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Single Fiber Analysis by Internal Reflection Infrared Microspectroscopy

ABSTRACT: Attenuated total reflection (ATR) is a convenient mode for single fiber analysis by infrared microspectroscopy, particularly when transmission spectra are difficult to obtain or when surface preferred sampling is desirable. Textile finishes such as spin finishes, anti-static finishes, and permanent press finishes are revealed by ATR techniques. Bicomponent fibers may be analyzed by a combination of ATR techniques, transmission techniques, and spectral subtraction.

KEYWORDS: forensic science, infrared microspectroscopy FT-IR, ATR single fiber spectroscopy, surface analysis, nondestructive fiber analysis, internal reflection spectroscopy, IRS

Infrared microspectroscopy has been used by forensic chemists to characterize polymer fibers using both transmission and internal reflection methods. Attenuated total reflection (ATR) microspectroscopy can reveal surface treatments on fibers that cannot be interrogated under transmission measurements because the fibers are too thick. Examples of common textile surface treatments include stabilizers, delustering agents, flame retardants, and anti-static agents. The use of each of these involves the surface application of a particular chemical. In most cases the chemistry of the surface differs from the chemistry of the host fiber. Because of this chemical difference, spectroscopy can be used to reveal the presence, absence, or amount of the surface treatment (1–4). ATR microspectroscopy can reveal the application evenness of finishes on the fiber surface as well as detect inorganic or organic chemicals retained on the surface. It is possible to determine if these materials were washed out or left behind in the manufacturing process. ATR microspectroscopy provides four notable features: it is a surface analysis technique, it is nondestructive, it requires little or no sample preparation, and it provides control of the depth of penetration. A zinc selenide (ZnSe) internal reflection element (ATR crystal) has an index of refraction of 2.4. In this case, for an angle of incidence of 45°, the depth of penetration into the surface is approximately 0.2 times the wavelength (λ) of the infrared radiation.

ATR crystals having a greater index of refraction have a lesser penetration. For example germanium, having an index refraction of 4.0, produces a depth of penetration of 0.066λ. Consequently, only the outermost part of the fiber's surface is analyzed. In this study, we are concerned with a permanent-press agent on cotton fibers, finishing agents on nylon carpet fibers, and finishes on acrylic fibers that are common to clothing. All of these are important in the area of forensic sciences in an effort to either have a match or a definite mismatch between fibers found at different places.

Experimental

Instrumentation for Micro ATR Work

The instrument used for ATR microspectroscopy was an IRμs™ infrared microspectrometer (Spectra-Tech, Shelton, CT). Details of the instrument and its configuration in the Microbeam Molecular Spectroscopic Laboratory have been previously described (5,6). This integrated combination of an infrared microscope and infrared spectrometer was designed as a unit to take advantage of compatible and efficient optics. A mercury cadmium telluride (MCT) liquid nitrogen cooled detector was used. The active surface on the detector was 0.25 mm in order to match the microbeam of the spectrometer. Projected image plane masks limited the portion of the specimen in view on the microscope stage to be interrogated by infrared radiation. In transmission, a second projected mask was used below the stage and just after the condenser to avoid incidental spectral contamination caused by the optical process of diffraction.

The ATR microscope objective (Model 0049-460, Spectra-Tech, Shelton, CT) used in this work consisted of a Schwarzschild mirror objective with a ZeSe hemispherical ATR crystal (7–9). The flat surface of the ZnSe crystal was coincident with the focal point of the objective. In ATR analysis, the crystal was placed in optical contact with the object being interrogated. The internally reflected rays are attenuated by the specimen to produce ATR spectra.

Successful micro ATR requires good operational skills, good instrumentation, and near perfect optical alignment. Sufficient incident intensity is essential to return a high signal intensity from the ATR objective to achieve a favorable signal to noise ratio and excellent spectra.

The ATR objective provides an aperture slide equipped for three different operational modes: survey, contact, and scan (10,11). Specifically, the ATR objective in a survey mode was used for finding the area of sample to be analyzed. An objective aperture stop with a round opening in the center was slid into position within the objective as shown in Fig. 1. In the survey mode, the fiber to be interrogated could be located by simply viewing it through the

binocular eyepiece or on the video monitor and placing it in the center of the field using the motorized stage.

The second mode of the ATR objective is the contact mode. In this mode, the aperture stop used has two oval-shaped apertures, each of which is offset from the center (Fig. 2b). When this stop is in position, the sample is raised gradually in order to place it into gentle contact with the ATR crystal. In this mode, rays are coming in at an angle of approximately 30° with respect to the normal. Optical contact can be confirmed because the portion of the sample in contact looks dark. Detecting contact is assisted by using a force transducer that gives a numerical scale reading of the contact force between the ZeSe ATR crystal and the sample surface. This device,

referred to as a "contact alert" (Model 0049-490), was supplied by Spectra-Tech Inc.

The scan mode of the ATR objective is that in which the actual spectroscopic measurement is made. To achieve ATR data, the angle of incidence is very important in order to allow total internal reflection. The angle of incidence is 45° from normal, and rays enter through the stop that is segmented into an arc at the edge (Fig. 3). Another arc (see pattern of the stop in Fig. 3b) matches; the first appears on the opposite side. The radiation enters through one arc and returns through the opposite arc back through the optics of the microscope to the MCT detector of the FT-IR spectrometer.
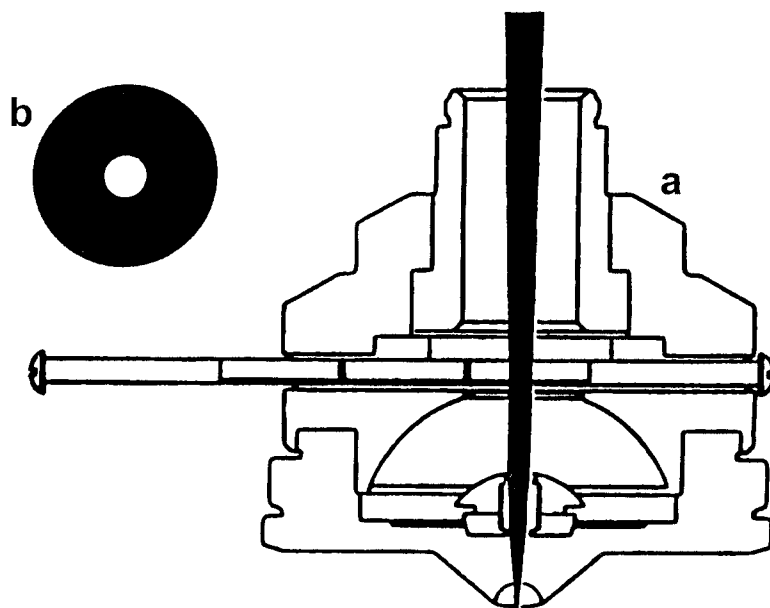

FIG. 1—Cross sectional sketch of the ATR objective in the survey mode showing the small angle of illumination (a) and the pattern of the aperture stop (b).
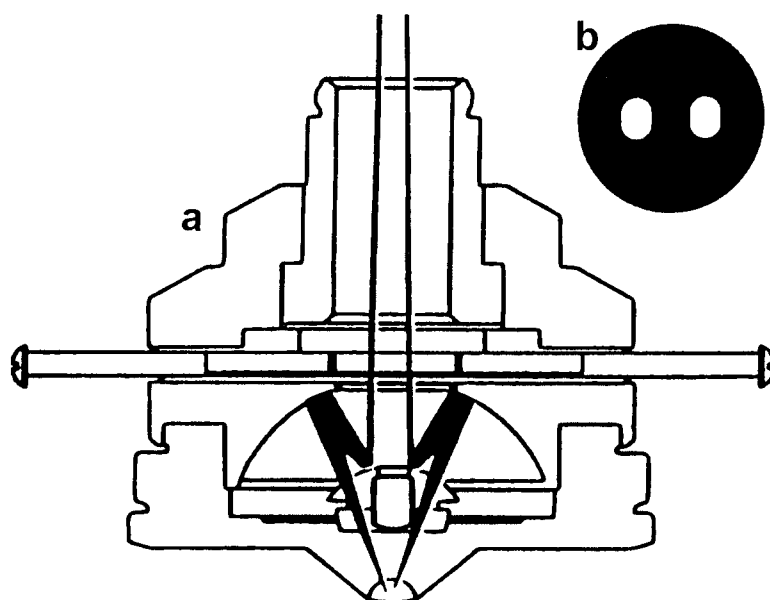

FIG. 2—Cross sectional sketch of the ATR objective in the contact mode showing the 30° angle of incidence (a) and the pattern of the aperture stop (b).
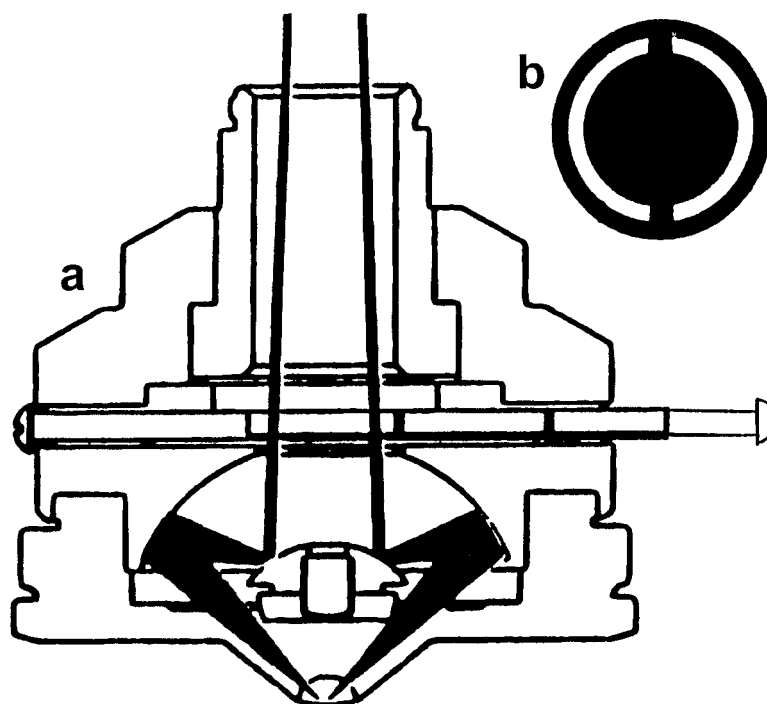
FIG. 3—*Cross sectional sketch of the ATR objective in the scan mode showing the 45° angle of incidence (a) and the pattern of the aperture stop (b).*

The typical configuration for collecting data with this ATR objective involves using a ZnSe crystal with a projected mask of 100 μm. The 100 μm mask illuminates a 42 μm diameter spot on the fiber. This spot size results from dividing the projected mask size by the refractive index of the ATR crystal. Typically, spectral resolution was set at 8 cm^{-1} and 256 scans were coadded to produce an ATR spectrum.

Fiber Samples and Sample Preparation

The acrylic fibers were treated with a dye carrier in the textile laboratory of Kansas State University (KSU) to produce a surface finish. Infrared spectra were taken on the single fibers before and after treatment to detect the finish on the fiber surface by using the ATR technique. Other fibers that were used to show the surface-preferred ATR technique were polyester fibers (Dacron 54, DuPont) and cotton fabric samples treated with a nonformaldehyde resin finish, BTCA (1,2,3,4-butanetetracaroxylic acid and sodium hypophosphite), which were supplied by Dr. N. M. Morris at the USDA/ARS Southern Regional Research Center (New Orleans, LA).

The carpet fibers selected for ATR spectroscopic analysis included six samples of 100% nylon 6 or 6,6 and 100% olefin carpeting furnished by S & S Carpet Mills, Dalton, GA (Table 1). These represented a variety of surface treatments (e.g., antistain, UV stabilizer, stain blocker, Scotchgard® fluorocarbon soil repellent) and different fiber manufacturers. Nylon carpet fibers can be treated with antistatic agents for reducing static charge generation, soil-repellent finishes to decrease soiling, or stain blockers to increase resistance to colored stains.

Sheath-core bicomponent fibers were analyzed by recording both their transmission and ATR spectra. By spectral subtraction of the ATR spectrum from the transmission spectrum, the spectrum of the core material can be obtained. Three different types of

TABLE 1—*Carpet fibers used to obtain the ATR spectra.*

Fiber Type	Trade Name, Finishes
Nylon	Anso
Nylon	Treated with 3M Scotchgard
Nylon	Dupont Stain Master
Nylon	Monsanto Weardated
Olefin	(No treatment)
Olefin	Treated with UV stabilizer

TABLE 2—*Bicomponent fibers analyzed by microspectroscopy.*

Sheath	Core
Polypropylene	PET
Polyethylene	PET
Nylon 6	PET

bicomponent fibers were analyzed using the ATR technique (Table 2).

Because ATR is based on the reflection of radiation from the surface of the sample, no special sample preparation is needed. In transmission measurement, it is often necessary to flatten or section fibers for analysis (12). The flattening step needed to thin fibers for transmission spectroscopy is eliminated using ATR. Hence, for ATR measurement, the fiber samples simply were placed on a microscope slide and taped on both ends. One layer of transparent or foam tape was used on the underside of the microscope slide to cushion the contact slightly.

Results

ATR is a convenient technique for single-fiber analysis by infrared microspectroscopy, particularly when transmission spectra are difficult to obtain or when surface-preferenced analysis is desirable. Although the total contribution to the transmission spectrum by the small amount of material on the surface may not be too great, the ATR spectrum enhance this surface contribution relative to that of the substrate. When the whole-fiber transmission spectrum is subtracted from the ATR spectrum, the differences are highlighted. This work showed the value of ATR microspectroscopy to reveal the presence of surface treatment and possibly the type of material used.

Some of the spin finishes in common usage employ natural or synthetic lipid-like material or esters. Spectroscopic data in Fig. 4 demonstrated the use of ATR spectroscopy on single fibers from the same manufacturer including one with a spin finish and one of the same composition without a finish. The spectrum of the finish is shown by spectral subtraction. Note that the band, at 1644 cm^{-1}, was from the finish on the surface of the fiber.

A polyester fiber (DuPont Dacron 54™) obtained directly after processing was used in this particular illustration. Although spectral subtraction is not perfect, what can be seen are the primary differences imposed on the spectrum of the original fiber sample by the finish. Fortunately, the surface-preferenced analysis of ATR microspectroscopy makes this possible. With this technique, the identity of the surface treatment of single fibers can be revealed, as well as the evenness of its application on a single fiber.

The cotton fabric was resin finished by a laboratory-scale procedure. Both the untreated and resin-treated fabrics from the same source were used for analysis. Figure 5 shows the spectrum of a single cotton fiber that had a finishing agent on its surface prepared from 1,2,3,4-butanetetracaroxylic acid (BCTA) and sodium hypophosphite. The ATR technique was used to produce surface-preferenced analysis of the single fiber with the finishing agent (middle spectrum). Also in Fig. 5 are the spectra of the untreated single cotton fiber (upper) and with a spectral subtraction (lower) highlighting the spectral contribution of the surface treatment. The BCTA treatment on the cotton formed crosslinks between the polymer chains via an ester linkage to give it permanent press functionality. Spectral subtraction showed the band at 1732 cm^{-1} due to the carbonyl groups from BCTA, and the 1176 cm^{-1} and 814 cm^{-1} bands due to residual unreacted sodium hypophosphite.
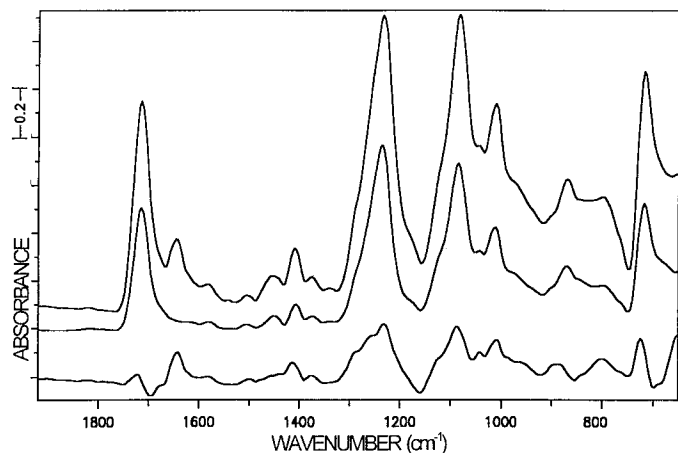

FIG. 4—*ATR spectra of a polyester fiber with finish (top), without finish (middle), and finish (bottom) via spectral subtraction.*
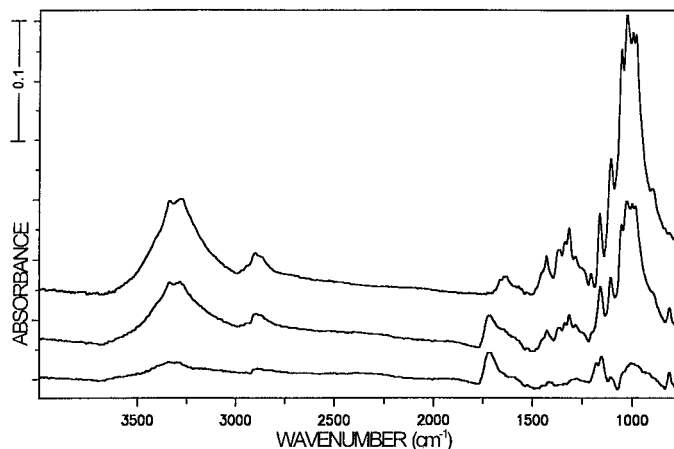

FIG. 5—*ATR spectra of a single cotton fiber untreated (top), treated (middle), and the result of spectra subtraction (bottom).*
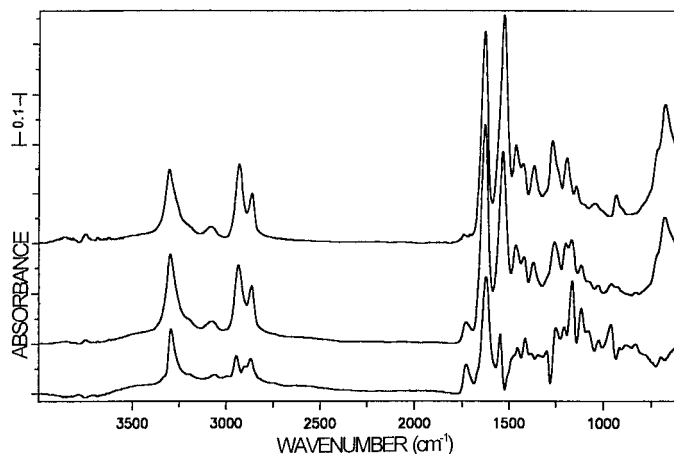

FIG. 6—*ATR spectra of single nylon carpet fiber untreated (top), treated (middle), and the result of spectral subtraction (bottom).*

Figure 6 shows spectra of untreated (upper) and treated (lower) nylon 6 carpet fibers. In this case, the commercial treatment was a Scotchgard® fluorocarbon stain repellent. This particular finish contains fluorocarbon side chains attached to a long hydrocarbon backbone (13). The subtracted spectrum shows the contribution to the spectrum of the chemical used for the finish. New bands occurred also at 1165 cm^{-1}, 1245 cm^{-1}, and 1115 cm^{-1}, which indicated the presence of CF_2 groups. CF_2 stretching is showed strongly in the 1280 cm^{-1} to 1120 cm^{-1} regions (14). Note that the new band at 1242 cm^{-1} (CF_2 stretching) replaced the nylon (C-N stretch) band at 1270 cm^{-1}. Also a carbonyl appearing at 1725 cm^{-1} was not present in the untreated nylon.

Figure 7 shows the spectra of two polypropylene (olefin) carpet fibers. One was factory treated (middle spectrum) with a UV stabilizer, and the other was untreated (upper spectrum). The lower spectrum was obtained from spectral subtraction. The sharp carbonyl absorption (1725 cm^{-1}) was probably a functional group present in the UV stabilizer.

Figure 8 shows the spectra of untreated acrylic fibers as well as the fiber treated in the KSU textile laboratory with dye carrier. The result of spectral subtraction also is shown. In the difference spec-
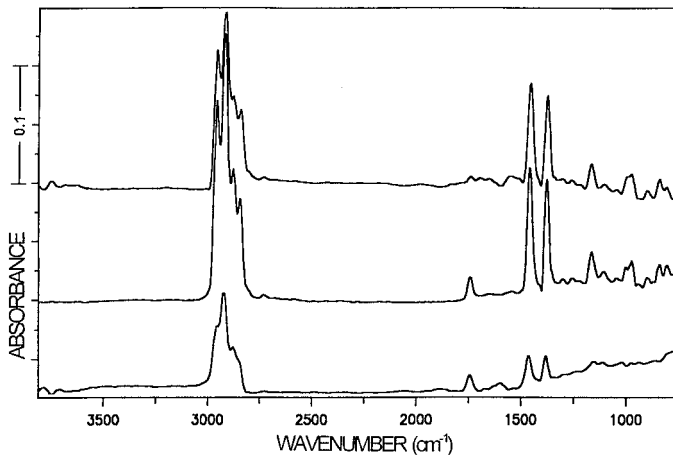
FIG. 7—*ATR spectra of olefin carpet fibers untreated (top), treated (middle), and the result of subtraction (bottom).*
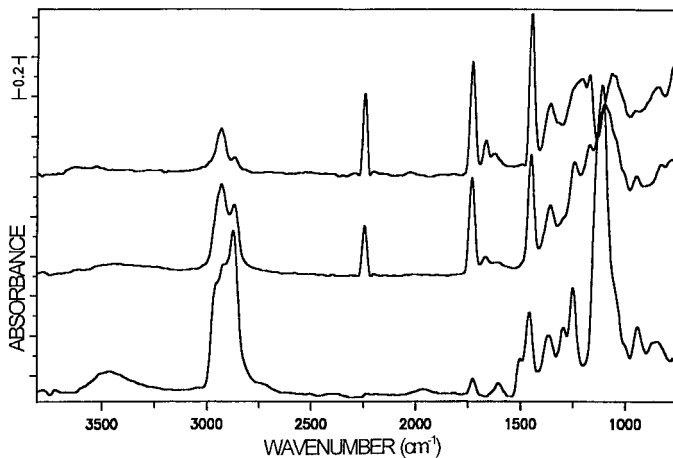

FIG. 9—*Bicomponent fiber transmission spectrum (top) combined core and sheath, ATR spectrum of polypropylene sheath (middle), and difference spectrum of PET core (bottom).*

FIG. 8—*ATR spectra of single acrylic fiber untreated (top), treated (middle), spectral subtraction result (bottom).*

FIG. 10—*Bicomponent fiber transmission spectrum (top), ATR spectrum of polyethylene sheath (middle), and difference spectrum of PET core (bottom).*

trum, notice the bands at 1455 cm^{-1}, 1231 cm^{-1}, 1112 cm^{-1}, and 941 cm^{-1} due to the dye carrier.

Bicomponent Fibers

Another task in forensic science that can be aided by ATR is analysis of single bicomponent fibers. The same fiber coming out of the spinneret can have either adjacent components fused together or a concentric arrangement of two materials with the core composed of one polymer and the sheath composed of another. Particularly in the case of sheath-core bicomponent fibers, getting the true spectroscopic picture is difficult without cross sectioning the single fibers. In the transmission mode, infrared spectra are a composite of both core and sheath. However, ATR spectra can be used to analyze the sheath. The sheath ATR spectrum can be subtracted from the transmission spectrum of the composite to yield the spectrum of the core. This technique is useful in qualitative analysis to determine the composition of a sheath-core bicomponent fiber. Difference spectra in Figs. 9,10, and 11 reveal the identity of the respective polyethylene terephthalate (PET) cores. Each of these figures contain the transmission spectrum of the combined bicomponent fiber; the ATR spectrum of each particular sheath
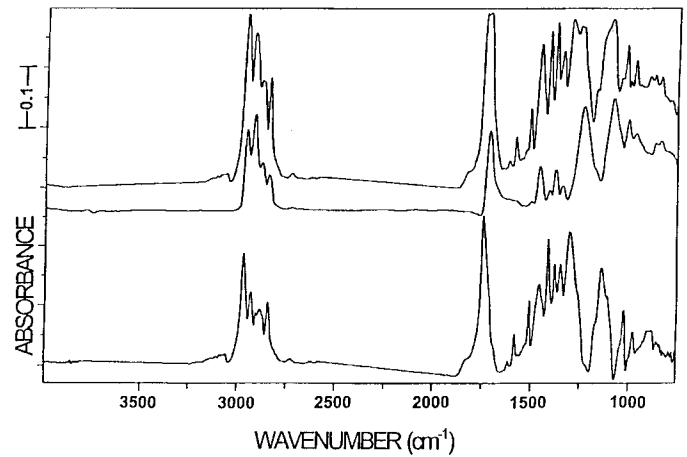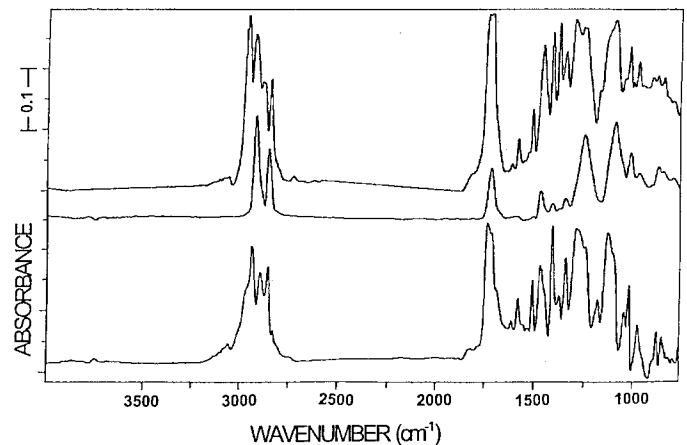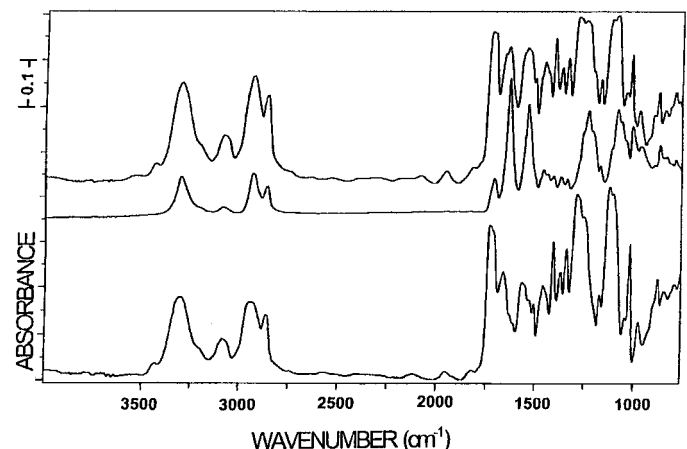

FIG. 11—*Bicomponent fiber transmission spectrum (top), ATR spectrum of Nylon 6 sheath (middle), and difference spectrum of PET core (bottom).*

(polypropylene, polyethylene, nylon 6); and the difference spectra of the PET core. Note that, although some details of the three different spectra in Figs. 9, 10, and 11 are not identical, a polymer spectral library search (Hummel) produced a top ranked "hit" for PET in each case. Side-by-side bicomponent fibers may be analyzed directly by ATR measurements.

The proceeding experimental results for thick, bicomponent, and surface fiber analysis illustrate the usefulness of ATR microspectroscopy. These methods can readily be applied to fiber evidences in forensic science. Newer, easy-to-use, ATR instruments and accessories reflect a trend toward routine everyday use of ATR in forensic and materials laboratories. With instrumental innovation, more laboratories can afford ATR equipment, and the user-friendly operation that it offers means that greater use can be made of these techniques.

Summary

Surface-preferred ATR infrared microspectroscopy allows spectra to be collected from samples that are too thick or opaque for transmission techniques. This is also useful for qualitative analysis of bicomponent fibers. ATR is particularly useful to detect spin finishes and other surface treatments or manufacturing reaction residues. The optical surface-preferred analysis enhanced the detection of finishes because of the localized concentration. Spectral subtraction of the proper background reveals the spectral features of the surface treatment.

ATR has been used commonly for macroanalysis. In fact, a number of ATR accessories fit into the sample compartment of a conventional FT-IR spectrometer. In contrast, ATR for single fiber analysis thus far has had limited use. In general, ATR has been used only when transmission techniques do not work, as is the case of a sample that is too thick to allow for sufficient transmission of infrared radiation or when it is necessary to preserve the sample morphology.

Single-fiber ATR presents both instrumental and optical challenges. Maintaining a high signal-to-noise ratio is essential, thus, good instrumentation is required and good operational skills must be developed. Alignment of every part of the FT-IR microscope is necessary to provide sufficient incident intensity for the ATR objective to return a high signal intensity, so that a good spectrum with a reasonable signal-to-noise ratio can be obtained without coaddition of an excessive number of scans.

This study demonstrated that nylon, acrylic, cotton, polyester, and olefin fibers too thick for transmission could be analyzed readily by ATR. Single-fiber ATR spectra have been reported in the past (7,8). However, this study focused on using ATR spectroscopy to learn about surface treatments. This information could potentially be used in forensic science to determine matches or mismatches of fibers found at different locations. A transmission spectrum from a single fiber shows mostly the chemical characteristic of the fiber itself. Because surface treatment represents a small percent of the overall content of the fiber, seeing those bands superimposed on the strong bands of the fiber itself may be difficult. However, the ATR spectrum of a surface-treated fiber can reveal spectral features of the surface treatment chemicals.

Another significant finding herein was showing that ATR can be used with transmission spectra in determining the identity of the core and sheath portions of a bicomponent fiber. This was done by using ATR to obtain the spectrum of sheath and subtracting the ATR spectrum from the transmission spectrum of the combined sheath and core. When difference spectra of the three bicomponent fibers were subjected to a computer spectral library search, PET was the highest ranked hit. Hence, for these three different bicomponent fibers, the PET core was correctly identified.

While this work was directed to analyzing commercial surface treatments, the micro-ATR method can be used to analyze residual artifacts on fabrics and fibers. These artifacts can be evidence of material transfer and be important as trace evidence. Single-fiber ATR presently is used by a limited number of forensic scientists. We hope that the findings of this systematic study may lead to the expansion of everyday use of the single-fiber ATR techniques described.

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