



GUIDELINE FOR THE FORENSIC EXAMINATION OF PAINT BY FOURIER-TRANSFORM INFRARED SPECTROSCOPY

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GENERAL REMARK

This guideline assumes prior knowledge in the forensic discipline. It is based on consensus among the relevant forensic experts and reflects the accepted practices at the time of writing. The requirements of the judicial systems are addressed in general terms only.

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1. AIMS

This guideline is intended to provide an understanding of the requirements, benefits and limitations of Fourier-transform infrared spectroscopy available for use by forensic paint examiners.

2. SCOPE

This guideline provides recommendations and basic information about FTIR-spectrometer components and accessories, performance assessment and test routines, sample preparation, spectral recording, data presentation and interpretation. It is intended to provide an understanding of the requirements, benefits, limitations and proper use of IR-spectroscopy and sample preparation techniques available for use by forensic paint examiners. It is used in conjunction to the Best Practice Manual for the Forensic Examination of Paint [1].

3. DEFINITIONS AND TERMS

For the purposes of this guideline, the relevant terms and definitions given in ENFSI documents, in ILAC G19 [2], in ISO/IEC 9000 [3], ISO/IEC 17020 [4] and ISO/IEC 17025 [5] standards, and in ASTM E1610-18 [6] are applied.

Specific technical terms used in this guideline are defined in ASTM E2937-18 [7].

4. BASIC PRINCIPLES

Atoms in molecules are made to vibrate by the supply of energy in the spectral range between 4000 cm^{-1} and 400 cm^{-1} (mid-IR radiation). Depending on the molecular structure (the size of the atoms and the strength of the bonds between them), radiation of characteristic wavelengths is absorbed. By measuring the intensity of absorption within the selected spectral range an IR spectrum is obtained.

Mid-IR spectra of coating materials are generally complex and provide numerous absorption maxima and minima that can be used for the identification, classification and comparison of coating materials by determination of chemical components like binders, fillers, pigments or additives.

5. SAMPLE PREPARATION

Initial inspection, search and recovery of forensic paint evidence are treated in EPG-GDL-001 [8].

Any impurity on the sample surface has to be noted, to be removed and, if forensically significant, to be analysed. These impurities can be removed from the paint either by scraping with a scalpel or washing with a piece of tissue soaked with water or a non-aggressive solvent like ethanol or methanol. Other organic solvents have to be avoided because of possible chemical reaction with or dissolution of the sample.

Sampled areas should be large enough to be representative for the item under analysis. To check for inhomogeneity of the sample, material from different areas should be taken and analysed.

Specific preparation of paint samples for their analysis by FTIR spectroscopy include the preparation of thin sections, the use of diamond compression cell, the pressed-disk method and sample flattening.

Sample preparation techniques should be the same for all samples being compared if possible.

5.1 Preparation of thin sections

This is the method of choice when measuring multilayered samples in relation to the EUCAP databases. It is limited to samples of at least 0,5 mm in size.

The sample is embedded in Technovit 2000 LC resin [9] (or similar embedding medium). This monocomponent resin is hardened by irradiating with blue (300 – 400 nm) light according to the instructions given by the supplier (Technotray). Always close the resin container to avoid polymer degradation by moisture take-up.

Some samples, e.g. some refinishing paints, may react with the embedding resin, often visible as a change in colour of the sample and penetration of the embedding resin in the sample. The embedding technique should not be applied in these circumstances.

The surface of the ensuing blocks is washed with alcohol in order to remove residual non hardened material. Samples are cut with a microtome using a tungsten carbide hardened steel knife to a thickness of 2 – 10 μm . Depending on the orientation of the sample during embedding, either thin cuts perpendicular to the paint surface or cuts parallel to the surface are being obtained.

Thin cuts perpendicular to the surface allow an overview of the layer system and provide easy accumulation of spectra of the individual layers from a single cut. However paint layers of 10 μm thickness or lower are near to the diffraction limit and therefore notoriously difficult to measure in this way. These cuts may also be used and documented with microscopy for illustrative purposes.

Cuts parallel to the surface require several cuts in order to cover the entire paint system and thus measurement is more time consuming. However they provide a larger measurable surface area and spectra of significantly better quality. Because the individual layers are sampled chronologically the inter-layer contamination issue is avoided. These cuts may also be used for MSP or Raman measurements.

Paint chips can also be cut in ice, by fixing the sample between two plastic plates, or without an embedding step.

Cross-sections are usually mounted free in air in order to measure them without interference of a support. In case they are too brittle and tend to shatter, they can be supported by a KBr disk or a diamond window.

5.2 Diamond compression cell

This preparation method is preferred for single layer paint samples (or easily separable layers of paint), and is intended to reduce the sample thickness and thus its absorbance by applying pressure to the sample.

The diamond anvil cell is a micro sampling accessory for use on the stage of an IR microscope or in the focal compartment of an FTIR spectrometer. The diamond windows (type II a quality) are transparent to most of the infrared spectrum except in the region of about 1650 cm^{-1} to 2600 cm^{-1} . Their contribution to the spectrum is minimal when using the appropriate background. If high pressure is exerted, this can alter the sample morphology and possibly its molecular characteristics such as crystallinity and orientation. The windows can be cleaned after use by wiping with a tissue moistened with ethanol.

The paint sample is mounted on one of the diamond windows using a stereo microscope. The second diamond window is then meticulously assembled and pressure is applied by tightening the screws. The sample is now flattened and its thickness reduced.

In case of resilient materials the sample is measured using the complete cell setup. In this way the sample thickness is kept constrained at the risk of generating interference fringes.

Paint sample thickness reduction is generally sufficiently permanent so the cell can be disassembled and the sample measured through only one window. The resulting beam will be more intense and interference fringes are avoided.

5.3 KBr pressed disk method

A portion of the paint layer to be analyzed is isolated and placed in a small mortar. One drop of e.g. dried dichloromethane can be added and the sample gently ground with a clean pestle. Approximately half of the required KBr can be added along with another drop of e.g. dichloromethane and the mixture thoroughly mixed. A pellet is formed from the mixture using a pellet press and following the instructions.

In order to obtain a good spectrum the sample must be ground to a particle size below the shortest wavelength of light – otherwise the spectrum quality will be considerably reduced due to scattering (Christiansen effect).

KBr is hygroscopic and therefore O-H stretching vibrations at 3450 cm^{-1} and O-H bending vibrations at 1650 cm^{-1} can be found in spectra taken from samples prepared as KBr pellets. The KBr and the prepared pellets should be kept in desiccators to minimize these water peaks.

13 mm pellets can be analyzed without a beam condenser, 3 mm pellets have to be measured by using a beam condenser.

5.4 Sample flattening

Samples can be pressed using a scalpel blade or rolled using a suitable tool, and then placed directly on a suitable support. This technique is useful when performing reflection – absorption measurements.

This technique requires special care during spectral acquisition in order to avoid mixed spectra of adjacent layers.

6. ANALYTICAL TECHNIQUES AND OPERATING CONDITIONS

Paint fragments and especially traces and smears are often small and require a beam condensing or focussing device.

Both transmission and reflectance measurements may be used for the analysis of coatings, but transmission methods are preferred. The latter spectra are less prone to distortions due to variations in collection parameters. Most of the reference data of coatings, binders, pigments and additives consist of transmission spectra.

Certain types of coatings, including automotive undercoats and many types of architectural coatings, contain significant amounts of inorganic pigments. These pigments tend to have most of their characteristic infrared absorption in the lower frequency range, and several have all their absorptions in the region below 700 cm^{-1} , e.g. metal oxides and silicates.

6.1 Main bench

It is possible to measure paint fragments using a diamond compression cell mounted in a beam condenser. Using the DTGS detector has the advantage of a lower wavenumber cut-off, thus enhancing the assessment of inorganic constituents.

This procedure however is not capable of discriminating areas of interest on the sample, and likewise it is not possible to visualize the sample as-measured.

6.2 FTIR microscope, transmission measurements

Infrared microscopes act as a beam condenser permitting the selection and documentation of the area of interest on a sample. It is possible to analyse very small samples (less than 1 mm) quickly, reproducibly and with a high degree of sensitivity.

The sample is presented either as a thin section mounted on a sample holder in a free-standing way, supported on a salt window, or as a fragment flattened on a diamond window.

Transmission measurements on free-standing thin sections is the standard method of obtaining the EUCAP database spectra and provides the optimal data to compare with these libraries.

The use of a microscope enables the selection of the area of analysis by using field apertures for selective sample illumination. Pairs of knife edges can be used to closely match the form and size of a paint layer of the fragment or thin section. Redundant aperturing ensures that the generation of stray light is minimized. Nevertheless all spectra of individual layers should be examined to determine if absorptions of adjacent layers are contributing to the spectrum.

The detector measurement aperture width should be adjusted to just slightly less than the width of the paint sample, but preferably not less than $10\text{ }\mu\text{m}$. The aperture length may vary with sample geometry, but should be large enough to allow the detector to be saturated when acquiring a background spectrum.

The illumination field aperture should be adjusted so that the image of its edges coincides with those of the detector measurement aperture. The size and position of the apertures should be the same for sample and background data acquisition.

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 pin-hole field aperture).

Objective and condenser should be adjusted for any IR window that lies between the optic and the sample in the beam path, to reduce spherical aberration and to permit more accurate focus.

6.3 FTIR microscope, reflection-absorption measurements

Reflection-absorption spectra are obtained using the reflectance mode of an infrared microscope.

The sample is mounted on a non-absorbing reflective surface, such as polished metal. The incident radiation passes through the sample, reflects off the substrate and passes through the sample a second time, i.e. double-pass transmission. A background spectrum is taken on a clean portion of the reflective surface.

The sample can be presented as a flattened particle or as a thin section stretched out using alcohol and tweezers.

Reflection-absorption (double transmittance) is carried out at near normal incidence (16 degrees) where it is very efficient (80%). It is a transmission type measurement, collected in a reflection mode, and so spectral distortions are few. However, for highly reflective samples, specular reflections from the sample surface may distort the strong bands in the absorption spectrum (Kramers-Kronig conversion should not be applied to spectra obtained by reflection-absorption, because it is only applicable to true specular reflectance spectra).

The use of the detector measurement aperture is similar to transmission measurements.

Because of the high sensitivity of this method, the sample should be sufficiently flattened to avoid saturation of the spectrum.

6.4 Attenuated total reflection (ATR)

Attenuated total reflectance (ATR) spectroscopy produces a spectrum by reflecting infrared radiation internally through a high refractive index crystal (Ge, KRS-5, diamond or ZnSe) and measuring that portion of the radiation absorbed by the area of a sample that is pressed against the crystal. It is a surface analysis technique yielding wavenumber dependent penetration depths up to a few μm . It is therefore used to measure coatings smears or trace material that cannot be separated from its support.

For good results it is very important that the sample is in intimate contact with the crystal.

Suitable crystals include:

Crystal	R.I.	Range	
KRS-5 (ThBr-ThI)	2.37	4000 – 400 cm^{-1}	Toxic, soft, easily damaged
ZnSe	2.4	4000 – 650 cm^{-1}	Toxic, brittle, susceptible to acids and bases
Ge	4.0	4000 – 700 cm^{-1}	Inert, brittle
diamond	2.4	4000 – 400 cm^{-1}	Inert, bands in range 1650 – 2600 cm^{-1}

As a control, the substrate itself (assuming it is not a metal) should also be analyzed to verify that its absorptions are not contributing to the spectrum of the smear. Any contribution from the substrate should be ignored.

ATR spectra are to be used with care as they present some important differences to transmission spectra. Band shifts to the higher wavelengths of up to 10 – 15 cm^{-1} are

observed. Bands at lower frequency are more intense compared to transmission spectra. There is enhancement in the fingerprint region and hence minor spectral differences may be more readily distinguished.

ATR may be used for comparison casework and for identification, but only if other methods fail. ATR spectra can be compared to ATR spectra but not to transmission libraries such as EUCAP.

6.5 Operating conditions

Equipment shall be handled and used according to the manufacturer's recommendations. Moisture shall be kept at a minimum by efficient desiccant cartridges and/or purging with dry, dust and oil free air or nitrogen. The air (nitrogen) pressure has to be adapted to the system in order to avoid vibrations of spectrometer components.

The spectrometer and the microscope must have reached overall stability, especially thermal stability and thermal equilibrium, before starting any operational runs. This may take up to 2 hours after switch-on depending on the thermal mass of the instrument and the laboratory conditions. Continuous operation is better for performance, stability and longer life time of the IR-source. It is recommended to leave the system in the stand-by mode for 24 hours a day.

Liquid nitrogen cooled detectors should be allowed to equilibrate for approximately 20 minutes after the addition of liquid nitrogen.

FTIR spectra of coatings materials are collected at a resolution of 4 cm⁻¹.

The standard spectral range used is:

- 4000 – 400 cm⁻¹ with a DTGS detector (main bench);
- 4000 – 600 cm⁻¹ with a middle-band MCT detector, liquid nitrogen cooled;
- 4000 – 450 cm⁻¹ with a broad-band MCT detector, liquid nitrogen cooled;
- 4000 – 670 cm⁻¹ with a thermoelectrically cooled MCT detector;
- 4000 – 900 cm⁻¹ with a FPA detector.

It is strongly recommended to use detection down to 650 cm⁻¹ or lower where characteristic bands of inorganic constituents may be present.

Samples are preferentially measured using a microscope in transmission mode, using 15x objective/condensor (or higher magnification). Measuring the samples without support yields spectra of better quality, although the use of salt or diamond windows is possible if required.

It is recommended to use automatically optimized gain settings.

The Blackman-Harris apodization algorithm is recommended [11].

Multi-layered coating samples that are intended for inclusion in the EUCAP databases are prepared as thin sections and measured using a microscope in transmission mode.

ATR measurements can be used when transmission measurements are not possible. They should only be compared to other ATR spectra or ATR databases and not to transmission measurements.

6.6 Background measurement

FTIR is a single beam technique and therefore a background measurement is needed to eliminate absorbance contributions of all system components, environment and sample holder. It consists of a reference absorption spectrum measured without sample and may be taken before or after the sample spectrum.

The system parameters for background spectra should be identical to the parameters used for sample spectra (with the possible exception of gain). These parameters include any automatic instrument control, pre-set frequency limits for spectra, wave number range, resolution, number of scans, and spectrometer aperture size.

If one background is used for more than one sample, the spectral baseline has to be checked carefully. The installation of new equipment, changing water or carbon dioxide concentrations in the air or baseline alterations (in shape, offset) will require a new measurement of the background.

Interference fringes in spectra for the diamond cell technique can be avoided if the background measurement is done with KBr between the two halves of the diamond cell.

7. **QUALITY CONSIDERATIONS**

In order to ensure good quality spectra, the functioning of equipment and the quality of the spectra have to be assessed.

7.1 Instrument performance tests

Depending on the frequency of use, quality assurance tests have to be made at least once per month. In continuous operation, a daily performance check should be made.

ASTM E1421-99 [9] describes how to measure the performance of Fourier Transform mid-IR spectrometers. Most equipment manufacturers offer automatic sequences incorporating these tests.

The following tests as described in ASTM E1421-99 [10] are recommended:

- Signal-to-noise ratio;
- 100% line;
- Interferogram amplitude;
- Energy test;
- Wavenumber calibration;
- Transmission reproducibility.

7.2 Spectral quality criteria

7.2.1 Transmission range

The optimal transmission (absorbance) range is 100% to 10% (0 – 1 AU).

Values in excess to 100% (negative absorbance) do not make spectroscopic sense and may be caused by an incorrectly acquired background spectrum.

Scattered and reflected radiation may cause a baseline shift to lower transmittance (higher absorbance). If the baseline is lower than 80%T (higher than 0.1 AU) the reasons for this displacement should be considered.

If the transmission is lower than 10% T (higher than 1 AU) the corresponding peaks may not be properly resolved. This would require a new preparation with less sample thickness.

7.2.2 Water and carbon dioxide

Water bands at 1650 cm^{-1} and above 3000 cm^{-1} should be minimal, otherwise interference with peaks of inorganic or organic compounds may occur. Minimize carbon dioxide to avoid bands at 668 cm^{-1} and between 2380 and 2300 cm^{-1} .

7.2.3 Signal-to-noise ratio

The signal-to-noise ratio criterion is set during validation of the method. Some samples such as highly filled metallic basecoats may not reach this criterion due to excessive scattering.

7.2.4 Interference fringes

Interference fringes are not allowed in order to avoid misinterpretation. They can be avoided by slightly tilting the sample during measurement.

8. CLASSIFICATION, COMPARISON, INTERPRETATION

Paint samples are often inhomogeneous at the microscopic level. It is therefore highly recommended to measure samples at several spots in order to assess the reproducibility of the spectral features.

These features can be exploited on different levels depending on the purposes of the analysis and the depth of detail required.

8.1 Identification of component classes

The absorption bands present in the spectrum may be evaluated with respect to band position, band shape and band intensity. They represent characteristic vibrations of functional groups, and their combination allows patterns to be assigned to classes of compounds.

All paint constituents contribute their characteristic pattern to the spectrum depending on their absorptivity and their concentration. This provides for complex spectra with strong overlapping, precluding quantitative exploitation in most cases.

Classification of binder, pigment and filler types is obtained by comparison to functional group charts and spectra of known materials.

Vigilance is required in order to accommodate sample inhomogeneity (especially with respect to pigment and filler distribution), artefacts and contaminations (from the support, the embedding resin or the glue of adhesive tape).

High filler content may result in difficulties for identifying other constituents. This is particularly the case with calcium carbonate where a treatment with 10 % HCl may dissolve the filler and help in detecting other constituents.

The classification may assist in determining the significance and end use of a coating.

8.2 Comparison between samples

Spectra to be compared shall be manipulated as little as possible. Raw data shall always be secured and the manipulations shall be temporarily. We recommend to limit manipulations to flatlining the CO₂ absorptions, to correct baseline slope and to normalize the spectra, when needed.

The comparison is made by superimposing the spectra in either transmission or absorbance mode. We recommend the following match criteria:

Presence of bands	:	All bands of the reference spectrum are present in the questioned spectrum.
Positions	:	Band positions correspond within $\pm 8 \text{ cm}^{-1}$.
Relative intensities	:	Pattern shape and relative intensity is similar, taking into account variability of especially pigment and filler signals in the reference spectrum.

Differences due to sample inhomogeneity, artefacts and contaminations shall not be considered significant.

Spectra are considered indistinguishable if they do not exhibit significant differences.

Spectra are considered dissimilar if they contain one or more significant differences.

If it is impossible to decide whether a difference is significant, the comparison is inconclusive.

8.3 Comparison of a spectrum to databases

The European Paint and Glass Expert Working Group provides a number of databases on its website that can be exploited using the KnowItAll software (Wiley, version 2015 or more recent) [12]. These databases contain various coating samples acquired by European laboratories and can be used to characterize the questioned sample.

The software enables the simultaneous search of the FTIR spectrum and of additional properties stored with the spectrum i.e. colour, use, make, etc.

Correction of the questioned spectrum must be temporary. Allowable corrections include flatlining CO₂ absorption bands (2390 – 2285 and 672 – 664 cm⁻¹), correcting a sloping baseline, and a range of optimized corrections [12].

The search classifies the database spectra according to a hit quality index (0 – 100) calculated using a choice of algorithms. It is advised to use both the ‘Correlation’ and the ‘1st Derivative Euclidian’ algorithms as they often give complementary results.

It is often advantageous to limit the search to those wavenumber ranges that contain information, i.e. excluding regions of background noise.

The reference samples do not necessarily originate from the same batch as the questioned sample. More variation on the relative intensities can therefore be expected. The match criterion on relative intensities in these conditions would become: within a pattern the highest band remains the highest.

8.4 Comparison of an automotive sample to EUCAP databases

IR spectra of automotive paint samples can be compared to the European Collection of Automotive Paint (EUCAP) databases using the KnowItAll software (Wiley, version 2015 or more recent), with the aim of identifying its make or obtaining statistical data on its rarity.

In addition to the comparison described in 8.3, a simultaneous search of the constituent layers of a paint sample can be executed, each layer in its corresponding databases. Additional properties, such as colour, car make, production dates etc., can also be included in this simultaneous search.

9. REFERENCES

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10. AMENDMENTS TO PREVIOUS VERSION

Not applicable

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