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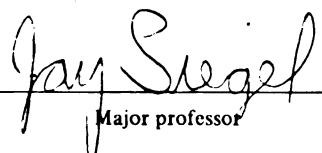
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Latent Prints Using An Argon Laser

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**AN EVALUATION OF EIGHT FLUORESCENT DYES
FOR VISUALIZATION OF CYANOACRYLATE DEVELOPED
LATENT PRINTS USING AN ARGON LASER**

By

Robert J. Soule

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ABSTRACT

AN EVALUATION OF EIGHT FLUORESCENT DYES FOR VISUALIZATION OF CYANOACRYLATE DEVELOPED LATENT PRINTS USING AN ARGON LASER

by

Robert J. Soule

Latent fingerprints can provide valuable information about placing a particular individual at a crime scene if a suitable development technique is employed. One technique relies on cyanoacrylate (super glue) vapors adhering to fingerprint residue. Unfortunately, the solid white polymer residue is difficult to detect on lightly colored backgrounds. Laser illumination has been successfully coupled with fluorescent dyes to provide greater contrast between the print and background. Combining fluorescent dyes instead of staining with a single dye has proven quite effective. Combinations dyes cover most of the visible range from 400 nm to approximately 600 nm. Despite much progress, fluorescent backgrounds still inhibit sufficient visualization of ridge detail. Four of the dyes tested provide red-shifted fluorescence which extends the useful range to well over 700 nm. In addition, these dyes can be used to virtually eliminate background fluorescence when viewed with an infrared camera.

To my father, for the continual guidance.

To my mother, for the eternal support.

To my son, Ian, may you grow to appreciate
the study of science: be it natural or social.

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Dr. Jay Siegel for the coordination of this research project.

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Introduction

The role of forensic evidence in criminal cases is to associate a particular person, weapon, or tool to a crime scene (Peterson, 1983). Latent fingerprints are considered one of the most important forms of physical evidence, yet of all criminalistics laboratories surveyed only 62% routinely check for fingerprint evidence. Although the interest of this paper is with the criminal identification of suspects, fingerprints are used routinely to identify amnesia victims, missing persons, and unknown deceased (U.S. Department of Justice, 1984).

The study of friction ridges is called dactyloscopy. Friction ridges exist for exudation of perspiration, tactile facility, and provision of a gripping surface (Lee, 1991). Pores along the ridges allow for oils, salts, and other biological substances to be secreted from the body. The transfer of these chemicals to any surface results in a fingerprint residue impression.

Fingerprints exist in several forms which are either visible, impressions, or latent prints. It is generally accepted that fingerprints are individual and immutable. Fingerprints are considered objective forms of evidence which lead to conclusions with a high degree of scientific certainty. Because of this, fingerprints are one of the most valuable types of physical evidence.

The exact beginning of the use of fingerprints as a means of criminal

identification is difficult to pinpoint. However, it is undisputed that several people were responsible for the impetus of fingerprint work with respect to criminal identification. Fingerprints as a means of personal identification were realized by Sir William J. Herschel (Lee, 1991).

Sir William J. Herschel, a British officer living in Bengal, India, declared that fingerprints possess immutable characteristics called "ridge persistency" and were unique (Lee, 1991). Throughout Herschel's twenty years of work with fingerprints, he concluded fingerprints were unique and unchanging. Noting this, he relied on fingerprints as a form of personal identification. Since Herschel used fingerprints only as a means of protection of documents in dealing with natives, he eventually acknowledged Faulds as the first person to identify fingerprints as a means of criminal identification.

It was not until 1880, that Dr. Henry Faulds published an article in Nature on the utility of fingerprints for criminal identification. Faulds, a Scottish doctor working in Japan, urged the use of printer's ink as a transfer medium and saw the potential of fingerprints as a means of criminal identification. Although there is a slight difference in concept between personal and criminal identification, Faulds is considered the pioneer in criminal fingerprint work. Faulds, as well as Herschel, noted the immutable characteristic of fingerprints and was first to demonstrate the utility of fingerprint evidence at a crime scene. Faulds stated, "[W]hen bloody finger marks or impressions on clay, glass, etc., exist, they may lead to the scientific identification of criminals" (Lee, page 28). A debate as to whether Herschel or Faulds is the true pioneer of fingerprint identification has continued for years.

In addition to Faulds and his pioneering work, Sir Francis Galton is considered another prominent contributor to fingerprint work. Galton, cousin of famous scientist Charles Darwin, expanded on Faulds' work by stating the individuality and immutability of fingerprints in his 1892 book entitled "Finger Prints". These two aspects lie at the foundation of the importance of fingerprints to criminal identification. Galton gave us the fingerprint terms bifurcation, ridge ending, island, and enclosure, which were termed "Galton Ridges" (Clements, 1987). Most importantly, Galton made the first attempt at classifying fingerprints.

In the tradition of Galton, Sir Edward Richard Henry contributed to fingerprint work by simplifying a classification system. Henry designed the classification system with the help of Azizul Haque and Hem Chandra from Bengal, India (Clements, 1987). Known as the Henry system, it forms the basis of the FBI classification system and is used today in law enforcement agencies in the United States and throughout the world.

A fingerprint pattern consists of fine ridges and furrows. Located along the ridges are tiny pores which allow for the secretion of perspiration. When an individual touches an object an impression of the print may be left on the object. A fingerprint weighs approximately 0.1 milligram. It consists of 99% water, which quickly evaporates, and 1% of approximately equal amounts of salts, amino acids, lipids, and vitamins (Menzel, 1980). The chemical composition of a typical fingerprint is represented in Figure 1.

A number of mature procedures in the form of flowcharts exist that have been successfully used to develop latent prints on a variety of surfaces. For example,

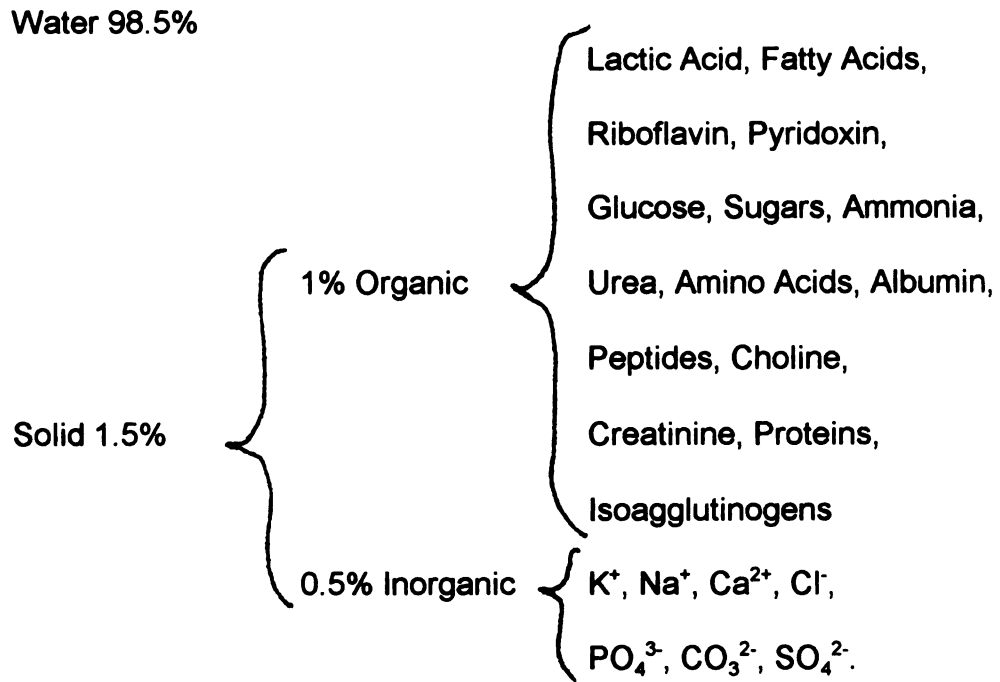


Figure 1. Fingerprint Composition Chart.

one chart may be designed to visualize prints found in a bloodstain whereas another might focus on paper products. The variety of surfaces, or substrates, is broken down into two simple categories. One is for porous substrates while the other is for non-porous. Porous products refer almost exclusively to paper products. Non-porous implies a relatively non-permeable surface upon which a latent print may reside.

Iodine crystals are heated which allowed the vapors to adhere to the print residue. Unfortunately, the iodine method is temporary and the need for a more permanent technique was eventually answered by the compound ninhydrin. This chemical reacts with amino acids to form a purple compound called Ruhemann's purple. This technique is still widely used, especially for paper evidence. Since 1891, silver nitrate has been used to react with the chloride present in fingerprint residue. The resulting compound, silver chloride, immediately turns black upon exposure to light. Over time, physical developer has replaced the use of silver nitrate as means of developing prints on paper evidence.

In 1978, latent print examiners in the U.S. Army Criminal Investigations Laboratory realized the potential of cyanoacrylate fuming as an additional method for processing latent prints. The use of methyl- or ethyl-cyanoacrylate has become a standard method for processing prints on non-porous substrates. Cyanoacrylate vapors are attracted to lipid residue in fingerprints. Cyanoacrylate fuming is excellent for all hard surfaces such as plastics, electrical tape, garbage bags, styrofoam, carbon paper, aluminum foil, guns, vinyl products, wood products, rubber products, metals, cellophane, and smooth rocks.

The heated glue vapor adheres to friction ridge residue, then hardens, and finally builds up the ridge detail as more glue particles condense. A white solid polymer is formed during the fuming process. Since the white polymer may be difficult to see on light colored surfaces, enhancements of the glue technique have been proposed. The print is usually dusted with a fluorescent or non-fluorescent powder or a dye staining method is employed. A number of dyes have been explored including gentian violet, coumarin 6, coumarin 540, ardrex, rhodamine 6G, rhodamine B, 3,3'-Diethyloxadicarbocyanine Iodide (DODC), 4-(Dicyanomethylene)-2-methyl-6-(p-dimethylaminostyryl)4H-pyran (DCM), 2'-7'-dichlorofluorescein, rosaniline chloride, 7-(p-methoxybenzylamino)-4-nitrobenzoxadiazole (MBD), yellow 40, and europium complexes.

Since latent prints are deposited on a variety of surfaces, a number of procedures have been designed to develop prints from these surfaces. It relies on crafting what scientists know about science to experiment with different aspects of fingerprint work. Mature procedures evolve out of trial and error based on scientific principles. The end result tends to focus on the qualitative aspect of developed prints rather than quantitative. The phrase of "as long as it works" fits in the development of new visualization techniques.

The critical point in the development of latent prints is centered around the initial conditions under which the prints were deposited. An ideal situation of successful development would involve five steps.

The first step involves the original conditions under which the print is left. Bobev (1995) identifies three factors that influence the degree to which the print

adheres to the surface. Since adhesive forces are inversely proportional to temperature, fatty residues tends to remain on the cooler surface. Adhesive forces are also affected by surface structure, therefore rougher surfaces tend to have greater adhesive attraction. Lastly, there are electrostatic forces that interact with the perspiration in print residue rather than the fatty secretions.

Second in the process of successful development of latent prints involves sufficient build-up of cyanoacrylate (super glue) on the suspected print. In the late 1970's, cyanoacrylate build-up was noticed on the underside of its container. Latent print examiners then realized that cyanoacrylate could be used to develop prints. This white residue that is left can be difficult to see so latent print examiners needed to visualize the fumed prints. It should be noted that excessive fuming can harm the potential visualization of the print.

Powders, both conventional and fluorescent, have been used along with fluorescent dyes to visualize fumed prints. Since fluorescent dyes are the focus of this research, it is presented as the third important element of print development. Choosing the proper fluorescent dye and concentration is critical.

A number of fluorescent dyes have been explored as a means of visualizing cyanoacrylate-developed prints. Rhodamine 6G is considered the standard fluorescent dye in print visualization, however, it is considered carcinogenic and careful use is necessary. Rhodamine 6G is an excellent dye for several reasons. It has good preferential adherence to the latent print. The absorption spectrum is well matched to the blue-green illumination of the argon laser. And finally, Rhodamine 6G has a high fluorescence quantum yield with a color that differs from

the illuminating laser light (Menzel, 1980).

The key to the fourth step is to select the proper of the illuminating light source and various filter in order to see the print. The argon-ion laser is considered standard since most dyes used are tailored for its use. Alternatives to laser illumination are called forensic light sources. Due to expenses of maintaining an argon laser, other light sources are explored to save costs.

The final step in the ideal situation to successfully develop a latent print revolves around recording the image. Once the image is recorded, either photographically or digitally, a search can be conducted on the latent print to compare with an inked print on file. If these conditions are met, a latent print at a crime scene will be matched to a particular person, weapon, or tool. This is the overall objective of designing latent print development techniques.

Numerous articles dealing with impression evidence have focused on improving methods of delivering the cyanoacrylate (Step 2), investigating new fluorescent chemicals (step 3), or exploring new illuminating light sources (Step 4). A significant recurring problem in the literature (discussed in the next chapter) is the fact that the background masks the fluorescence of the dye used on the fumed print. This obstacle has not been adequately addressed in prior articles, focusing instead on time-resolved photography and imaging techniques to capture the print. What was needed is a separation by distance rather than time.

The purpose of this research was to examine the potential use of eight fluorescent dyes for visualization of cyanoacrylate developed prints. Specifically, new dyes were selected that either could replaced Rhodamine 6G (due to its

carcinogenicity) or that could shift the color of fluorescence far beyond that of the interfering background. For the former, 5-[(4,6-Dichlorotriazin-2-yl)amino]fluorescein Hydrochloride (DTAF), Ethidium Bromide, Evans Blue, 5-Fluorescein Isothiocyanate, LISSAMINE (Rhodamine B Sulfonyl Chloride), and Nile Blue A Perchlorate were selected. These dyes were selected due to excitation wavelengths near that of the argon-ion laser output and/or for the electron donating groups based on their structure. For the problematic background, Styryl 7 and IR-144 were specifically selected for investigation into extending the range into the infrared region.

A two liter Coke label was selected as the fluorescent background in this research. This non-porous substrate was the independent variable and the fluorescent dye were the dependent variable. The dye combination called RAM (Rhodamine, Ardrox, and MBD) works well in the visible region of the electromagnetic spectrum, however, it does not adequately overcome the background fluorescence. The idea is to optimize the distance between the background and substrate. In scientific terms what is needed is a highly fluorescent dye with a large Stokes shift. Since there are far more fluorescent dyes possible light sources, it is therefore prudent to explore new fluorescent dyes.

Literature Review

In 1977, Dalrymple, Duff, and Menzel used an argon laser to visualize latent prints. This was the first major article to deal with the union of fingerprints and laser light. Although they did not look at fluorescent dyes, but rather native, or inherent luminescence, they provided much of the impetus for research involving luminescent chemicals.

Then in 1979, Menzel and Duff identified problems with laser fingerprint development. Namely the substrate luminesced strongly, overwhelming the usually weak fingerprint luminescence. Also the substrate did not accept the fingerprint sufficiently well. And lastly, fingerprints deposited by a minority of individuals did not show sufficient inherent luminescence. This research focused on luminescent dusting powders or chemical treatments yielding a luminescent reaction product.

A follow-up to the previous article involved a similar approach but looked at extending time variable into phosphorescence instead of fluorescence. Menzel (1979) explored the utility of using luminescent lifetimes and illumination decay. So, in essence he attempted to delay the fluorescence in time but not to remove the influence of substrate fluorescence.

By 1979, Dalrymple considered the substrates glass, metal, wood, cloth, stone, and plastic exhibits. From his research he arrived at four conclusions. 1) All

lines lasing was much more efficient than in single line use. 2) The argon laser and ninhydrin may work on different components in fingerprint residue, thereby adding to the likelihood of identifying a print. 3) The argon laser good for otherwise different surfaces. 4) Fingerprints were within reach of laser method even under unfavorable conditions.

Starting in 1980, Menzel and Fox investigated fluorescent dusting powders. Menzel states, "Dyes providing near-infrared fluorescence seem to be of little use since the dusted latent prints cannot be located by visual inspection." (Menzel & Fox, page 153). The focus would eventually change when technology advanced in visualizing prints with alternative to visible light.

Creer (1983) presented an article on operational experience with latent print detection and photography. This article is of interest because of 396 articles looked at with laser illumination, 0 of 19 prints on wood were identifiable. He notes that "wood fluoresces strongly under laser excitation and this will mask any fingerprint fluorescence." (Creer, page 157). Wood, along with other types of fluorescent substrates, makes developing latent prints difficult.

Kobus, Warrener, and Stoilovic (1983) published an article that began to center on the use of cyanoacrylate as a means to receive fluorescent dye/powder. Gentian Violet and Coumarin 540 were explored as fluorescent dyes. A Xenon arc lamp with 150W tube instead of an argon laser used as the illuminating source. Their research was designed to improve contrast between the ridges and the background of fingerprints developed with cyanoacrylate on non-porous substrates.

By 1983 Menzel, Burt, Sinor, Tubach-Ley, and Jordan have now

incorporated the use of the argon laser to visualize fluorescent dyes on cyanoacrylate-developed latent prints. Two years later, Burt and Menzel (1985) center on detection of prints on difficult surfaces. They used chemical development with dansyl chloride and vapor-staining with 9-methylanthracene on highly fluorescent backgrounds. This was possible only with UV lamp or argon laser operating in the UV. No interest was placed on the visible region of the argon laser.

Menzel (1985) hints of using a monitor rather than photography to visualize prints. In a visionary statement he also suggests electronic development (visualization) would lend itself to computer image processing. There was a decrease of major works done in this area until 1993.

Wilkinson and Watkin (1993) explored the use of europium aryl β -diketone complexes for detection of cyanoacrylate developed fingerprints on skin. They determined four sources that contribute to background fluorescence. 1) Light of similar wavelength to the emission wavelength will reflect off the background thereby reducing contrast. 2) Background fluorescence occurs when the surface upon which the print has been deposited is excited by the same wavelength used to excite the stain. 3) Background fluorescence may also result from an excess of stain adhering to the surface. 4) Cyanoacrylate that has developed on the background the stain will adhere to this in exactly the same way it adheres to the print, thereby reducing contrast during examination. Prints were deposited under medium pressure and only the middle 3 fingers were used (due to roughly equal surface area). Finally, Wilkinson and Watkin suggest using a two phase system of 20% Methyl Ethyl Ketone (MEK) and water to allow penetration into polymer instead

of dissolving it.

A major article was published by Cummings, Hollars, and Trozzi (1993). They report that the polymerized latents were sometimes difficult to detect and preserve. Of historical note, one of the first dyes used was Rhodamine 6G. In addition, Ardrex, MBD, and Yellow 40 have been used to visualize prints. By combining dyes, one dye solution could be applied to the suspected surface and then scanned by any number of light sources. They also caution against over-fuming which could mask print fluorescence. This implies that varying the light source and illuminating the dye combination is more reasonable than applying one dye and illuminating it with proper wavelength and then using another dye and wavelength if unsuccessful.

Murdock and Menzel (1993) again focus on problematic backgrounds. They suggest trying to trick the eye, monitor, or recording device into seeing only the fingerprint fluorescence and not background fluorescence. In essence, this does nothing to eliminate or deviate from the existence of background fluorescence, but rather separate both in time by employing a gating technique. They explain this is designed for rare earth fingerprint treatment chemistry. This may be too heavily equipment-laden for typical forensic crime laboratories.

Campbell (1993) notes that recent research has focused on improved methods of fuming prior to dye staining and new forensic light sources, or new chemicals and formulations to render them fluorescent. He, like Murdock and Menzel (1993) are concerned with luminescent lifetime and illumination decay (a focus on separation of time rather than distance).

Weaver and Clary (1993) present the ability to fume in tandem with fluorescent dye application by means of co-volatilization of a subliming 3M thermal dye of the styryl family. A vapor wand directs the stream of cyanoacrylate and dye. A suggestion is made as to the ability of styryl dye to sufficiently visualize cyanoacrylate-developed prints.

An important article was published recently by Mazzella and Lennard (1995). As of January 1995, Styryl 7 is mentioned by Mazzella and Lennard while this research was in progress. They state, "On highly luminescent of multi-colored surfaces, the choice of a particular stain may be critical. Ideally, the fingerprint luminescence should be as far removed as possible from that of the substrate." Stain formulations based on Pet ether (volative 30-50°C fraction) were used because of low cost, readily available, low toxicity, low polarity, and high volatility. It does have the disadvantage however of being highly flammable and a risk of explosion. Since the substrate of this research was plastic, a fluorescent background was needed to test the ability of Styryl 7 to visualize developed prints in the infrared region.

Finally Bobev (1995) presents the notion that the mechanism of latent fingerprint origins depends on a number of surface phenomena. These phenomena are linked to adhesive and electrostatic forces. He states the interdependence on physico-chemical structures of surfaces of the different items, the environmental conditions, and the amount of time since the latent deposition. Since many variables are present, a varied protocol for successful development of latent fingerprints is mandatory.

The literature has shown the evolution of latent print detection. In the late-1970's, laser light and fingerprints were brought to the attention of the forensic community. With the realization of cyanoacrylate fuming as an influential method coming soon after this report, the likelihood of improved methods was evident. By 1983, the combination of cyanoacrylate-developed prints, staining with fluorescent dyes, and illumination with laser light was available and sufficiently ripe for experimentation. A few years later, background fluorescence was an obstacle to securing good ridge detail from fluorescing prints. The utility of using a set of fluorescent dyes in one mixture and applying this mixture to the fumed object was an improvement in time and effectiveness.

What can be distilled from the forensic literature is that because the fluorescent background is a recurring problem with visualizing latent prints developed with cyanoacrylate, a different approach is needed. The fluorescent background and fluorescent print may be more effectively separated by distance (IR-shifted fluorescent dyes) rather than time (time-resolved photography/imaging). Attempts have been made to improve fuming methods, explore new dyes, and employ alternative light sources. Greater flexibility is possible to overcome background fluorescence due to numerous new or future fluorescent chemicals.

In order to "visualize" infrared radiation, an infrared monitor is needed. Once detected, the print can be processed by a thermal printer. Or as technology advances, and crime laboratories follow close behind, the monitor may be linked to an image processing system which in turn may be linked to AFIS (Automated Fingerprint Identification System).

Methodology

It is necessary to preface this chapter with a few remarks. No emphasis was placed on measuring or recording the temperature, relative humidity, or other factors affecting the laboratory environment. Laboratory conditions are atypical of crime scene scenarios, therefore the laboratory conditions under which the experiments were conducted had minimal environmental monitoring.

Basically the experiments were conducted in several stages and more attention was placed on qualitative results rather than quantitative. The goal was to test various dyes using mature development techniques on fluorescent non-porous substrates. In principle, the interest was whether or not these dyes could be used to visualize prints.

An Eastman Kodak book of laboratory chemicals was obtained. The interest was primarily in fluorescent dyes and laser dyes. Laser dyes by necessity are often highly fluorescent, thus making them excellent candidates for this research. Eight dyes were selected from the catalog. Only eight were selected because of research costs and in addition eight would provide enough research to be conducted. All dyes were specifically chosen using three criteria. First, the dyes must be at or near the required excitation wavelength of the argon laser. Second, if the excitation wavelength values were slightly outside the required wavelength, then dye structure

was examined. Fluorescent chemicals with a strong electron-donating group were sought. Since fluorescence relies on the ease of promoting electrons, selecting strong electron-donating groups was obvious. Third, two of the dyes selected were IR-shifted dyes. These dyes were chosen because the likelihood of viewing the dye-stained prints on an infrared monitor was greater. Infrared-shifted dyes were chosen to combat the background fluorescence problem noted in the literature. In the following section, fluorescence principles are explained in greater detail.

Fluorescence is the emission of radiation following absorption of more energetic radiation. It is the emission of radiation from substances which arise from a radiative transfer between an excited state to a ground state (Figure 2). A typical excitation curve is depicted in Figure 3. The corresponding emission, or fluorescence spectrum, is presented in Figure 4.

A substance first absorbs radiation which causes it to be promoted to an excited state. Some energy is lost as heat or conversion to internal energy. As energy is lost, the excited state is reduced to its lowest energy level for the excited state. The energy returns to the ground state and in the process emits a photon of light of longer wavelength than the absorbed light.

Excited states involve promotion of one electron of an electron pair. These electrons are paired in each orbital and following promotion, one electron remains paired to the other electron in the ground state. Such a phenomenon is termed an excited singlet state. Molecular orbitals in organic compounds, such as fluorescent dyes, encompass the entire molecule. Since the electrons are delocalized within the compound, chemical bonding is enhanced which aids in the promotion of

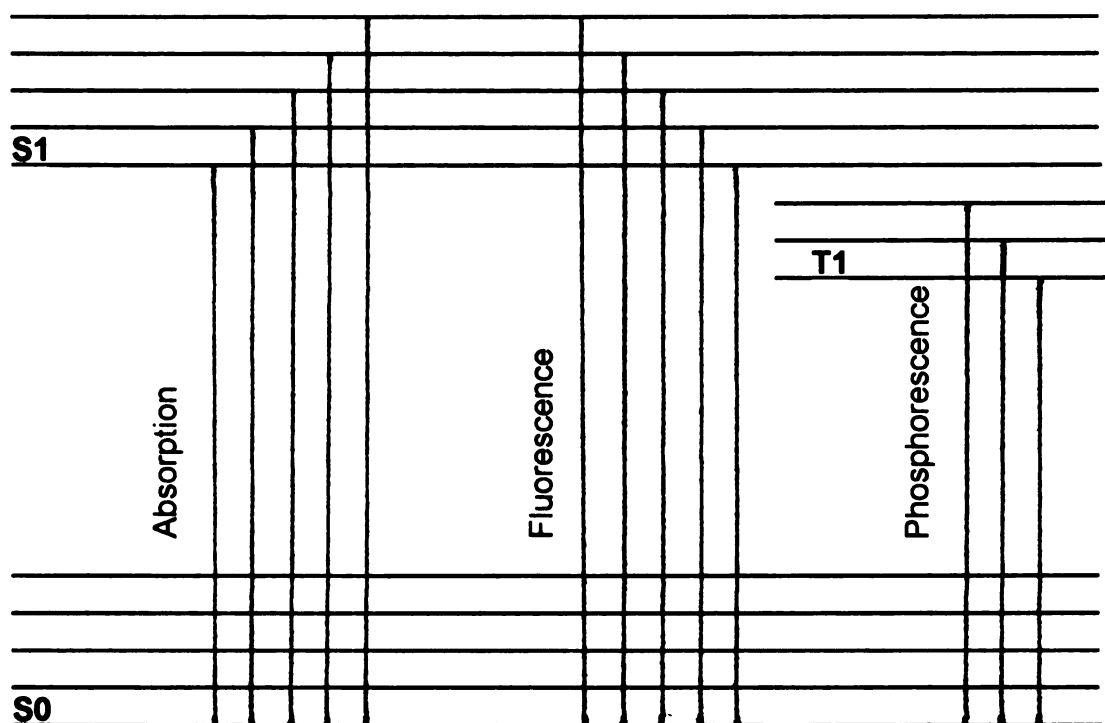


Figure 2. Absorption, Fluorescence, and Phosphorescence Energy Levels.

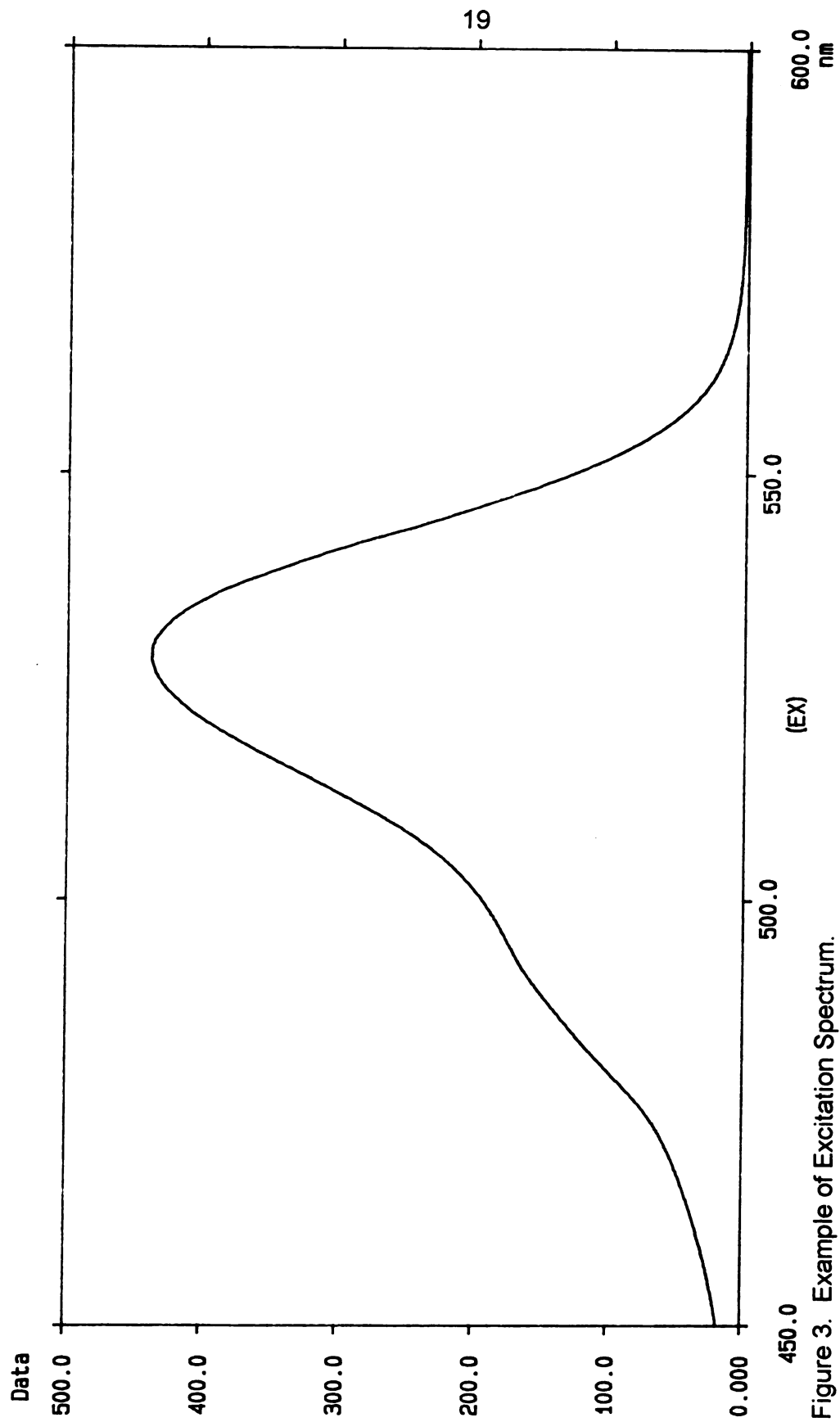


Figure 3. Example of Excitation Spectrum.

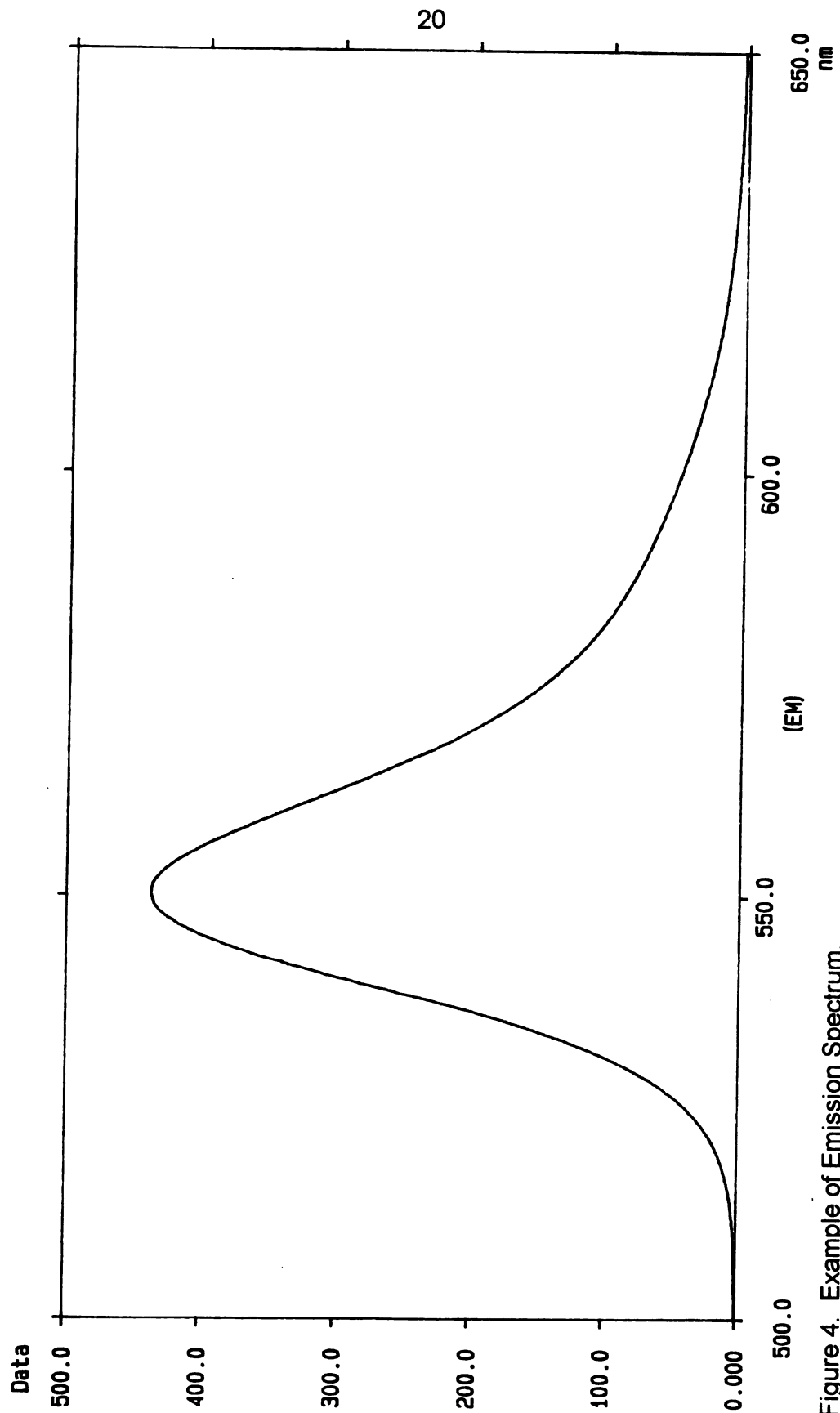


Figure 4. Example of Emission Spectrum.

electrons. Excited states possess different geometries with different interatomic distances and varying dipole moments.

With respect to organic chemical systems, a low-energy state involves primarily two states. One involves the $\pi\text{-}\pi^*$ state which means a π -bonding molecular orbital is promoted to a π -antibonding molecular orbital. The other involves the $n\text{-}\pi^*$ state which involves a nonbonding orbital to a π -antibonding orbital.

Maximum absorption of energy occurs at a higher energy (smaller wavelength) than fluorescence. Fluorescence, therefore, occurs at a lower energy (longer wavelength) than the maximum absorption. The distance between maximum absorption and maximum emission is called the Stokes shift. In other words, this distance is the amount of energy released between the excitation state and the eventual return to the ground state. Since fluorescence does not involve a change in electron spin, they are short-lived emissions with strong absorptions, large rate constants, and short lifetimes (Demas & Demas, 1991).

A rigid structure increases fluorescence as well as compounds that contain electron donating groups. A rigid structure diminishes the effect of the internal conversion rate, intersystem crossing rate, and the photochemical decomposition rate, thereby increasing the fluorescence efficiency. In competition with fluorescence is a term called quenching. Of the several types of quenching, concentration quenching involves a decrease in fluorescence intensity with increasing concentration. At low concentrations, fluorescence intensity is linear which allows for the optimal selection of dye concentrations.

For this research, fluorescent dyes were chosen based on having the maximum absorption close to the output of the argon laser. If dyes were reported to have an absorption value slightly outside that of interest for laser excitation, dyes with amino or dimethylamino groups were sought as visualizing agents from latent prints. These are strong electron donating groups which would assist in fluorescence.

Since the illumination source must closely match the absorption spectrum of the dye, few sources are perfect as sources of illumination of dye-stained prints. One source is the argon laser; the other non-laser illumination sources are collectively known as "forensic light sources".

Fluorescence techniques provide increased sensitivity as well as having the fluorescent radiation being proportional to incident power. This allows the examiner to take advantage of the power of most lasers. Also, the examiner could utilize the tuneable wavelengths of a forensic light source.

Fluorescent dyes provide greater sensitivity because the absorbed light is remitted as a form of light. Of course, the light emits at a longer wavelength than the absorbed light. Colors that the eye normally sees are the result of complementary wavelengths after certain wavelengths are absorbed. Certain colors can be used to provide contrast between background and dyed prints, therefore increasing detectability.

With the fluorescent dyes in hand, initial effort was directed at targeting an effective concentration for dye application. This involved placing prints on microscope slides. All prints were placed using only the three middle fingers. This

was noted in prior research that would allow prints of roughly the same surface area. All prints were placed under medium pressure. This is a subjective measure and no attempt was made to determine the force applied per unit area.

With the prints placed on microscope slides, the fuming chamber was prepared by first humidifying for five minutes. A moist paper towel was placed under a hair-dryer. For heat acceleration of the cyanoacrylate fuming, a hair dryer was used.

The cyanoacrylate must first be volatilized in order for polymerization on the latent print to occur. After humidifying the chamber, 10-20 drops of cyanoacrylate were placed in an aluminum weigh boat and placed on the moist paper towel beneath the hair dryer.

The chamber occupied approximately thirty square feet. Microscope slides were placed in the chamber and exposed for 20-25 minutes. A test print was placed on the chamber window to signal sufficient fuming. Ventilation of the fumes was accomplished by operating one fan at the north end and one at the south end which connected to an exhaust hose. After a few minutes of ventilation, the chamber was opened and the fumed prints were allowed to dry.

While fuming was in progress, dye solutions were prepared using 50 mg of dye dissolved in 50 mL of methanol. Methanol was used due to low cost, readily available, low toxicity, high volatility, and reduced risk of explosion that is associated with pet ether. However, flammability is still a concern in the laboratory. Since there is greater control over the concentration of the dyes, a range of dye solutions were prepared.

From this stock solution, aliquots ranging from .01 to .10 mL were pipetted into ten test tubes. Methanol was then poured to a 10 mL mark on the test tube. A second series of dye solutions was prepared using aliquots ranging from .1 to 1.0 mL of stock solution. To each of these methanol was added to the 10 mL mark.

The dye solutions were taken to a fume hood where application of the dye was performed. A pasteur pipet and suction bulb were used to draw up from each concentration. Initially two applications of the dye solution was applied to each slide. However, this lead to excessive staining of the print when later viewed with the argon laser. Therefore, only one application of the dye solution was used. The volume dispensed was approximately 2 mL. The carrier solvent (methanol) was allowed to evaporate. Laser operating principles are discussed in the following section.

L.A.S.E.R. stands for light amplification of stimulated emission of radiation. In order for a laser to work, energy must first be channeled into the unit. The energy required to excite electrons can come from an electrical discharge, electrical current, or exposure to a radiant source, such as a flashlamp. This is known as pumping the laser and is used to attain population inversion. Population inversion is a condition where more electrons are in the excited state than in the ground state.

Once energy is pumped into the laser, electrons are promoted to a higher electronic state and soon return to the ground state. Known as spontaneous emission, this is an important part of laser action. During spontaneous emission, stimulated emission may also occur. This is when a photon of energy value of X

collides with an excited atom having that same energy X and results in two atoms with the same phase, polarization, and direction. Since stimulated emission requires atoms in the excited state, population inversion must be present. Otherwise, the majority of atoms are in the ground state where the probability of absorption over population inversion would occur. While under the influence of population inversion, a metastable state exists wherein the electrons remain excited longer than in ordinary excited states.

The familiar output of a laser, commonly known as the "beam", is produced by using two coated mirrors. One mirror is fully reflecting and the other is partially reflecting or may contain a small hole in the center. This allows the avalanche of photons to be directed into a narrow beam of coherent and monochromatic light. Coherent and monochromatic light refer to all light waves being in phase with each other and of only a few select wavelengths, respectively. Laser light is the result of stimulated emission, whereas fluorescence is the result of spontaneous emission.

One benefit of using a laser to excite fluorescence in a substance is the fact that the power of fluorescent radiation is proportional to the radiant power of the excitation beam that is absorbed by the system ($F = K' (P_o - P)$). Therefore, the intensity or brilliance of fluorescence is directly related to intensity of the light source. It should be noted that the fluorescent power versus concentration plot is linear at low concentrations.

Since lasers can produce outputs of several watts, the intensity of the fluorescent dye is dramatically increased. If stimulated emission occurs in a

contained laser cavity, highly directional monochromatic light is produced. Although a lamp may operate at 100 Watts, the output light is polychromatic, incoherent, and emits multidirectional light. So by using a light bulb of 100 W, the needed wavelength for the maximum absorbance of a fluorescent dye excites the dye with minimal radiant power.

The copper vapor laser is a pulsed laser as opposed to the continuous wave of the argon laser. Its shortest line at 510 nm which emits green light. Complexes such as Ruhemann's purple and zinc chloride absorb around 490 nm. The difference of 20 nm is sufficient to render the copper vapor laser less effective than the argon laser, since optimal excitation of the fluorescent dye is dependent upon wavelength of the source. The primary advantage of the argon laser over the copper vapor laser is that the argon can be operated in the near ultraviolet between 350 and 365 nm.

Another laser in fingerprint work is the frequency doubled neodymium:yttrium aluminum garnet (Nd:YAG). This laser is pulsed like the copper vapor laser and emits at 532 nm. The Nd:YAG suffers from similar disadvantages as the copper vapor laser, specifically pulsed lasers with inadequate average powers to generate fluorescence. Tradition has also hindered the use of other lasers since treatment methods have been tailored for use with an argon laser.

Once the fumed and dyed prints were dry, the slides were viewed under a 17W argon laser. A Spectra-Physics model 171 was used in all lines lasing instead of the single line mode. This was done to ensure that several intense wavelengths struck the fluorescent dye-stained print. With orange laser goggles on,

wavelengths of 530 and above were transmitted to the eye. Each dye-stained slide was examined under argon laser light and notes on the degree of brilliance of fluorescence were determined qualitatively. Each slide containing the varying concentrations were observed. Since Rhodamine 6G is a standard fluorescent dye, the dye-stained prints were compared alongside a stained print of Rhodamine 6G.

Photographs were taken of the prints visualized with each dye. A 4 x 5 camera was used which was mounted on a tripod. Kodak Orthochromatic and Technical Pan films were used. Single sheet film permitted viewing the exposure times and correcting them if necessary. Development of the film employed Developer B and then Kodafix solution to fix the negative.

As noted earlier, successful adherence of the dye to the fumed print relates directly to the initial amount of fingerprint residue deposited. Accordingly the degree to which the dye adhered to the print varies with each fuming session. Visual attempts were made to ensure that similar slides produced relatively uniform distribution of cyanoacrylate per print per slide.

The fumed prints were then dyed with each of our combination dye sets; RAMS, RAM-E, RAM-N, RAMIR. The success of using a combination dye set with a red-shifted fluorescent dye is depicted in a series of pictures in Figures 5a through 5f. Print outs were obtained from the Doya J-700 and the Mitsubishi printer.

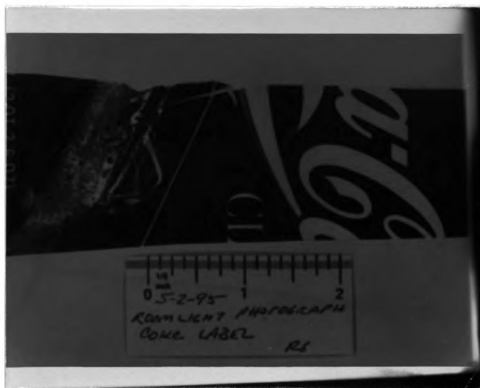


Figure 5a. Room Light Photo of Fumed and Dyed Print.



Figure 5b. Laser Illumination of Fumed and Dyed Print.



Figure 5c. Infrared Illumination of Fumed and Dyed Print (Styryl 7).



Figure 5d. Infrared Illumination of Fumed and Dyed Print (Nile Blue A Perchlorate).



Figure 5e. Infrared Illumination of Fumed and Dyed Print (Ethidium Bromide).

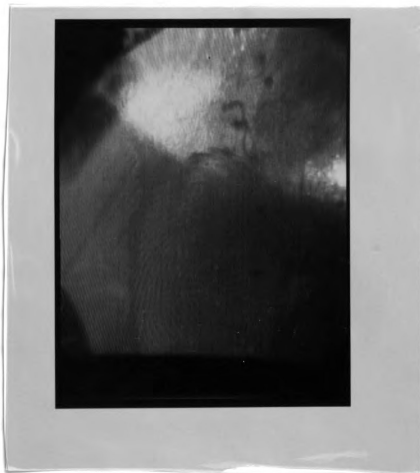


Figure 5f. Infrared Illumination of Fumed and Dyed Print (IR - 144).

Findings

The results of the research indicate four major areas of knowledge. First, Evans Blue did not produce sufficient intensity to warrant further study beyond the two sets of concentrations. The dye lacked fluorescence at the level needed for the latent print examiner.

Second, DTAF and 5-FIT can be used as a replacement for the carcinogenic reagent Rhodamine 6G. It should be noted that these dyes emit significantly low levels of fluorescence when compared to Rhodamine 6G. Furthermore, additional research with these dyes may provide greater support for the use of these dyes.

Third, LISSAMINE (Rhodamine B Sulfonyl Chloride) produced average results indicating that other dyes are more suitable for latent fingerprint work. Since other dyes tested produced overwhelming fluorescence when compared to LISSAMINE, further testing was suspended.

Fourth, Styryl 7, Ethidium Bromide, Nile Blue A Perchlorate, and IR-144 generated profound interest in the ability to shift fluorescence into the infrared region. By doing so, any background fluorescence is practically eliminated. Room light photos revealed no detail of the fumed print. The two liter Coke label produced fluorescence when illuminated with the argon laser thus masking any fluorescence generated by the dye. However, when viewed with the infrared camera a print was able to be identified. Once identified a thermal print of the ridge

detail was produced. A series of photos are presented to illustrate the findings.

The findings of the research can be condensed into one table. Table 1 represents all findings condensed onto a single page. On Table 1, molecular weight is given following the name of each dye tested. The excitation (ex) and emission (em) wavelengths are presented. Next is the concentration of the initial stock solution followed by the ideal volume to be used for dye application. From these two items the ideal concentration to be used is calculated and presented. Next is the volume of ideal concentration to be added to the RAM solution to make 100 mL combination dye solution. Lastly, the cost of each dye is presented.

All things being equal, the brilliance of fluorescence, the amount of dye used, and cost were variables used to determine the rank for the infrared dyes. Court presentation does not hinder on a quantity associated with the degree of fluorescence but rather if the prints were made identifiable by a certain technique.

Styryl 7 was chosen as the best infrared fluorescing dye due to low cost, greater brilliance, and small amounts needed to produce satisfactory results. Nile Blue A Perchlorate was second despite the slightly higher price per gram than Ethidium Bromide because Nile Blue produced better results than Ethidium Bromide. IR - 144 was ranked fourth due to the cost of IR - 144 and the not so satisfactory results. It should be noted that all dyes appear to have potential were interested in shifting the fluorescent dye range to the infrared region of the electromagnetic spectrum.

Problems with the method relate to proper fuming and staining of suspected latent prints. Once sufficient amount of cyanoacrylate is deposited on the print,

FLUORESCENT DYE NAME	MW	EX WL	EM WL	STOCK CONC.(M)	IDEAL VOLUME	IDEAL CONC.(M)	COMBINATION DYE VOLUME	COST /g
DTAF	531.74	495	530	1.911E10-3	1 mL	1.911E10-4	N/A	66.15
Ethidium Bromide	394.32	545	610	2.551E10-3	1 mL	2.551E10-5	10 mL	27.25
5-Fluorescein Isothiocyanate	389.39	492	513	2.575E10-3	0.6 mL	1.540E10-4	N/A	50.05
IR-144	1008.36	745	825	1.032E10-3	1 mL	1.032E10-4	6 mL	258.40
LISSAMINE	577.12	570	590	1.802E10-3	0.4/0.6 mL	7.200E10-5	N/A	77.45
Nile Blue A Perchlorate	417.85	627	660	2.441E10-3	0.2/0.4 mL	4.880E10-5	4 mL	66.70
Styryl 7	506.42	560	704	1.997E10-3	0.1 mL	1.990E10-5	2 mL	48.75

Table 1. Comparison Among Seven Fluorescent Dyes.

only a smooth application of the dye solution is needed to visualize the print.

Overfuming and overstaining need to be addressed in order to avoid obtaining an unidentifiable print.

Conclusions & Recommendations

After a careful review of the research literature, this research attempted to find suitable replacements for the carcinogenic reagent Rhodamine 6G. Although DTAF and 5-FIT were found to produce satisfactory results, albeit with reduced intensity, further research is needed to determine if these dyes can be adapted to fingerprint work as a suitable replacement for Rhodamine 6G.

This research was also interested in minimizing the amount of background fluorescence experienced throughout the forensic literature. Styryl 7, Nile Blue A Perchlorate, and Ethidium Bromide proved to be of significant interest to be used to visualize latent prints on non-porous substrates fumed with cyanoacrylate.

The labor, cost, and results of the infrared dyes are comparable to other dye staining methods. An additional advantage is that the background fluorescence is practically eliminated. Consequently, only the stained print is visible under the infrared monitor. A printout can be obtained or can be digitized into a computer to be search with AFIS. In sum, an improvement in detecting, developing, and visualizing latent prints has been made.

As with all research projects, suggestions are made as to what should be tested next. Several authors indicated success with using methyl ethyl ketone and water as the carrier solvent. This would allow penetration into the cyanoacrylate

generated with the argon laser light.

An additional suggestion for future research is to explore these red-shifted and infrared dyes on other items of evidence. Prints were captured on an infrared monitor and printed by a thermal printer, perhaps prints on other difficult or fluorescing backgrounds could be rendered identifiable as well.

APPENDIX

Excitation and Emission Spectra of Fluorescent Dyes and Combination Dyes.

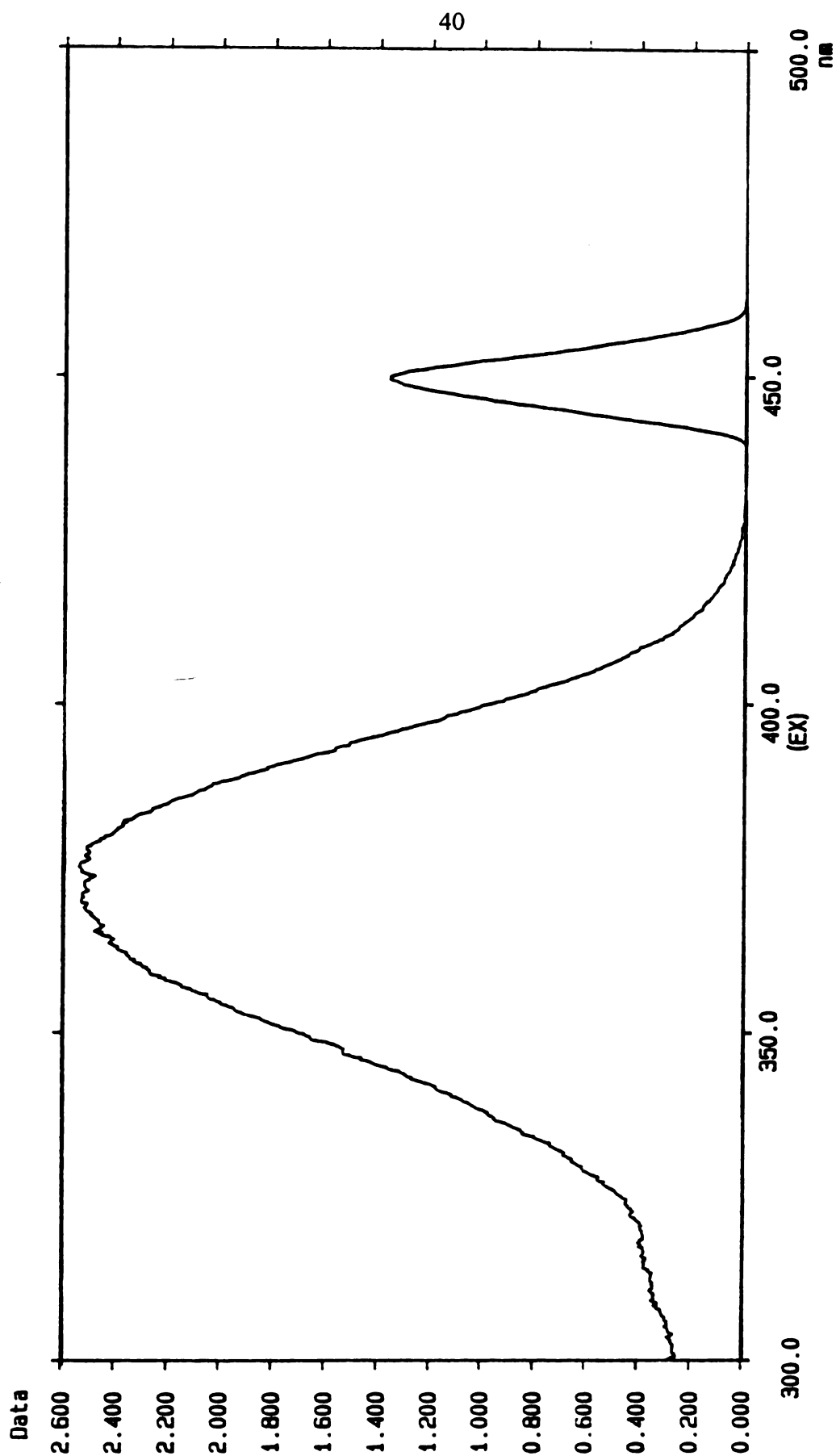


Figure 6. Ardrox Excitation Spectrum.

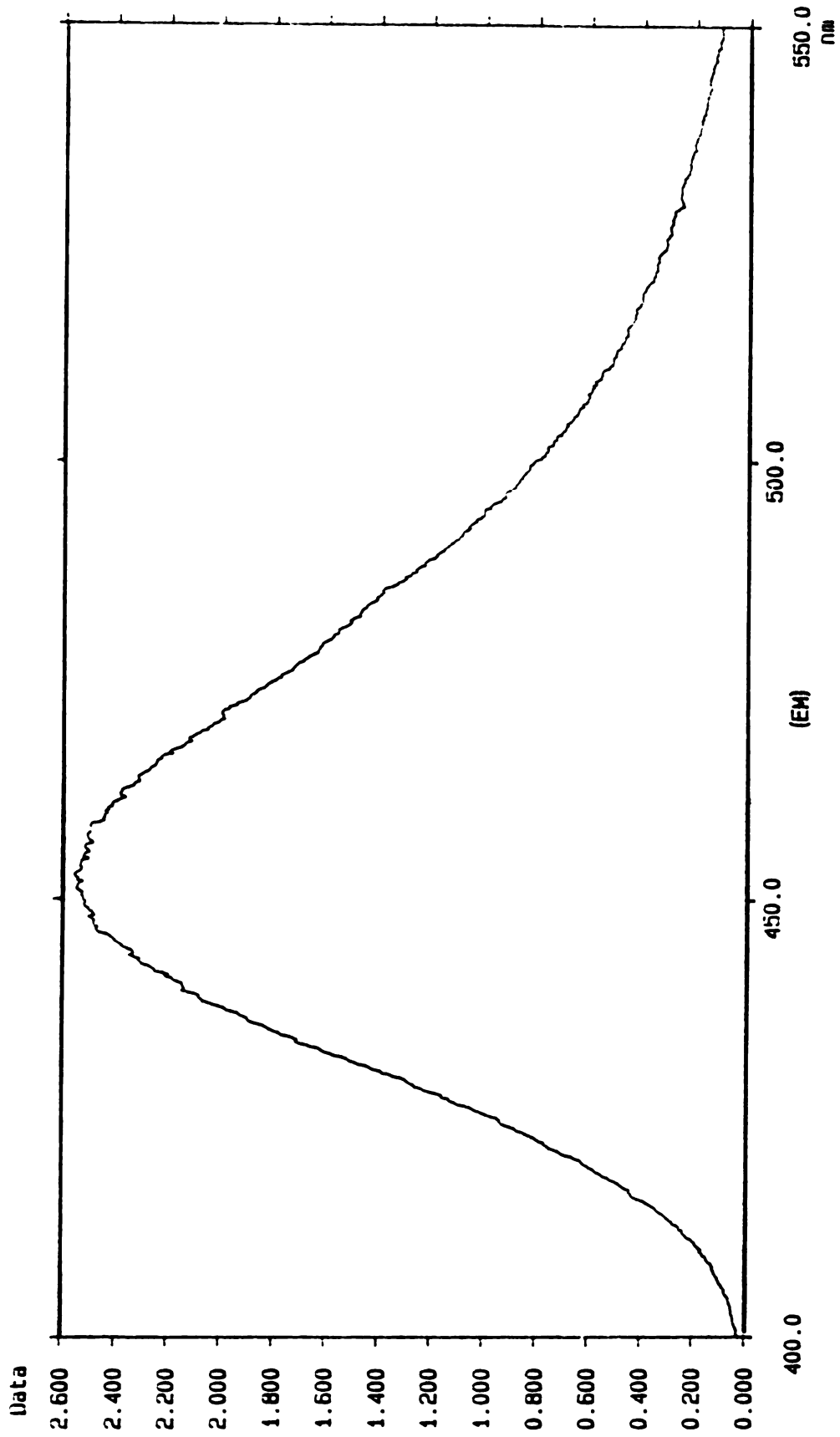


Figure 7. Ardrox Emission Spectrum.

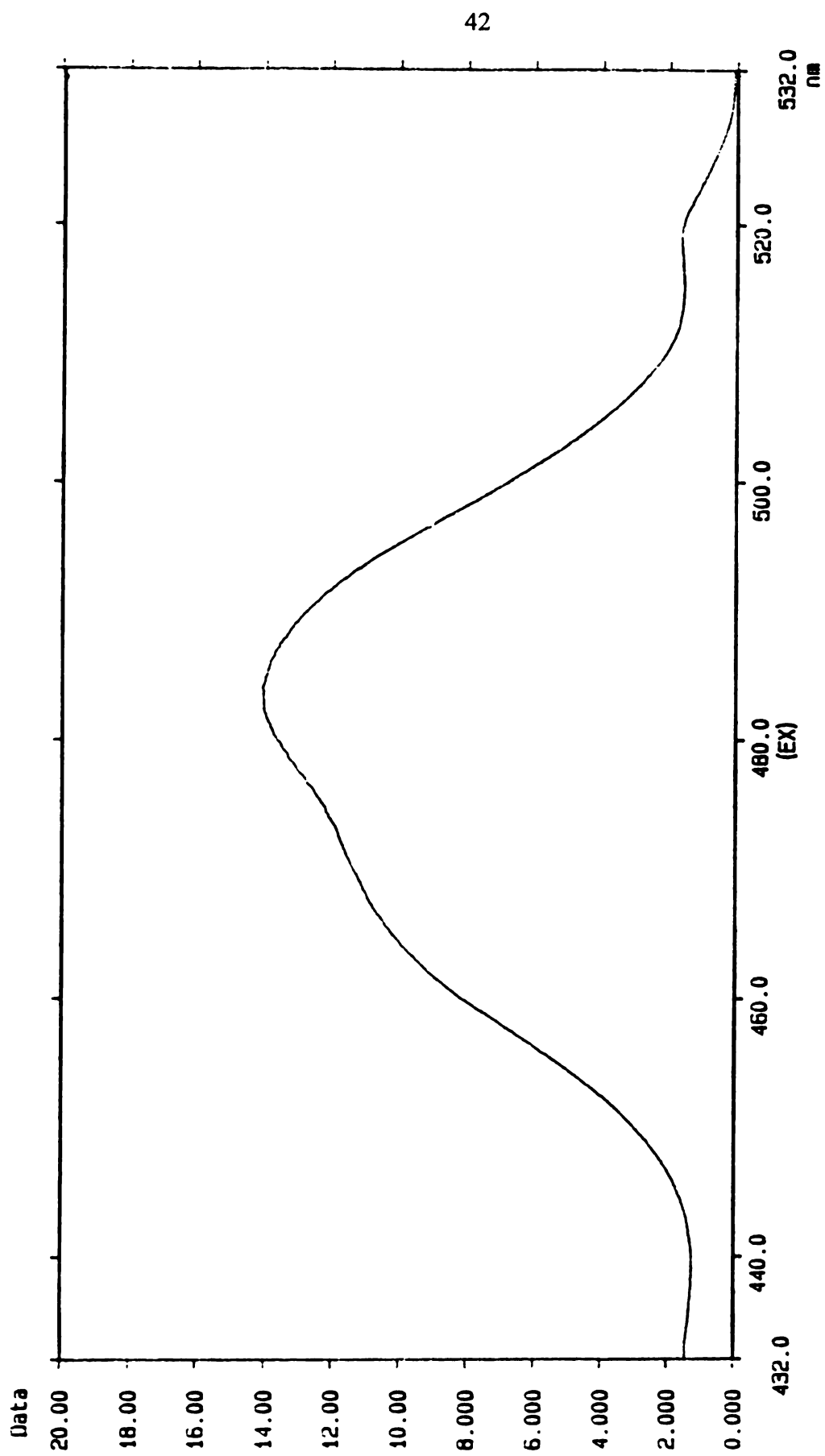


Figure 8. DTAF Excitation Spectrum.

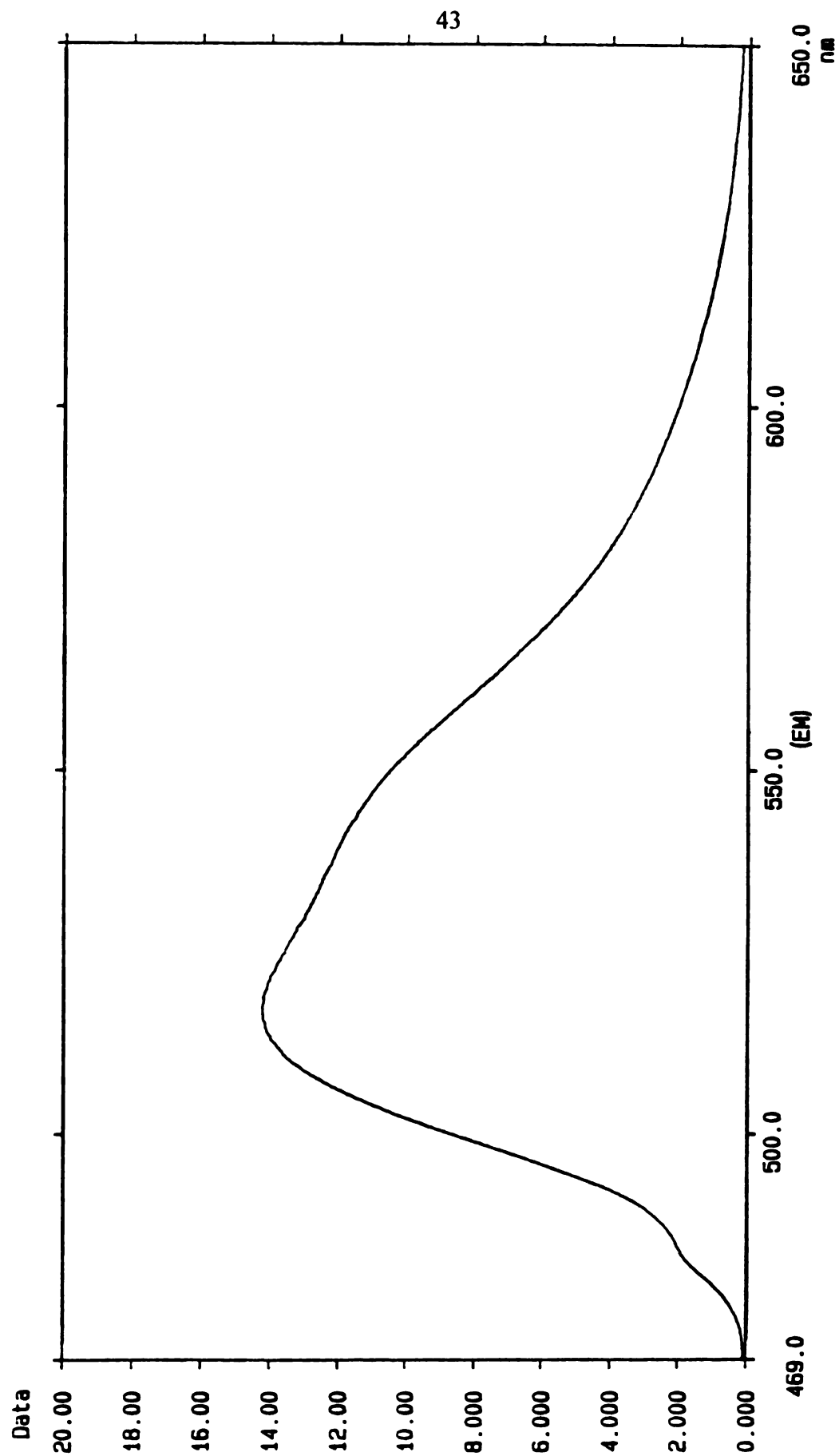


Figure 9. DTAF Emission Spectrum.

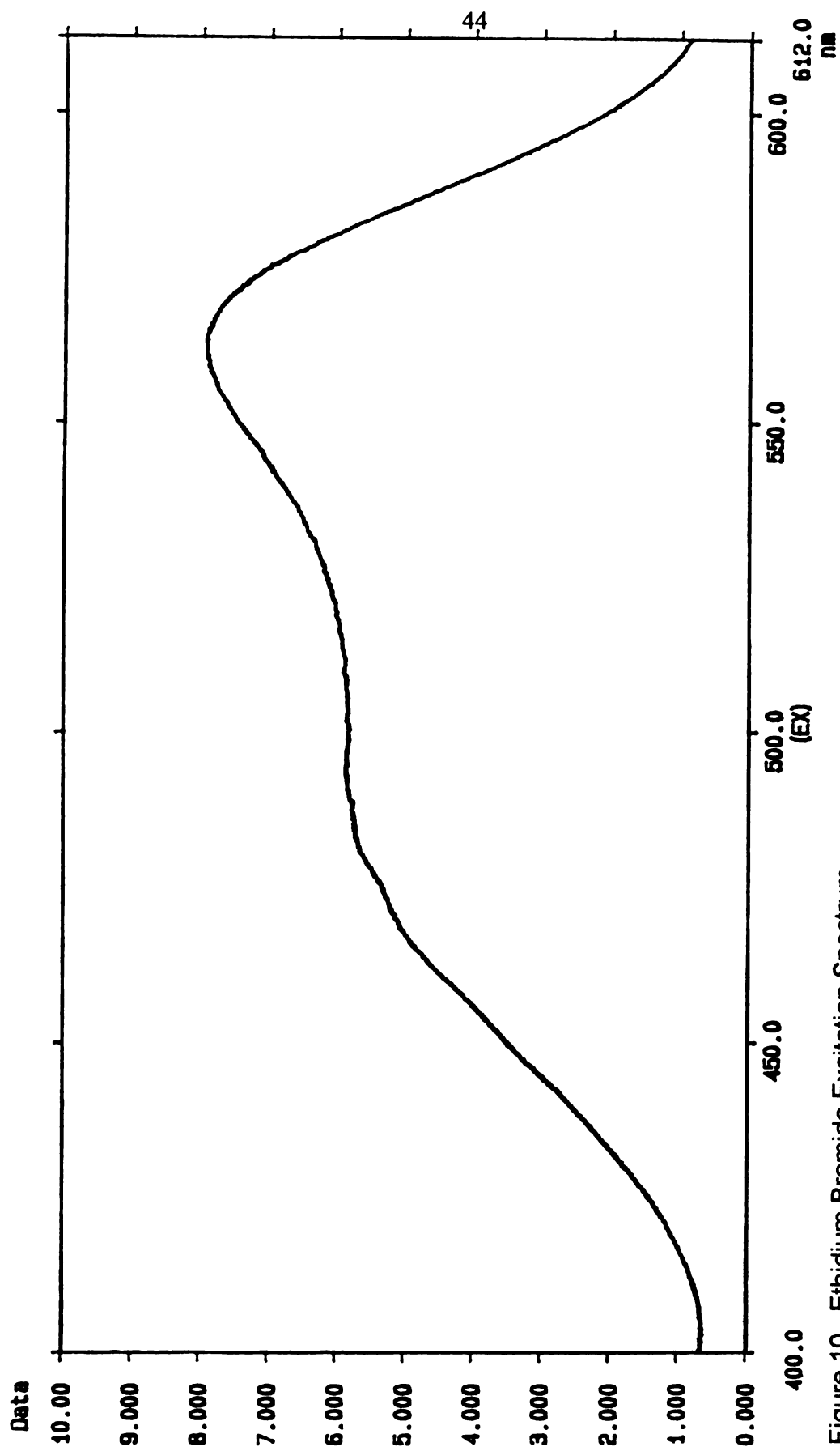


Figure 10. Ethidium Bromide Excitation Spectrum.

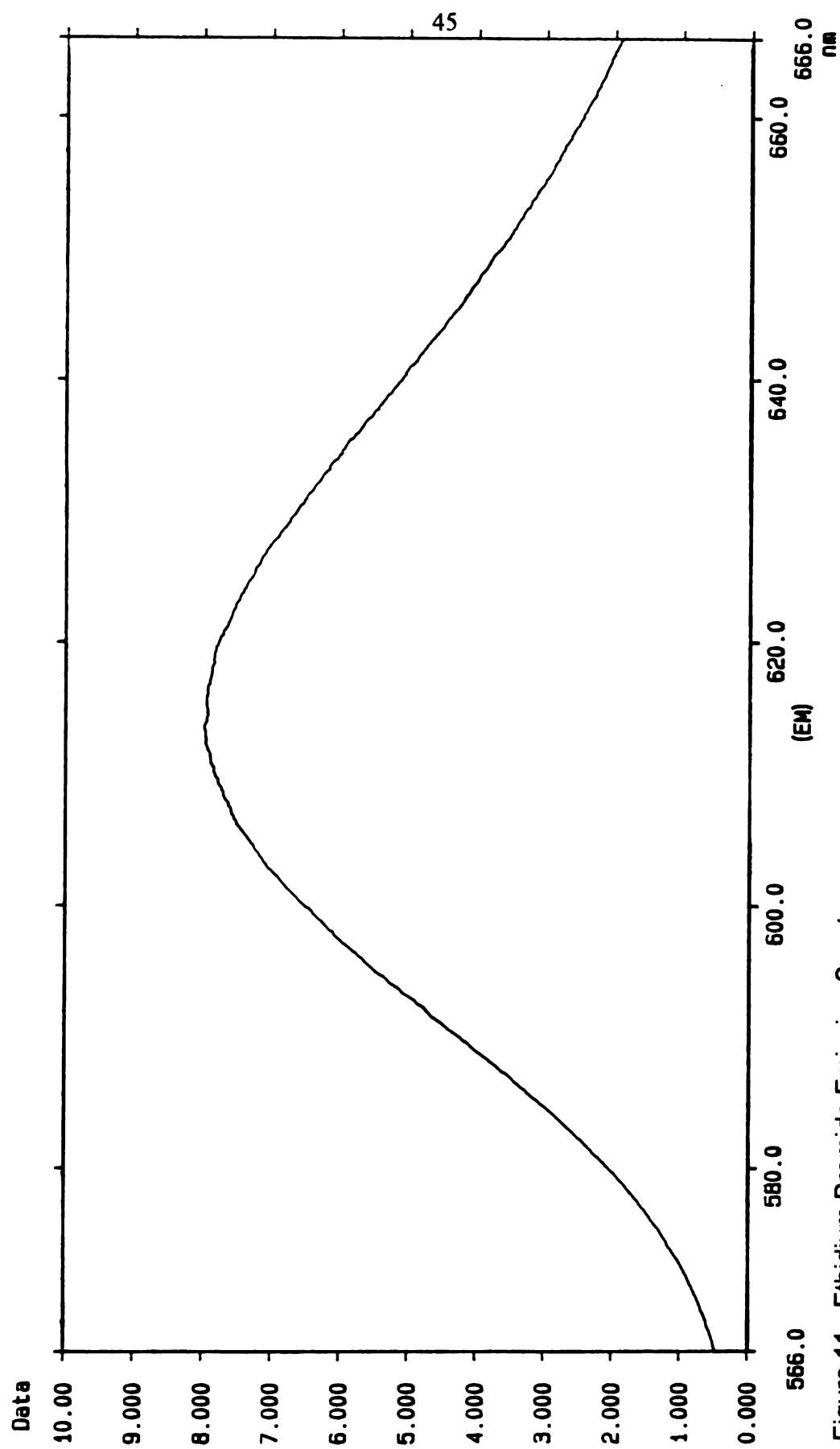


Figure 11. Ethidium Bromide Emission Spectrum.

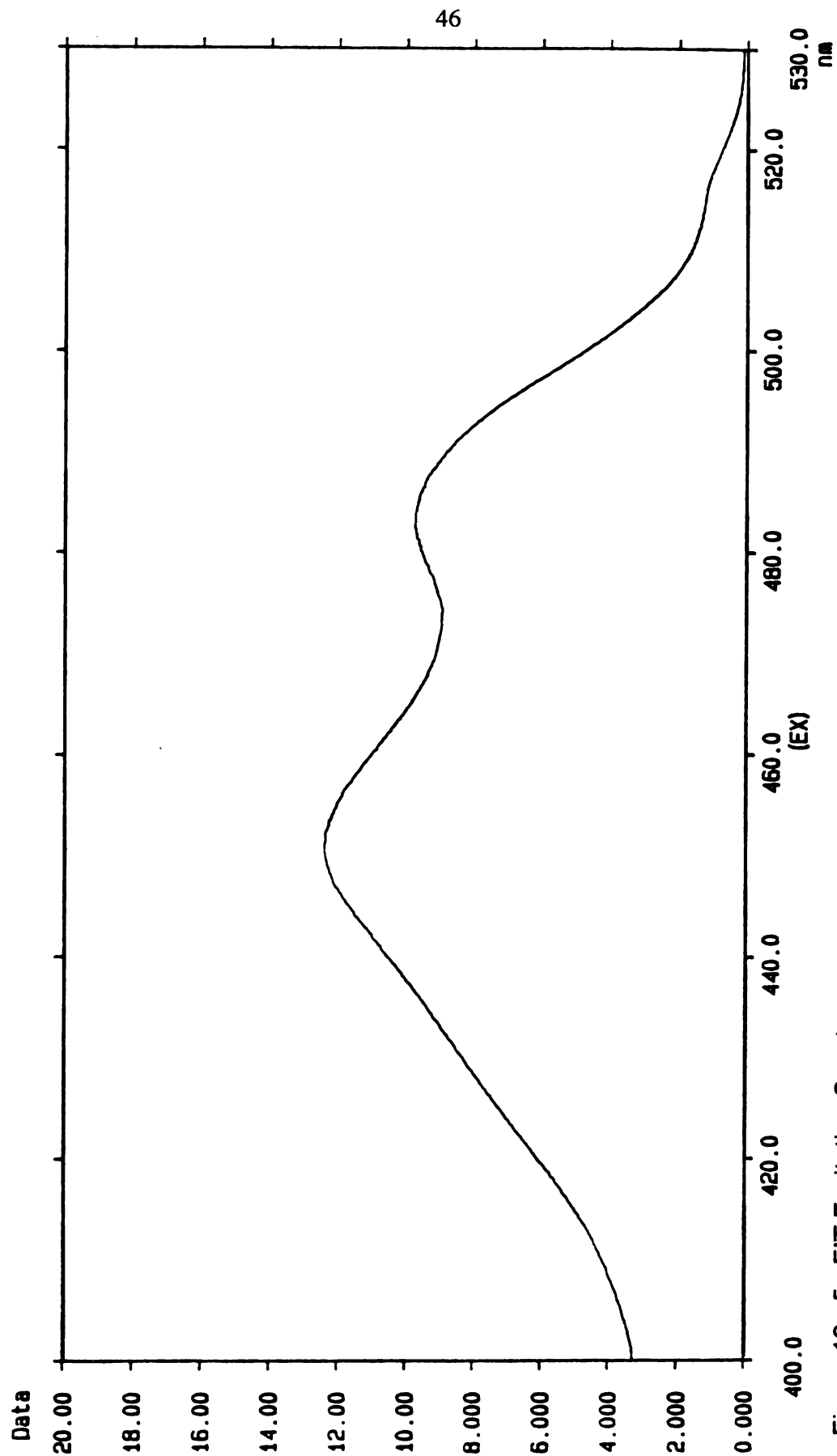


Figure 12. 5 - FIT Excitation Spectrum.

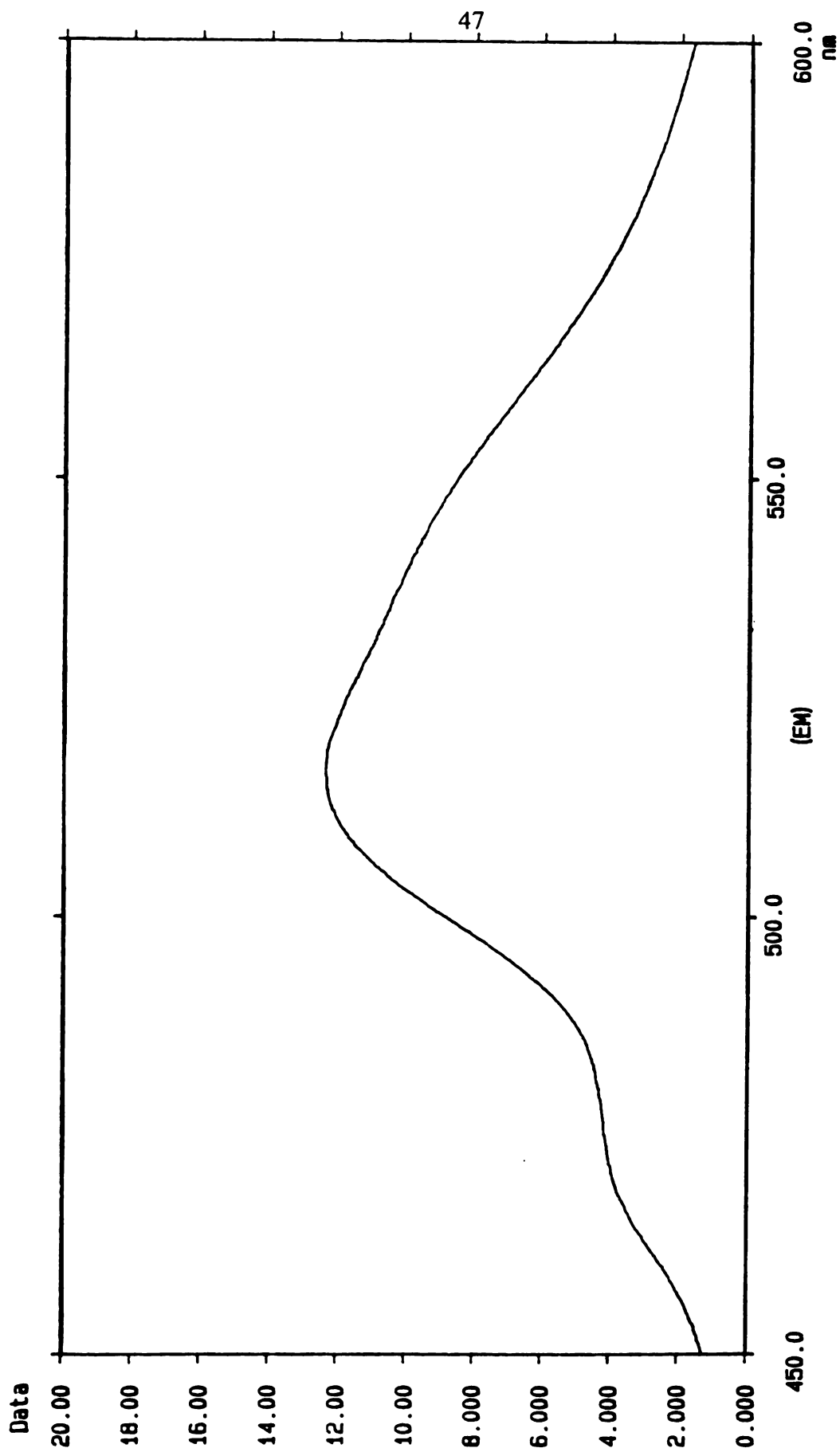


Figure 13. 5 - FIT Emission Spectrum.

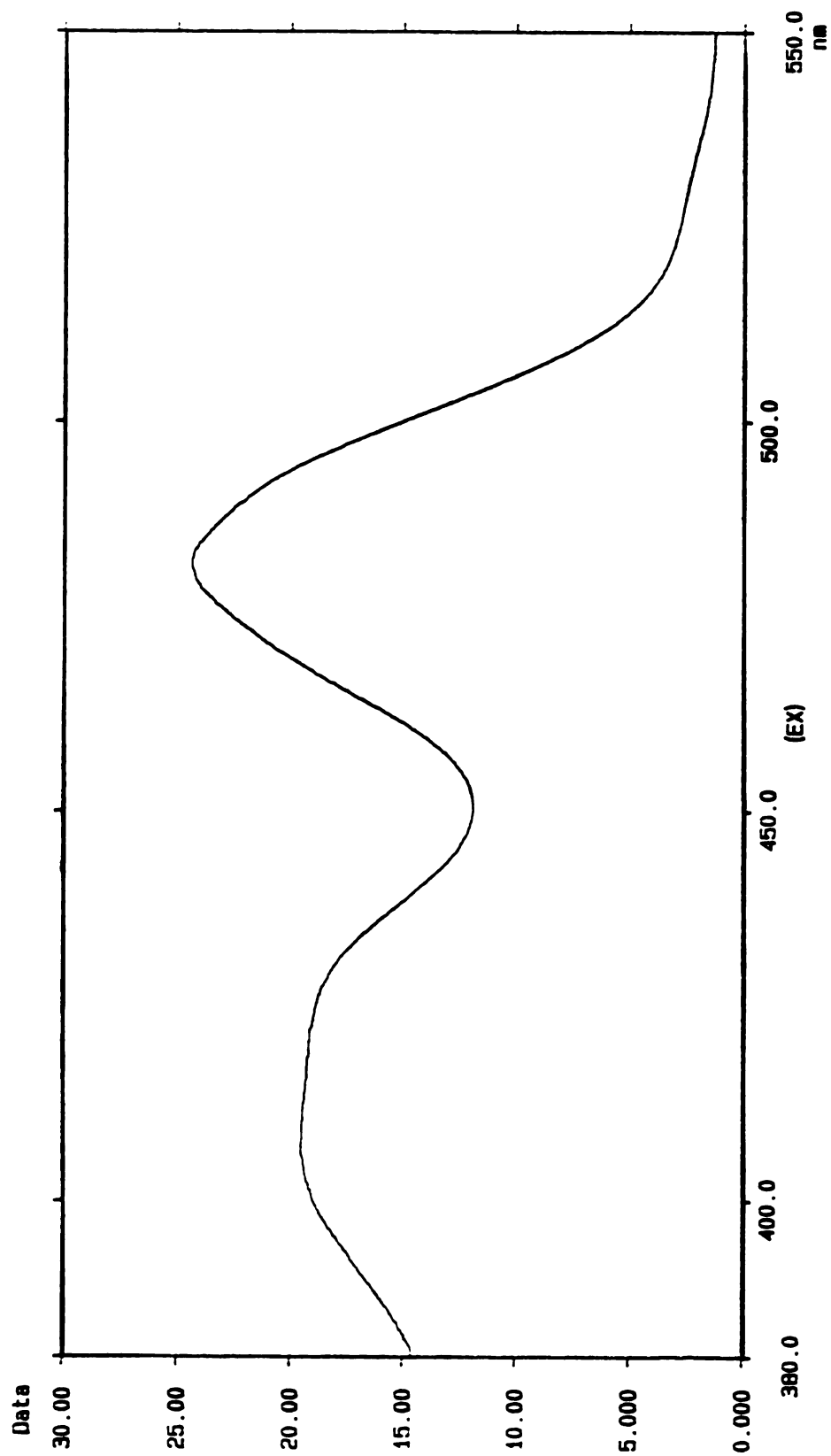


Figure 14. LISSAMINE Excitation Spectrum.

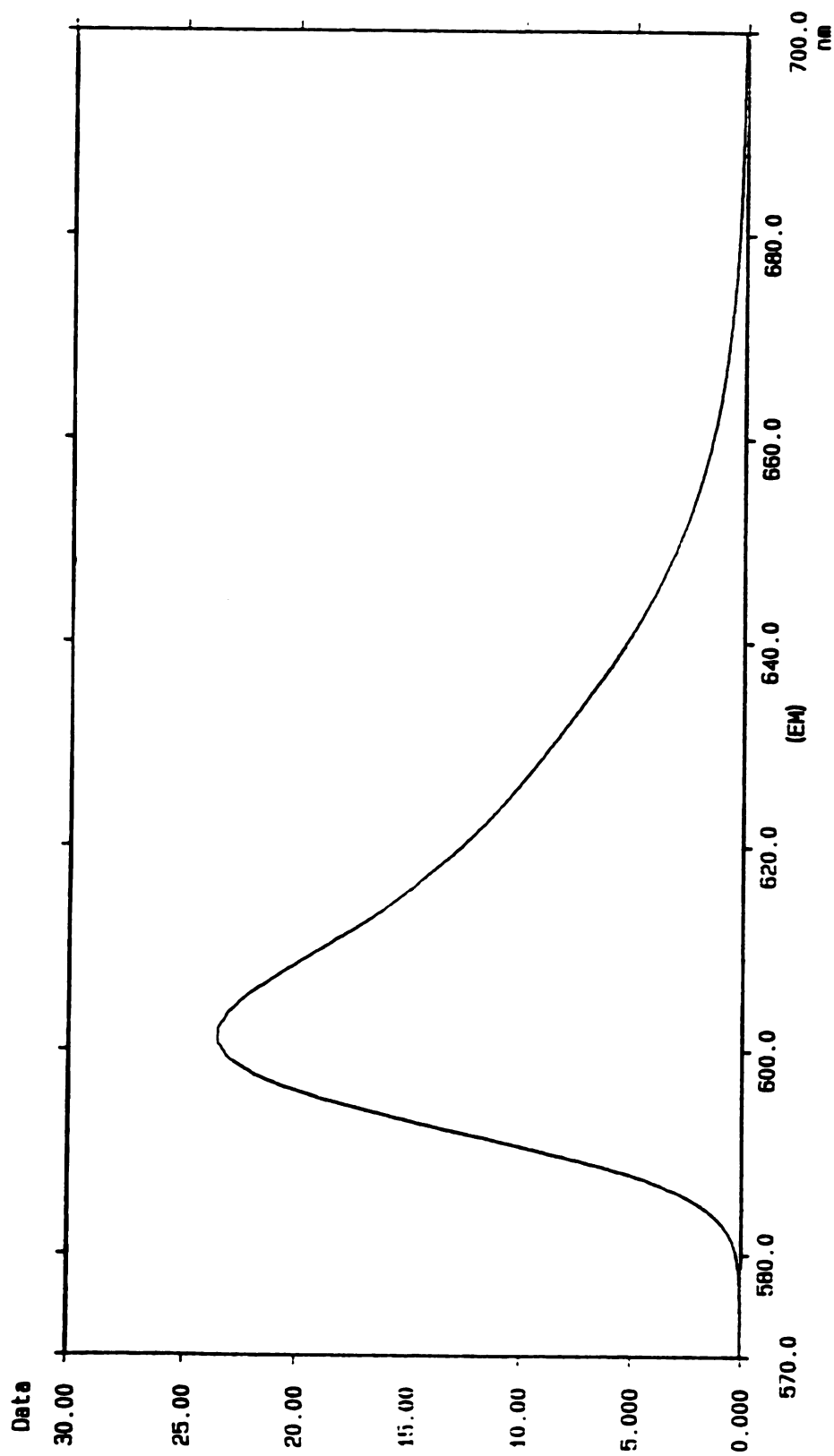


Figure 15. LISSAMINE Emission Spectrum.

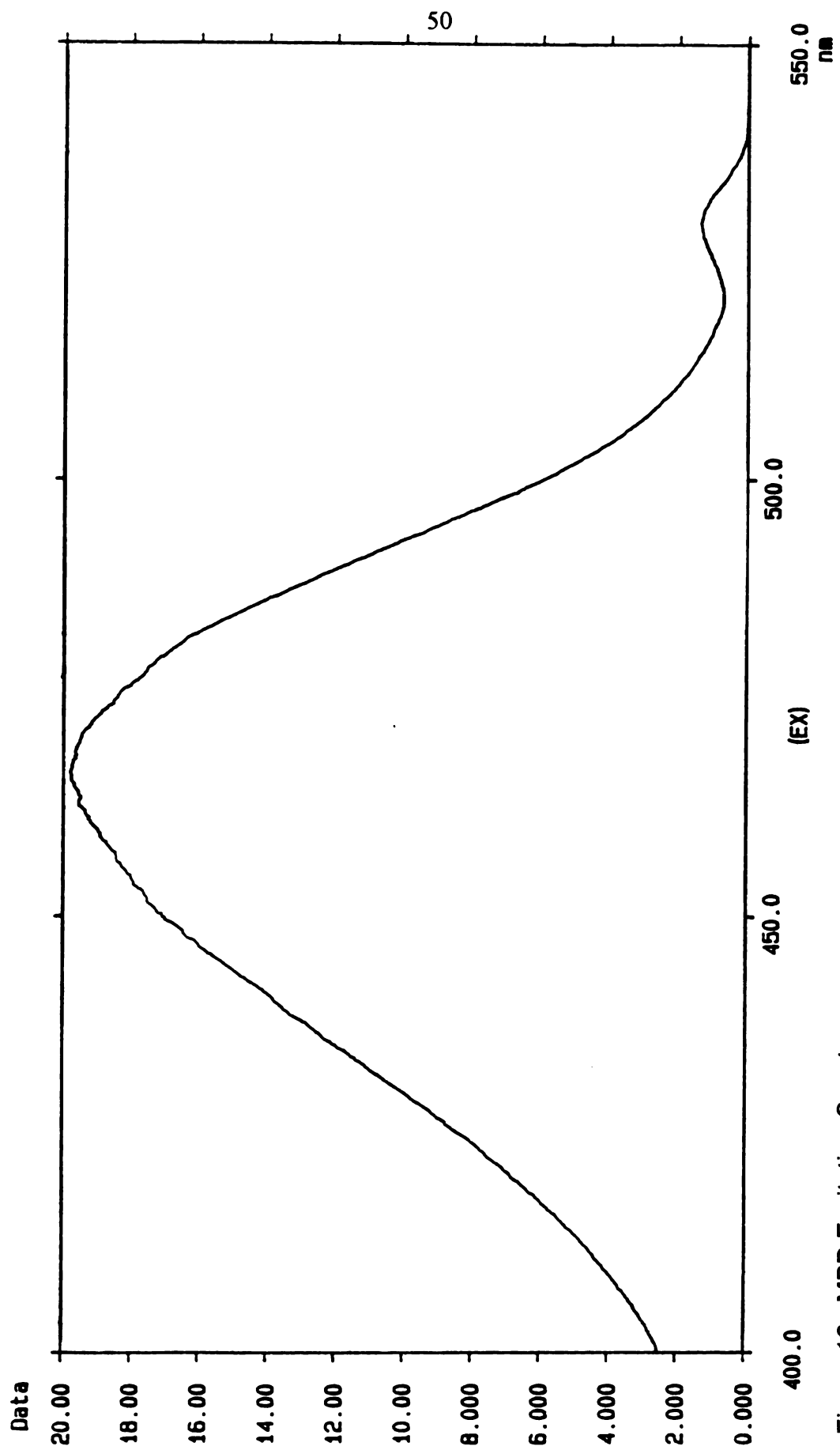


Figure 16. MBD Excitation Spectrum.

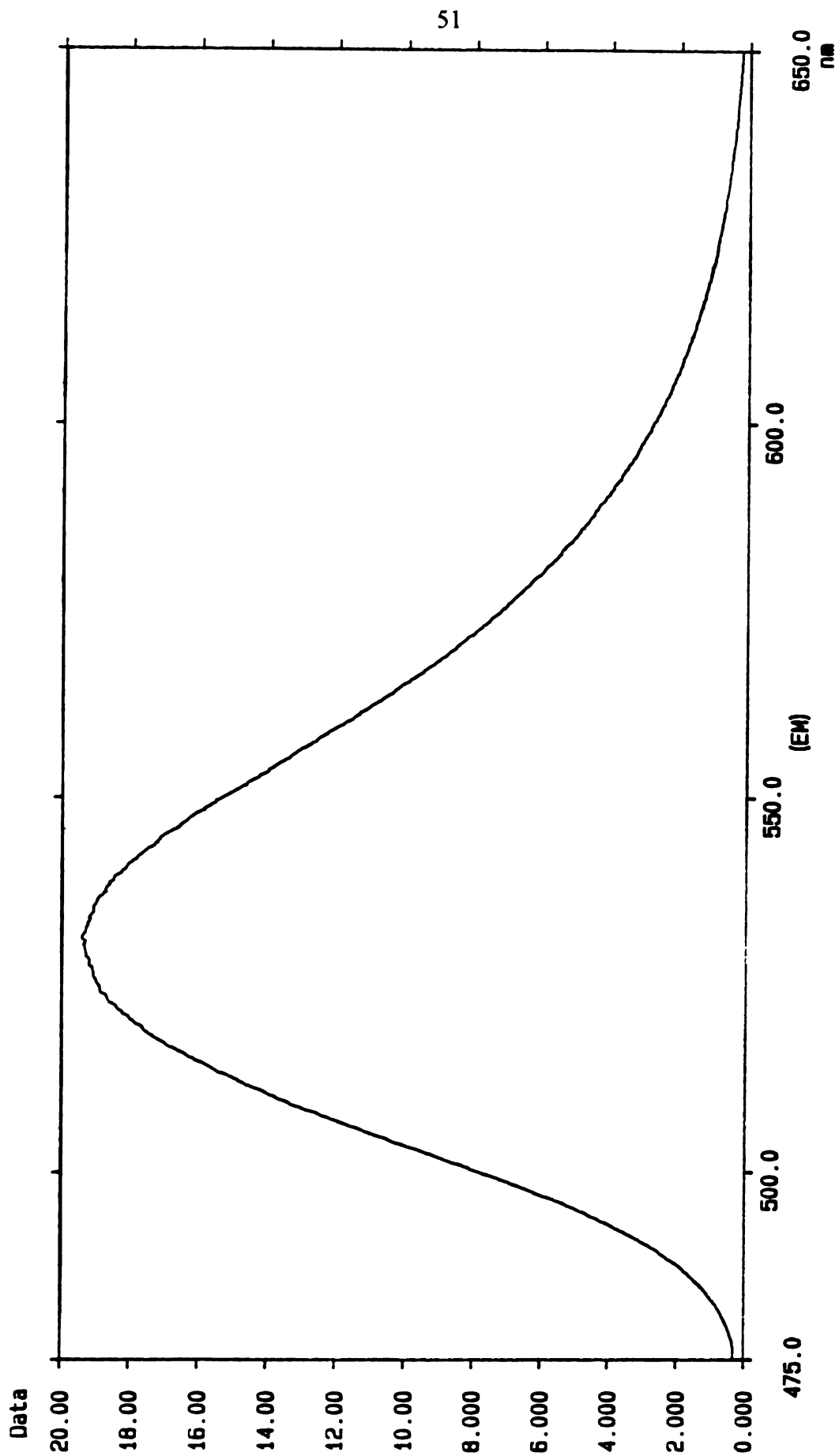


Figure 17. MBD Emission Spectrum.

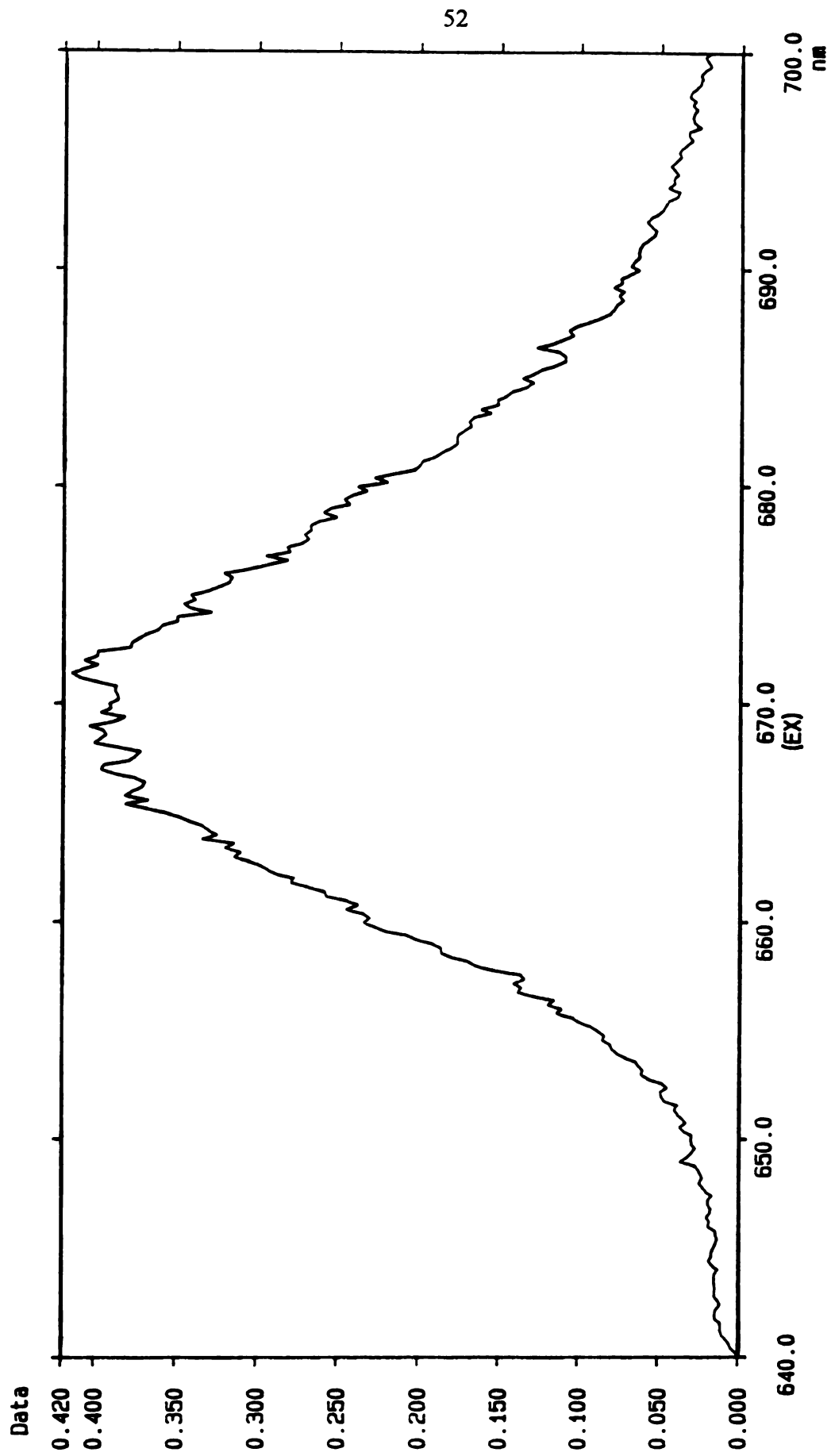


Figure 18. Nile Blue A Perchlorate Excitation Spectrum.

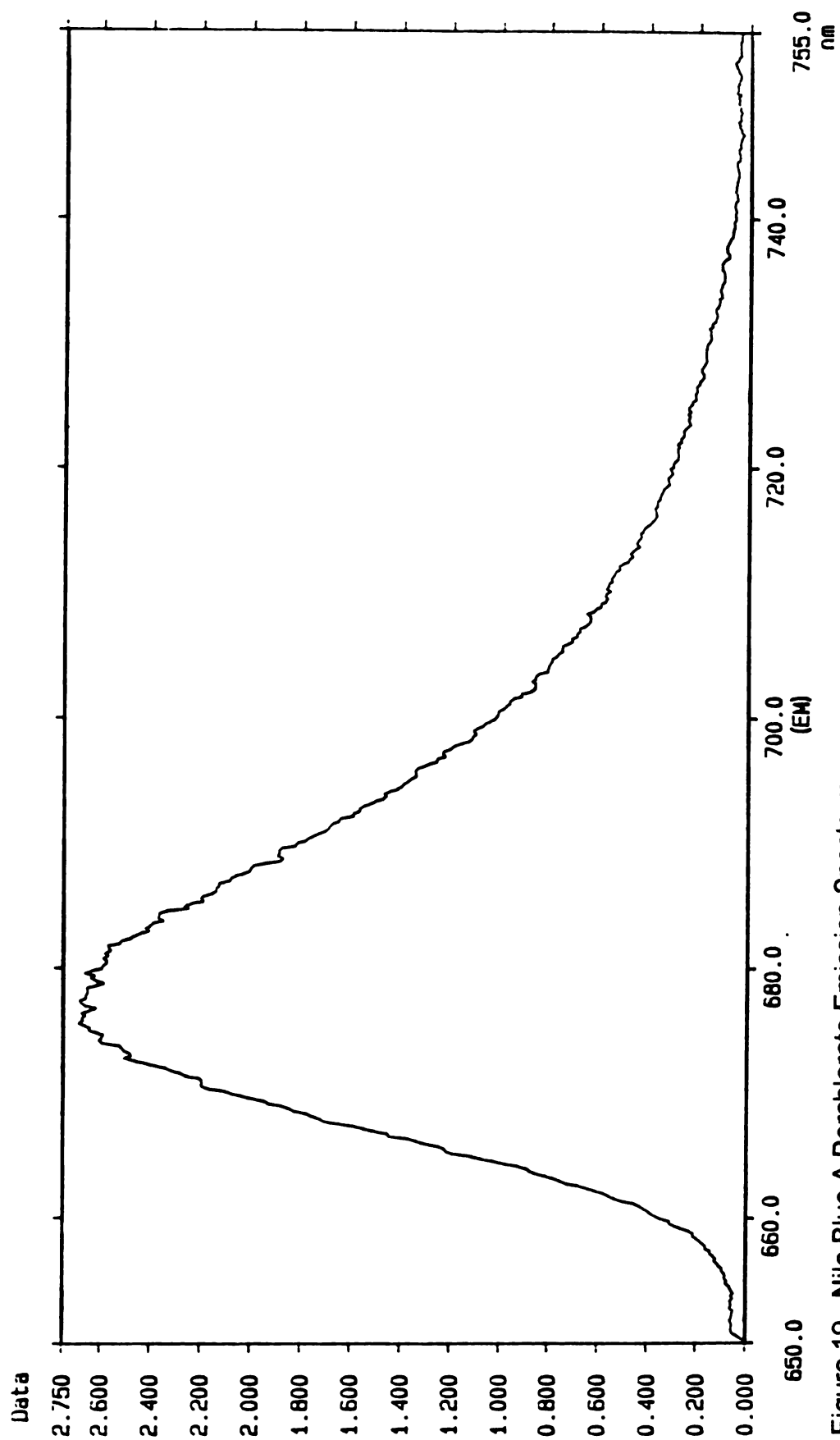


Figure 19. Nile Blue A Perchlorate Emission Spectrum.

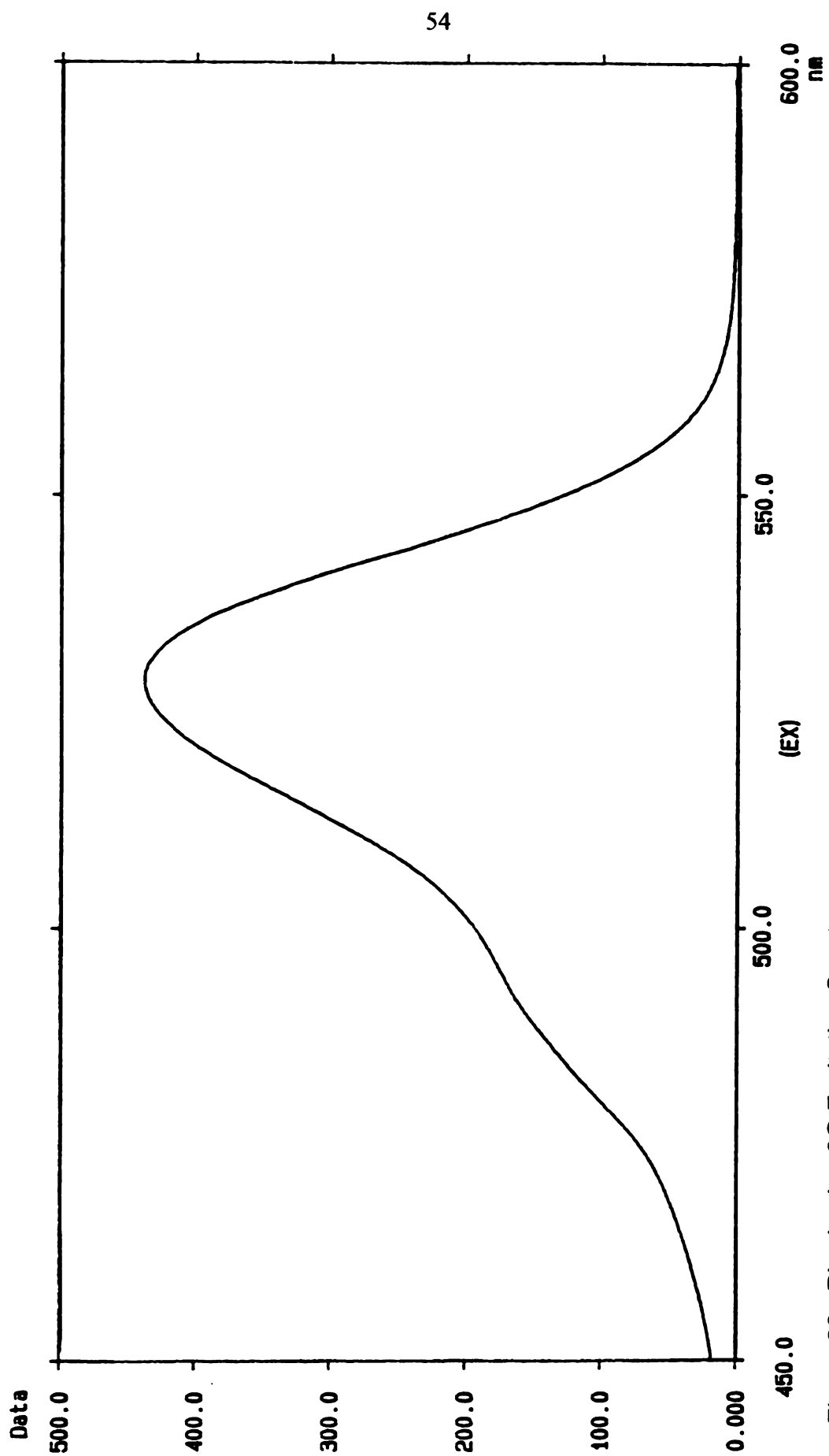


Figure 20. Rhodamine 6G Excitation Spectrum.

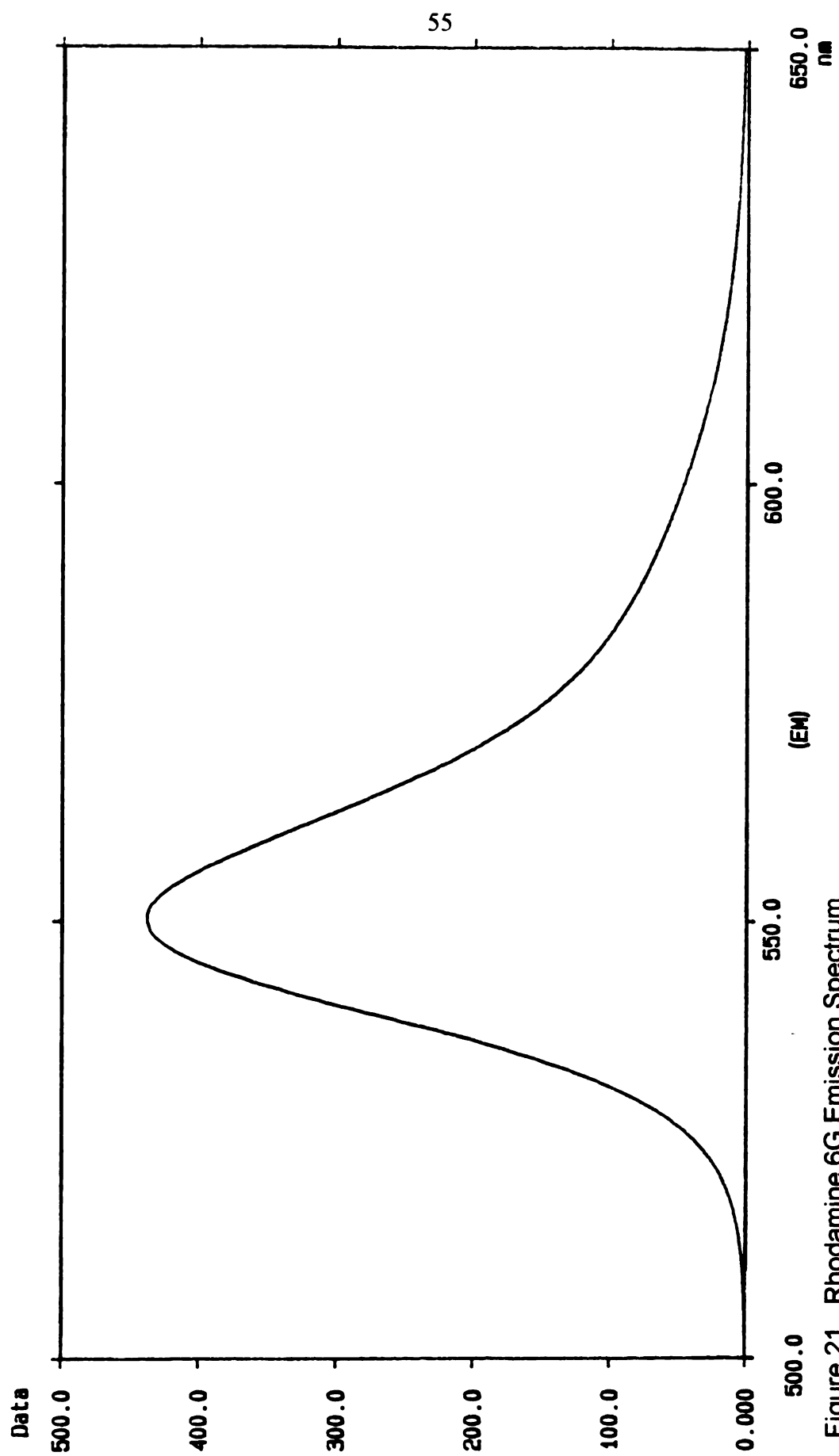


Figure 21. Rhodamine 6G Emission Spectrum.

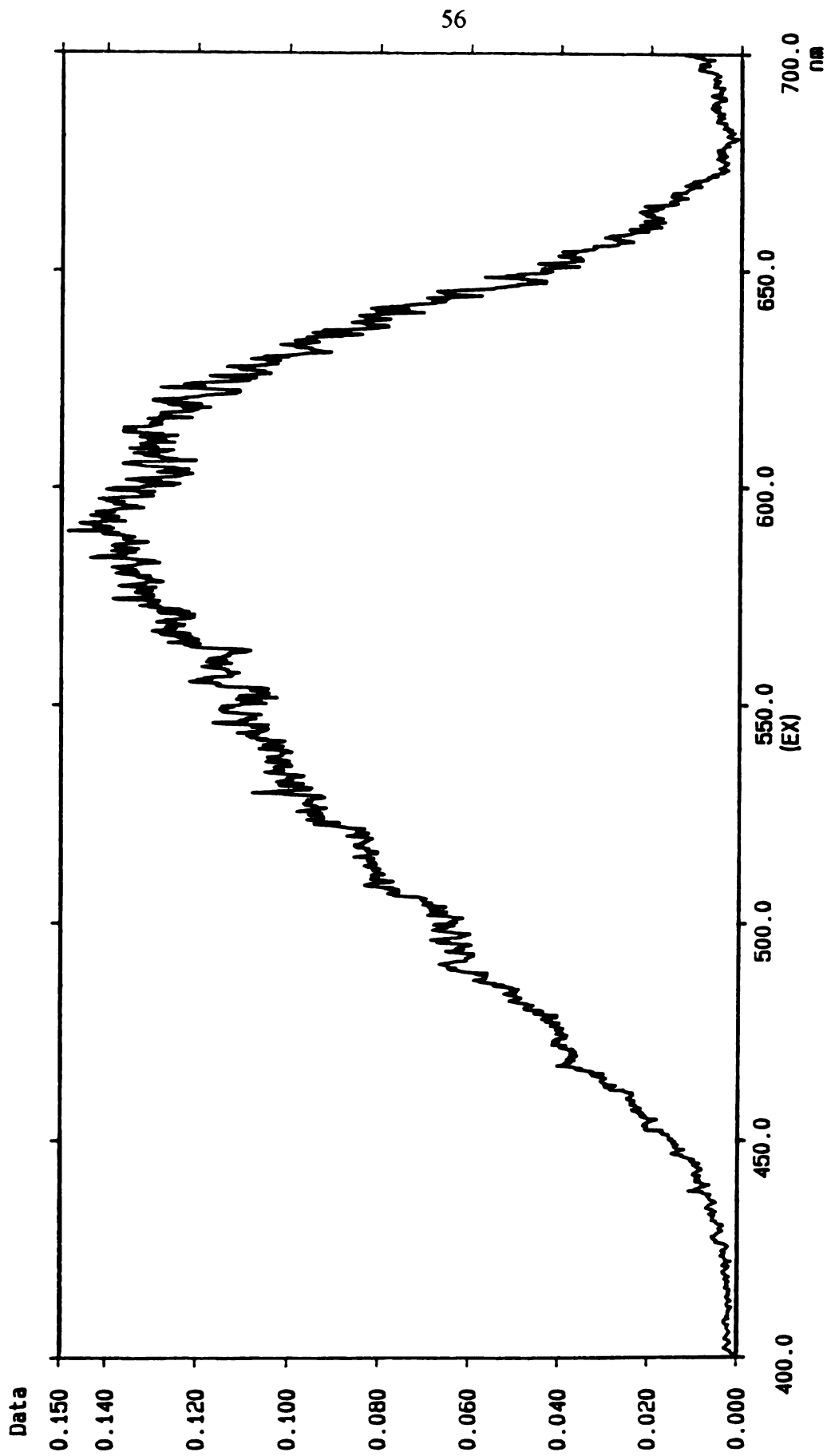


Figure 22. Styryl 7 Excitation Spectrum.

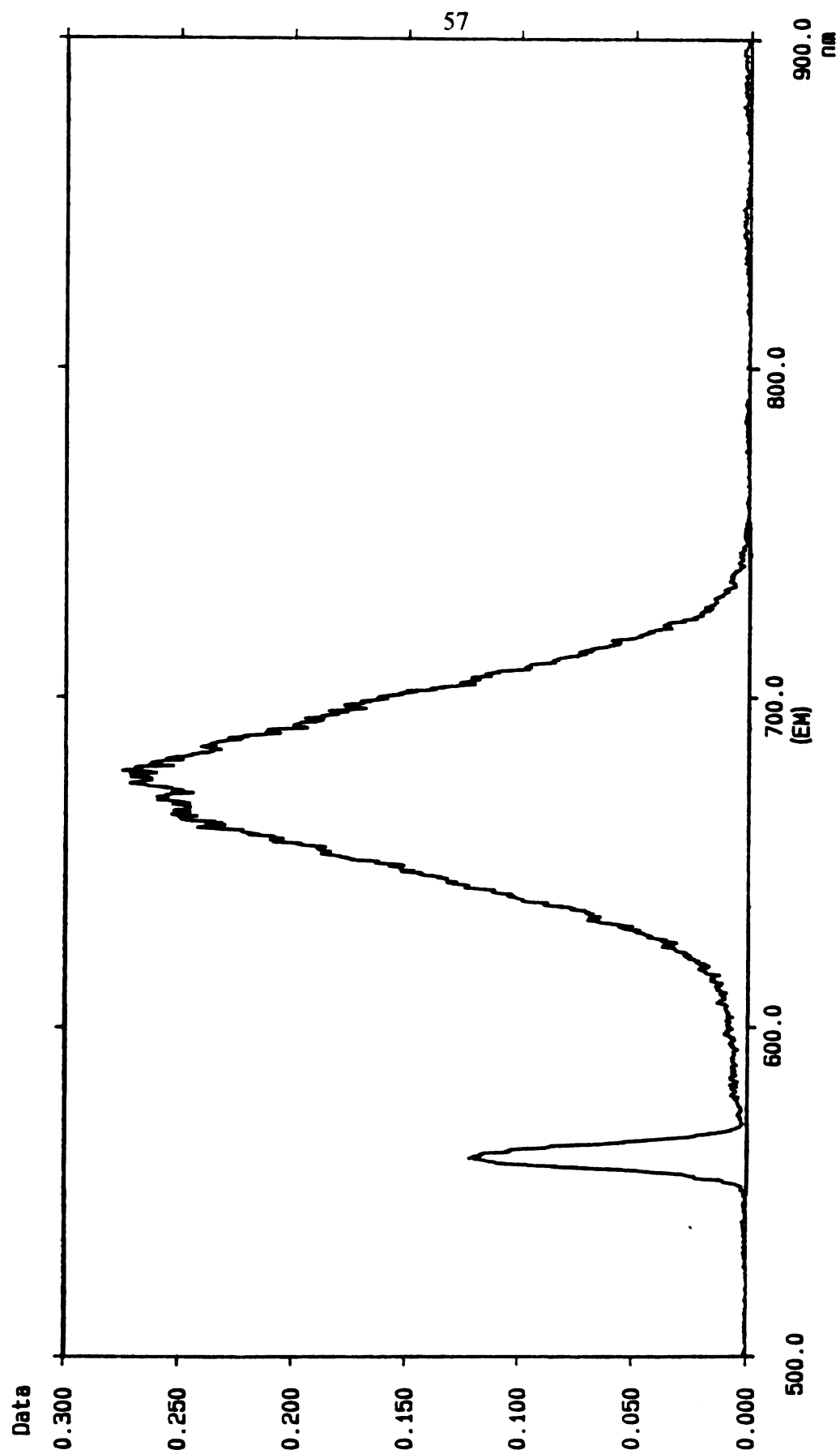


Figure 23. Styryl 7 Emission Spectrum.

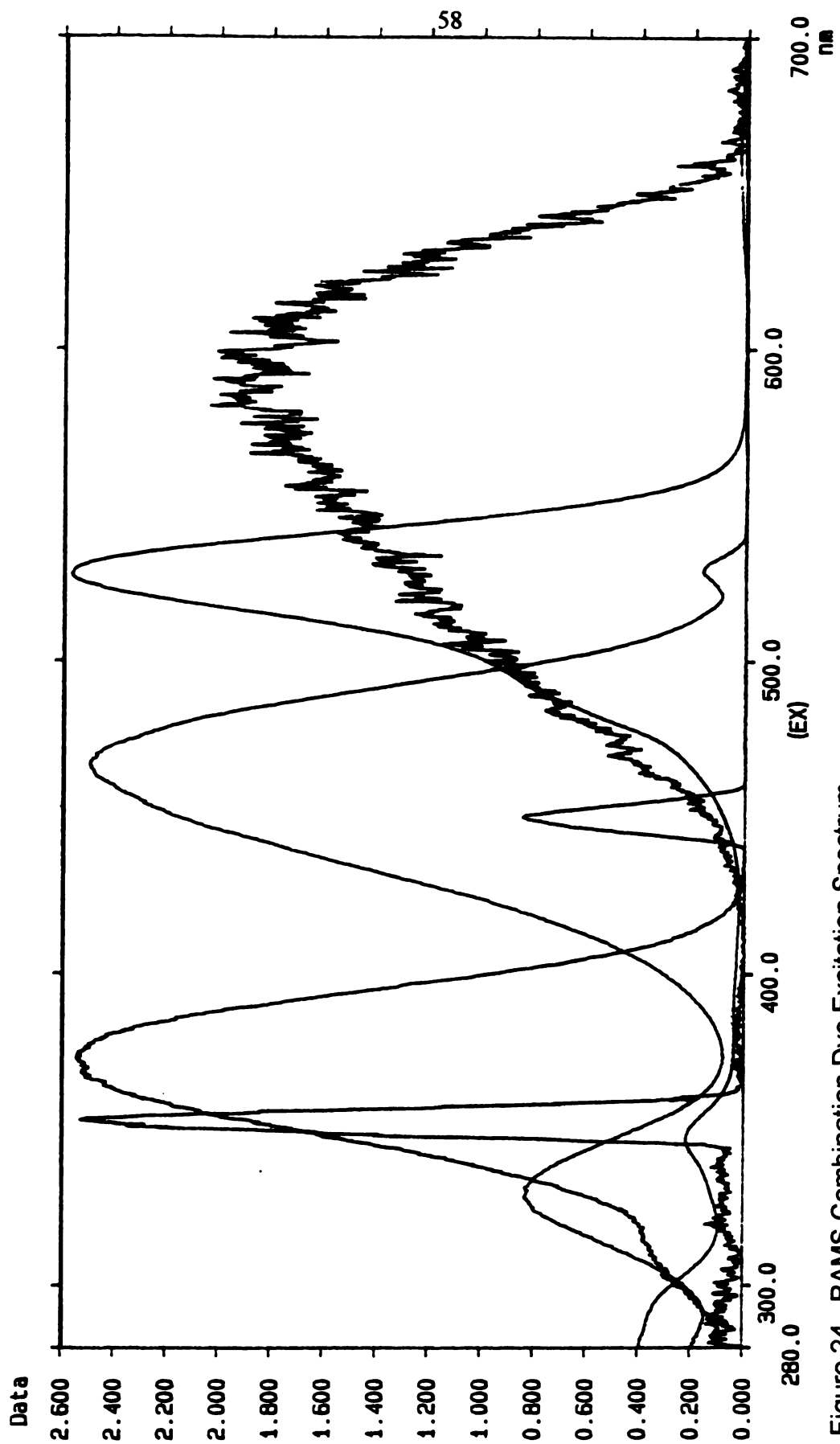


Figure 24. RAMS Combination Dye Excitation Spectrum.

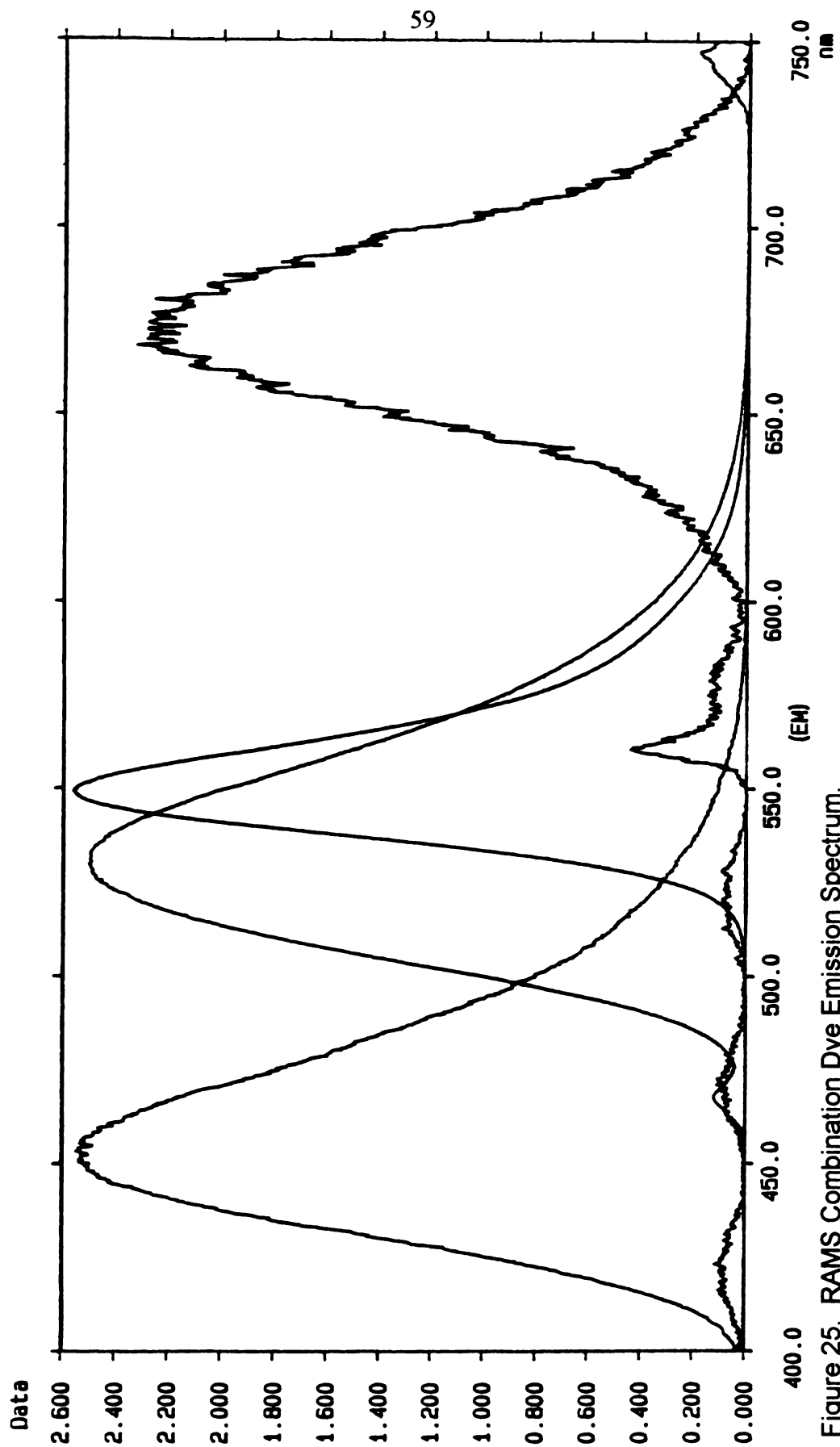


Figure 25. RAMS Combination Dye Emission Spectrum.

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