FTIR Analysis of Paints, Tapes, and Polymers

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1 INTRODUCTION

This document describes the sample preparation and suggested instrumental parameters for the Fourier transform infrared spectroscopy (FTIR) analysis of paints, tapes, and other polymeric materials.

2 SCOPE

This procedure applies to Chemistry Unit caseworking personnel who analyze paints, tapes, and polymers via FTIR.

3 EQUIPMENT

- FTIR Spectrometer with operating and search software: Nicolet iS50 FTIR spectrometer with Omnic software (or equivalent)
- Microscope Accessory: Continuum microscope with Mercury Cadmium Telluride (MCT)/A detector (or equivalent)
- Attenuated Total Reflectance (ATR) Accessory: Smart iTX (or equivalent)
- Liquid Nitrogen
- Diamond compression cell (Spectra-Tech Inc., Shelton, CT or equivalent)
- IR inactive windows (e.g., Potassium Bromide (KBr)) (Spectra-Tech Inc., Shelton, CT or equivalent)
- Stereo microscope (~6X to ~100X) with appropriate light source (e.g., an annular ring light, fiber optic light)
- General laboratory supplies
- Standards and Controls

4 STANDARDS AND CONTROLS

A. Manufacturer-supplied and commercially available paints, tapes, polymers, adhesives, and sealants are maintained within the FBI Laboratory. These materials are used in casework in accordance with CHEM-100.
B. Refer to IOSS-751 for details on the performance checks and necessary supplies to conduct the check and operate the instrument.

5 SAMPLING

Refer to PP-800 for guidance on sample(s) selection. Record the sample(s) selected for analysis in the case notes.

6 PROCEDURE

Cease comparison examinations whenever a test reveals an exclusionary difference between the samples being compared. Record any factors limiting the analysis (e.g., sample size, condition) in the case notes.

A. If using the microscope accessory, determine whether the detector has been cooled. If it has not, fill the detector reservoir with liquid nitrogen.

B. Verify that the daily performance check has been successfully completed and recorded before proceeding to sample analysis.

C. Sample an item from a clean, core area (e.g., cut into the sample and discard the top portion, or clean the surface). If appropriate, dried material (e.g., cured spray paint on the nozzle) can be sampled from the container of an uncured specimen. Alternatively, a portion of an uncured sample (e.g., glues, two-part adhesive systems, liquid paint) can be mixed, applied to a clean microscope slide or other suitable substrate, and permitted to dry/harden according to the manufacturer's recommendations.

   As described below, samples are prepared in a manner suitable for analysis by transmission infrared microscopy. ATR is also noted as an alternative where applicable.

   1. Paint: Prepare either thin peels of individual layers or a cross-section of a multi-layered specimen. Thin peels can be achieved by manually cutting through individual layers with an angled scalpel blade or similar tool. Cross-sections are achieved manually or with a microtome. Compress each thin layer or cross-section with a roller, scalpel blade, between two IR inactive windows, or between the two windows of a diamond compression cell. Alternatively, analyze an area free of visible contaminants directly by ATR.

   2. Tape:
      i. Adhesive: Sample a core area, free of any contamination, with a scalpel or similar tool. Smear the adhesive evenly onto an IR inactive window. Alternatively, analyze an area free of visible contaminants directly by ATR.

      ii. Backing: For duct tapes, clean the top side of the backing as needed. Thoroughly remove the adhesive and reinforcement fabric from an area of the tape. Proceed to step E and analyze both sides of the backing by ATR. For other types of tapes, clean the tape backing as needed. Take a thin peel of a core area of the backing with a scalpel or similar tool. Compress with a roller, scalpel blade, between two IR inactive windows, or between the two windows of a diamond compression cell. Alternatively, analyze the backing directly by ATR.

      iii. Fibers: For fabric reinforced tapes, a cutting of one fiber from each of the warp and weft directional yarns is analyzed by compressing it with a roller, scalpel blade, between two IR inactive windows, or between the two windows of a diamond compression cell. Each fiber analysis involves two steps: a comparison of the known and/or

questioned fibers to one another and an identification of the polymer class of the fiber. Natural fibers (e.g., cotton) are not typically analyzed using FTIR.

3. Glues, sealants, elastomers, and plastics: Sample a core area with a scalpel or similar tool. Compress with a roller, scalpel blade, between two IR inactive windows, or between the two windows of a diamond compression cell. Alternatively, analyze directly by ATR.

D. If using the microscope accessory, remove the top window if the sample was compressed between two windows. Place the IR inactive window containing the sample into the appropriate holder and place the window and holder on the microscope stage. Adjust the compensator to accommodate the sample holder. View the sample of interest through the microscope. Adjust the apertures so that the sample fills the field of view. Collect a spectrum using the instrumental conditions listed below. After analyzing the sample, move to a clear area of the window without making any other adjustments and collect a background spectrum. Proceed to step F.

E. If using an ATR accessory, clean the crystal surface with a cotton swab or disposable wipe. Collect a background spectrum using the instrumental conditions listed below. For tape adhesives, place the sample area of interest in direct contact with the crystal and collect a spectrum using the instrumental conditions listed below. For cured material (e.g., paints, polymeric films, elastomers), place the sample with the area of interest on the crystal. Turn the compression device until the sample area is in direct contact with the crystal surface. Collect a spectrum using the instrumental conditions listed below.

F. Clean the IR windows or ATR crystal between samples and after daily use.

7 INSTRUMENTAL CONDITIONS

The following instrumental conditions are a guide for all standards and samples described herein:

Parameter	Microscope	ATR
Detector:	MCT/A	DTGS[1]
Spectral range (cm^{-1}):	4000 - 650	4000 – 400
Beam splitter:	KBr	KBr
Source:	IR	IR
Gain:	Auto	Auto
Resolution (cm^{-1}):	4	4
Minimum number of sample scans:	128	32
Minimum number of background scans:	128	32

8 ACCEPTANCE CRITERIA

8.1 Spectrum suitability

A. Proper sample preparation is critical for obtaining a suitable spectrum from FTIR absorption/transmission analysis. The following are some common sample preparation problems encountered in FTIR analysis. If not addressed, they can complicate the assessment of whether spectral differences are exclusionary.

1. Over absorption of a sample is characterized by rounded peaks or peaks that flatten out along the baseline, (i.e., not sharply-defined). To resolve this issue, the specimen should be re-sampled with a smaller sample size or compressed further to achieve a thinner analysis area.

2. Under absorption can occur when insufficient sample is placed in the field of view. To resolve this issue, adjust the aperture opening or repeat sampling to obtain a larger sample size.

3. Interference fringes are often observed in the transmission spectrum of a thin film introduced to the beam on an IR inactive window due to internal reflections of the IR radiation. The interference fringe can alter the relative band intensities or give the appearance of additional peaks. This phenomenon is most commonly observed for clear, colorless films. To reduce this effect, break direct contact between the specimen and the IR inactive

[1] Deuterated TriGlycine Sulfate Detector

window, transfer the specimen to a different IR inactive window, or roughen the surface of the prepared specimen. Alternatively, repeat the sample preparation and analyze the newly prepared sample.

8.2 Spectral comparison

A. Spectral comparisons should be conducted with spectra collected using similar sample preparations, similar sample characteristics (e.g., thickness, topography), and similar instrumental parameters, as appropriate.

B. Spectra are compared and interpreted based on the observation of any spectral differences, or lack thereof, between the sets of infrared data.

    1. Spectral overlay is a recognized approach for comparing data where the presence or absence of peaks, peak shapes, and relative intensities are all considered in the evaluation as to whether exclusionary differences exist between compared samples.

    2. When assessing differences between spectra, consider sample limitations (e.g., small samples, thin layers, dirty samples, sample smears that eliminate layer structure) and instrumentation limitations (e.g., sampling size, limits of detection).

C. Possible reasons for spectral differences include dissimilar sample conditions (e.g., size, thickness, surface topography), lack of representativeness of the specimen or source material, contribution from extraneous materials, or origination from different source materials. Additional samples can provide supplemental data to assist in assessing such differences.

D. If suitable infrared spectra are produced, comparisons can provide information regarding the potential relationship of the sources of the samples.

    1. Distinguishable sources: When exclusionary differences are observed between compared spectral features, the sources of the samples are considered distinguishable by infrared spectroscopy. Exclusionary differences in spectral comparisons 1) are outside the variability of spectra originating from the same source; and 2) cannot be explained by considerations such as sample heterogeneity, contamination, different sample conditions, or different sample histories.

    2. Indistinguishable sources: When no exclusionary differences are observed between compared spectral features, the sources of the samples are considered indistinguishable by infrared spectroscopy. Differences that are not considered exclusionary 1) are within the variability of spectra originating from the same source; or 2) can be explained by considerations such as sample heterogeneity, contamination, different sample conditions, or

different sample histories. If no exclusionary differences are observed in an infrared comparison, samples can be analyzed by other analytical techniques to provide additional information about the potential relationship between the sources of the samples.

E. Infrared spectral comparison is one part of a multi-analytical comparative approach. Infrared data alone can be used to distinguish the sources of compared samples but is otherwise not used independent of data obtained from other analytical techniques to reach an overall opinion regarding the potential relationship between the sources of the samples. An overall opinion that sources are indistinguishable is only reported when no exclusionary differences are observed in the analytical techniques that were applied.

9 LIMITATIONS

A. The inability to discriminate color and/or texture differences between layers (e.g., adjacent white paint layers) can result in inadequate sampling.

B. Some useful characteristic IR peaks occur outside of the chosen accessory's detector spectral range (e.g., inorganic pigment absorption bands).

C. The spectrum of a mixture can be difficult to interpret due to spectral overlap (e.g., calcite and isoprene at ~1450 and ~1375 cm^{-1}, tackifier and butadiene at ~967 cm^{-1}).

D. The sub-generic class of polymers cannot always be determined by FTIR analysis (e.g., type of acrylic).

E. Available sample size can limit or preclude analysis by this technique. A cross-section less than 15 microns wide cannot be analyzed.

10 PRECAUTIONARY STATEMENT

A. As with any procedure involving trace evidence, ensure actions minimize the potential for loss or contamination of the sample.

B. The presence of some pigments can cause difficulty with interpretation of the resulting spectrum. For example, carbon black causes an upward slant to the spectrum and organic red pigment(s) often have very sharp peaks in the region of interest for paint components.

C. The elasticity inherent in some polymers can cause the flattened sample to curl up when the object used to flatten the specimen is removed.

11 REFERENCES

CHEM-100, FBI Laboratory, Chemistry Unit

IOSS-751, FBI Laboratory, Research Support Unit

PP-800, FBI Laboratory, Chemistry Unit
ASTM E1421, Standard Practice for Describing and Measuring Performance of Fourier Transform Mid-Infrared (FT-MIR) Spectrometers: Level Zero and Level One Tests ASTM International, West Conshohocken, PA

ASTM E1610, Standard Guide for Forensic Paint Analysis and Comparison. ASTM International, West Conshohocken, PA

ASTM E2224, Standard Guide for Forensic Analysis of Fibers Using Infrared Spectroscopy. ASTM International, West Conshohocken, PA

ASTM E2937, Standard Guide for Using Infrared Spectroscopy in Forensic Paint Examinations. ASTM International, West Conshohocken, PA

ASTM E3085, Standard Guide for Fourier Transform Infrared Spectroscopy in Forensic Tape Examinations. ASTM International, West Conshohocken, PA

ASTM E3260, Standard Guide for Forensic Examination and Comparison of Pressure Sensitive Tapes. ASTM International, West Conshohocken, PA.

12 REVISION HISTORY

Revision	Issued	Changes
06	08/15/2022	Reformatted to conform with LAB-100 revisions. Minor grammatical changes throughout. Simplified and updated equipment. Moved references to training manual.
07	07/31/2023	Revised to include analysis of duct tape fibers.
08	01/02/2025	Removed Polystyrene from equipment list and removed details from general laboratory supplies; removed section 6.C.2.iii; updated ATR spectral range in Section 7.