I. Scope

Fourier Transform infrared spectroscopy (FTIR) is a valuable method of identification and comparison in forensic exams. Both transmittance and reflectance techniques may be used for analysis of explosives and explosives residues.

The absorption bands can provide enough characteristics to specifically identify a substance. The IR spectra of thousands of compounds have been collected, indexed and catalogued to serve as invaluable references for identifying substances.

II. References

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Miller, F.A. & C.H. Wilkins, Infrared Spectra of Characteristic Frequencies of Inorganic Ions, Analytical Chemistry, V24, 1952, p. 1253-1294

Yinon, J & Zitrin, S, The Analysis of Explosives, Pergamon Series in Analytical Chemistry, Volume 3, Chapter 11

Ryland S. G., Infrared Microspectroscopy of Forensic Paint Evidence, Practical Guide to Infrared Microspectroscopy, Edited by Humecki H. J., 1995, p163-243

Tungol M. W., Bartick E. G., & Montaser A., Forensic Examination of Synthetic Textile Fibers by Microscopic Infrared Spectrometry, Practical Guide to Infrared Microspectroscopy, Edited by Humecki H. J., 1995, p245-285

Colthup N. B., Daly L. H., & Wiberley S. E., Introduction to Infrared and Raman Spectroscopy, 3rd Edition, Academic Press, 1990

Hopen T. J. Tricks of the Trade: Microtome Glass Knives Employed for Micro-FTIR Preparation, The Microscope, Vol. 50, No.1, 2002, p4.

III. Safety Precautions

- wear eye protection when appropriate
- use care when pressing a pellet (high pressures)
- wear face shield and protective gloves when handling liquid nitrogen

IV. Apparatus/ Instrument Conditions

The instruments available vary between laboratories. Any validated FTIR instrument can be used. See parameter sheets and/or spectral reports for instrument settings.

Some FTIRs are equipped with two different detectors:

- The BENCH uses a DTGS (deuterated triglycine sulfate) detector which operates at room temperature.
- The MICROSCOPE uses an MCT (mercury cadmium telluride) detector that must be cooled with liquid nitrogen.

V. Procedures

Sampling and Sample Prep

Sampling and sample preparation will vary depending on the physical state of the sample (e.g., solid, liquid, or gas) and the available accessories.

Instrument Performance

There are four aspects of instrument performance that may be monitored:

1. Interferogram
2. Single-beam spectrum for microscope or bench
3. 100% T line
4. Polystyrene standard

It is each analyst's responsibility to ensure that a polystyrene standard has been evaluated and an energy check has been performed within the last 31 days. Other tests of instrument performance may be run at the analyst's discretion.

1. Interferogram
    - Refer to instrument manufacturer specifications. It may be useful to monitor interferogram position and voltage. Every detector is different so keeping track of the "normal" voltage is useful when trying to identify problems.
    - It is a good practice to check the interferogram energy for each detector before use.

2. Single-Beam Spectrum

    The single beam spectrum of the open beam instrument (no accessories in the beam) can be diagnostic of instrument performance and alignment:

    - Small peaks around 2900 cm^{-1} indicate hydrocarbon contamination, probably oil contamination on the beamsplitter.
    - Bands due to water (centered around 3750 and 1650 cm^{-1}) and carbon dioxide (around 2300 cm^{-1}) indicate the presence of these residual gases in the instrument. If these bands appear larger than normal after a reasonable purge time, the seals and purge setting should be checked.
    - With an MCT detector, apparent absorption around 3300 cm^{-1} may indicate the presence of ice in the detector. (primary operator should be notified)

3. 100% T Line

    The 100 percent line is the ratio of two consecutive open-beam spectra and is used to measure system noise. Compare to the manufacturer's specifications for the noise in the monitored region. Increased noise may indicate fogged mirrors.

4. Polystyrene Standard

This procedure confirms that selected peaks in a known spectrum correspond to the known wavenumber values of those selected peaks.

- Collect spectrum, in transmittance mode, for a known polystyrene standard.
- Compare the wavenumber values of the collected spectrum to the wavenumber values of known identifying peaks (as indicated on the standard card or in ASTM standard E1421-94). Values should not vary by more than 5-6 wavenumbers. Also, compare new wavenumber values to those of previous standard runs.

Running Samples/Blank

A blank background must be run before (or after, depending on the accessory) the sample. The accessory and conditions must be the same for the background and for the sample.

Possible Sources of Error

- Excessive water and/or carbon dioxide interference due to wet sample or poor background.
- Excessive noise in ATR spectrum due to inadequate contact between crystal and sample.
- Complete absorbance (spectrum bottoms out) due to sample concentration (too concentrated) or pellet thickness (too thick).
- Strongly absorbing crystals or mulls used in sample preparation may interfere with regions of the resultant sample spectrum.
- Improper peak height ratios due to failure to perform ATR spectrum correction when necessary.

VI. Quality Assurance

Through regular calibration checks, use of known standards, and upkeep of instrument logbooks, the quality of the FTIR method is assured.

Glossary

Absorbance (A): The logarithm to the base 10 of the reciprocal of the transmittance (T). $A = \log_{10}(I/T) = -\log_{10}(T)$

Absorption Spectrum: a plot, or other representation, of absorbance, or any function of absorbance, against wavelength, or any function of wavelength.

Attenuated Total Reflectance (ATR): reflection that occurs when an absorbing coupling mechanism acts in the process of total internal reflection to make the reflectance less than unity.

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

DTGS: Deuterated Triglycine Sulfate – refers to type of detector used on the FTIR bench and TravelIR.

Far-Infrared: pertaining to the infrared region of the electromagnetic spectrum with wavelength range from approximately 400 to 10 cm^{-1}.

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

Fourier Transform Infrared (FT-IR) 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.

Infrared: Pertaining to the region of the electromagnetic spectrum with wavelength range from approximately 0.78 to 1000 µm (wavenumber range 20,000 to 40,000 cm^{-1}).

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

MCT: Mercury Cadmium Telluride – refers to the type of detector used on the microscope accessory.

Mid-Infrared: pertaining to the infrared region of the electromagnetic spectrum with wavelength range from 4000 to 400 cm^{-1}.

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

Transmittance (T): the ratio of radiant power transmitted by the sample, I, to the radiant power incident on the sample, $I_{0.}$

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}.