FORENSIC ANALYSIS

Introduction

Sir Arthur Conan Doyle is believed by many to have first popularized the application of forensic analysis through his newspaper serials originally published in 1887 featuring the fictional character Sherlock Holmes. This work is thought to have inspired many of the early forensic scientists. One of these was Frenchman Edmond Locard, who proposed that when two objects come into contact with one another, a cross-transfer of evidence occurs (1,2). This is the basis of Locard’s Exchange Principle and is the foundation of how we can often use physical evidence to link or at least associate a suspect to a crime scene or a victim. Depending on the nature of the evidence, a wide range of analytical methods are used in forensic casework.

A broad definition of the term forensic, according to Webster’s New World Dictionary, is “suitable for a law court or public debate.” With the application of forensic science, one must demonstrate in court that the evidence analyzed has relevance to the case in question. The significance of evidence related to a case is often determined by whether the physical evidence has individual or class characteristic properties. Individual characteristics are properties of evidence that can be attributed to a common source with an extremely high degree of certainty. Class characteristics are properties of evidence that can only be associated with a group and never with a single source. (3)

Fingerprint and DNA evidence are accepted as having individual characteristics. Fibers or copy toners, however, are identified by their class characteristics, and because of the large production of these materials, they cannot be
individualized. The strength of fiber evidence depends on the likelihood of those type fibers being randomly found on the suspect. Common fibers such as blue or white cotton from jeans or shirts, respectively, have little evidential value. But, blue Nylon 6,6 fibers with an unusual cross section would have more significant value because there are fewer in existence. Forensic scientists have thoroughly developed statistical values for DNA and fingerprint data to demonstrate individual characteristics. Statistics are more difficult to apply to class evidence, but approaches to apply them are being investigated. The information obtained during polymer analysis is usually characteristic of classes of materials, but in some instances the identification of specific components and physical properties demonstrates an uncommon characteristic. If a contaminant found on an evidential material is identified as a rare substance specific to the crime scene, the evidence would demonstrate a high likelihood of originating from the crime scene. Therefore, forensic polymer analysis is used to identify chemical and physical properties that contribute in varying degrees to the evidential value in criminal forensic analysis.

Forensic science is a hybrid, applied science encompassing any of the natural, engineering, or medical sciences that may be used in analysis for the administration of criminal or civil justice. Criminalistics is a branch of forensic science. Although variously defined, it is generally thought of as utilizing the physical sciences, especially chemistry, physics, and biology to characterize, identify, compare, and individualize items of physical evidence. The forensic scientist may be a full-time employee of a municipal, state, federal, or private laboratory, or a specialist from an academic or industrial laboratory, who is called upon to conduct forensic examinations and provide expert testimony in courts of law.

A forensic scientist must not only possess expertise in an area of specialization, but must also be able to communicate with clarity, because of the importance of conveying accurate scientific results and their interpretation to the court. The forensic scientist, whose qualifications have been accepted by the court, is given the status of expert. This status allows the scientist/witness to offer opinions on the basis of reasonable scientific certainty—an option not allowed by lay witnesses. Because a person’s property, reputation, and, very often, life may be at stake in a trial, a special burden of responsibility is placed on the scientist who testifies as an expert.

Polymers as Evidence

This article is concerned principally with the utilization of polymers as items of trace evidence. The small size of samples usually available makes their examination nonroutine. Methods such as tensile testing, fractography, and burning are rarely conducted on a microscale in forensic investigations. A significant part of the forensic examination of polymeric substances is concerned with factors other than those derived from the polymer itself. Criminalistics is distinguished from the other sciences by its unique attempt to individualize as opposed to most natural sciences, where the emphasis is on generalization and the establishment of laws that can be universally applied.

It has only recently become possible to identify microscopic polymer samples by spectroscopic and other instrumental methods. Even with this advantage, and
in spite of the many possible modifications in polymer composition, it is the trace components that serve to individualize these substances and distinguish them from their close relatives. The identification of low concentration additives makes polymer materials more specific, and therefore more evidentially important. However, when trace elements, resulting as random constituents of polymer starting materials and fillers, are identified and quantified, they can render the sample as unique. When crime scene material in question and a known material in the possession of a suspect are analytically identical to these random trace elements, a strong link is realized. This is an area that has not been significantly explored and is open to extensive research.

It is not only important to analyze the composition of a polymer, but to look for and identify subtle post-manufacturing changes that may have occurred. Changes resulting from mechanical or environmental effects can make a sample uniquely identifiable to its source.

Polymers are of interest to the forensic scientist for one or the following reasons:

*Trace Evidence.* Polymers may be crushed to powder, melted, left behind or carried away, burned, or broken. Particles—usually microscopic—of fibers, paint chips or smears, and rubber or plastic particles may be transferred to the clothing or environment of a suspect or victim. Evidence may also be in the form of soluble or dispersable polymers, such as gums, resins, adhesives, asphalts, etc.

*Failures.* Polymeric materials, like others, fail. Such failures are often studied as a result of civil liability litigation; however, they occasionally bear importance in criminal cases. Examples include the failure of a suture in an operation, peeling paint from a bridge or building, or failure of plastic parts in a prosthetic implant.

*Burned Polymers.* Most cases of this type are civil, but on occasion may arise in a criminal investigation. Examples include the flammability of various fabrics or plastics and their suitability for a particular use, determination of the quantity and identity of toxic gases that may have been given off by polymer products in a fire, and the determination of the fiber composition of a fabric after a fire.

**Evidence Collection**

Successful forensic trace evidence analysis is characterized by the ability to locate, collect, manipulate, identify, and compare microscopic particles. However, sample poverty is common in legal investigations. The sample size is frequently limited, and oftentimes only a portion of the sample can be used, pending the need for additional analysis. This places a further burden on the analyst, techniques, or instruments used. Accordingly, microscopy is the first choice for most forensic examinations.

Once particles of interest are located, they must be isolated for further study and analysis. This may be accomplished by handpicking with fine, pointed forceps.
or sharpened tungsten needles while observing through a stereomicroscope. In some cases, the evidence may be collected with sticky, transparent tape. This collection method is not recommended for paint or lacquer particles because of the inevitable mixing of the polymeric evidence and adhesive. In other cases, vacuuming, washing, or scraping with a spatula are useful techniques. Criteria for choosing the proper collection method are given in the literature (4–6).

It is rare that an item of trace evidence can be completely examined in situ. Since the original location of the specimen is changed and at least a portion of the specimen is frequently altered in testing, photography at each step of the examination is recommended, and often required, particularly in civil cases. Equipment should be available for ordinary studio photography, macrophotography, and photomicrography. The recent widespread use of digital cameras has made recording images almost routine. These permanent records not only serve to document the course of the investigation, but also help to explain the examination to a jury in the courtroom or to enhance written reports. The value of such exhibits to help the court understand the process cannot be overemphasized. For example, a comparison color photomicrograph of polished cross sections of known and questioned multiple layered paint flakes from a hit-and-run accident offers the jury a visual presentation that is easier to understand than a statement that the paint chips have the same layer structure. Photographs showing the colors of the coat layers, especially a repainted vehicle, can show a vivid match of two compared paints.

Alphabetical/numerical designations are used to label evidence exhibits of known and suspect samples for comparison. In the example cited above, the questioned paint chips recovered from the victim’s clothing could be labeled “Q-1,” and the street where the accident took place labeled “Q-2.” Paint samples from the suspect vehicle would have a known origin and be designated with K-numbers, e.g., K-1 “Paint from damage to the driver’s side fender.” This provided systematic references that are easily understood.

Analysis

In most cases, the analytical methods of the forensic chemist are different from those of the usual analytical, quality control, or materials chemists. The most important tests are usually those that lead to identification of the substances under examination. Tests, such as those found in compilations of standard methods of analysis, are rarely of use in the criminalistics laboratory, because they generally require more sample than is available and are usually intended to measure some quantitative aspect of a material. For forensic purposes, initially, a qualitative identification is more important than a quantitative determination. Before the analyst can compare or attempt to individualize a trace sample, it is essential that it be identified. Comparisons performed on traces that have not been accurately identified represent a fault in principle and may come back to haunt the scientist during cross-examination.

Microscopical methods are most commonly employed, because they allow the examination of minute specimens and are usually nondestructive. Table 1 describes many of the microscopes and instruments useful for the examination of polymer microtraces. Other equipment less frequently used, because larger
Table 1. Methods for Examining Minute Specimens

<table>
<thead>
<tr>
<th>Methods</th>
<th>Uses</th>
<th>Refs.</th>
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</thead>
<tbody>
<tr>
<td><strong>Microscopical</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stereo binocular</td>
<td>Upright image and long-working distance are excellent for particle</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>manipulation and preliminary examination</td>
<td></td>
</tr>
<tr>
<td>Comparison</td>
<td>Comparison of hairs and fibers, paint chips, layer structure; physical matches</td>
<td>8,9</td>
</tr>
<tr>
<td>Polarizing (PLM)</td>
<td>Essential for the identification of vegetable and synthetic fibers</td>
<td>10–12</td>
</tr>
<tr>
<td>Phase contrast and interference contrast</td>
<td>Qualitative systems allow image enhancement; qualitative interference systems permit the most accurate measurement of refractive indexes of synthetic fibers for patent work</td>
<td>12,13</td>
</tr>
<tr>
<td>Fluorescence</td>
<td>Autofluorescence can distinguish certain plastics and various layers of white house paints; optical brighteners can be detected on single fibers; fluorochromes can be used to detect substance such as polymer coatings on fibers</td>
<td>14</td>
</tr>
<tr>
<td>Scanning electron microscope (SEM)</td>
<td>Useful alone but enhanced by energy dispersive X-ray analyzer (EDS) system</td>
<td>15</td>
</tr>
<tr>
<td>Analytical electron microscopy (AEM)</td>
<td>Of exceptional use in the study of fractures and failure of fibers; the elemental-analysis capability assists in identifying polymers containing characteristic elements, e.g., silicone (Si), and neoprene (Cl)</td>
<td>16</td>
</tr>
</tbody>
</table>
Table 1. (Continued)

<table>
<thead>
<tr>
<th>Methods</th>
<th>Uses</th>
<th>Refs.</th>
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<tbody>
<tr>
<td>Micro-Fourier transform infrared spectroscopy (FT-IR)</td>
<td>The single most useful instrument for identifying microtraces of polymers of all types</td>
<td>17–20</td>
</tr>
<tr>
<td>The addition of a microscope to an FT-IR, especially when coupled to a mercury cadmium telluried (MCT) detector, allows the collection of IR spectra on particles down to ∼10 µm in size</td>
<td></td>
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<tr>
<td>Micro-Raman spectroscopy</td>
<td>Identification of polymers and pigments</td>
<td>21–23</td>
</tr>
<tr>
<td>Ultraviolet, visible, and fluorescence microspectrophotometry (MSP)</td>
<td>Comparison of questioned and known materials, especially fibers and paints, by their spectral characteristics</td>
<td>24</td>
</tr>
<tr>
<td>Electron microprobe analyzer</td>
<td>Quantitative analysis of element in small particles; detects elements of low atomic number</td>
<td>25</td>
</tr>
<tr>
<td>A more dedicated elemental analyzer than the SEM, although the distinction between electron microprobes and SEM has lessened with time</td>
<td></td>
<td></td>
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<tr>
<td>Surface analytical</td>
<td>Provides elemental and chemical analysis of surfaces; can reveal thin layers of corrosion of deposition</td>
<td>26</td>
</tr>
<tr>
<td>Secondary ion mass spectrometry (SIMS)</td>
<td></td>
<td></td>
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<tr>
<td>Auger spectroscopy</td>
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<tr>
<td>Electron spectroscopy for chemical analysis (ESCA)</td>
<td></td>
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<tr>
<td>Separation</td>
<td></td>
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<tr>
<td>Pyrolysis gas chromatography (Py-GC)</td>
<td>Sensitive separation of components of polymer mixtures and blends; identification by mass spectra</td>
<td>27–29</td>
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<tr>
<td>Pyrolysis gas chromatography/mass spectrometry (Py-GC/MS)</td>
<td></td>
<td></td>
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<tr>
<td>Thin-layer chromatography</td>
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<td>High performance liquid chromatography (HPLC)</td>
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samples are required, include those used to perform other tests such as Instron testers, thermal analysis instruments (differential thermal analysis, differential scanning calorimetry, thermogravimetric analysis) and apparatuses for determining molecular weights, such as size exclusion chromatography. Micromodifications of some of these instruments and techniques have been described and may have occasional significance in forensic investigations (30,31).

Separation methods such as thin layer chromatography (TLC) and pyrolysis-gas chromatography (Py-GC) are useful for comparison of questioned and known specimens when there is sufficient material and the destruction of the specimens is not an issue. In order to identify polymers and certain additives, numerous trace evidence examiners have established libraries of known Py-GC. Commercial
libraries of Py-GC chromatograms have not successfully been established, because analysts have difficulty on agreeing to standard GC conditions. Pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) can be used successfully to identify materials with commercial mass spectrometry libraries.

The nature of the specimen and the question that has been raised about it determine the course of action and the avenue of the analysis. After consideration of all known facts, and after nondestructive observations are completed, a particular test is selected in an attempt to answer a specific question. The results of this test determine the next step chosen. Some of the methods that may be employed for specific groups of polymers are discussed in the following sections. Microscopic and spectroscopic methods yield a great amount of information in the least amount of time, and, subsequently, are most frequently used by forensic trace examiners. Therefore, microscopy and spectroscopy are discussed in the greatest depth.

**Microscopy.** Visual light microscopes come in several optical configurations that are used for specific purposes. Low magnification *stereomicroscopes* (SMs) are of particular value in searching large areas for items of question and then separating them as potential evidence. The areas could include portions of garments to scan for foreign debris. Pill boxes of garment scrapings are scanned with SMs to seek potential fibers for comparisons. In addition, they are used for manipulation of the items that have been isolated to prepare toward more detailed microscopical or instrumental analysis. SMs are required in virtually any laboratory that examines micro-traces regardless of what other microscopes or instruments are employed.

The most useful microscope in the hands of a trained microscopist is the *polarizing light microscope* (PLM). Although considerable training and experience are necessary to fully utilize the capabilities of this microscope, a relatively short period of training can give a chemist the necessary skills to use the microscope to identify both natural and synthetic fibers. With minimal training, one can utilize morphological and optical properties to compare polymers regardless of their form or composition when received as items of trace evidence.

Additional microscopes include the *comparison microscope* that permits the microscopist to look at two specimens side by side. This is a useful early step in the comparison of two fibers or paint chips believed to have originated from the same source. The items can be observed and photographed side by side, permitting detailed scrutiny by both the forensic scientist and the court. Other light microscopes such as *fluorescence*, *hot stage*, *phase contrast*, and *interference* instruments may be of value in certain investigations, as shown in Table 1.

The scanning electron microscope (SEM) has some value to the forensic study of polymers, but it is principally the elemental information provided by an energy dispersive X-ray spectrometer (EDS) attached to most SEMs that usually gives the most information in forensic analyses. Using an EDS, the elemental composition of an isolated paint smear or fiber dye may be determined on even the smallest samples. The SEM provides high magnification images of the surfaces of materials. It is less useful for the examination of the interior of a particle of evidence. In this case, microtomed cross sections and freeze fractures can be used to look at interiors. A fairly recent and valuable application of the imaging capability of the SEM in the study of polymers is the examination of the ends of fibers to determine the cause of failure. Cutting with various instruments, crushing, breaking, etc, can
all be studied with the SEM and conclusions can be drawn by careful analysis of the images. Care must be taken, however, since all of the fibers in a multistrand cord or rope may not show the same characteristics as the fibers that initially failed. For example, some of the strands may have been cut with a knife under tension and the rest of the fibers (once there were too few to support the load) may have failed under tension. Other scanning microscopes, such as atomic force microscope (AFM), and instruments have yet to find significant forensic applications (see ATOMIC FORCE MICROSCOPY).

Spectroscopy. The ability to obtain spectroscopic information from microscopic samples has considerably increased the value of spectroscopy in the forensic study of microtraces. Vibrational Spectroscopy (qv) is applicable to a wide range of physical evidence. Polymeric materials, such as fibers, paints, and adhesive tapes, are frequently analyzed to identify characteristic information regarding the composition. Modern infrared and Raman spectrometers with microscopes attached are capable of obtaining chemical information from even the smallest samples. With the development of Fourier transform infrared (FT-IR) spectroscopy, the application of infrared to forensic analysis became more prevalent because of the increased speed and sensitivity of FT-IR. The development of diffuse reflection (DR) accessories provides ease of sample introduction for several forensic applications. Samples with matte-finished surfaces can be directly analyzed with no sample preparation, thus avoiding difficult pellet preparation by grinding the sample and subsequent mixing in potassium bromide. Internal reflectance spectroscopy (IRS), commonly referred to as attenuated total reflectance (ATR), has become widely used with a variety of recently developed accessories. Sample areas of less than one millimeter in diameter can be analyzed using single-reflection bench compartment accessories and diameters on the order of 10 µm can be analyzed with microscope attachments. Raman spectroscopy requires even less sample preparation than FT-IR, and artist’s pigments are being identified today by their Raman spectra obtained directly from a painting without removal of sample material (32).

Applications, General Polymers

Because polymers are so common and vary so widely in composition, they are frequently found at crime scenes and subsequently play an evidentiary role in criminal cases. Polymeric materials, such as fibers, paints, and adhesive tapes, are frequently analyzed to identify characteristic information regarding their composition. Physical and chemical information on these materials is increasingly being stored in computer databases to help determine the manufacturer or supplier, or simply to discriminate between many similar samples of material. Some of the available databases will be described as a part of the analyses mentioned in the following pages. Other general polymeric materials found as evidence do not fall into a particular category and must be studied on a case-by-case basis without the aid of comparison to similar material in a database.

The following is a case example where a polymeric material became important evidence. Early one morning on a luxury cruise ship off the coast of California, a man reported to the captain that his wife had been blown overboard. Considering
the minimal wind conditions, the captain became suspicious and alerted the law enforcement authorities. Several hours after the overboard report, the woman’s body was recovered by the U.S. Coast Guard. The clothing that both the man and woman were wearing at the time of the incident was forwarded to the FBI Laboratory. The woman’s running pants appeared soiled with an orange substance on both legs. Careful examination of her pants with a stereomicroscope revealed orange colored, rubbery particles. Examination of the man’s running pants also revealed rubbery particles that appeared identical. On the ship’s deck, at the location of the overboard incident, there was an orange colored, rubberized running track. A portion of the track material was removed from the ship and forwarded to the laboratory for analysis. The particles were removed from both pairs of running pants and flattened in a compression cell to make them sufficiently thin to perform transmission analysis using an FT-IR microscope system. Particles from the track material were prepared in the same way and the spectra of all three samples were compared as shown in Figure 1.

The three spectra of the rubberized material compared closely. The material was heavily filled with calcite (hexagonal CaCO₃), identified by the intense, broad C—O asymmetric stretch near 1450 cm⁻¹, and narrow out-of-plane and in-plane bends near 880 and 710 cm⁻¹, respectively. To determine the force required to embed the particles in the pants, a fabric similar to that of the pants was rubbed across the removed track piece at different degrees of pressure. The investigators found that it was necessary to rub the fabric with significant pressure, such as in the case of dragging a person, to cause the transfer and embed the material in the fabric. They determined that the transfer of particles suggested an altercation

![Figure 1](image_url)

**Fig. 1.** Cruise ship homicide case. Spectra of rubber particle evidence from, sweat pants from both (A) victim and (B) the suspect, (C) running track and (D) calcite reference.
between the individuals, and, therefore, this evidence was heavily weighed and re-
sulted in a homicide conviction. The combined comparison of evidential materials
by microscopical examination, infrared analysis, and physical testing played a
significant role in this case without witnesses.

Particles of plastic or rubber are often recovered from crime scenes or from
victim’s and suspect’s clothing. Occasionally, these have forensic significance and
must be identified and compared as described above. Rubber particles mounted
on a microscope slide are recognizable because they can be compressed when
pressure is applied to the coverslip with a needle, and recover fully when the
pressure is released. Plastics are more easily recognized by an experienced eye
by ruling out other types of particles. Particles of plastic are readily identified
today by FT-IR analysis.

Plastics may provide evidence in determining passenger location with ve-
hicles in serious accidents when questions arise as to who was driving when the
accident occurred. This question is often answered by examination of hairs embed-
ded in the dashboard, sun visor, etc. It has been shown that many thermoplastics
can melt and transfer to clothing in the high energy environment that momentarily
exists during a high impact collision. Molten plastic from clothing (eg, nylon
jackets, cotton polyester shirts) can be collected from dashboards, airbags, and
window pillars and identified. Colored polymers may sometimes be compared by
light microscopy alone, but any comparison of unknown polymers should always
be confirmed by FT-IR spectroscopy.

Fiber Applications

In cases of sexual assault and homicide, the transfer of single fibers often have
important forensic significance. The case that most significantly impacted the real-
ization of the importance of fiber evidence was the Atlanta murders that occurred
between 1979 and 1981 (33,34). The bodies of 28 boys and young men were found
under similar conditions. Although many of the bodies contained fiber and hair
evidence that compared closely, Wayne Williams was prosecuted and convicted for
only two of the homicides. The conviction was based solely on multiple transferred
hairs and fibers with an emphasis on uncommon carpet fiber found in the bedroom
of Williams’s home.

In the forensic study of fibers, five questions are commonly asked:

(1) What is the polymeric composition of the fiber?
(2) Could the questioned fiber have the same source as the known?
(3) How was the fiber broken?
(4) Who manufactured the fiber or fabric?
(5) What is the commonality of the fiber?

The first question can almost always be answered by PLM, and often more
specifically by FT-IR microspectroscopy, regardless of how little fiber is available.
The other four may often be more difficult.
In fiber examinations, the analyst receives evidence fibers from a known source and fibers from a suspect source that must be compared to decide whether or not the questioned and known fibers could have a common origin. As part of this comparison, the fibers must be classified according to their generic type. The foremost method of analysis for this type of evidence is light microscopy; however, IR is often valuable to further specify fiber type. Fibers from the clothing of the victim and suspect are screened microscopically for similarity by closely comparing physical and optical properties of the fibers. Laboratories that collect fibrous evidence on clear tape now have the option of using fiber finders that automatically search for target fibers, which saves considerable time in complex cases involving many exhibits. The useful properties may vary significantly because of the color, shape, texture, and chemistry of the fibers. Polarized light microscopy is used to determine the generic classification (e.g., nylon, polyester, acrylic) and FT-IR microspectroscopy plays an important role in identifying subclasses of synthetic and regenerated fibers. A spectral library of 83 polymeric fiber types, obtained by transmission spectroscopy on flattened single fibers, was developed to aid forensic examiners in the identification of fiber composition (35–37). IR spectroscopy is particularly useful for subclassifying acrylic fibers that are seen frequently as a wool alternative in sweaters. These fibers are readily transferred between individuals during contact. According to U.S. Federal Trade Commission rules, acrylic fibers must contain at least 85% polyacrylonitrile (38). The other 15% may be copolymers and ionic end groups that enhance the dying properties of the otherwise undyeable fibers. Figure 2 shows spectra of the three most common acrylic

![Fig. 2. IR spectra of acrylic copolymer fibers: (A) poly(acrylonitrile:vinyl acetate); (B) poly(acrylonitrile:methyl acrylate); and (C) poly(acrylonitrile:methyl methacrylate).](image-url)
The band shape of the C–O stretch, as shown in the region between 1300 and 1000 cm$^{-1}$, varies as a result of its position or environment within the different comonomer structures. Over 20 variations of acrylics can be identified by IR (39). Thus, IR is a very useful tool in providing information that further discriminates fiber types in order to enhance the evidential value of a sample.

Tests designed to distinguish the fibers from each other are used to complete a comparison. If the fibers cannot be distinguished at the conclusion of the tests, they are reported as nondistinguishable and it can be said that they may have a common origin. However, at best, fibers provide class-type evidence; they are not as individual as fingerprints or body fluids. It is not the number of tests that are performed, but the discriminating power of each test selected, as well as the independence of each test performed from the others, that determines the completeness of the examination and thus the strength of the conclusions that can be drawn. Table 2 lists various measurements and tests that can be performed on synthetic fibers. Most of the methods shown in Table 2 are applicable to regenerated fibers as well as synthetics. For identification of vegetable fibers (natural cellulose polymer), one must rely almost entirely on a detailed study of morphology for identification. Identification to the genus level of the plant from which the fibers originate is usually as far as a comparison can be taken. For example, having identified both known and questioned fibers as ramie ($Boehmeria nivea$), other tests of comparison are not possible (other than dyed or oiled cordage or rope), since the fibers consist of almost pure cellulose.

The optical and morphological properties of fibers are useful in comparisons when trying to determine possible end use and in manufacturer of the fiber. The optical properties of fibers include color (as well as pleochroism and fluorescence), refractive indices (parallel and perpendicular to the length of the fiber), birefringence (the numerical difference between the two refractive indices), and sign of elongation. The latter is determined by convention. A fiber is said to have a positive sign of elongation if the higher refractive index is parallel to the length of the fiber. The possibility of determining the manufacturer of a single fiber is nearly impossible in most cases. However, in some cases, where the fiber possessed a very characteristic property and manufacturers have given assistance, it has been done. In the Atlanta murder case the manufacturer of the carpet fibers from Williams’s home was determined from the unique cross-sectional shape.

The solution of a child murder in Alaska was brought to a successful conclusion by a forensic examination of particles of polymeric trace evidence recovered from her body, which was found lying in a secluded area, not far from her home. These included short (~1 mm long), brittle red and blue polypropylene fibers and single layered particles of paint in a wide variety of colors. Iron spheres and fragments were also found on the victim’s clothing. The girl was freshly dressed when she went off to meet her friend after school. There was no source of particles such as these in her normal environment. A suspect developed in the case had a workshop surrounded by nonfunctioning automobiles and trucks, and he often did repairs on children’s bicycles.

It was possible to trace the manufacturer of the fibers by an examination of their cross sections, which were made with difficulty, because of their brittle nature. Infrared microspectroscopy revealed that the fibers were photo-oxidized on the basis of a significant carbonyl absorption band of ~1730 cm$^{-1}$. The fibers were
Table 2. Fiber Comparison Techniques for Single Fibers and Fiber Fragments

<table>
<thead>
<tr>
<th>Method</th>
<th>Measurement</th>
<th>Information</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comparison microscope</td>
<td>Side-by-side viewing</td>
<td>Diameter, color, pigment, and/or delustrant density and distribution</td>
</tr>
<tr>
<td>Polarized light microscopy</td>
<td>Crystallographic properties: refractive indexes&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Fiber-identity differences in draw ratio, heat setting</td>
</tr>
<tr>
<td></td>
<td>Sign of elongation</td>
<td>Distinguishes fibers with high bond polarization perpendicular to fiber axis, eg, acrylics</td>
</tr>
<tr>
<td></td>
<td>Birefringence</td>
<td>Fiber identity (qualitative), draw ratio, and end use (quantitative)</td>
</tr>
<tr>
<td>Cross section</td>
<td>May be deduced to some extent by longitudinal view; most information is obtained from cut sections</td>
<td>Determination of fineness (tex or denier), modification ratio: can aid in manufacturer identification</td>
</tr>
<tr>
<td>Fluorescence microscopy</td>
<td>Autofluorescence</td>
<td>Blues and blue-whites indicate optical brighteners: other colors due to dyes</td>
</tr>
<tr>
<td>Microspectrophotometry</td>
<td>Visible spectrophotometry on a microscale</td>
<td>Dye comparison of dye components from known and questioned fibers</td>
</tr>
<tr>
<td>Thin-layer chromatography</td>
<td>Separation of dyes</td>
<td>Comparison of dye components from known and questioned fibers</td>
</tr>
<tr>
<td>Electron microprobe</td>
<td>Elemental composition</td>
<td>Identity of catalyst residue and elemental tags for comparison and manufacturing origin</td>
</tr>
<tr>
<td>Micro FT-IR and Raman</td>
<td>Polymer comparison</td>
<td>Recognition of copolymers in acrylics and modification to polyesters, etc</td>
</tr>
<tr>
<td>Thermal microscopy</td>
<td>Melting range</td>
<td>Distinguishes nylon; crystallinity differences</td>
</tr>
</tbody>
</table>

<sup>a</sup>The refractive indexes measured perpendicular (η<sub>perpendicular</sub>) and parallel (η<sub>parallel</sub>) to the length of the fiber. The isotropic refractive index (η<sub>iso</sub>) is the refractive index the fiber would exhibit in the absence of orientation.

made by Phillip's Fibers and consultation with experts at the company suggested that, most likely, they originated from a “fake” oriental rug that had been left out-of-doors. This carpet, if it ever existed, was never found, but the fibers from the suspect’s environment made their way onto the body of the victim.

Fibers identical in all respects to those found on the victim’s body were discovered in the truck and workshop of the suspect. Single-layered paint chips in a wide variety of colors and metal particles and spheres were also found in the suspect’s workshop. The finding of particles identical to those from the suspect’s environment on the victim was a practical example of Locard’s Exchange Principle. Since the girl did not have these particles on her clothing when she left the
house with fresh clothing and she did not move after she was murdered, the particles must have been associated with the environment of the murderer. The jury convicted the suspect of the child’s murder.

Raman spectrometry promises to complement IR analysis of textile fibers because of the ease of sampling and the additional information it can provide. Light microscopy analysis requires fiber samples to be mounted in a liquid medium, under coverslips, on a glass slide. Because glass absorbs strongly in the IR, the fibers must be removed and cleaned prior to IR analysis. Raman analysis, on the other hand, has been successfully performed on single fibers while mounted on glass microscope slides (21), thus omitting the need to remove the fibers from the slide mount. The additional sample preparation time is not required and, once mounted, the chance of fiber loss is minimal. Figure 3 illustrates the process of obtaining a Nylon 6 fiber spectrum using microscopical Raman analysis. Figure 3A includes spectral contributions from the fiber, Permount mounting medium, and glass from the coverslip. Figure 3B shows the result of Permount subtracted from the original spectrum. The Nylon 6 spectrum that remains after the glass contributions are subtracted is shown in Figure 3C. The baseline is flattened for the final spectrum in Figure 3D. The signal-to-noise ratio is less than obtaining a spectrum without being mounted under a coverslip, but it is sufficient to identify the fiber by the prominent characteristic bands as labeled. The band assignments of the major peaks are labeled in accordance with Hendra and co-workers (40). Raman spectra differ from IR spectra, because the selection rules

![Fig. 3. Raman spectra of a nylon-6 fiber mounted under a coverslip on a glass microscope slide: (A) original spectrum; (B) Permount mounting medium subtracted; and (C) baseline flattened with the major characteristic bands labeled.](image-url)
for Raman vary from that of IR, thereby producing complementary information. The information obtained by Raman is at times more definitive in determining the polymeric structure. Since Raman spectroscopy demonstrates spectral response from dyes, the dye information can be useful. However, the dye spectral features can interfere with identification of the polymeric composition of fibers. To further characterize the fibers, dye spectral features could provide information regarding the dye type. Studies have been conducted using surface enhanced Raman spectroscopy (SERS) to study dye composition using silver colloid substrates \(41,42\). While the spectral features are significantly enhanced by SERS, this method requires that the fibers are removed from the glass slides, resulting in an additional step and chance of fiber loss. Raman analysis has demonstrated certain advantages over IR, but the strengths and limitations of both are still under study to determine where each of the methods can be used to obtain the greatest information with the most convenient analysis procedure.

**Paint**

Paint evidence is usually submitted to the forensic scientist for comparison with paint from a known source. Automotive, architectural, art, marine, aircraft, tool, and other types of paints may become evidence in a variety of crime scenarios \(43\). Within the United States, most of these examinations involve automotive finishes as related to automotive accidents and hit-and-run cases. The question frequently posed is, what kind of vehicle could have contributed the paint flakes recovered from the scene of a hit-and-run homicide case? Additionally, house paints may be examined in connection with burglaries, and paint from tools in cases involving industrial sabotage. Rarely is it necessary to determine the manufacturer of a particular paint.

The examination proceeds differently, depending on whether the questioned evidence is in the form of flakes or a smear. Individual spray-paint spheres are occasionally encountered and treated in the same manner as individual particles from a smear. Table 3 summarizes the comparison methods employed.

After light microscopy, IR analysis offers the most information in forensic paint examinations. The organic binders are frequently identified by IR, and both organic and inorganic pigments can often be identified. Since the 1970s, scientists from the Royal Canadian Mounted Police (RCMP) have been classifying automotive paints on the basis of chemical composition \(50–52\). The original analysis was performed with the use of high pressure diamond anvil cells in beam condensers on dispersive IR spectrometers. Since then, the RCMP and other analysts have changed to using the less cumbersome, low pressure, compression diamond cells with beam condensers in FT-IR systems. Inorganic pigment components in paints have revealing spectral features at the lower wave numbers. Beam condensers are used rather than FT-IR microscopes to overcome the limited frequency range of liquid nitrogen cooled mercury cadmium telluride (MCT) detectors used in IR microscopes. For paint analysis, the extended range to near 200 cm\(^{-1}\) is obtained with CsI optics and a standard deuterated triglycerine sulfate (DTGS) detector in the spectrometer bench.
### Table 3. Comparative Methods for Paint Traces

<table>
<thead>
<tr>
<th>Methods</th>
<th>Measurement</th>
<th>Information</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color comparison</td>
<td>Chips laid side by side under a stereo microscope</td>
<td>Visual matching, adhering debris, possible to automotive-paint reference collection</td>
<td></td>
</tr>
<tr>
<td>Spectrophotometry</td>
<td>Visible spectrum</td>
<td>Nonsubjective comparison of color and aid in identifying some pigments</td>
<td>24,44</td>
</tr>
<tr>
<td>Cross section</td>
<td>Layer structure</td>
<td>Proof of similarity or dissimilarity for multilayered flakes; even white house paints can be studied by staining with rhodamine and observing with a fluorescence microscope</td>
<td>45</td>
</tr>
<tr>
<td>Physical match</td>
<td>Observation of fit between two chips of paint</td>
<td>Only positive form of paint identification; a physical match is regarded as the equivalent of a fingerprint</td>
<td></td>
</tr>
<tr>
<td>Polarized light microscopy</td>
<td>Magnification, optical properties</td>
<td>Observation of properties; identification of a filler</td>
<td></td>
</tr>
<tr>
<td>Microchemical tests</td>
<td>Identification of chemical and physical properties</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Solvent tests (emperical or select)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Microchemical reaction</td>
<td>Identification of inorganic fillers and crystalline organic pigments</td>
<td>43,46,47</td>
</tr>
<tr>
<td>X-ray diffraction</td>
<td>Identifies crystalline phases</td>
<td>Identification of inorganic fillers and crystalline organic pigments</td>
<td>48</td>
</tr>
<tr>
<td>Electron microprobe</td>
<td>Elemental analysis</td>
<td>Identification of inorganic pigments and fillers</td>
<td></td>
</tr>
<tr>
<td>Micro FT-IR</td>
<td>IR spectrum</td>
<td>Identification of polymers and copolymer comprising vehicle; limited identification of pigment</td>
<td>19,43,49</td>
</tr>
<tr>
<td>Pyrolysis gas chromatography</td>
<td>Separation of pyrolysis product</td>
<td>“Fingerprint” for comparison; some limited chemical information on chemical type</td>
<td>28</td>
</tr>
</tbody>
</table>

Databases are maintained to search for unknown automotive paints from hit-and-run cases. The FBI Laboratory in Quantico, Va, maintains the National Automotive Paint File, which is the largest automotive paint collection in the United States. The largest forensic collection in the world, with over 50,000 samples, is maintained at the Bundeskriminalamt Research Laboratory in Wiesbaden,
Germany. Scientists at the RCMP have developed a software package called PDQ, ie, Paint Data Query (53). This database uses microscopic and IR spectroscopic analysis results to search for automotive information leading to the identity of make, model, and year of vehicles in question, typically from hit-and-run cases. Through the FBI-sponsored Scientific Working Group for Materials Examination (SWGMAT), this database has expanded to include entries from North American, European, Japanese, and Australian Collections. The international cooperation of forensic scientists has served to assist in casework involving paint evidence from international automobiles that have a global market. This worldwide effort helps everyone that applies the PDQ database for searching an unknown automobile paint found on a hit-and-run victim.

When two paint samples are compared, and comparison results are analytically the same, the analyst may report that the two are similar in all respects and that they may, therefore, have originated from the same source. Comparisons of two paint specimens are made on the layer structure, elemental composition, polymer identity, fillers, and pigments. The analyst must take great care to point out that in the case of an automotive finish, this does not mean that the paint necessarily came from a particular car. From the scientifically determined facts, it could have originated from any of hundreds, or perhaps thousands, of vehicles painted with the same topcoat. However, significance would be attached to the fact that the suspect car was registered and driven in the state where the accident occurred; that this particular car sustained damage to the front end, for example, and that evidence stuck to the bumper was in the form of fiber fragments identical to the fibers from the victim’s trousers. If a fragment of paint from the victim’s clothing or the accident scene can be found and fits like a jigsaw puzzle in the damaged areas of the suspect car, the association is unequivocal.

Most paints do not usually display as much diversity in chemistry, color, and layer structure as do automotive ones. Therefore, a wider variety of analytical instruments are often used to characterize them. Along with microscopy and IR spectroscopy, other methods frequently used are pyrolysis GC/MS and inorganic elemental analysis by X-ray spectroscopy in the SEM. X-ray diffraction is also of use in the identification of crystalline pigments and fillers.

The study of coatings is also important in litigation concerning peeling paint. The examination in these cases focuses on the two surfaces that were once in contact with each other. Light and scanning electron microscopy of the surfaces are often able to pinpoint the cause, usually improper or inadequate surface preparation. In a very few cases, the surfaces appear to be perfectly clean and yet will still not adhere to each other. Surface analysis techniques such as electron spectroscopy for chemical analysis and Auger spectroscopy can reveal thin layers of otherwise invisible coatings on the surface of the substrate. The chemical composition of these thin coatings can be determined with these techniques, which in turn can help assess the cause of nonadhesion. FT-IR microspectroscopy was used to identify crystals that were implicated in a peeling paint problem. The IR spectra identified the crystals as a fungicide which had exsolved from the paint and recrystallized on the undersurface, pushing the film away from the wood substrate.

Paint comparisons are most often conducted in conjunction with criminal proceedings, but civil cases often arise. In one civil case, the owners of a high rise
office building suspected that their building, especially the windows, was being coated by paint from a bridge a half-mile away that was being spray-painted. Microscopical examination of the glass windows revealed the presence of tiny green spherical particles that were compared visually and by visible microspectrophotometry. The elemental composition was determined using energy-dispersive X-ray spectroscopy and the polymer was identified by FT-IR. These tests could all be conducted on a single sphere and compared with spheres that had formed and fallen around the bridge. The paints from both sources were identical in all respects and the painting contractors were held liable for the damage to the high rise.

A criminalist in California was assigned to rework a murder investigation originally tried in the early 1960s in 1987 after the U.S. Supreme Court overturned

![Fig. 4](image_url)  
**Fig. 4.** IR and Raman spectra of yellow acrylic melamine enamel auto paint with pigments: (A) IR spectrum of the auto paint; (B) IR spectrum of chrome yellow pigment; (C) Raman spectrum of chrome yellow pigment; (D) Raman spectrum of the yellow auto paint; (E) Raman spectrum of rutile. Spectra provided by E. Suzuki, Washington State Patrol, Forensic Laboratory, Seattle, Wash.
the conviction of the defendant on a technical issue. The murdered 16-year-old
girl was found in a dry drainage canal near the California desert, some distance
from her home. The original suspect in the case was placed at the crime scene on
the basis of a partial footprint and tire track in the soil outside the victim’s home.
During the reinvestigation, the criminalist was surprised to find small, pale green
football-shaped particles among the items of evidence associated with the victim
and the suspect. Consulting a forensic microscopist, he was informed that they
were originally wet spheres of spray paint that had deformed by capillary action
because they had a fiber running through them. These particles, whatever their
origin, were significant because they were associated with both the suspect and
the victim. They had been observed during the original investigation 25 years
earlier, but the analysts involved did not feel that they could be analyzed by the
techniques available at the time. The forensic microscopist took over the investi-
gation of the particles when the criminalist discovered their source. The headliner
of the suspect’s vehicle, which was still in custody, had been spray-painted green.
The headliner was cotton at that time and many of the droplets dried around
the fibers. When the cotton became brittle, the particles broke away and dusted
the car with these green football shaped particles. Microanalysis of the parti-
cles was conducted for the purpose of comparing the particles from the victim
(shoelace, dust from her house, etc) and the suspect (his clothing, dust from his
hotel room, etc) to the paint particles from the vehicle headliner. The analysis
was exhaustive and it was possible to say that the paint from all three sources
was identical in elemental composition, polymer composition, color, fluorescence,
and microscopical examination of the fillers and pigments in terms of size and
quantity. In addition, the particles were all spray paint, and all of the particles
had been sprayed over cotton fibers. These fibers also had the same properties
among the three sources. The jury convicted the defendant for the murder a second
time.

Researchers are beginning to demonstrate the usefulness of Raman analysis
for organic and inorganic pigment identification in paint (22,23). Figure 4 com-
pares IR and Raman paint spectra of a yellow acrylic melamine enamel automo-
tive paint. The IR spectrum in Figure 4A clearly shows the resin binder features.
The N–H stretch near 3350 cm\(^{-1}\), the C–H stretching near 3000 cm\(^{-1}\), the C=O
stretch near 1730 cm\(^{-1}\), the C–N stretch near 1540 cm\(^{-1}\), and the typical C–O
envelope from 1300 to 1000 cm\(^{-1}\) are observed in the IR. Of particular interest
in paint analysis are any contributions by pigments. The weak, broad band at
868 cm\(^{-1}\) appears to be contributed by chrome yellow, as shown in the Figure 4B
reference spectrum. However, because of the band’s comparatively low intensity
and lack of detail in the paint spectrum, it would be difficult to positively identify
chrome yellow by this method alone. The peaks labeled at 659, 425, and 357 cm\(^{-1}\)
are rutile, a polymorph of titanium dioxide. Figure 4D is the Raman spectrum
of the yellow auto paint. The major peaks at 843 and 365 cm\(^{-1}\) match up with
the Raman spectrum of chrome yellow shown in Figure 4C. Peaks at 611 and 446
cm\(^{-1}\) are contributed by rutile, as shown in Figure 4E. With Raman spectroscopy,
the high scattering efficiency of some of the pigments, relative to those of the
binders, helps to easily determine the pigment components, as interfering binder
peaks are not a problem.
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