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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 can then be used to identify probable types of paint such as architectural, automotive, or maintenance. Additionally, the use of automotive paint databases allow for the determination of information such as potential vehicle year, make and model. Databases can 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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

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

[1] This guide is under the jurisdiction of ASTM Committee E30 on Forensic Sciences and is the direct responsibility of Subcommittee E30.01 on Criminalistics.

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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.

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

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

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

3.2.4 *coating, n*—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.

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

3.2.6 *meaningful difference(s), n*—a feature or property of a sample that does not fall within the variation exhibited by the comparison sample, considering the limitations of the sample or technique, and therefore indicates the two samples do not share a common origin. The use of this term does not imply the formal application of statistics.

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

3.2.8 *paint, n*—a pigmented coating.

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

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

4. Summary of Guide

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 bonds to substrates and can contain 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 reflection techniques. These measurements can be taken with a variety of equipment configurations and accessories, the most common being the use of an infrared microscope. A variety of accessories can also be used in the system's main bench. However, the use of a non-microscope 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, reflection techniques (ATR, internal total reflection) can be employed using microscope objectives or bench accessories.

4.5 *Basic Principles:*

4.5.1 Infrared spectroscopy (mid-range) is the 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 calculating the ratio of the transmitted or reflected infrared spectrum to a background spectrum.

4.5.3 Transmission spectra can be plotted either in percent transmittance (%T), or in absorbance (A). Reflection spectra can be plotted either in percent reflectance (%R) or in –log10 (R) units.

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 use 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 can 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 used for comparison purposes, the goal of the forensic examiner is to determine whether any meaningful 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 using 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 can be of interest and therefore can 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. If possible, analyze a number of areas to ensure reproducibility and understand inter/intrasample compositional 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. Therefore, cleaning with organic solvents should be considered the method of last resort. If solvents are used, known and unknown samples should be treated the same, making sure no residual solvent remains.

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

7. Analytical Techniques and Operating Conditions

7.1 Paints can be analyzed by transmission or reflection methods using the microscope accessory or 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. Use multiple preparation or analytical techniques, or both, as necessary 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 A 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 can be used for multiple samples or a new one can 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 can 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 can be obscured if the diamond path length is too long.

7.7 *Attenuated Total Reflectance (Main Bench):*

7.7.1 Numerous in-bench single reflection ATR accessories are commercially 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 force applied when using the ATR accessory can 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 can 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 commonly used for acquiring the infrared spectrum of a paint. Spectra can be obtained from samples as small as 10 to 20 µm in diameter, using transmission and reflection methods. MCT detectors are commonly used with microscopes due to the higher sensitivity needed for small samples. These detectors 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} and an area of $0.25 \times 0.25\ mm^2$ 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 can 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}.

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 can 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 high 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 can also be used in the reflectance mode. However, most of the reference IR spectral 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.

7.8.4 *Reflection/Transmission (Transflection):*

7.8.4.1 This method is used to analyze thin films of a sample on an infrared reflective surface, such as a glass slide made of infrared light reflecting architectural glass (low e-glass), or metal. The sample 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}. 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.

7.8.5 *ATR:*

7.8.5.1 ATR microscope objectives can be fitted with a silicon, ZnSe, diamond, KRS-5, or germanium internal reflecting crystal element. Different internal reflection elements (IREs) offer a variety of penetration depths and physical or chemical 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.