol Content of Liqueurs

sample	ethanol content, % vol	height of 2978-cm ⁻¹ peak relative to baseline 2775–3030 cm ⁻¹
pure fruit syrup	0.00	0.0064
mixture 1	6.99	0.0243
mixture 2	14.06	0.0371
mixture 3	19.00	0.0483
mixture 4	28.50	0.0718
mixture 5	36.10	0.0900

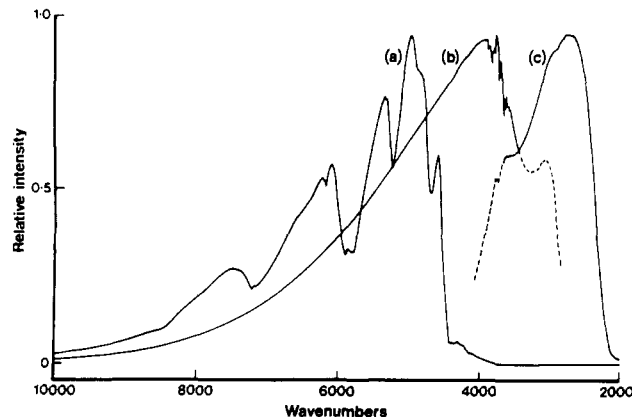


Figure 1. Single beam spectra of (a) PCS fiber and (b) fluoride fiber, obtained with near-IR source and beamsplitter, and (c) fluoride fiber, obtained with mid-IR source and beamsplitter.

addition of ethanol to fruit syrup to manufacture a synthetic liqueur. A peristaltic pump was connected to the solenoid valve, to deliver a measure of diluent (water or ethanol) to a sample reservoir. For a given pump pressure, the amount of liquid delivered is a function of the length of time for which the valve is opened. This time interval is set by the control algorithms in response to spectroscopic measurements. The relay switches were used to activate the valve delivery pump, a stirrer in the sample reservoir, and a second pump for passing sample through the transmission cell. Spectroscopic measurements for each of the processes were made in the near-IR and mid-IR, using the transmission and ATR cells, respectively.

3. RESULTS AND DISCUSSION

3.1. Instrumentation. Single-beam spectra (Figure 1) obtained from the 5-m lengths of PCS and LeVF fibers demonstrate clearly the regions available for spectroscopic purposes, by showing the spectral characteristics of the respective source and beamsplitter combinations. The transmission window of fluoride fibers covers the whole of the near-IR to around 2000 cm⁻¹ in the mid-IR. In this region, the attenuation of fluoride fibers is low, typically less than 0.1 dB/m. PCS fibers also have good attenuation characteristics in the near-IR (typically around 0.01 dB/m). However, the cutoff in transmission occurs at 5000 cm⁻¹, restricting the useful spectral range.

Mechanically, the PCS fibers are robust and will withstand relatively rough handling. Termination, polishing, and cabling with a protective sheath were carried out in the laboratory. Fluoride glass fibers are more fragile, and it was impractical to perform sheathing, termination, and polishing with nonspecialist equipment. These fibers were thus supplied terminated and polished to specification by the manufacturers and with sufficient protective sheathing to allow normal handling.

3.2. Calibrations. 3.2.1. Fruit Juice Concentrate. The near-IR region is dominated by two strong water bands, at 6400–7300 and 4800–5400 cm⁻¹. By ratioing the spectra of aqueous samples to a water background, weaker spectral features which may be hidden or distorted can often be revealed. The spectrum of the undiluted fruit juice concentrate ratioed to a water background obtained

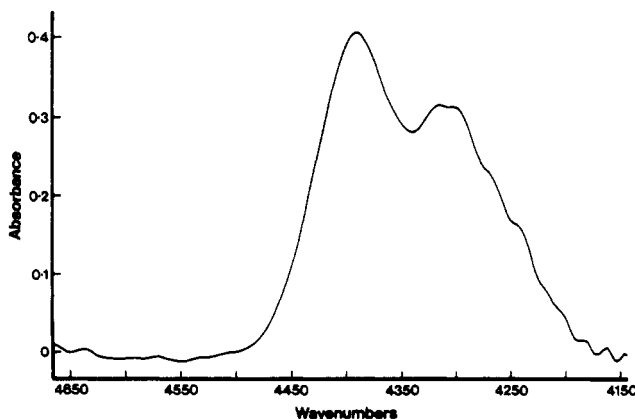


Figure 2. Near-IR absorbance spectrum of fruit juice concentrate.

with the transmission cell is shown in Figure 2. The carbohydrates contained in the concentrate give rise to measurable bands at 4200–4500 cm^{-1} .

The height of the 4391- cm^{-1} band with respect to a baseline between 4500 and 4550 cm^{-1} was measured for the spectra of the concentrate and diluted samples. A linear regression of peak height against carbohydrate content was performed according to the method of least squares. The intercept a , slope b , and correlation coefficient were determined. The carbohydrate content X_c of an unknown fruit juice sample may then be calculated: a spectrum is obtained and the appropriate peak height Y_c measured and inserted into the calibration equation:

$$X_c = (Y_c - a)/b$$

$$a = 0.00442; b = 0.00534; \text{corr coeff} = 0.99985$$

Conventional statistical procedures were used to determine the 95% confidence interval for results obtained from the calibration, which was found to be ± 0.9 g/100 mL. Single-component calibrations of this kind are particularly suitable for process control applications: few calibration standards are required, and the subsequent analysis using the calibration data is fast and may be easily integrated into a control routine.

3.2.2. Alcohol Content of Liqueur. The "fingerprint" region of the mid-IR, 800–1300 cm^{-1} , lies outside the spectral range of the fiber optic probe. Nevertheless, there are a number of bands that arise from sugars and alcohols in the region 2800–3000 cm^{-1} , which may be used for quantitative analysis. The spectra of the fruit syrup calibration samples ratioed to a water background and corrected to a carefully chosen baseline are shown in Figure 3. Although the spectral features are severely overlapped, there is a prominent ethanol peak at 2978 cm^{-1} which is relatively isolated and a possible candidate for quantitative measurements. The height of this peak was measured, and a linear regression again performed.

The calibration equation in this case was found to be

$$X_c = (Y_c - 0.00634)/0.00229$$

$$\text{corr coeff} = 0.99902$$

The 95% confidence interval for results calculated from this calibration was found to be $\pm 1.4\%$ ethanol by volume.

3.3. Process Control Systems. For the dilution of the fruit juice concentrate, the calibration information already obtained was built into the control program and used to calculate the carbohydrate content during the course of the process. The procedure can be divided into the following steps:

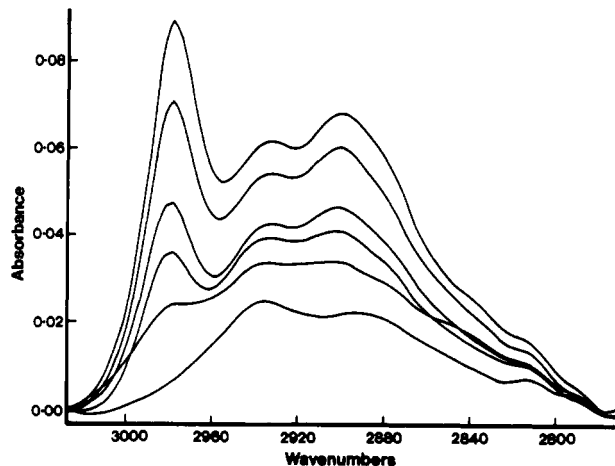


Figure 3. Mid-IR absorbance spectra of fruit syrup calibration samples, showing the peak at 2978 cm^{-1} increasing with alcohol content.

(i) The desired final carbohydrate content is set (either as a keyboard input or as an integral part of the control program).

(ii) The cell is filled with water and a background spectrum collected.

(iii) The cell is pumped full of sample and a spectrum acquired and ratioed to the water background.

(iv) The spectrum is analyzed; the instantaneous carbohydrate content is calculated and compared with the required value; the approximate amount of water to be added is determined, underestimating slightly to avoid overshooting the process end-point.

(v) The solenoid valve is opened for the appropriate length of time, the diluent is pumped into the sample reservoir, and the sample is mixed for a time related to its total volume.

(vi) Steps iii–v are repeated until the required final concentration is reached, at which time the process is terminated.

The number of repetitions depends on the accuracy with which the pump and valve system can dispense the required amount of diluent. As a result, three or four iterations are normally required. Spectral acquisition conditions are the same as those used for the calibration; thus, each scanning step, including Fourier transformation of the spectrum, takes around 45 s. A further 20 s is required for the subsequent spectral analysis step. The overall duration of the process then depends on the volume of sample being analyzed and the final concentration, as these will determine the duration of the addition and mixing steps.

It has been found that the acquisition of a new water background (step ii) at the start of the process, or at least at the start of the day, increases the reliability of the results, as it can compensate for small fluctuations in the throughput of the system. The final concentration can then be controlled to within the limits of the calibration error, estimated for this process at around ± 0.9 g/100 mL of carbohydrate.

The procedure outlined above relies on the existence of a valid calibration. An alternative approach was investigated for the addition of alcohol to fruit syrup. Instead of the daily water background, a specimen of the desired final product is used for the reference spectrum. A rough estimate of the alcohol concentration during the course of the process is made from the calibration data already obtained, to provide a value for the volume of alcohol to be added in the initial steps of the process. However, toward the end of the procedure, the alcohol is added in small predetermined volumes and the end-point deter-

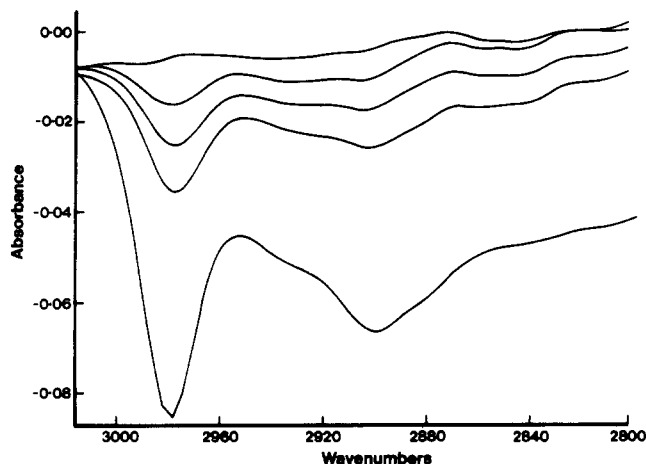


Figure 4. Spectra obtained during the course of an alcohol addition process, showing the negative peak at 2978 cm^{-1} decreasing in size as alcohol is added, until complete cancellation occurs (upper trace).

mined directly by comparison of the sample and reference spectra, rather than a concentration measurement. The procedure is summarized as follows:

(i) The ATR cell is immersed in a specimen of the desired final product and a reference spectrum acquired.

(ii) The ATR cell is immersed in the sample reservoir and a spectrum acquired and ratioed to the reference spectrum.

(iii) The spectrum is analyzed; the size of the negative ethanol peak is measured; the amount of ethanol to be added is set, either from an estimate of the instantaneous alcohol content or, as the end-point of the process is approached, at a pre-set small volume.

(iv) The solenoid valve is opened for the calculated length of time and ethanol pumped into the sampling reservoir.

(v) Steps ii–iv are repeated until the ethanol peak is canceled completely, at which point the sample and reference spectra are essentially the same, and the process is terminated.

A series of spectra obtained during the course of this process are shown in Figure 4. The advantage of this approach is that an accurate calibration need not be performed. The reference spectrum, which replaces the water background, essentially functions as a daily one-point calibration.

4. CONCLUSIONS

The work described in this paper has demonstrated the potential of fiber optic FT-IR spectroscopy for on-line process control. The interfaces constructed to couple the optical fibers to the FT-IR spectrometer have proved highly efficient. In the interests of economy, fiber lengths of 5 m only have been used, but the high throughput of the system and low fiber attenuation suggest that much longer lengths (for example, 50-m circuits) are viable. The spectral range of the system is at present limited by the transmission characteristics of currently available fibers, which fall short of the information-rich fingerprint region of the mid-IR. However, continuing advances in optical fiber technology suggest that fibers with extended transmission windows and acceptably low attenuation characteristics are no longer a distant prospect (McEnroe et al., 1987); short lengths of mid-IR-transmitting chalcogenide glass fiber are already commercially available. Future developments may thus include remote spectroscopy at these longer wavelengths, particularly the fingerprint region. This has been demonstrated to be a valuable region for food analysis.

Notwithstanding the current limitations, the spectroscopic work undertaken has demonstrated that high-quality spectra and useful information can be obtained from a variety of samples. In addition to the samples considered in detail here, we have also obtained useful spectra from systems such as fats, oils, and dairy produce.

The two types of sampling cell (near-IR transmission cell for liquid samples, mid-IR ATR cell for solids and semisolids) perform satisfactorily. However, the mid-IR cell comprises an ATR crystal of zinc selenide, a toxic material, and consequently in its present form can only be used to monitor pilot processes. We are currently investigating the possibility of constructing an alternative cell from the food-acceptable material of sapphire.

The good throughput of the system has enabled high signal-to-noise ratios to be obtained from relatively few co-added scans, keeping acquisition times typically below a minute. Thus, both the sensitivity and the speed necessary for effective process control have been achieved. Demonstration procedures have been devised based on the calibrations already obtained, which are able to carry out concentration determination and control rapidly, and with accuracy of the order generally required by industry. If speed is not paramount, improved accuracy and precision could be achieved by using longer acquisition times, larger calibration sets, and replicate spectra. We conclude that fiber optic FT-near-IR and FT-mid-IR spectroscopies have great potential value as quality control techniques for the food industry.

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