Standard Guide for
Using Infrared Spectroscopy in Forensic Paint Examinations[1]

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INTRODUCTION

Infrared (IR) spectroscopy is commonly used by forensic laboratories for the analysis of paints and coatings received in the form of small chips, residues, particles, or smears, and serves as a staple comparative technique in the assessment of whether or not questioned paint could have come from a particular source. IR spectroscopy provides molecular structure information on many of the organic and inorganic constituents contained within a single paint layer. This information can be used to classify both binders and pigments in coating materials. The classification information may then be utilized to identify probable types of paint such as architectural, automotive, or maintenance. Additionally, the use of automotive paint databases may allow the determination of information such as potential vehicle year, make and model. Databases may also aid in the interpretation of the significance (for example, how limited is the group of potential donor sources) of a questioned paint.

1. Scope

1.1 This guide applies to the forensic IR analysis of paints and coatings and is intended to supplement information presented in the Forensic Paint Analysis and Comparison Guidelines (**1**)[2] written by Scientific Working Group on Materials Analysis (SWGMAT). This guideline is limited to the discussion of Fourier Transform Infrared (FTIR) instruments and provides information on FTIR instrument setup, performance assessment, sample preparation, analysis and data interpretation. It is intended to provide an understanding of the requirements, benefits, limitations and proper use of IR accessories and sampling methods available for use by forensic paint examiners. The following accessory techniques will be discussed: FTIR microspectroscopy (transmission and reflectance), diamond cell and attenuated total reflectance. The particular methods employed by each examiner or laboratory, or both, are dependent upon available equipment, examiner training, specimen size or suitability, and purpose of examination. This guideline does not cover the theoretical aspects of many of the topics presented. These can be found in texts such as *An Infrared Spectroscopy Atlas for the Coatings Industry* (Federation of Societies for Coatings, 1991) (**2**) and *Fourier Transform Infrared Spectrometry* (Griffiths and de Haseth, 1986) (**3**).

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[3]

D16 Terminology for Paint, Related Coatings, Materials, and Applications
E131 Terminology Relating to Molecular Spectroscopy
E1421 Practice for Describing and Measuring Performance of Fourier Transform Mid-Infrared (FT-MIR) Spectrometers: Level Zero and Level One Tests
E1492 Practice for Receiving, Documenting, Storing, and Retrieving Evidence in a Forensic Science Laboratory

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[2] The boldface numbers in parentheses refer to the list of references at the end of this standard.

[3] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

E1610 Guide for Forensic Paint Analysis and Comparison

3. Terminology

3.1 *Definitions*—For definitions of terms used in this guide other than those listed here, see Terminologies D16 and E131.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *100 % line*—calculated by ratioing two background spectra taken under identical conditions; the slope and noise of 100 % lines are used to measure the performance of the instrument.

3.2.2 *absorbance (A)*—the logarithm to the base 10 of the reciprocal of transmittance T, written as $A = \log 10\ (1/T) = -\log^{10} T$.

3.2.3 *absorbance spectrum*—a representation of the infrared spectrum in which the ordinate is defined in absorbance units (A); absorbance is linearly proportional to concentration and is therefore used in quantitative analysis.

3.2.4 *additive (modifier)*—any substance added in a small quantity to improve properties; additives may include substances such as driers, corrosion inhibitors, catalysts, ultraviolet absorbers, and plasticizers.

3.2.5 *attenuated total reflectance (ATR)*—a method of spectrophotometric analysis based on the reflection of energy at the interface of two media that have different refractive indices and are in intimate contact with each other.

3.2.6 *aperture*—an opening in an optical system that controls the amount of light passing through a system.

3.2.7 *background*—the signal produced by the entire analytical system apart from the material of interest.

3.2.8 *beam condenser*—a series of mirrors that focus the infrared beam in the sample compartment to permit the examination of smaller specimens.

3.2.9 *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.

3.2.10 *binder*—a nonvolatile portion of the liquid vehicle of a coating, which serves to bind or cement the pigment particles together.

3.2.11 *coating*—a generic term for paint, lacquer, enamel, or other liquid or liquefiable material that is converted to a solid, protective, or decorative film or a combination of these types of films after application.

3.2.12 *deuterated triglycine sulfate (DTGS) detector*—a thermal detector that operates at room temperature but lacks the sensitivity for use with microscope accessories.

3.2.13 *extraneous material (contaminant, foreign material)*—material originating from a source other than the specimen.

3.2.14 *interferogram*—a plot of the detector output as a function of retardation.

3.2.15 *microtomy*—a sample preparation method that sequentially passes a blade at a shallow depth through a specimen, resulting in sections of selected thickness.

3.2.16 *mercury cadmium telluride (MCT) detector*—a quantum detector that utilizes a semi-conducting material and requires cooling with liquid nitrogen to be operated; this type of detector is commonly used in microscope accessories due to its sensitivity.

3.2.17 *paint*—a pigmented coating.

3.2.18 *pigment*—a finely ground, inorganic or organic, insoluble, and dispersed particle; besides color, a pigment may provide many of the essential properties of paint such as opacity, hardness, durability, and corrosion resistance; the term pigment includes extenders.

3.2.19 *representative sample*—a portion of the specimen selected and prepared for analysis that exhibits all of the characteristics of the parent specimen.

3.2.20 *significant difference*—a difference between two samples that indicates that they do not share a common origin.

3.2.21 *smear*—a transfer of paint resulting from contact between two objects; these transfers may consist of co-mingled particles from two or more sources, fragments, or contributions from a single source.

3.2.22 *specimen*—a material submitted for examination; samples are removed from a specimen for analysis.

3.2.23 *transmittance (T)*—the ratio of the energy of the radiation transmitted by the sample to the background, usually expressed as a percentage.

3.2.24 *transmittance spectrum*—a representation of the infrared spectrum in which the ordinate is defined in %T; transmittance is not linearly proportional to concentration.

3.2.25 *wavelength*—the distance, measured along the line of propagation, between two points that are in phase on adjacent waves.

3.2.26 *wavenumber*—the inverse of the wavelength; or, the number of waves per unit length, usually conveyed in reciprocal centimeters (cm^{-1}).

4. Summary of Practice

4.1 The film forming portion of a paint or coating is the organic binder, also referred to as the resin. The binder forms a film that protects as well as displays the organic and inorganic pigments that make a coating both decorative and functional. Infrared spectroscopy is commonly employed for the analysis of paint binders, pigments and other additives that are present in detectable concentrations.

4.2 Paints and coatings absorb infrared radiation at characteristic frequencies that are a function of the coating's composition. These absorption frequencies are determined by vibrations of chemical bonds present in the various components.

4.3 The analysis of coatings using infrared spectroscopy can be carried out using either transmission or reflectance techniques. These measurements can be taken with a variety of equipment configurations and sampling accessories, the most common being the use of an infrared microscope. A variety of accessories can also be utilized in the system's main bench.

However, the use of a nonmicroscope accessory typically requires a larger sample size than those that can be analyzed using a microscope.

4.4 For transmission FTIR, a thin-peel of each paint layer, or a thin cross-section of a paint sample is made either by hand with a sharp blade or using a microtome. It is then analyzed using either a microscope attachment or other suitable accessory, such as a diamond anvil cell. When thin samples suitable for transmission FTIR are not obtainable, reflectance techniques (ATR, reflection) may be employed using microscope objectives or bench accessories.

4.5 *Basic Principles:*

4.5.1 Infrared spectroscopy (mid-range) is capable of utilizing a spectral range between 4000 and approximately 400 cm^{-1}. Extended range instruments are needed to take measurements down to approximately 200 cm^{-1}. The actual spectral cutoff depends upon the type of detector and optics used.

4.5.2 An FTIR spectrometer measures the intensity of reflected or transmitted radiation over a designated range of wavelengths. The spectrum of a sample is produced by ratioing the transmitted or reflected infrared spectrum to a background spectrum.

4.5.3 Transmission spectra may be plotted either in percent transmittance (%T) or in absorbance (A). Reflectance spectra may be plotted either in percent reflectance (%R) or in absorbance (A).

4.6 *Instrumentation:*

4.6.1 An FTIR instrument consists of a source to produce infrared radiation, an interferometer, a detector and a data processing device. A micro-FTIR instrument also has a microscope equipped with a detector and infrared compatible optics.

4.6.2 Most FTIR systems are equipped to collect data using the main bench in the range of 4000 to 400 cm^{-1}. Extended range systems are equipped with a beamsplitter and optics that allow transmission down to approximately 200 cm^{-1}. Systems equipped with an FTIR microscope utilize a more sensitive detector type. Depending on the specific detector type, microscopic samples can be analyzed in the range of approximately 4000 to 450 cm^{-1}.

5. Significance and Use

5.1 FTIR spectroscopy may be employed for the classification of paint binder types and pigments as well as for the comparison of spectra from known and questioned coatings. When utilized for comparison purposes, the goal of the forensic examiner is to determine whether any significant differences exist between the known and questioned samples.

5.2 This guide is designed to assist an examiner in the selection of appropriate sample preparation methods and instrumental parameters for the analysis, comparison or identification of paint binders and pigments.

5.3 It is not the intent of this guide to present comprehensive theories and methods of FTIR spectroscopy. It is necessary that the examiner have an understanding of FTIR and general concepts of specimen preparation prior to using this guide. This information is available from manufacturers' reference materials, training courses, and references such as: *Forensic Applications of Infrared Spectroscopy* (Suzuki, 1993) (**4**), *Infrared Microspectroscopy of Forensic Paint Evidence* (Ryland, 1995) (**5**), *Use of Infrared Spectroscopy for the Characterization of Paint Fragments* (Beveridge, 2001) (**6**), and *An Infrared Spectroscopy Atlas for the Coatings Industry*(**2**).

6. Sample Handling

6.1 The general collection, handling, and tracking of samples shall meet or exceed the requirements of Practice E1492 as well as the relevant portions of the SWGMAT's Trace Evidence Quality Assurance Guidelines (**7**).

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

6.3 As stated in Guide E1610, a paint specimen should first be examined with a stereomicroscope, noting its size, appearance, layer sequence, heterogeneity within any given layer, and presence of any material that could interfere with the analysis (for example, traces of adhesive, surface abrasion transfers, or zinc phosphate conversion coating residue on the underside of the base primer on electro-coated parts). Some surface materials may be of interest and therefore may be worthy of analysis before removal.

6.4 Each layer of a multi-layered paint should be analyzed individually.

6.5 When analyzing difficult items (for example, smears, dirty or heterogeneous specimens) care shall be taken when sampling the paint and in choosing appropriate analytical conditions. An attempt should be made to remove any extraneous material from the exhibit before sampling. It may be necessary to analyze a number of samples to ensure reproducibility and understand inter/intrasample variation.

6.6 Extraneous material should be removed either by scraping with a suitable tool such as a scalpel or washing with water. If needed, alcohols or light aliphatic hydrocarbons can be useful for cleaning. However, it should be noted that the use of organic solvents for cleaning paint can alter the composition by extracting soluble components such as plasticizers or dissolve the paint binder. If solvents are used, known and unknown samples should be treated the same, making sure no residual solvent remains.

6.7 For the accurate comparison of paint evidence, samples should be prepared and analyzed in the same manner.

7. Analytical Techniques and Operating Conditions

7.1 Paints may be analyzed by transmission or reflectance utilizing the microscope accessory or the bench accessories. The technique chosen is dependent upon the physical nature of the paint, the quantity of sample, preparation and analysis time, available equipment, and access to reference libraries for that technique. The same technique should be used on both known and questioned samples. It may be necessary to use multiple preparation or analytical techniques, or both, in order to analyze all layers and characteristics.

7.2 The type of detector and beam splitter dictates the spectral range of the FTIR spectrometer. Mid-range infrared instruments use alkali halide beam splitters that are made from either cesium iodide (CsI) or potassium bromide (KBr).

7.3 The most common infrared detector used on the main bench is a deuterated triglycine sulfate (DTGS) detector. The DTGS detector operates at room temperature. A spectrometer equipped with a DTGS detector and CsI optics has an approximate spectral range of 4000 to 200 cm^{-1}. With KBr optics and a DTGS detector, the spectral range of the spectrometer is approximately 4000 to 400 cm^{-1}.

7.4 The detector commonly used with the microscope accessory is a mercury-cadmium-telluride (MCT) detector. The MCT detector is approximately 40× more sensitive than the DTGS detector, but has a narrower spectral range with a lower limit of 700 to 450 cm^{-1}, depending on the type.

7.5 Infrared data are collected from both the sample and a previously stored or newly acquired background. Taking the ratio of the sample spectrum to the background enables removal of absorptions from the cell or support material (for example, diamond absorptions) or from the atmosphere (for example, carbon dioxide and water vapor), or both. The latter absorptions can be minimized by purging with dried and filtered air desiccant packs or nitrogen gas. The number of scans acquired for each specimen can vary depending on sample type and size.

7.6 *Main Bench Transmission Techniques:*

7.6.1 The most common bench transmission technique for the analysis of paint is the use of the diamond cell with a beam condenser.

7.6.1.1 Either prior to or after analysis, a background spectrum of the empty diamond cell is collected. The same background spectrum may be used for multiple samples or a new one may be collected for each sample analysis.

7.6.1.2 A sample from a single paint layer is placed on the clean diamond anvil cell and compressed between the windows to a desired thickness. Both high-pressure and low-pressure diamond cells can be used in conjunction with a beam condenser. Sample compression is normally done under a stereomicroscope to ensure uniform coverage. The cell is then placed in the sample holder in the main bench of the instrument. The instrument is allowed to equilibrate. This process is dependent upon the type of instrument and efficiency of the purge. A spectrum is then collected with the sample in place. Typically 16 to 256 scans are collected with a resolution of 4 cm^{-1}. These parameters may vary depending on the instrument and size and nature of the sample. The same instrumental parameters, including the number of scans, should be acquired for the background as for the sample.

7.6.1.3 Diamond absorbs infrared radiation in the 2300 to 1900 cm^{-1} region; therefore, sample absorptions in this region may be obscured if the diamond path length is too long.

7.7 *Attenuated Total Reflectance (Main Bench):*

7.7.1 A number of in-bench single reflection ATR accessories are available. The general principles of operation are the same for each accessory. The sample of interest is placed in direct contact with the internal reflecting crystal, such as diamond or KRS-5. Some accessories employ a viewing microscope to facilitate proper placement of the sample or area of interest.

7.7.2 In contrast to transmission methods, ATR methods require little or no sample preparation, although the pressure applied when using the ATR accessory may deform the sample.

7.7.3 Once in contact with the crystal, multiple scans are collected. The material is then removed and the crystal is cleaned. Background scans are collected with the item removed, either before or after the sample scans. Typically 16 to 256 scans are collected at a resolution of 4 cm^{-1}. These parameters may vary depending on the instrument and size and nature of the sample.

7.8 *FTIR Microscope Accessory:*

7.8.1 In forensic science, infrared microspectroscopy is the most commonly used method for acquiring the infrared spectrum of a paint. Spectra can be obtained from samples as small as 10 to 20 µm in diameter, using transmittance, reflectance and ATR methods. MCT detectors are commonly used with microscopes due to the higher sensitivity needed for small samples. They are available in configurations usually designated as narrow band and broad (wide) band with the lower energy cut-off ranging from approximately 700 to 450 cm^{-1}. There is a compromise between sensitivity and spectral range with these detectors. A detector with the spectral range of 4000 to 650 cm^{-1} is typically used for paint examination since it offers the optimal balance between spectral range and sensitivity. These detectors shall be cooled by liquid nitrogen before use. When using the lower sensitivity/broader spectral range detector, larger samples are required.

7.8.2 *Transmission Measurements:*

7.8.2.1 Transmission methods generally require more extensive sample preparation. The sample shall be thin enough not to over-absorb. For transmission data viewed in % transmittance, spectral peaks optimally should not fall below 10 % T. For spectra displayed in absorbance, the maximum absorbance optimally should be 1.0 or less.

7.8.2.2 A prepared and mounted sample is placed on the microscope stage and focused. The condenser on some instruments may have to be adjusted to account for the thickness of a support window. The sample is observed with visible light and the area to be analyzed is centered in the field of view. The area of interest is isolated from the remainder of the field of view with one or two apertures.

7.8.2.3 The number of apertures corresponds to the instrument configuration. The apertures control the area and location of the infrared beam striking the sample and the transmitted light reaching the detector.

7.8.2.4 Apertures also block unwanted radiation originating outside of the area of interest. If stray light is allowed to reach the detector, absorption intensity is reduced.

7.8.2.5 As a sample area of interest becomes smaller, or as the aperture(s) are reduced so that a portion of the sample can be isolated, diffraction effects rapidly increase. These effects can be experienced when using aperture sizes smaller than 25 µm × 25 µm.

7.8.2.6 To minimize the effects of heterogeneity, aperture areas greater than 2500 μm^2 (for example, 50 µm × 50 µm or

25 µm × 100 µm) should be used when possible. Alternatively, multiple areas of the sample can be analyzed to determine the range of spectral characteristics.

7.8.2.7 Once the area of interest is isolated by adjusting the magnification and apertures of the microscope, the infrared spectrum of the sample is collected. Typically 16 to 256 scans are collected at a resolution of 4 cm^{-1} or better.

7.8.2.8 The background spectrum is collected from an unused area of the support window using the same aperture configuration as used for the sample.

7.8.2.9 If sample size is limited, the resulting spectrum may be noisy. To increase the signal to noise ratio (S/N), the number of scans can be increased. It is important to collect spectra with good S/N to permit visualization of fine detail such as small sharp peaks or shoulders in the resultant spectrum.

7.8.3 *Reflection Measurements (Microscope):*

7.8.3.1 The FTIR microscope can also be used in the reflection mode. However, in most cases, transmittance methods are preferred for several reasons. Refractive index changes, and differences in infrared absorption coefficients for different wavelengths, give rise to distortions in reflectance spectra. Reflectance spectra are not absorption spectra and cannot be compared in detail to transmission spectra due to shifts in spectral peak wavelengths and variations in spectral peak intensities (**8**). Also, most of the reference data of coatings, binders, pigments and additives consist of transmission spectra. Furthermore, being surface analysis techniques, inconsistencies in the preparation of surfaces subject to comparative assessments can be problematic for data interpretation. Additionally, when analyzing individual layers in cross section and using the requisite small apertures, signal-to-noise constraints are even greater than those encountered in transmission analyses.

7.8.3.2 If samples are compressed directly on a glass slide made of infrared light reflecting architectural glass (low e-glass), the microscope's reflection mode can be used to produce spectra mimicking double-pass transmission spectra. The technique is sometimes referred to as "transflection" or "reflection/absorption". Some wavelength maxima shifts may be observed in intense absorption bands.

(1) For transflection, the thinned sample is placed on an infrared reflective surface, such as a glass slide made of infrared light reflecting architectural glass (low e-glass), or a gold mirror, and placed on the microscope stage. It is viewed using visible light and the area to be analyzed is centered in the field of view. The area of interest is isolated from the remainder of the field of view with an aperture and the infrared spectrum is collected. Typically, 16 to 256 scans are collected at a resolution of 4 cm^{-1} or better. The background spectrum is collected from an unused area of the reflective support using the same aperture configuration and number of scans as used for the paint sample.

7.8.4 *ATR Objectives for Infrared Microscopes:*

7.8.4.1 ATR microscope objectives may be fitted with a silicon, ZnSe, diamond, KRS-5, or germanium internal reflecting crystal offering a wide variety of penetration depths and crystal physical attributes. The sample is viewed using visible light and the area to be analyzed is centered in the field of view. The crystal is then placed in direct contact with the area of interest. Monitoring the single beam spectrum provides an indication of whether there is sufficient contact between the sample and crystal. Typically 64 to 512 scans are collected at a resolution of 4 cm^{-1} or better and ratioed against an air background. The number of scans collected for each sample can vary with size or type.

8. Sample Preparation Methods and Sampling Accessories

8.1 The method chosen for sample preparation depends on the size, nature, and condition of the specimen, as well as the particular FTIR technique/accessory that is employed for analysis. It may be necessary to use multiple preparation or analytical techniques, or both, in order to analyze all layers and characteristics.

8.2 *Transmission Techniques (Main Bench):*

8.2.1 Samples prepared for analysis by main bench transmission techniques shall be thin enough to allow infrared radiation to pass through without over-absorption. For transmission data that are viewed in absorbance, the sample optimally should be thin enough to produce a maximum absorbance of 1 absorbance unit. For transmission data viewed in % transmittance, spectral peaks ideally should not fall below 10 % T. This typically requires thicknesses of approximately 5 to 10 µms.

8.2.2 The separation and analysis of individual layers is recommended in order to determine chemical composition and detailed spectral characteristics of each layer. This may be achieved by microtomy or by hand using a sharp blade while observing the evidence under a stereomicroscope.

8.2.3 Sample preparation techniques which may be employed for transmission analysis using the main bench include a thin peel stretched over an aperture, an alkali halide pellet (for example, potassium bromide), or a diamond cell.

8.2.4 Thin peels of each layer can be placed on a glass microscope slide and compressed with the flat beveled surface of a scalpel blade, a roller bearing tool, or other equivalent technique, and then placed directly over a small masking aperture for analysis. Given the small sample sizes encountered, a beam condenser is typically employed.

8.2.5 Potassium bromide (KBr) pellets are made by grinding a small aliquot of the individual paint layer with dry spectroscopic grade KBr using a mortar and pestle. The powder is then transferred to a die maker and a press is used to generate the pellet. As KBr is deliquescent, the pellets, KBr powder and die maker should be stored in an oven or desiccator. Given the small sample sizes encountered, one to three millimeter diameter pellets mounted in a beam condenser are typically employed.

8.2.6 The diamond anvil cell is a useful sampling technique when the greatest spectral range is required and for laboratories that do not have a microscope accessory for their infrared spectrometer. It is possible to obtain spectra down to approximately 200 cm^{-1} with cesium iodide (CsI) optics, or down to 400 cm^{-1} with KBr optics. Both high- and low- pressure diamond cells can be used in conjunction with a beam condenser. Pliable and powdered samples are amenable to low-pressure diamond cells, while harder paints may require the use of high-pressure diamond cells. Low pressure diamond cells have the advantages of costing less, are compatible with an infrared microscope accessory and do not obscure spectral information in the 2400 to 1800 cm^{-1} region because they contain thinner diamonds than high pressure cells.

8.2.7 Diamond cells permit relatively simple sample preparation. The cell consists of two diamond windows, a holder for each diamond and a means of compression that achieves an appropriate sample thickness. There are a variety of designs available. The paint is simply placed on one of the diamond faces, the second diamond is positioned on top, and sufficient pressure is applied to form a film. This is normally done under a stereomicroscope to ensure uniform coverage of the diamond face.

8.2.8 For non-elastic paints, one diamond may be removed prior to analysis. This leaves the thin compressed film adhering to one of the diamond faces and avoids diffraction fringes in the recorded spectrum resulting from the two parallel diamond faces.

8.2.9 The diamond cell sampling technique is essentially non-destructive because of diamond's inertness. After analysis, the paint can be recovered uncontaminated from the diamond face using a scalpel blade or other suitable tool.

8.2.10 The chief drawback of this technique is that a larger sample size is required than with a microscope accessory. This can be particularly significant when examining small paint chips that have multiple layers because extraction of sufficient paint from interior layers can represent a significant challenge. Furthermore, each sample shall be placed in the cell and removed prior to mounting the next sample, unlike the microscope method where multiple samples may be placed on the support material and analyzed sequentially.

8.3 *Internal Reflection Techniques (Main Bench):*

8.3.1 Attenuated Total Reflectance (ATR) spectroscopy may be used to analyze exposed paint layers. Although ATR spectroscopy accessories are available in both multi-reflection (macro scale) and single reflection (micro scale), only single reflection accessories will be discussed because they are more suitable for forensic paint examination. In contrast to transmission methods, ATR methods require virtually no sample preparation when examining an already exposed surface. In some instances ATR methods may lend themselves to conducting the examination *in situ*. Since ATR is a surface technique it is necessary to remove any extraneous material from the area to be examined.

8.3.2 The bench ATR (single reflection) accessory utilizes an internal reflection crystal to condense the beam onto a spot-sized sampling area. The crystal is mounted horizontally in a purged box within the sample compartment. The sample is placed in contact with the center of the crystal, and an adjustable piston is used to apply sufficient pressure to ensure contact. Mirrors focus the beam such that the infrared light reflected by the sample is directed to the detector.

8.3.3 ATR techniques are subject to inter-sample variations resulting from variations in pressure on the sample surfaces and variations in surface contact areas. Being reflectance techniques, they are also prone to the same type of spectral distortions noted for reflection spectroscopy.

8.4 *FTIR Microscope Accessory:*

8.4.1 The use of a microscope accessory is preferred for very small samples and has several advantages over bench techniques. Spectra can be obtained from flattened paints as small as 10 to 20 µm in diameter. The microscope attachment permits the sequential analysis of multiple samples placed on an appropriate support material. The method also affords the advantage of optical viewing and choosing specific regions of interest in either heterogeneous samples or those having varying thickness.

8.4.2 Although it is a popular IR accessory for paint analysis, the microscope attachment has some disadvantages. Unlike DTGS detectors, the MCT detectors used in microscope accessories require cooling with liquid nitrogen to minimize electronic noise. There is a compromise to be considered between sensitivity and spectral range with these detectors. Narrow band detectors that cut off in the 700 cm^{-1} range are more sensitive than the broad band detectors that cutoff in the 450 cm^{-1} range. Care shall be taken with very small samples as the use of small measurement apertures can limit the energy from the longer wavelengths (smaller wavenumbers) from reaching the detector. Heterogeneity issues are also more pronounced when using very small apertures.

8.4.3 The chief drawback of this technique is its limited spectral range. Microscope optics and detectors have a cutoff of approximately 450 cm^{-1} as contrasted to the diamond anvil cell/beam condenser method with extended range optics affording a lower cutoff of approximately 200 cm^{-1}. The lower range can be advantageous in the classification and comparison of inorganic pigments.

8.4.4 *Transmission Measurements (Microscope):*

8.4.4.1 Transmission measurements are commonly used as they generate spectra with fewer artifacts. However, transmission methods generally entail more extensive sample preparation than reflection techniques. The paint shall be thin enough to avoid over-absorption.

8.4.4.2 Analysis of individual layers is required in order to spectrally characterize each layer in a multi-layered paint. For transmission FTIR spectroscopy with a microscope accessory, individual layers of multi-layered paints can be analyzed either as thin peels of each layer or as individual layers in a thin cross section of the intact chip.

8.4.4.3 The paint layers may be separated by hand using a sharp blade while observing the sample under a stereomicroscope. Thin peels of each layer can be placed on a glass microscope slide and compressed with the flat beveled surface of a scalpel blade, a roller bearing tool, or other suitable technique. The sample obtained can then be placed either directly over a small masking aperture or on an appropriate salt plate for analysis; a thickness on the order of 5 µm is desired.

8.4.4.4 When selecting an appropriate infrared support material (for example, salt plate), several factors should be taken into consideration including cost, availability, environmental sensitivity, transparency of the material to infrared radiation, and the durability of the material.

8.4.4.5 The low pressure diamond cell can also be used as a support medium under the FTIR microscope. The paint is simply placed on one of the diamond faces, the second diamond is positioned on top, and sufficient pressure is applied to form a film. This is normally done under a stereomicroscope to ensure uniform coverage. For non-elastic paints, one diamond is typically removed prior to analysis. This leaves the thin compressed film adhering to one of the diamond faces and avoids diffraction fringes in the recorded spectrum resulting from the two parallel diamond faces. The sampling technique is essentially non-destructive because of diamond's inertness. The paint sample can be recovered uncontaminated from the diamond face using a scalpel blade or other appropriate tool.

8.4.4.6 The microscope attachment also affords FTIR analysis of multi-layered paints without physical separation of the layers. A thin cross section with intact layer structure can be cut by hand using a sharp blade or with a microtome (thicknesses on the order of 5 µm are typical). The cross sectioned sample is either flattened on a microscope slide and placed on a support material or flattened directly on the support material. If the sample is used for analysis by another technique (for example, elemental analysis), contributions from the support material may be detected. Individual layers may then be analyzed after observing with visible light and centering the sample in the field of view, delineating areas of interest using the microscope's aperture controls. Care shall be taken to avoid contributions from adjoining layers.

8.4.4.7 Cross section analysis has the advantage of viewing the sample optically and then selecting the specific region for analysis, thus permitting rapid analyses of individual layers. It also permits analyses of specific regions of inhomogeneous materials and compositional mapping. However, it typically requires smaller target apertures which can result in diffraction effects, heterogeneity concerns, and signal to noise constraints.

8.4.5 *Reflection Measurements (Microscope):*

8.4.5.1 If samples are compressed directly on a glass slide made of infrared light reflecting architectural glass (low e-glass), the microscope's reflection mode can be used to produce spectra mimicking double-pass transmission spectra. The technique is sometimes referred to as "transflection" or "reflection/absorption". Some wavelength maxima shifts may be observed in intense absorption bands. Transflection samples need to be approximately half the thickness of that which is optimal for transmission measurements.

8.4.5.2 The FTIR microscope can also be used in the reflection mode, but in most cases, transmittance methods are preferred for several reasons. Refractive index changes, and differences in infrared absorption coefficients for different wavelengths, give rise to distortions in reflectance spectra. Reflectance spectra are not absorption spectra and cannot be compared in detail to transmission spectra due to shifts in spectral peak wavelengths and variations in spectral peak intensities (**8**). Also, most of the reference data of coatings, binders, pigments and additives consist of transmission spectra. Furthermore, being surface analysis techniques, inconsistencies in the preparation of sample surfaces can present problems in detailed comparisons. Additionally, when analyzing individual layers in cross section and using the requisite small apertures, signal-to-noise constraints are even greater than those encountered in transmission analyses.

8.4.6 *Internal Reflection Techniques (ATR Microscope Objective):*

8.4.6.1 ATR objectives are available for infrared microscope accessories. The technique requires little or no sample preparation and is non-destructive.

8.4.6.2 An ATR microscope objective may be used to analyze exposed paint layers. In some instances ATR methods may lend themselves to conducting the examination in situ. Since ATR is a surface technique it may be desirable to analyze any existing surface material of interest and then remove the surface material from the area and reanalyze the area.

8.4.6.3 The analysis of thin surface smears may result in contributions from substrate material or underlying layers. If the substrate material does not transmit infrared radiation, such as metal or glass, the ATR spectra appear more like transmission spectra the thinner the sample becomes. Hence, ATR spectra of thin samples (on the order of 1 to 2 microns) should not be directly compared to ATR spectra of thicker ones.

8.4.6.4 ATR is subject to inter-sample variations resulting from variations in pressure on the sample surface and variations in surface contact areas. Also, intra-sample variations may result from sample heterogeneity. Being a reflectance technique, it is somewhat prone to the same type of spectral distortions noted for reflection spectroscopy (**9**, **10**).

9. Performance Checks

9.1 The instrument shall be checked to ensure it is operating properly. Results of the check shall be documented. Before any performance checks, the instrument shall be thermally stable. It is recommended that the system be left on, or in a stand-by mode, as continuous operation is better for performance, stability, and prolonging the lifetime of the IR-source. For detectors that require liquid nitrogen, the detector takes approximately twenty minutes to cool and stabilize.

9.2 Performance checks should be conducted at least once a month (or before use if used less frequently) depending upon how often the instrument is used, or the laboratory's protocol. It is recommended that the built-in instrument test from the manufacturer be used for the performance checks, if available. Instrument performance tests should include evaluation of conditions such as wavenumber accuracy, signal-to-noise ratio, signal strength, and 100 % line. Performance tests recommended by the manufacturer or those outlined in Practice E1421 may also be utilized. A performance check should also be used for FTIR accessories.

10. Classification, Comparison, and Interpretation

10.1 Binder classification of commonly encountered coatings is based on the interpretation of characteristic infrared absorption bands. Similarly, some pigments and additives may be identified.

10.2 Classification of a coating may be achieved by evaluating the absorption bands present in the spectrum with respect to band position, band shape and band intensity. After evaluating the absorption bands, interpretation and classification of a spectrum may be accomplished through comparison of the collected data to spectra of reference materials, use of flow charts and published findings. Spectral libraries of known materials may also be used to characterize the binder, additives, or pigments, or a combination thereof, present in the paint.

10.2.1 There are many sources of flow charts and functional group frequency charts. Flow charts are easy to use and offer an examiner a place to start in classifying paints. However, classification should not be solely based on comparison to flow charts. The spectrum should be compared to representative reference spectra before a classification is made. Moreover, new formulations may not be represented in existing paint classification systems.

10.3 Binder classification may be hindered by the presence of certain pigments. If the paint binder is soluble, a micro extraction may be performed to isolate the binder for analysis. If the paint is not soluble, then an alternative analytical technique, such as pyrolysis-gas chromatography, may be utilized to elucidate the classification of the binder.

10.4 Binder classification may be difficult in contaminated paints and smears. Contributions from substrate or other co-mingled materials shall be considered. Particle picking may be utilized to obtain spectra which are suitable for interpretation. Spectral subtraction may also be utilized to assess the presence of co-mingled materials.

10.5 Classification of the binder type, pigments, or additives, or a combination thereof, may assist in determining the significance and end use of the coating. The classification of the binder may differ from the manufacturer's designation, however, due to changes in polymer chemistry or component migration that occur during curing. Also, trade names given to the coating by the manufacturer may not reflect the actual chemistry of the paint. This conflict in designation results from the use of marketing trade names and historical designations that are technically inaccurate or incomplete.

10.6 Comparison of known and questioned evidence may be conducted with both spectra displayed in transmittance or absorbance, or both, although certain information may be seen more readily in one format or the other.

10.6.1 There are a number of significant factors to consider when assessing whether or not spectra can be distinguished from one another: the presence or absence of absorption bands, their positions, shapes, and relative intensities.

10.6.1.1 Characteristic absorption bands present in one spectrum should be present in the comparison spectrum. The position of the absorption bands should have reasonable agreement with each other and is somewhat dependent on the shape of the absorption band. A rule of thumb is that the positions of corresponding peaks in two or more spectra be within ± 5 cm^{-1}. For sharp absorption peaks one should use tighter constraints. One should critically scrutinize the spectra being compared if corresponding peaks vary by more than 5 cm^{-1}. Replicate collected spectra may be necessary to determine reproducibility of absorption position.

10.6.1.2 The absorption bands should have comparable relative intensities and shapes for the spectra being compared. If there is variation between spectra it may be necessary to acquire additional spectra to determine if the variation is reproducible.

(1) If there are notable differences among spectra of a single sample, the collection of additional spectra may be necessary to assess the range of variation.

(2) If differences are noted between questioned and known items, the collection of additional spectra may be necessary to demonstrate whether the differences are repeatable and therefore significant.

10.7 One of three conclusions can be reached after evaluating and comparing the known and questioned spectra.

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

10.7.2 Spectra are indistinguishable if they contain no significant differences.

10.7.3 A spectral comparison is inconclusive if sample size or condition precludes a decision as to whether differences are significant.

11. Spectral Libraries

11.1 Several infrared spectral libraries and databases relating to paint are available. The Federation of Societies for Coatings Technology offers a library in both printed and digital formats. It is a compilation of the infrared spectra of the various chemical compounds commonly found in coatings. Other libraries relating to polymers, pigments, and additives found in coatings are marketed by various companies. The ability to search the library of spectra and compare them to the spectrum of a specific paint layer may assist in the identification of the chemical components in that layer.

12. Paint Data Query Database (PDQ)

12.1 For forensic purposes, one of the most comprehensive compilations of OEM (original equipment manufacture) automotive paint information is the Paint Data Query (PDQ) database. PDQ is used to aid in the identification of make, model, and year of an unknown vehicle, to assess the relative significance of a paint system when conducting a paint comparison, and to stay current with automotive paint trends. PDQ consists of a text-based database and spectral libraries. It was created in the early 1970s and is maintained by the Royal Canadian Mounted Police Forensic Laboratory Services. **This database is only available to law enforcement agencies through contractual agreement.**

12.1.1 The PDQ text-based database consists of two parts; the source-based information and the paint layer information. The source-based information includes topics such as production plant, make, model, and year for each paint specimen in the database. The paint layer information includes the layer system (number, color, sequence, etc.) and the chemical composition of each layer.

12.1.2 The PDQ spectral libraries include the infrared spectra of individual paint layers.

12.1.3 To aid in the identification of make, model, and year of an unknown vehicle, the data acquired from an evidentiary paint system is coded according to PDQ format and is searched against the text-based portion of the database. The spectral library is also available for searches and comparisons to the data obtained from evidentiary paints to further narrow the range of possible sources.

12.1.4 The database may also serve to assist in assessing the relative significance of a correspondence between a questioned and known OEM paint system. For example, accessing the database provides information as to how many other makes and models of vehicles in the database utilize the same paint system.

12.1.5 The database is also a source of information to keep the forensic paint examiner aware of current trends in OEM automotive coating systems. These include changes in technology such as paint compositions and paint layer structures.

12.2 PDQ is intended to be a source-based database, not a population-based database. In other words, PDQ does not contain information on finish systems of all vehicles in existence. This shall be taken into consideration whenever the database is used.

13. Documentation

13.1 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 item designation, the operator's name or initials, and the date of analysis.

13.2 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.

13.3 See SWGMAT's Trace Evidence Quality Assurance Guidelines (7) for further requirements.

14. Keywords

14.1 analysis; coatings; forensic examinations; infrared spectroscopy; paint

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