3.10 Fibers FTIR

3.10.1 Introduction

Consideration should be given to the potential for additional compositional information that may be obtained by IR spectroscopy over PLM alone.

The extent to which IR spectral comparison is indicated will vary with specific sample and case evaluations.

If polymer identification is not readily apparent from optical data alone, an additional method of analysis should be used such as microchemical tests, melting point, IR spectroscopy, or pyrolysis gas chromatography. Infrared analysis offers the advantage of being the least destructive of these methods.

Infrared (IR) spectroscopy is a valuable method of fiber polymer identification and comparison in forensic examinations. This instrumental technique is generally not applicable for vegetable fibers or animal hair fibers.

Because of the large number of subgeneric classes, forensic examination of acrylic and modacrylic fibers is likely to benefit significantly from IR spectral analysis. Useful distinctions between subtypes of nylon and polyester fibers can also be made by IR.

Fiber samples may be prepared and mounted for infrared analysis by a variety of techniques. Infrared spectra of fibers are obtained using an IR spectrometer coupled with an IR microscope, ATR accessory, or diamond compression cell with beam condenser. Fiber polymer identification is made by comparison of the fiber spectrum with reference spectra.

Attenuated Total Reflectance (ATR) accessories for FTIR spectrometers as well as stand-alone ATR instruments and diamond anvil cells with a beam condenser enable the analyst to collect infrared spectra from manufactured textile fibers with minimal sample preparation.

Although natural fibers may also be analyzed by IR spectroscopy, this is not a method to replace light microscopy.

3.10.2 Safety Considerations

Standard Laboratory Precautions - See FSD Health & Safety Manual

Liquid nitrogen precaution - extreme cold, NFPA is 3-0-0
The FTIR contains a laser; precautions apply

3.10.3 Preparations

Standard Laboratory Practices

The dewar must be filled with liquid nitrogen a minimum of thirty minutes before the first sample run.

Care should be taken to eliminate or lessen the effects of interference fringes, contaminants, and pressure effects due to sample preparation.

3.10.4 Minimum Standards & Controls

Worksheets shall indicate the instrumental tests performed and their results.

All spectra of case exhibits shall be preserved in the case record.

Relevant parameters shall be recorded and included in the case record. The data shall be properly identified.

3.10.5 Instrumentation

Fourier transform infrared spectrometer (FTIR) with microscope attachment

See TRACE-PM 7.2 FTIR Verification for general FTIR information and minimum standards and controls

3.10.6 Procedure or Analysis

FTIR Sample Preparation

The quantity of fiber used and the number of fiber samples required will differ according to the following:

- Specific technique and sample preparation;
- Sample homogeneity;
- Condition of the sample; and
- Other case-dependent analytical conditions/concerns, or both.

These are examples of how to prepare fiber evidence for analysis on the FTIR. Not all techniques will give the best results with each type of fiber. Fibers like Acrylic, Acetate, and Triacetate crush easily and care should be taken when pressed. Spandex, plasticized man-made fibers, and irregular shaped fibers need to be compressed in order to hold their flattened shape.

Sample preparation should be similar for all fibers being compared. Samples mounted in oil or removed from adhesive should be cleaned with an appropriate solvent.

Except when using ATR, fibers should be flattened prior to analysis in order to obtain the best quality spectra. Flattening the fiber alters the morphology, and therefore, the minimum length of fiber necessary for the analysis should be used. Flattening the fibers can alter the crystalline/amorphous structure of the fiber and result in minor differences in peak frequencies and intensities. This must be taken into consideration when making spectral comparisons. Leaving the fiber unflattened, while allowing crystallinity-sensitive bands to be observed unaltered, results in distortion of peak heights due to variable pathlengths. In certain situations, a combination of both approaches may be advisable. Fibers analyzed via Attenuated Total Reflectance (ATR) do not require flattening prior to analysis. Sample fibers are flattened by a hand-operated press when the sample is mounted against the diamond surface.

Flattening with a Roller - Cut piece of fiber (recommend no larger than 100 µm). Flatten fiber on glass slide with roller by pressing firmly and pushing in one direction. Repeated rolls back and forth can result in fiber adhering to roller surface. Repeat until fiber is flattened.

The flattened fiber may be mounted across an aperture, on an IR window, between IR windows or on a Low e- microscope slide suitable for use on the microscope FTIR.

It is important that the longitudinal plane (flattened surface) of the fiber be as nearly parallel to the IR window or other mount as possible. Common IR window materials used for this purpose include but are not limited to KBr, CsI, BaF2, ZnSe, and diamond. The choice of window material should not reduce the effective spectral range of the detector being used. Where the fiber is mounted between two IR windows, a small KBr crystal should be placed next to the fiber. The background spectrum should be acquired through this crystal to avoid interference fringes that would arise if the spectrum were acquired of an air gap between the two IR windows.

Where several fibers are mounted on or in a single mount, they should be well separated (microscopically) so that their positions can be unambiguously documented for later retrieval, reanalysis, or both and to prevent spectral contamination from stray light that might pass through another fiber.

3.10.7 Data Collection

Refer to FTIR instrument operation specific to your laboratory's instrument.

Samples should be focused as close to the center of the sample volume as possible.
The detector measurement aperture width should be adjusted to just slightly less than the width of the fiber but preferably not less than 10 µm.

The size and position of the apertures should not vary between sample and background data acquisition for a given analysis.

Background Spectrum - A background spectrum refers to a reference absorption spectrum, which includes the absorbance contributions of all system components except the sample of interest. The IR window or windows with KBr crystal are all considered part of the system. The system parameters for

background spectra should be identical to the parameters used for sample spectra (with the possible exception of gain and number of scans). These parameters include resolution, mirror velocity, and spectrometer aperture size.

Resolution - Resolution should be set at 4 cm^{-1} (one data point every 2 cm^{-1}). Higher resolution may be used. The additional data points, however, typically yield no further analytical information for polymer samples.

Scan from 4000 to 550 cm^{-1}. This range may vary depending on the type of accessory and detector used. Replicate analyses may be employed to ensure reproducibility or to demonstrate variability within a sample.

Generally speaking, data manipulation, including baseline correction, is discouraged and smoothing of data is prohibited. If baseline correction is conducted, a copy of the original, uncorrected spectrum will be included in the case file.

3.10.8 Fiber Type Identification and Comparison

Identification - Successful identification of fiber polymers by IR spectra depends on experience and familiarity with fiber reference spectra. Spectral identification is accomplished by comparison with spectra of known reference standards. A library of reference IR spectra is essential. A library of reference fiber IR spectra obtained using the same technique used for the unknown fiber is desirable. It is also desirable to have available authenticated reference samples of the fibers.

For identification, the positions of the absorption bands according to wavelength or wavenumber and their relative intensities must be compared with those of a known reference spectrum. It is desirable to confirm the identification by other methods (i.e., previously performed analytical techniques such as PLM).

The generic class of manufactured textile fibers can be unequivocally identified with the exception of rayon versus lyocell (these generic classes may be differentiated by their optical properties). The subgeneric class of synthetic manufactured fibers may be identified.

Comparison – Comparisons of the positions of absorption bands according to wavelength or wavenumber and their relative intensities must be performed. Overlaying spectra is recommended for making comparisons. No meaningful (or unexplainable) differences shall be observed between a questioned and known sample when making an association.

Any major discrepancies between the two are reason for elimination. It may be necessary to sample several known or questioned fibers or to take several spectra along the length of a given fiber to determine the reproducibility of the spectra.

3.10.9 Documentation

Departures from procedures and requirements listed in this procedure shall be noted in the case record.

Similarity or dissimilarity in the IR spectra should be noted when making a fiber comparison. The examination documentation should contain sufficient detail to support conclusions.

Worksheets or spectra shall indicate the instrumental tests performed and their results.

All spectra of case items shall be preserved in the case record.

Relevant parameters shall be recorded and included in the case record.

3.10.10 References

ASTM E2224-19 Standard Guide for Forensic Analysis of Fibers by Infrared Spectroscopy

Scientific Working Group for Materials Analysis, “Forensic Fiber Examination Guidelines”, www.swgmat.org

Bartick, E. G.; Tungol, M. W. In Forensic Science Handbook; Saferstein, R., Ed.; Prentice Hall: Englewood Cliffs, N.J., 1993; Vol. III, Chapter 4.

Robertson, J., Ed. Forensic Examination of Fibers; Ellis Horwood: New York, 1992.