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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 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

[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.

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.