TIME-RESOLVED LUMINESCENCE IMAGING: APPLICATION
TO LATENT FINGERPRINT DETECTION

by

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CHAPTER I

INTRODUCTION

1.1 Luminescence Detection

Luminescence detection is commonly used throughout chemistry, biology, and physics. In physics, for example, scintillation materials which fluoresce when excited by particles from nuclear collisions are used to detect single events. Similarly, in chemistry and biology, luminescence detection enables the assay of amino acids down to concentrations in the picomole range [1,2]. The sensitivity and ease of application of the luminescence method of detection results from the technological improvements made in photomultiplier tubes and photon-counting electronics. This sensitive spectroscopic equipment now permits the counting of individual photons emitted from fluorophores, making luminescence measurement one of the most sensitive methods of detection in many scientific fields.

However, one problem encountered in luminescence detection is that in many cases undesired fluorophores interfere with the luminescence of interest. In the case of immunoassays employing fluorescence detection, for instance, competing fluorophores make the detection less sensitive than radioimmunoassays. To circumvent this problem, time-resolved fluorescence immunoassay has used both

rare earth chelates [3,4] and coordination compounds such as ruthenium(II)tris(1,10-phenanthroline) as long lifetime fluorescent labels [5].

In our specific detection problem, namely the detection of latent fingerprints, not only is the intensity and color of luminescence important, but its spatial distribution as well. Time-resolved imaging allows us to detect luminescent fingerprints on brightly fluorescent surfaces. The crux of time-resolved imaging is to devise fingerprint treatments such that fingerprint luminescence lifetimes are much longer than those of the substrates. To set the stage for our approach to the problem, we first describe how fingerprints are developed conventionally and also how fingerprint detection by laser is currently practiced. As we shall see, compatibility between conventional fingerprint processing and laser detection constitutes an important issue.

1.2 Latent Fingerprints in Crime

The motivation for studying fingerprint detection comes from the fact that crime is such a serious problem in our society. Homicide is the second leading cause of death for people 15-34 years of age, second only to accidents, and the chance of being the victim of a violent crime is greater than that of being hurt in a traffic accident [6]. The lifetime risk of becoming a homicide victim [6] is shown in Table 1.1. As shown in Table 1.2, the estimated cost of crime to victims exceeded \$13 billion in 1986 [7]. While this cost to society is staggering,

Table 1.1: Lifetime Risk of Being a Homicide Victim

One out of:	Group
179	White Males
30	Black Males
495	White Females
132	Black Females

Table 1.2: Economic Loss to Victims of Crime

Type of Crime	Gross Loss in Millions of Dollars
Crimes of Violence	1,000
Crimes of Theft	2,592
Household Crimes	9,447
Total Crime	13,039

local, state, and federal government only spends about \$48.5 billion per year for police, judicial services, and correctional facilities [6].

Rehabilitation of criminals during their prison term does not seem to have the desired effect on reducing crime since over a 20-year period, half of all those released eventually will be imprisoned again, the majority within their first three years after release [6]. One positive way of affecting the rate of crime is to ensure that those crimes which are committed do not go unpunished. Because a latent fingerprint can be unambiguously linked to the identity of a person, it is usually the strongest of all physical evidence introduced into a court. In cases where this kind of physical evidence can be produced, the trials are usually expedited quickly, thus reducing investigative and court costs.

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With the development of Automated Fingerprint Identification Systems (AFIS) used for computer matching of prints, the improvements in techniques for detecting latent fingerprints are especially timely. In crimes where there are no suspects and no other clues, there is little chance that a fingerprint match will be made from existing fingerprint files with manual searching. However, the AFIS system employs a computer to scan fingerprint impressions, pinpointing important features for identification. The computer is thus able to match the entered print with those print files that have been previously entered into the computer's database. The speed and accuracy of computer searching makes possible the comparison of a single latent print against millions of prints in a matter of minutes.

In 1985, after the San Francisco Police Department installed an AFIS system, it was able to match latent fingerprints of criminals and clear over 816 cases, including 52 homicides. This is contrasted with the 58 cases cleared the previous year using only latent print identifications. After helping to convict over 900 burglars, the AFIS system has been credited for the city's 26 percent drop in burglaries [8]. Obviously, the ability to detect latent fingerprints is fundamental to the success of AFIS.

1.3 Conventional Detection of Fingerprints

Fingerprints were first applied to the positive identification of individuals in 1858 when William James Herschel used fingerprints to identify people receiving pensions. Sir Francis Galton devised a system of fingerprint classification and in 1892 wrote a textbook on fingerprints in which he correctly claimed that they are never duplicated and remain unchanged for life. It was not until 1902 that the first man was identified solely by fingerprints on record. About this time, police departments began to use fingerprints systematically for identification [9].

1.3.1 Chemical Composition of Latent Fingerprint Residue

Latent fingerprints consist mainly of perspiration residue and in some cases contaminants, which have been picked up by fingers and transferred to a surface. The fingerprint contains typically about 10^{-4} grams of material. Most of a fingerprint is made of perspiration, of which 99.0% to 99.5% is water; of the remainder, about one half of the solids are organic substances such as amino acids, fats, and oils from the sebaceous glands, and the other half is comprised of inorganic salts, mostly sodium chloride and potassium chloride [10-12]. Because there is so little material in a fingerprint to begin with, and since this material must be detected with its spatial information intact, the detection of fingerprints is difficult.

The method selected to detect latent fingerprints depends on what type of surface the print is on. If the surface is smooth, such as plastic, metal, or glass, then either dusting or superglue fuming is the most sensitive method; if the surface is porous, such as paper, cardboard, or wood, then a chemical treatment is used.

1.3.2 Smooth Surfaces

The earliest method of fingerprint detection and still the most used by law enforcement personnel is dusting. When dusting for latent prints, a fine powder is brushed across a fresh fingerprint, and the powder adheres to the moisture left in the print. The powder provides the contrast necessary to make the fingerprint visible. Except for fresh prints, however, dusting is not effective. The moisture left in a print quickly dries, leaving little material for the powder to adhere to.

Another more recent development has been the use of superglue fuming. In this method, a surface is exposed to vapors of methyl- or ethyl-cyanoacrylate ester molecules that comprise the main ingredient of superglue. When a fingerprint on a smooth surface is exposed to fumes of these molecules, the cyanoacrylate polymerizes on the fingerprint residue. When water vapor is combined with the cyanoacrylate vapor, the polymerized print will be white in color, thus making the print visible. Superglue fuming is now in wide use and is often followed by dusting.

1.3.3 Porous Surfaces

The reason that the methods discussed above are not used with porous surfaces is that these methods have a tendency to be absorbed by the porous surface as well as the fingerprint residue. Therefore, several chemical treatments have been used to develop latent fingerprints on porous surfaces. A chemical reagent that reacts with the fingerprint residue, but not with the porous surface, yields a product that contrasts with the background. These treatments are usually limited not only to porous surfaces, but can be applied to smooth surfaces as well. However, with smooth surfaces there is a danger of washing away faint prints by the solvent delivery system [13].

Iodine fuming takes advantage of the way lipids left in the fingerprint residue absorb iodine fumes, forming a brown stain where the lipids were deposited. Because the iodine tends to sublime away with time, prints developed with this technique should be photographed immediately.

The silver nitrate method relies on the reaction of silver with the salts left in a fingerprint. As in silver halide photography, when exposed to light, the silver ions are reduced to metallic silver. This metallic silver, when visible, is seen as a black stain revealing the latent print.

In 1954, Svante Oden and Bengt von Hofsten reported the use of ninhydrin (2,2-dihydroxy-1,3-indanedione) in the detection of latent fingerprints [14]. This compound, shown in Figure 1.1, had been discovered and recognized to react

with amino acids by Siegfried Ruhemann in 1910 [15]. The purple product formed in the reaction of ninhydrin with an amino acid is a molecule called Ruhemann's Purple (RP) shown in Figure 1.2. To detect fingerprints using the ninhydrin treatment, the ninhydrin is dissolved into a volatile solvent, which acts as a carrier for the ninhydrin molecule. When this solution is sprayed onto the surface, the volatile solvent evaporates quickly and prevents the bleeding of fingerprint residue and any inks which may be present on the surface. The ninhydrin molecule is then free to react with any amino acids left on the surface by a latent fingerprint. If there are enough amino acids to react with the ninhydrin and form the RP, the purple latent fingerprint will be visible on a lightly colored surfaces. This is the most popular treatment for porous surfaces because of its sensitivity and ease of use. The ninhydrin treatment has also been shown to be compatible with chemical tests used to detect drugs [16,17] and the electrostatic detection apparatus used in the examination of questioned documents [18]. Other chemical reagents have been explored, including 4-dimethylamino-cinnamaldehyde (DMAC). Nevertheless, DMAC has been found to be inferior to the ninhydrin treatment [19], and ninhydrin remains the most common fingerprint reagent used.

A common problem with all of these conventional methods is that they rely upon producing differences in absorption and reflection to make the latent fingerprint visible on a surface. If the latent fingerprint is faint, the the small

Figure 1.1: Ninhydrin Molecule

Figure 1.2: Ruhemann's Purple

difference in reflection and absorption may not contrast enough to yield the detail needed for identification. The problem is with the detection method itself. When detecting differences in reflection/absorption, small differences in relatively large signals are compared. Luminescence detection, on the other hand, is an inherently more sensitive method of detection since small signals are detected with little background.

1.4 Laser Detection of Fingerprints

In 1976 it was discovered that fingerprints could be detected by their inherent fluorescence [20,21]. This inherent fluorescence is due to the presence of several materials in the sweat deposited by a fingerprint, including lipids, amino acids, and vitamins such as riboflavin [22]. The inherent fluorescence of latent fingerprints is excited by blue-green light, typically from an argon laser. The laser method of detection has a great advantage over conventional methods because it uses only light, thus not interfering in any way with other methods of detection, and lending itself to surfaces that could not be examined using conventional methods. However, the same intense light responsible for the faint inherent luminescence sometimes excites the surface on which the print is deposited to fluoresce and overwhelm the faint inherent fluorescence of the fingerprint. Methods thus were developed to enhance the fingerprint luminescence by making it stronger than the background or of a different color

than the fluorescence of the background. These laser methods were made compatible with the traditional methods of fingerprint detection as much as possible so that they would be accepted more readily by those working in the field. Compatibility is a critical issue in that evidence is often processed using conventional methods and only subsequently subjected to laser examination.

1.4.1 Smooth Surfaces

For smooth surfaces, fingerprint dusting powders were tagged with dyes to improve their fluorescence detection [23- 26]. Dusting powders that exhibit phosphorescence were also developed to eliminate background fluorescence. A sample is enclosed by a rotating cylinder. A slit, which is cut through the cylinder, rotates about the sample, alternately allowing the laser to excite the phosphorescent powder, and then, after enough time has elapsed for the background to die out, allowing a camera to photograph the phosphorescent print [27].

The superglue method can also be adapted for use on smooth surfaces. The fingerprint is fumed with a cyanoacrylate ester (superglue) which goes preferentially to the fingerprint as in the traditional method where it polymerizes on the fingerprint residue [28]. To make this method more sensitive, the object with the fingerprint fixed within the superglue polymer is stained with a highly fluorescent dye such as rhodamine 6G dissolved in a solvent. The dye is selected

which has the proper physical properties which allow it to go preferentially into the superglue and not everywhere onto the surface. The dye solution must not dissolve either the surface which is to be stained or the superglue polymerized fingerprint. When illuminated by a laser, the traces of dye remaining in the superglue make the polymerized fingerprint readily visible [29].

Another method of getting the dye into the superglue polymer that works even for surfaces that normally could not be solution dye stained dye is the vapor staining method. The superglue-fumed latent fingerprint is immersed in fumes of a dye that is being vaporized by heating. The vaporized dye, while still highly fluorescent, goes preferentially into the polymerized fingerprint residue revealing the position of the fingerprint residue under laser examination [30]. Some surfaces fluorescence very strongly when illuminated with visible light, but have little background fluorescence when excited with UV laser light or UV lamps. One staining dye which can be used effectively for such surfaces because of its UV excited fluorescence is 9-methylanthracene [31].

1.4.2 Porous Surfaces

Several chemical treatments that react with fingerprints creating a luminescent product have been investigated for their detection on porous surfaces, including 4-phenylspiro[furan-2(3H),1'-phthalan]-3,3'dione (fluorescamine) [26], 8-anilinonaphthalene-1-sulfonate (ANS) [32], dansyl chloride

[31], ortho-phthalaldehyde (OPA) [26,24], and 7-chlor-4-nitrobenzo-2-oxa-1,3-diazole (NBD chloride). All of these treatments exploit the improvement in sensitivity possible with luminescence detection, but all require UV excitation, which usually increases the background fluorescence of surfaces. However, in cases where visible excitation causes excessive background fluorescence, UV can in some circumstances produce less fluorescence [33,34]. Of these reagents, NBD chloride has become the most widely used because it is sensitive and easy to use. Recently 7-nitro-4-benzofurazanyl ethers, which are comparable in sensitivity with their parent NBD chloride, have demonstrated smaller background fluorescence and an additional advantage that they can be applied in the vapor phase [35].

Because the ninhydrin treatment is the most commonly used conventional fingerprint detection method, it was desirable to make this method compatible with the laser method. A treatment was discovered whereby treated ninhydrin prints could be made to fluoresce under argon laser excitation. When the ninhydrin-developed prints are sprayed with ZnCl_2 or CdCl_2 dissolved in a volatile solution, a highly fluorescent coordination compound is formed [36-38]. Shown in Figure 1.3 is the coordination compound formed with ZnCl_2 -RP treatment. Other transition metal salts also make coordination compounds with RP, but only group II B metals, Zn, Cd, and Hg show appreciable fluorescence. The fluorescence in metal-RP coordination compounds has been interpreted in

Figure 1.3: Ruhemann's Purple, ZnCl_2 Coordination Compound

terms of twisted intramolecular charge transfer (TICT) states [39]. X-ray structural determinations of Cd-RP coordination compound have shown that the RP acts as a tridentate ligand, as shown previously in Figure 1.3, with one anion bound to the metal cation, and two water molecules completing the distorted octahedral configuration, forcing the two indandione groups to be nearly coplanar [40]. The structure of protonated RP has been determined by x-ray diffraction to be twisted, thus quenching fluorescence because the overlap of the π orbitals of the 1,3-indandione moieties is minimized [40,41].

For the group II B metals, the fluorescence intensity of the RP coordination compounds decreases with increasing atomic number, due to greater spin-orbit coupling, which quenches the ligand fluorescence. Thus Cd-RP and especially Hg-RP are not as strongly fluorescent as the coordination compounds formed with Zn [39]. To improve the fluorescence, Zn-RP treated latent fingerprints can

Figure 1.4: Benzo(f)ninhydrin

be cooled down to liquid nitrogen temperatures [42,43]. The ninhydrin- ZnCl_2 treatment is also useful in the detection of weak bloody prints [44,45].

Several compounds have been made that have chemical properties similar to ninhydrin. These compounds also produce highly fluorescent coordination compounds when treated with ZnCl_2 that are in many cases superior to ninhydrin [46-48]. Two of the most successful compounds that have been tried are benzo(f)ninhydrin and 5-methoxyninhydrin shown in Figures 1.4 and 1.5 respectively. Because of their enhanced luminescence, these reagents are at times used instead of ninhydrin.

1.5 Lasers in Forensic Science

Lasers are used not only in the detection of latent fingerprints, but they can also enhance the detection of fluorescence in general, making them useful for gathering physical evidence in a variety of ways. Fiber classification [49], erased

Figure 1.5: 5-methoxyninhydrin

writing, differences in inks or transfers of ink to other surfaces [50,51], stains on clothing, differences in paints, and shoeprints can all be examined for fluorescence using the laser [26,52,53]. Lasers can also be used in emission spectroscopy, which finds many uses in identifying chemicals [54].

Reconstruction of broken glass has also been explored using laser interferometry [55]. The use of the laser for latent fingerprint detection as well as other forensic applications has justified the inclusion of the laser as a laboratory instrument in over 100 crime labs across the country.

The main problem encountered while detecting latent fingerprints via laser-excited luminescence is that such prints are often located on intensely fluorescent surfaces. The relatively weak luminescence of the fingerprint is overwhelmed by the large fluorescence of these surfaces. To overcome this problem, fingerprint treatments compatible with conventional methods of

detection were developed to give the fingerprint a long luminescent lifetime for use in time-resolved imaging.

1.6 Time-Resolved Imaging of Fingerprints

Numerous surfaces ubiquitous at crime scenes display very intense fluorescence under laser illumination. Many of these surfaces exhibiting such a strong background have short 0.5-2.0 nanosecond lifetimes [56]. These short luminescence lifetimes suggested a method of eliminating the background by making the fingerprint have a longer lifetime than its background as was first done with phosphorescent fingerprint powders discussed earlier [27].

By devising fingerprint treatments that give the fingerprint a longer luminescent lifetime than the background, the fingerprint can be separated from the background using the following method. The fingerprint is illuminated with a laser beam modulated either by a mechanical light chopper or an electro-optic modulator. The imaging system is gated off during the time that the laser is illuminating the sample and gated on as soon as the laser light has been turned off and the rapidly decaying background has completely decayed. The imaging system will then image only the long-lived luminescence of the latent fingerprint. Just before the laser again illuminates the latent fingerprint, the imaging system is turned off. By repeating this cycle for each modulation of the laser beam, the

imaging system will only be gated on when the fingerprint's long-lived luminescence is present and the background fluorescence is removed completely.

With this method of background suppression in mind, the objective of this thesis research then is to (1) design staining compounds or chemical reagents that will not only have the requisite physical and chemical properties, but will also display long-lived and intense luminescence, and (2) to design and construct a time-resolved imaging system that serves as a prototype for a second generation laser device for law enforcement personnel in criminal investigations.

CHAPTER II

SPECTROSCOPIC MEASUREMENTS

Two different approaches were taken in creating treatments for fingerprints useful for time-resolved imaging. For porous surfaces, rare earth salts replace the ZnCl_2 in the RP- ZnCl_2 treatment, forming coordination compounds of the rare earths. The rare earth ions that are excited by intramolecular energy transfer have long luminescence lifetimes. For smooth surfaces, for which the usual laser method of treatment is to fume the surface with superglue and then to stain with a solution containing a strongly fluorescent dye, several coordination compounds of ruthenium that have long lifetimes were investigated for use as staining dyes. Spectroscopic measurements were made in order to optimize these treatments for time-resolved imaging.

2.1 Ruthenium Compounds

These compounds are of interest because they have the physical properties needed to be suitable for use as a solution staining dye, and they have intense, long-lived emission at room temperature [57].

One ruthenium molecule that has received extensive study because of its possible use in splitting water is tris(2,2'-bipyridyl)ruthenium(II) chloride

hexahydrate (BIPY) [58]. At room temperature this molecule has a luminescence quantum yield of about .27 and a lifetime of .93 μs [59]. The intense luminescence of this molecule has been assigned to a charge transfer (CT) ($d-\pi^*$) transition [60,61]. This assignment of the luminescence to a CT emission is based upon the magnitude of the observed lifetimes (.5-10 μs) and a quantum yield greater than 10% when measured at 77°K. The multiplicity has been assigned to a spin forbidden transition in which the phosphorescence has a shorter lifetime than would normally be expected because of nonradiative decay from the triplet state due to the strong heavy-atom perturbation [59,60,62]. While this assignment to a spin forbidden transition seems true for low temperatures (77°K), it may not be possible to assign only one multiplicity to the luminescence for this molecule, especially at room temperature [63].

Several other coordination compounds of ruthenium that have similar spectroscopic properties but physical properties that give them superior adherence to the superglue/fingerprint residue in solution staining were investigated, including: tris(1,10-phenanthroline)ruthenium(II) chloride hexahydrate (PHEN) and tris(4,4'-dimethylbipyridine)ruthenium(II) hexafluorophosphate (DMB). In order to find the most effective pumping wavelength of these ruthenium compounds, excitation and emission spectra were taken.

2.1.1 Excitation Spectra

To find the best possible wavelength to excite luminescence, excitation spectra were taken of samples of the ruthenium compounds which had been deposited on thin layer chromatography (TLC) plates. The TLC plates, consisting of glass covered by silica gel without UV indicator, were chosen for their porous surface which resembles the solid environment that the ruthenium molecules would experience in a fingerprint. For spectroscopic measurements, these TLC plates have little background fluorescence to distort the spectra taken. The excitation spectra were taken using the setup shown in Figure 2.1. A xenon arc lamp is used for excitation, and its illumination is sent through monochromator 1. The light illuminates the sample, and the luminescence from the sample is focused on the entrance slit of monochromator 2, which is tuned to the maximum emission wavelength for each of the three ruthenium molecules measured. A photomultiplier tube is mounted at the exit of monochromator 2, sending its output to a chart recorder via an amplifier-discriminator and photon-counter. By scanning monochromator 1 through a range of excitation wavelengths, the peaks in luminescence could be recorded, revealing the best excitation wavelengths to use. The resulting spectra are shown in Figure 2.2. The sharp peaks in the excitation spectra are due to the sharp peaks in the xenon lamp excitation source.

Figure 2.1: Excitation Measurement Experimental Setup

Excitation Spectra

Figure 2.2: Excitation Measurements of Ruthenium Molecules

2.1.2 Emission Spectra

Emission spectra were taken with an argon laser (458 nm) exciting the samples of ruthenium molecules dissolved in methanol and spotted on a TLC plate. The experimental setup was identical to that in Figure 2.1 except that the xenon arc lamp and monochromator 1 are replaced with the argon-ion laser. Monochromator 2 is scanned through the entire emission spectra for each of the three ruthenium compounds. The emission spectra of the ruthenium compounds on a solid TLC substrate are shown in Figure 2.3, and the solution spectra for the ruthenium compounds dissolved in methanol are shown in Figure 2.4.

2.2 RP Rare Earth Coordination Compounds

While the ZnCl_2 coordination compound is highly fluorescent, its luminescence lifetime is too short (about the same as highly fluorescent backgrounds) to be suitable for time-resolved imaging. In order to make the treatment suitable for time-resolved imaging, coordination compounds of rare earths are made. These coordination compounds' ligand fluorescence is less than that produced with the ZnCl_2 treatment since the higher atomic number of rare earths tends to quench fluorescence due to spin-orbit coupling, but the rare earth ion can be excited through intramolecular energy transfer to luminesce. Rare earth transitions are highly forbidden and thus have long luminescence

TLC Emission Spectra

Figure 2.3: Emission Spectra of Ruthenium Molecules on TLC plate

Solution Emission Spectra

Figure 2.4: Emission Spectra of Ruthenium Molecules in Methanol

lifetimes. This luminescence of rare earths excited by intramolecular energy transfer was first observed by Weissman in 1941 [64].

2.2.1 Rare Earths

The rare earths are a group of elements that have in common an open 4f shell. They are chemically similar, forming mainly trivalent ions, although cerium, praseodymium, and terbium can also be tetravalent, and samarium, europium, and ytterbium are sometimes divalent. The interesting luminescence of the rare earth ions involve highly forbidden transitions in the 4f electron shell. The transitions between the levels of the 4f configuration are all forbidden as electric dipole transitions by the parity rule. Because these rare earth transitions are so highly forbidden, they typically have long luminescence lifetimes, usually on the order of milliseconds. The following transitions are responsible for the luminescence of rare earth ions.

1. Forced electric dipole
2. Magnetic dipole
3. Electric quadrupole

Electric quadrupole and magnetic dipole transitions are extremely weak. The rare earth spectra come mainly from forced electric dipole transitions, which are

allowed by admixtures of opposite parity. These admixtures come from the interaction of the $4f^n$ wavefunction with wavefunctions of opposite parity (s,d).

$$\Psi = A\Psi^+ + B\Psi^-. \quad (2.1)$$

The wavefunction Ψ will include Ψ^+ with the parity of $4f^n$ and Ψ^- of opposite parity, with coefficients $A \sim 1$ and $B \ll 1$ [65,66].

When a rare earth salt is reacted with ninhydrin, benzo(f)ninhydrin, or 5-methoxyninhydrin, a coordination compound is formed much like that which was formed for ZnCl_2 treatment. The forming of this coordination compound dramatically changes the color of the RP. Shown in Table 2.1 are the colors of these coordination compounds which are formed with the RP of ninhydrin and the two ninhydrin analogs. Rare earth coordination compounds were made of the following rare earths: Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, and Er. These coordination compounds were spotted on a TLC plate and excited with the an argon and dye laser. No rare earth luminescence was observed for these coordination compounds except for Eu and Tb which have a strong luminescence when excited with UV.

2.2.2 Energy Transfer

The energy transfer from the RP ligand to the rare earth ion for europium and terbium is shown in Figure 2.6 and Figure 2.5 respectively. The rare earth coordination compound is formed, and light is absorbed by the ligand of the RP,

Table 2.1: Colors of Ruhemann's Purple

Ninhydrin Molecule	Ruhemann's Purple Color	Rare Earth Compound Color
Ninhydrin	Purple	Orange
Benzo-Ninhydrin	Green	Red
5-Methoxyninhydrin	Blue	Red-Orange

which then transfers some energy to the rare earth ion, which in turn luminesces with a long lifetime.

Ideally, there would be substantial resonance energy transfer from the first excited singlet state of the ligand to the 5D_4 state of Tb^{3+} or the 5D_0 state of the Eu^{3+} . The Tb^{3+} ground state $^7F_6 - ^5D_4$ energy is about $20,300\text{ cm}^{-1}$ and coincides with the 488 nm line of the Ar-laser. The Eu^{3+} ground state $^7F_0 - ^5D_0$ energy is about $17,267\text{ cm}^{-1}$ and can be pumped with a dye laser. However, the oscillator strengths of the Tb^{3+} $^7F_6 - ^5D_4$ and the Eu^{3+} ground state $^7F_0 - ^5D_0$ transitions are too low to render the direct ligand to excited state energy transfer effective [67]. On the other hand, near-UV excitation of the excited ligand states leads to efficient energy transfer to a group of Eu^{3+} and Tb^{3+} states that have higher oscillator strengths. From there, cascading takes place to the Eu^{3+} 5D_0 and Tb^{3+} 5D_4 states, leading to intense luminescence corresponding to transitions to the Tb^{3+} $^7F_{3,4,5,6}$ and the Eu^{3+} $^7F_{0,1,2}$ levels of the F ground J-manifold. The visible transitions measured from rare earths in $LaCl_3$ are shown in Table 2.2 [68,69].

Figure 2.5: Energy Levels of Terbium (III)

Figure 2.6: Energy Levels of Europium (III)

Table 2.2: Visible Rare Earth Luminescence

Rare Earth	Transition	Wavelength (nm)
Tb ³⁺	⁵ D ₄ - ⁷ F ₆	489
Tb ³⁺	⁵ D ₄ - ⁷ F ₅	544
Tb ³⁺	⁵ D ₄ - ⁷ F ₄	584
Tb ³⁺	⁵ D ₄ - ⁷ F ₃	620
Eu ³⁺	⁵ D ₀ - ⁷ F ₀	579
Eu ³⁺	⁵ D ₀ - ⁷ F ₁	592
Eu ³⁺	⁵ D ₀ - ⁷ F ₂	615

2.2.3 Emission Spectra

Measurements of rare earth luminescence were made using an argon laser operating in the UV (334-364 nm) to excite rare earth salts dissolved in methanol. The luminescence was measured with a monochromator using the same photomultiplier tube, amplifier discriminator, photon counter, and chart recorder as previously mentioned for the emission spectra taken of the ruthenium compounds. The spectra of Eu³⁺ and Tb³⁺ are shown in Figure 2.7. These spectra show the characteristic sharp emission lines seen for rare earth ions and agree with the energy levels observed for rare earth ions in crystalline environments as previously listed in Table 2.2.

2.3 Luminescence Lifetime Measurements

There are two widely used methods for the measurement of luminescence lifetimes: the pulse method and the phase-modulation method. The pulse method utilizes either single photon counting, or pulse-sampling, to measure a

R.E. Emission Spectra

Figure 2.7: Emission Spectra of Rare Earth Salts in Methanol

luminescence response function $F(t)$ to a given excitation pulse. For an impulse excitation (infinitely sharp pulse), the observed decay would be fitted to a sum of exponentials

$$F(t) = \sum_i \alpha_i e^{-t/\tau_i}. \quad (2.2)$$

For an excitation corresponding to a laser beam's being turned on and then off, the response is an exponentially decaying curve.

The phase-modulation method uses phase shift and demodulation of luminescence signals to determine the lifetime of the sample luminescence. If a sample is excited with light modulated at an angular frequency ω , the emission will have the same frequency ω but the modulated emission will be delayed with phase angle ϕ relative to the excitation,

$$\tan\phi = \omega\tau, \quad (2.3)$$

where τ is the fluorescence lifetime. The amplitude of the emission will be demodulated by a factor m where

$$m = [1 + \omega^2\tau^2]^{-1/2}. \quad (2.4)$$

For the long lifetimes of the rare earths, measurements were taken using laser excitation chopped with a mechanical beam chopper. The luminescence was sampled using a boxcar averager which was scanned over the entire period of sample excitation and decay. This essentially corresponds to the pulse method of detecting fluorescence. When a sample is pulsed with a laser beam, the emission

decays exponentially. From the shape of the decay, the lifetime is derived by fitting to an exponential decay. The system response is measured with the boxcar averager measuring the laser excitation decay. Since the chopped laser signal will not have an exponential decay, the decay that is measured is the instrument response of the boxcar averager.

Lifetime measurements for the Eu-RP and Tb-RP were determined by making the RP compound, reacting it with the rare earth salt to form the coordination compound, and then spotting it on a TLC plate. The samples were then excited by UV argon-ion laser light which was chopped by a mechanical chopper at 169 Hz. The luminescence was detected with a photomultiplier tube mounted on a monochromator. The signal of the photomultiplier was sent to the boxcar averager which was triggered by the mechanical chopper. The boxcar measurements were then recorded on a chart recorder. The measurements gave a lifetime of .4 ms for Eu and 1.3 ms for Tb.

Measurement of lifetimes of the ruthenium molecules were determined using the phase modulation method. The experimental setup is shown in Figure 2.8. The sample is excited by a sinusoidally modulated laser light source. The luminescence is focused on the entrance slit of a monochromator with a photomultiplier mounted on the exit slit. The anode of the photomultiplier is hooked up to the signal input of the lock-in amplifier which measures the phase difference and modulation of the photomultiplier anode signal. The lifetimes

Figure 2.8: Lifetime Measurement Using Lock-in Amplifier

Table 2.3: Ruthenium Compound Lifetimes

Ruthenium molecule	Measured Lifetime
$\text{Ru}(\text{bipy})_3\text{Cl}_2$	$.8\mu\text{s}$
$\text{Ru}(\text{phen})_3\text{Cl}_2$	$1.4\mu\text{s}$
$\text{Ru}(\text{dmb})_3\text{Cl}_2$	$.4\mu\text{s}$

were calculated according to Equation 2.3 and are given in Table 2.3. Because of the multicomponent nature of the ruthenium luminescence and the instrumental uncertainty in the measurement of phase angles using the lock-in amplifier, the uncertainty of these lifetimes is $\pm 10\%$. For the purposes of this research, however, the accuracy of the lifetimes is not a critical issue.

CHAPTER III

TIME-RESOLVED IMAGING SYSTEM

The time-resolved imaging system is shown in Figure 3.1. The system consists of a laser, modulator, and microchannel plate image intensifier. Each component was chosen to provide versatility to the system so that a wide variety of treatments of latent fingerprints could be explored using time-resolved imaging.

3.1 Laser

To excite luminescence of the treated fingerprint, the laser was chosen for its ability to provide intense illumination. The monochromatic reflected laser light is also easily filtered out with long wavelength pass filters. Also, to make the time-resolved imaging applicable to short lifetime treatments of fingerprints, some method of switching off and on the illumination of the sample as quickly as possible was desired. Because of the narrow beam width, lasers are the only source of illumination capable of being modulated with nanosecond risetimes.

A Coherent Innova 90-6 argon-ion laser that was used in this research operates in the near UV when Eu^{3+} or Tb^{3+} fingerprint treatment is employed and in the blue-green when one of the ruthenium compounds is used. In

Figure 3.1: Time-Resolved Imaging System

addition, the argon laser was used to optically pump a Coherent Model 599 dye laser when investigating treatments requiring illumination in the 570-630 nm range.

3.2 Laser Modulation

The laser light is modulated by an EG&G Princeton Applied Research Model 125A mechanical light chopper operating at 169 Hz when rare earths are used. At this modulation rate, the mechanical chopper is the most economical and easiest to work with. Since the emission lifetimes of the ruthenium compounds are too short (about $0.9 \mu\text{s}$) for mechanical chopping, a Quantum Technology Model 3050 electro-optic modulator is used. This modulator has a useful bandwidth of 50 MHz. The electro-optic modulator was chosen for its high bandwidth for faster decaying fingerprint treatments that would be investigated in future research. The laser beam is then focused onto an optical fiber which illuminates the sample. The sample luminescence passes through a filter, which blocks reflected laser light, and enters a 35 mm photographic camera with a Hamamatsu V3036U gated proximity-focused microchannel plate image intensifier mounted on its image plane.

3.3 Microchannel Plate Image Intensifier

The mounting of the image intensifier on the camera was chosen for ease in changing lenses and apertures, with the added advantage of providing a convenient shutter. Originally it was thought that the image intensifier could be mounted on the image plane of a pinhole camera box, but the amount of light from the pinhole limited the image intensifier's useful amplification of the weak signals we were detecting, thus necessitating the added optics. The image intensifier is operated in the gate-on mode. The gating signal is shown in Figure 3.2. The high voltage for the microchannel plate and phosphor screen is provided by a Bertan Model 320N high voltage power supply. A schematic diagram of the intensifier biasing electronics is shown in Figure 3.3. The reverse bias of the photocathode is provided by 1.5 Volt battery. A negative 15 Volt gating pulse is applied to an RC circuit to turn on the image intensifier. The depicted values of R and C in Figure 3.3 correspond to values that are used for the slow modulation of the image intensifier used when the mechanical light chopper is employed. The RC time constant is such that the complete laser-off portion of the modulation period can be spanned. The gating pulse is provided by a Hewlett Packard Model 8015A pulse generator, which is triggered by the light modulator. The fingerprint images on the microchannel plate image intensifier are then photographed using an ordinary 35 mm camera.

Figure 3.2: Microchannel Plate Image Intensifier Gating Signal

Figure 3.3: Microchannel Plate Image Intensifier Biasing Circuit

CHAPTER IV

RESULTS

In this time-resolved imaging system, the fingerprint images, which are visible on the image intensifier phosphor screen, are simply photographed. They could also be recorded by CCD camera and interfaced with a computer for further image processing or computer cold searching with a system such as AFIS.

To demonstrate the background fluorescence suppression capability of the imaging system, two sample fingerprint treatments are presented: (1) a fingerprint deposited on a porous surface developed using 5-methoxyninhydrin followed by treatment with $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ and overlaid with a second fingerprint that is highly fluorescent to demonstrate background fluorescence suppression and (2) a fingerprint deposited on a smooth surface and developed with the superglue/dye-staining method using tris(2,2'-bipyridyl)ruthenium(II) chloride hexahydrate (BIPY) dissolved in methanol as the staining solution.

4.1 5-methoxyninhydrin/ $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ Treatment

A fingerprint was placed on a TLC glass plate. The print was treated first with 5-methoxyninhydrin and then with $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$. Next to this first print, a second print stained with dichlorofluorescein was placed. The dichlorofluorescein

Figure 4.1: Room-Light Photo Showing Only Dichlorofluorescein Fingerprint

print fluoresces very intensely in the same spectral range as Tb^{3+} . This second print serves to show the fluorescence suppression capability of the imaging system. In Figure 4.1, a room-light photograph of the fingerprint shows the dichlorofluorescein print, but the print treated with the 5-methoxyninhydrin/ $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ is not visible. This photograph corresponds to what would normally be seen if only the conventional method of fingerprint detection were used without the improved sensitivity of luminescence detection. While detail is clearly visible in original photographs, the reproduction of such photographs results in a significant loss of detail.

In the photograph of the fingerprint shown in Figure 4.2, luminescence is detected by the image intensifier, which is gated on while the laser is on. This

corresponds to what would be seen when fingerprints are detected by laser. The luminescence of the 5-methoxyninhydrin/ $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ print is faintly visible, as is the intense fluorescence of the dichlorofluorescein print. In fact, the latter's emission was so strong that it grossly overexposed the image intensifier phosphor screen and photographic film.

In the photograph of the fingerprint shown in Figure 4.3, the image intensifier was gated on only while the laser was off so that only the long lived luminescence of the 5-methoxyninhydrin/ $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ print is seen. Complete suppression of the fluorescence of the dichlorofluorescein print was achieved. Time-resolved imaging has also been demonstrated using 5-methoxyninhydrin/ $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ [70], and for more realistic circumstances with fingerprints developed on paper [71].

4.2 Tris(2,2'-bipyridyl)ruthenium(II)chloride Treatment

To demonstrate the capabilities of the imaging system with smooth surfaces, a fingerprint was placed upon a Coke can, which under argon laser illumination has extremely fluorescent paint. This fingerprint was then placed in superglue fumes in the conventional manner and stained with a dye containing BIPY dissolved in a methanol solution. In Figure 4.4 a photograph of the Coke can after treatment with superglue shows virtually no detail. In Figure 4.5 the Coke can is photographed under the usual CW argon laser illumination. The

Figure 4.2: Photo of Image Intensifier Ungated

Figure 4.3: Photo of Image Intensifier Gated

Figure 4.4: Room-Light Photo of Coke Can After Superglue Fuming

fluorescence of the dye-stained fingerprint is visible except for where it overlaps the brightly fluorescent paint of the can. In the photograph of Figure 4.6, the luminescence is detected by the image intensifier during the laser off period. Almost complete suppression of the background paint fluorescence is achieved, and fingerprint detail, which could not be seen in Figure 4.5 because of the paint fluorescence is visible. The background fluorescence that is seen in this photograph is due to the residual laser light that gets through the electro-optic modulator during the laser off period. Time-resolved imaging has also used PHEN as a dye in solution staining [72]. Also, several solvents including cyclohexane, chloronaphtalene, and different solutions of water/methanol have been investigated in order to optimize the dye's adherence to the

Figure 4.5: Photo of Coke Can Under Laser Examination

superglue/fingerprint and minimize its adherence to the surface. Of the solutions which have been tried so far, ethylene glycol seems to work the best.

4.3 Discussion of Results

From the results presented, the time-resolved imaging system obviously shows improvements over conventional fingerprint detection methods and current laser fingerprint detection methods. Moreover, the RP-rare earth and superglue/staining treatments retain compatibility with conventional fingerprint processing. However, there remains some room for improvement. Presently Eu and Tb only give energy transfer under UV illumination, whereas the ruthenium staining dyes require blue-green excitation. When argon lasers are used,

Figure 4.6: Photo of Coke Can Using Time-Resolved Imaging

switching the excitation wavelength from blue-green to near-UV involves changing the mirrors of the laser cavity, and this is cumbersome from a practicality perspective. If a rare earth can be found to work under blue-green argon laser excitation or dye laser excitation, the sensitivity would be greatly improved. Conversely, staining compounds that are amenable to UV excitation should be investigated so that one does not have to switch excitation wavelengths if one has to use Eu and Tb compounds on porous items.

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