

Guideline for Using Fourier Transform Infrared Spectroscopy in Forensic Tape Examinations

Scientific Working Group on Materials Analysis (SWGMAAT)

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1.0 Scope

This document is part of a series of SWGMAAT guidelines relating to the forensic analysis of tape. Infrared spectroscopy (IR) is a valuable method for the identification and comparison of pressure sensitive tape components. This document provides basic recommendations and information about FTIR-spectrometer components and accessories, with an emphasis on sampling techniques specific to tape components. The particular method(s) employed by each examiner and/or laboratory will depend upon available equipment, examiner training, sample suitability, and sample size. It is assumed that the examiner has a basic knowledge of the theory and proficiency in the use of infrared spectroscopy.

2.0 Reference Documents

ASTM International Standards

E1492-05 *Practice for Receiving, Documenting, Storing, and Retrieving in a Forensic Laboratory*

E131-98 *Terminology Relating to Molecular Spectroscopy*

1421-99 (2004) *Standard Practice for Describing and Measuring Performance of Fourier Transform Mid-Infrared (FTMIR) Spectrometers: Level Zero and Level One Tests*

E 573-01 (2007) *Standard Practices for Internal Reflection Spectroscopy*

SWGMAAT Trace Evidence Quality Assurance Guidelines [Online] (January 2000). Available:

<http://www.fbi.gov/hq/lab/fsc/backissu/jan000/swgmat.htm>.

SWGMAAT Trace Recovery Guidelines [Online] (October 1999). Available:

<http://www.fbi.gov/hq/lab/fsc/backissu/oct1999/index.htm>

SWGMAAT Forensic Fiber Examination Guideline [Online] (April 1999) Available:

<http://www.fbi.gov/hq/lab/fsc/backissu/april1999/index.htm>

SWGMAAT Guideline for the Forensic Examination of Pressure-Sensitive Tapes [Online] (October 2008) Available:

<http://www.fbi.gov/hq/lab/fsc/backissu/Oct2008/index.htm>

3.0 Terminology

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

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

Absorbance band: a region of the absorption spectrum in which the absorbance passes through a maximum.

Absorbance spectrum: a plot or other representation of a function of absorbance against any function of wavelength.

Absorptivity: an absorbance divided by the product of the sample pathlength (b) and the concentration of the absorbing substance (c). The units of b and c shall be specified.
 $a = A/bc$.

Aperature: an opening in an optical system that controls the amount of light passing through a system.

Attenuated total reflectance (ATR): a method of spectrophotometric analysis based on the reflection of energy at the interface of two media which have different refractive indices and are in intimate contact with each other; also known as Internal Reflection Spectroscopy (IRS).

Background: absorption caused by anything other than the substance for which the analysis is being made.

Beam condenser: a series of mirrors that focus the infrared beam to a small area in the sample compartment to permit the examination of smaller samples than would otherwise be possible.

Beam splitter: an optical component that partially reflects and partially transmits radiation from the source in such a manner as to direct part to a fixed mirror and the other part to a moving mirror.

Deuterated triglycine sulphate (DTGS) detector: a thermal detector that operates at room temperature but lacks the sensitivity for use with microscope accessories.

Double-pass transmission spectra: spectra that results from incident radiation passing through the sample, reflecting off the substrate, and passing through the sample a second time.

Far-infrared: the infrared region of the electromagnetic spectrum with wavelength range from approximately 25 to 1000 μm (wavenumber range 400 to 10 cm^{-1}).

Filler/extender: an inorganic material that is added to a tape to modify a physical property or reduce cost.

Fourier transform (FT): the mathematical process which is used to convert an amplitude-time-spectrum to an amplitude-frequency spectrum, or *vice versa*. In FTIR spectrometry, retardation is directly proportional to time; therefore, FT is commonly used to convert an amplitude-retardation spectrum to an amplitude-wavenumber spectrum, and *vice versa*.

Fourier transform infrared spectrometry (FTIR): 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.

Infrared: the region of the electromagnetic spectrum with wavelength range from approximately 0.78 to 1000 μm (wavenumber range 12,800 to 10 cm^{-1}).

Infrared spectroscopy (IR): the study and interpretation of spectra within the infrared region of the electromagnetic spectrum.

Interferogram: a plot of the detector output as a function of retardation.

Interferometer: a device used to split a beam of radiant energy into two paths, generate an optical path difference between the beams, and recombine them in order to produce repetitive interference maxima and minima as the optical retardation is varied.

Internal reflection element: a high refractive index material (e.g., ZnSe, Ge, or diamond) used as a substrate for the sample to internally reflect the IR electromagnetic radiation.

Internal reflection spectroscopy (IRS): see Attenuated Total Reflection (ATR)

Low E-Glass: glass that is coated with an IR reflective surface. Such glass is suitable for use as a sample support when performing IR reflection techniques.

Mercury Cadmium Telluride (MCT) detector: a quantum detector that utilizes a semi-conducting material and requires cooling with liquid nitrogen to operate. This type of detector is commonly used in microscope accessories due to its sensitivity.

Mid-infrared: the infrared region of the electromagnetic spectrum with wavelength range from approximately 2.5 to 25 μm (wavenumber range 4000 to 400 cm^{-1}).

Retardation: optical path difference between two beams in an interferometer; also known as the "optical path difference" or "optical retardation".

Spectrometer: an instrument for the measuring of some function of spectral power, or other physical quantity, with respect to spectral position within a spectral range.

Spectroscopy: the study of the theory and interpretation of spectra generated by any phenomenon, such as electromagnetic waves or particles, ordered in accordance with the magnitude of a common physical property (wavelength, frequency, or mass).

Spectrum: an arrangement of the component parts of any phenomenon, such as electromagnetic waves or particles, ordered in accordance with the magnitude of a common physical property.

Transmittance, (T): ratio of the energy of the radiation transmitted by the sample to the background, usually expressed as a percentage.

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 Guideline

This guideline covers the analysis of components used in tape backings and adhesives by infrared spectroscopy. It can be applied to a wide range of infrared spectrometers and accessory configurations.

For the infrared analysis of the fibers in the reinforcement component of tapes, one should refer to SWGMAAT Chapter 6 of Forensic Fiber Examination Guidelines: Infrared Analysis of Textile Fibers.

5.0 Significance and Use

This guide is designed to assist an examiner in the selection of appropriate sample preparation methods for the analysis, comparison, and identification of pressure sensitive tape components. If no significant differences are noted in the physical measurements, then IR should be the next step in the analytical scheme.

Infrared spectroscopy can provide molecular information regarding major organic and inorganic components. For various reasons, components in lesser amounts are typically more difficult to identify unequivocally. Reasons for this include interference of the absorption bands of the major components with the less intense bands of minor constituents and sensitivity issues whereby the minor components are present at concentrations below the detection limits of the instrument.

Infrared spectroscopy can be used to obtain spectra for elucidation of the chemical composition of a tape and for comparison of two or more samples. When used for comparison of spectra, the goal is to determine whether any significant differences exist between the samples.

6.0 Sample Handling

6.1 The general collection, handling, and tracking of samples should meet or exceed the requirements of ASTM 1492-05 as well as the relevant portions of the SWGMAAT's Trace Evidence Quality Assurance Guidelines and Trace Recovery Guidelines.

6.2 The work area and tools used for the preparation of samples must be free of all materials that could transfer to the sample.

6.3 When analyzing difficult samples (e.g., residue, dirty samples, or inhomogeneous samples), care must be taken when sampling the tape and in choosing appropriate analytical conditions. An attempt should be made to remove any extraneous material from the specimen before sampling. In order to ensure reproducibility and/or evaluate intra-sample variations, repeat analysis of any samples is recommended.

6.4 If the tape has been processed by the latent print unit and an unprocessed piece of tape has not been retained, a number of options are available to obtain a representative sampling for infrared analysis. Tape backing can be cleaned with an appropriate solvent. Alternatively, a clean portion can be obtained by manually removing the residue from the latent print processing by gentle scraping of the surface. A representative adhesive sample can be obtained by exposing and sampling the underlying portion.

6.5 Attenuated Total Reflection (ATR), also known as Internal Reflection Spectroscopy (IRS), is a rapid sampling method for the analysis of the tape backing and the adhesive as virtually no sample preparation is necessary. Single or multiple reflection elements can be used depending on the amount of clean area available for sampling. When only a small clean area is available, a single reflection element is desirable to avoid contamination.

6.6 Transmission microspectroscopy is possible by sampling a small portion of the tape component (backing, adhesive) and analyzing it as a thin film.

6.7 A diamond anvil cell may be used to analyze both the backing and the adhesive portions of tape. This may be used in the bench with a beam condenser or placed under the microscope accessory.

6.8 If the sample backing is opaque, pyrolysis/IR may be used. The condensed pyrolyzate cast as a film on an IR window is normally sufficient to identify the polymer by transmission. No inorganic information can be obtained from this technique. Caution should be exercised when comparing spectra obtained by this technique as the pyrolysis conditions are not optimally controlled.

6.9 Tackifiers and/or plasticizers may be extracted from the adhesive or backing using a mild solvent such as hexane or acetone. They are subsequently analyzed in transmission by casting a thin film.

6.10 Samples being compared should be prepared and analyzed in the same manner.

7.0 Analysis

A standard mid-IR range FTIR spectrometer is acceptable to conduct the necessary analyses. The detector cutoff should be no higher than 750 cm^{-1} . A mid-infrared FTIR spectrometer with an extended range to near 200 cm^{-1} is optimum, as it is advantageous for the classification and comparison of inorganic fillers and pigments.

7.1 Instrument Parameters

7.1.1 Performance and Calibration

It is essential that instrument performance and calibration be evaluated routinely, at least once a month (or before use if used less frequently).

7.1.2 The preferred performance evaluation method is in accordance with ASTM-1421-99 (2004), Sections 1-7, 9.5 and 9.5.1. In brief, this includes evaluation of the following:

- System throughput;
- Single-beam spectrum;
- 100% T line;
- Polystyrene reference spectrum.

7.1.3 Sample and background scans should be run under the same instrument conditions.

7.1.4 A resolution of 4 cm^{-1} is optimum (one data point every 2 cm^{-1}). Higher resolution may be used. The additional data points, however, typically yield no further analytical information for polymeric samples.

7.2 Main bench

7.2.1 Transmission

7.2.1.1 Samples prepared for analysis by transmission techniques must be thin enough to allow infrared radiation to pass through without being over-absorbed by the sample. For transmission data that are viewed in absorbance, the sample should be thin enough to produce a maximum absorbance of 1 absorbance unit. For transmission data viewed in % Transmittance, optimally, spectral peaks should not fall below 10% T. This typically requires a sample thickness of approximately 5 – 10 micrometers.

7.2.1.2 Sample preparation techniques that may be employed for transmission analysis in the main bench include backing and/or adhesive pressed in a diamond cell, a thin backing sample stretched over an aperture, or adhesive deposited onto an alkali halide pellet (e.g., KBr, NaCl, or AgCl).

7.2.2 ATR

7.2.2.1 ATR methods may lend themselves to conducting the examination of the tape intact. Since ATR is a surface technique it is necessary to remove any extraneous material from the area to be examined. The bench ATR (single reflection) is useful for forensic casework size samples. These accessories utilize an internal reflection crystal to condense the beam onto a spot-sized sampling area.

7.2.2.2 ATR is also useful in the analysis of duct tape backings for layer structure determination. The adhesive is removed, and the backing is analyzed on both sides. The compositions are then compared.

7.3 FTIR Microscope accessory

7.3.1 The use of a microscope accessory is preferred for very small samples. Spectra can be obtained from samples as small as 10-20 micrometers in diameter after flattening.

7.3.2. There is a trade off between sensitivity and spectral range with the MCT detectors. The low energy cut off for most detectors is in the 700-450 cm^{-1} range. The smallest apertures particularly limit the energy from the longer wavelengths (smaller wavenumbers) reaching the detector due to diffraction. Heterogeneity issues are also more pronounced when using very small apertures.

7.3.3 The microscope attachment permits the analysis of multiple samples placed on an appropriate support material. The method affords the advantage of viewing the sample optically and choosing the most appropriate area for analysis.

7.3.4 Spectral measurements using an FTIR microscope can be obtained in transmission, reflection, or ATR mode.

7.3.4.1 Transmission

7.3.4.1.1 Transmission measurements are commonly used because they generate spectra with fewer artifacts. However, transmission methods generally entail more sample preparation than reflection techniques. The tape sample must be rendered thin enough not to over-absorb. Samples can be placed directly over a small aperture for analysis or placed on an appropriate salt plate. This typically requires a sample thickness of approximately 3-5 micrometers.

7.3.4.1.2 A diamond cell can also be used as a sample support medium under the FTIR microscope. The adhesive can simply be smeared on one of the diamond faces. The tape backing sample is placed on one of the diamond faces, the second diamond is positioned on top, and sufficient pressure is applied to form a film. For nonelastic samples, one diamond is typically removed prior to analysis once the sample has been compressed. This leaves the thin compressed film adhering to one of the diamond faces.

7.3.4.2 Reflection

7.3.4.2.1 If samples are flattened directly on an infrared light reflecting surface (e.g., low e-glass or gold mirror), the reflection mode can be used to produce spectra mimicking double-pass transmission spectra. The technique is sometimes referred to as "transflection" or "reflection/absorption." Samples need to be approximately half the thickness of an optimum transmission sample.

7.3.4.2.2 The FTIR microscope can also be used in the specular reflection mode; however, it is not useful for tape unless the surface of the sample is highly reflective.

7.3.4.3 ATR

ATR objectives are available for infrared microscopes. Consistent pressure should be applied to each sample to mitigate spectral variations. Intra-sample variations may result from sample heterogeneity; therefore, multiple samplings should be considered.

8.0 Spectral Interpretation

8.1 Spectral comparison

Comparisons of the tape component spectra can be accomplished by digital overlays with full scale expansion.

8.1.1 Comparison of samples may be conducted with both spectra displayed in transmittance and/or absorbance. Certain information may be seen more readily in one format or the other.

8.1.2 There are a number of significant factors that should be considered when comparing spectra including the presence or absence of absorption bands, and their position (wavenumber), shape and relative intensity. Additional sample replicates may be necessary to evaluate reproducibility of these spectral characteristics

8.1.2.1 The presence of additional absorption bands could be from true differences between the samples or from extraneous material adhering to the tape. If extraneous material is suspected as the source of the difference, the sample should be cleaned or additional samples prepared. If the sample cannot be cleaned or resampled, then spectral subtraction may be an option.

8.1.2.2 For spectra to be considered indistinguishable, the position of the absorption bands should have reasonable agreement with each other. A rule of thumb is that the positions of corresponding peaks in two or more spectra being compared should be within a few wavenumbers of each other, depending on whether the peak is sharp or broad. For sharp absorption peaks one may use tighter constraints and with broad peaks the variation may be slightly greater.

8.1.2.3 For spectra to be considered indistinguishable, the shape of the absorption bands should be consistent between comparison samples. The peak width and the symmetry of each peak should be evaluated. Sample thickness may affect the peak width and resolution.

8.1.2.4 For spectra to be considered indistinguishable, the relative intensities of respective absorption bands should be similar between comparison samples. The relative intensity may be affected by the heterogeneity of the sample.

8.1.3 Three possible conclusions can be reached after evaluating and comparing spectra: 1) the spectra are dissimilar, 2) the spectra are indistinguishable, or 3) inconclusive.

8.1.3.1 The spectra are dissimilar if there are one or more significant differences in the spectra. Significant differences are differences in which the spectral variation cannot be explained other than as differences between samples.

8.1.3.2 The spectra are indistinguishable when there are no significant differences in the spectra. Differences are not significant if the spectral variation can be explained as something other than differences between samples.

8.1.3.3 An inconclusive determination is one in which the significance of the differences cannot be completely assessed due to the constraints of sample size and/or condition.

8.2 Component Characterization

8.2.1 Tape is often comprised of a number of components that result in overlapping bands in the IR spectra; therefore, caution must be exercised while evaluating the data. Not all of the components of tape can be elucidated by IR due to overlapping bands and/or relative concentration.

8.2.2 Tools that can assist in the characterization of the spectra include, but are not limited to, spectral libraries, flow charts, and reference standards. It should be noted that most commercial spectral libraries consist of transmission (as opposed to reflection) spectra. It is desirable to use reference spectra that were obtained using the same sample preparation and collection technique.

8.2.3 The following components, if present, may be characterized by IR spectroscopy depending on the condition of the tape and on the concentration of the material.

- Backing
 - Polymer film
 - Plasticizers
 - Fillers/Extenders
 - Flame retardants
- Adhesive
 - Elastomer
 - Tackifiers
 - Fillers/Extenders
- Release coating
- Fiber reinforcement

9.0 Documentation

9.1 When making comparisons of tape samples, similarity or dissimilarity in the IR spectra should be noted.

9.2 For chemical identification of tape components, the positions of the absorption bands according to wavelength or wavenumber and their relative intensities must be compared to those of known reference spectra. It is desirable to confirm the identification by other methods such as polarized light microscopy (PLM), pyrolysis gas chromatography (Py-GC), scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS), X-ray fluorescence (XRF), and/or X-ray diffraction (XRD).

9.3. Case notes should include a copy of all of the instrumental data that was used to reach a conclusion. All hard copies should include a unique sample designation, the operator's name/initials, and the date of analysis.

9.4. Case notes should also include a description of the evidence analyzed by IR, the method of sample preparation, the analytical instrumentation used, and its operating parameters.

9.5 See SWGMAAT's Trace Evidence Quality Assurance Guidelines for further requirements.

10.0 References

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