

Forensic Fiber Examination Guidelines: Infrared Analysis of Textile Fibers

Scientific Working Group for Materials Analysis (SWGMAAT)

1.0. Scope

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, infrared (IR) spectroscopy, or pyrolysis gas chromatography. Infrared analysis offers the advantage of being the least destructive of these methods.

IR spectroscopy is a valuable method of fiber polymer identification and comparison in forensic examinations. The use of IR microscopes coupled with Fourier transform infrared (FTIR) spectrometers has greatly simplified the IR analysis of single fibers, thus making the technique feasible for routine use in the forensic laboratory.

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.

This guideline is intended to assist individuals and laboratories that conduct forensic fiber examinations and comparisons in the effective application of infrared spectroscopy to the analysis of fiber evidence. Although this guide is intended to be applied to the analysis of single fibers, many of its suggestions are applicable to the infrared analysis of small particles in general.

2.0. Reference Documents

SWGMAAT Trace Evidence Quality Assurance Guidelines (January 2000)

SWGMAAT Trace Evidence Recovery Guidelines (October 1999)

SWGMAAT Forensic Fiber Examination Guidelines (April 1999)

ASTM E1492-11 Standard Practice for Receiving, Documenting, Storing, and Retrieving Evidence in a Forensic Science Laboratory

ASTM E131-10 Standard Terminology Relating to Molecular Spectroscopy

ASTM 1421-99(2009) Standard Practice for Describing and Measuring Performance of Fourier Transform Mid-Infrared (FTIR) Spectrometers: Level Zero and Level One Tests

ASTM E2224-10 Standard Guide for Forensic Analysis of Fibers by Infrared Spectroscopy

3.0. Terminology

Absorbance (A): the logarithm to the base 10 of the reciprocal of the transmittance, (T).

$$A = \log_{10}(1/T) = -\log_{10} T$$

Absorption Band: A region of the absorption spectrum in which the absorbance passes through a maximum.

Absorptivity (a): Absorbance (A) divided by the product of the sample pathlength (b) and the concentration of the absorbing substance (c). $a = A/bc$

Absorption Spectrum: A plot, or other representation, of absorbance or any function of absorbance, versus wavelength, or any function of wavelength.

Attenuated Total Reflection (ATR): An instrumental method of FTIR spectrum collection in which an infrared beam is reflected within an optically dense crystal (e.g., diamond), creating a wave that extends beyond the crystal's exterior surface into a sample that is placed in direct contact with the crystal.

Background: Apparent absorption caused by anything other than the substance being analyzed.

Cellulosic Fiber: Fiber composed of polymers formed from glucose.

Evanescent wave: a wave that is created when a beam of infrared light is reflected within an optically dense crystal. This evanescent wave extends beyond the surface of the crystal and into an adjoining sample.

Far-Infrared: Pertaining to the infrared region of the electromagnetic spectrum with wavelength range from approximately 50 to 1,000 μm (wavenumber range 200 to 10 cm^{-1}).

Fourier Transform (FT): A mathematical operation that converts a function of one independent variable to that of a different independent variable. In Fourier transform infrared (FTIR) spectroscopy, the Fourier transform converts a time function (the interferogram) to a frequency function (the infrared absorption spectrum). Spectral data is collected through the use of an interferometer, which replaces the monochromator found in a dispersive infrared spectrometer.

Fourier Transform Infrared (FTIR) Spectrometry: A form of infrared spectrometry in which an interferogram is obtained. This interferogram is then subjected to a Fourier transform to obtain an amplitude-wavenumber (or wavelength) spectrum.

Generic Class: A group of fibers having similar, but not necessarily identical, chemical composition. A generic name applies to all members of a group and is not protected by trademark registration. Generic names for manufactured fibers include, for example; rayon, nylon, and polyester. Generic names used in the United States for manufactured fibers were established as part of the Textile Fiber Products Identification Act enacted by Congress in 1954.

Infrared: Pertaining to the region of the electromagnetic spectrum with wavelength range from approximately 0.78 to 1,000 μm (wavenumber range 12,820 to 10 cm^{-1}).

Infrared Spectroscopy: Pertaining to spectroscopy in the infrared region of the electromagnetic spectrum.

Manufactured Fiber A class name for various families of fibers produced from fiber-forming substances, including synthetic polymers, modified or transformed natural polymers and glass.

Mid-Infrared: Pertaining to the infrared region of the electromagnetic spectrum with wavelength range from approximately 2.5 to 50 μm (wavenumber range 4,000 to 200 cm^{-1}).

Near-Infrared: Pertaining to the region of the electromagnetic spectrum with wavelength range from approximately 0.78 to 2.5 μm (wavenumber range 12800 to 4,000 cm^{-1}).

Spectrometer: Photometric device for the measurement of spectral transmittance, spectral reflectance, or relative spectral emittance.

Subgeneric Class: A group of fibers within a generic class that shares the same polymer composition. Subgeneric names include, for example; nylon 6, nylon 6,6, and poly(ethylene terephthalate).

Transmittance (T): The ratio of radiant power transmitted by the sample, (I), to the radiant power incident on the sample, (I_0). $T = I/I_0$.

Wavelength: The distance, measured along the line of propagation, between two points that are in phase on adjacent waves.

Wavenumber: The number of waves per unit length, in a vacuum, usually given in reciprocal centimeters (cm^{-1}).

4.0. Summary of Guidelines

This guideline covers identification of fiber polymer composition by interpretation of absorption spectra obtained by infrared spectroscopy. It is intended to be applicable to a wide range of infrared spectrometer and microscope configurations. Spectra may also be obtained by a variety of alternative IR techniques not covered in this document.

This analytical method covers the analysis of manufactured textile fibers (with the exception of inorganic fibers). Although natural fibers may also be analyzed by IR spectroscopy, light microscopy is the preferred method for the identification of natural fibers.

5.0. Significance and Use

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.

Consideration should be given to the potential for additional compositional information that may be obtained by IR spectroscopy over PLM alone (see the Microscopy chapter of SWGMAAT's Forensic Fiber Examination Guidelines). The extent to which IR spectral comparison is indicated will vary with specific sample and case evaluations.

IR analysis should follow visible and fluorescence comparison microscopy, polarized light microscopy, and UV or visible spectroscopy. However, it should be conducted before dye extraction for thin-layer chromatography due to the semi-destructive nature of the technique. 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.

6.0. Sample Handling

The general handling and tracking of samples should meet or exceed the requirements of ASTM 1492-05 (14).

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.

Sample preparation should be similar for all fibers being compared. 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. During ATR analysis, sample fibers are flattened by a hand-operated press when the sample is mounted against the diamond surface.

The flattened fiber may be mounted across an aperture, on an IR window, or between IR windows. 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 through the air gap between the two IR windows.

Where several fibers are mounted on or in a single mount, they should be well separated (physically) 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.

7.0. Analysis

A mid-infrared spectrometer and an infrared microscope that is compatible with the spectrometer or diamond compression cell with beam condenser are recommended. The lower frequency cutoff varies with the microscope detector used (preferably no higher than 750 cm⁻¹).

Useful sample preparation accessories include, but are not limited to, sample supports, infrared windows, presses, dies, rollers, scalpels, and tungsten probes.

7.1. Equipment Readiness

All spectrometer and microscope components should be turned on and allowed to reach thermal stability prior to commencement of calibration and operational runs. It should be noted that some FTIR instruments are designed to work best when left on or in the standby mode 24 hours a day.

Analysts should refer to the manufacturer's guidelines for the optimum performance of their instruments.

7.2. Instrument Performance and Calibration

It is essential that instrument performance and calibration be evaluated routinely, at least once a month, in a comprehensive manner.

The preferred performance evaluation method is in accordance with ASTM 1421-99(2009). In brief, this includes evaluating system throughput, single-beam spectrum, 100% T line, and polystyrene reference spectrum.

Instrument performance records should be maintained on hard copy, computer disk, electronically or all of the above. Case documentation may vary by laboratory but should include the date, the operator, the system parameters, and the original instrumental output data.

7.3. Sample Illumination and Detector Measurement Apertures

The apertures that control the areas (fields) of sample illumination and detector measurement in an IR microscope may be of fixed or variable size and may be either rectangular or circular in shape. Variable rectangular apertures are recommended because they can be more closely matched to the fiber shape. Light throughput, stray light reduction, and aperture focus in the sample image plane are some of the considerations in selecting aperture parameters and positioning. Fiber width, length, flatness, and linearity will usually limit the size of the illumination and detector apertures used for analysis. In general, the illuminating and detector fields should lie within the boundaries of the fiber edges.

7.4. Objective and Condenser Adjustment

The objective, condenser, or both should be optimized, if possible, for any IR window that lies between the optic and the sample in the beam path. This compensation reduces spherical aberration and permits more accurate focus.

7.5. Polarization Bias of the Infrared Spectrometers and Microscopes

Infrared spectrometers and microscopes exhibit a polarization bias. It is essential that fiber alignment be consistent throughout an analysis.

7.6. Focusing

Samples should be focused as close to the center of the sample volume as possible and centered on the optical axis of the system. The condenser should be focused and re-centered if necessary. This is best accomplished using a circular field aperture.

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 aperture length may vary with sample geometry but should not be so great as to allow the detector to be saturated when acquiring a background spectrum. The illuminating field aperture should be adjusted so that the image of its edges coincide with those of the detector measurement aperture. The size and position of the apertures should not vary between sample and background data acquisition for a given analysis.

7.7. 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. Because the apertures are adjusted to fit the sample, it is usually most convenient to acquire the sample spectrum prior to acquiring the background spectrum.

7.8. 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.

7.9. Spectral Quality and Data Storage

The quality of a spectrum is dependent on the focus, size of the window, thickness of the fiber, nature of the fiber, delustrant, etc.. A spectrum should be repeated, for example, if the baseline is noisy, or diffraction effects and/or interference fringes are pronounced. These hamper the identification of fibers and comparison of spectra.

It is generally useful to save all data after it is generated and prior to any modification.

7.10. Identification of Fiber Polymers by IR Spectra

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

8.0. Examination Documentation

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.

9.0. References

Bartick, E. G. Considerations for fiber sampling with infrared microspectroscopy. In: *The Design, Sample Handling, and Applications of Infrared Microscopes*, ASTM STP 949. Ed., P. B. Roush. American Society for Testing and Materials, Philadelphia, 1987, pp. 64-73.

Bartick, E. G., Tungol, M. W., and Reffner, J. A. A new approach to forensic analysis with infrared microscopy: Internal reflection spectroscopy, *Analytica Chimica Acta* (1994) 288:35-42.

Carlsson, D. J., Suprunchuk, T., and Wiles, D. M. Fiber identification at the microgram level by infrared spectroscopy, *Textile Research Journal* (1977) 47:456-458.

Cook, R. and Paterson, M. D. New techniques for the identification of microscopic samples of textile fibres by infrared spectroscopy, *Forensic Science International* (1978) 12:237-243.

Federal Trade Commission Rules and Regulations Under the Textile Products Identification Act, Title 15, U. S. Code Section 70, et seq. 16 CFR 303.7.

Fox, R. H. and Schuetzman, H. I. The infrared identification of microscopic samples of man-made fibers, *Journal of Forensic Sciences* (1968) 13:397- 406.

FTIR Spectroscopy, Attenuated Total Reflectance (ATR), Technical Note; PerkinElmer Life and Analytical Sciences; Shelton, CT., 2005.

Gál, T., Ambrus, I., and Urszu, S. Forensic analysis of textile fibres by Fourier transform infrared diamond cell technique, *Acta Chimica Hungarica* (1991) 128:919-928.

Garger, E. F. An improved technique for preparing solvent cast films from acrylic fibers for the recording of infrared spectra, *Journal of Forensic Sciences* (1983) 28:632-637.

Grieve, M. C. Another look at the classification of acrylic fibres: Using FTIR microscopy, *Science and Justice* (1995) 35:179-190.

Grieve, M. C. and Kotowski T. M. Identification of polyester fibres in forensic science, *Journal of Forensic Sciences* (1977) 22:390-401.

Hartshorne, A. W. and Laing, D. K. The identification of polyolefin fibres by infrared spectroscopy and melting point determination, *Forensic Science International* (1984) 26:45-52.

Hatch, K. L. *Textile Science*. West Publishing, Minneapolis/St. Paul, 1993, pp. 84.

Messerschmidt, R. G. Minimizing optical nonlinearities in infrared microspectrometry. In: *Infrared Microspectroscopy: Theory and Applications*. Eds. R. G. Messerschmidt and M. A. Harthcock. Marcel Dekker, New York, 1988, pp. 1-19.

Read, L. K. and Kopec, R. J. Analysis of synthetic fibers by diamond cell and sapphire cell infrared spectrophotometry, *Journal of the Association of Official Analytical Chemists* (1978) 61:526-532.

Tungol, M. W., Bartick, E. G., and Montasser, A. Forensic examination of synthetic textile fibers by microscopic infrared spectrometry. In: *Practical Guide to Infrared Microspectroscopy*. 2nd. ed. Ed., H. Humecki. Marcel Dekker, New York, 1995.

Tungol, M. W., Bartick, E. G., and Montaser, A. The development of a spectral data base for the identification of fibers by infrared microscopy, *Applied Spectroscopy* (1990) 44:543-549.