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HPLC Analysis of Black Ballpoint Pen Ink Exposed to Different Light Conditions

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HPLC ANALYSIS OF BLACK BALLPOINT PEN INK EXPOSED TO DIFFERENT LIGHT CONDITIONS

By

Amanda Jeanne Slebodnik

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ABSTRACT

HPLC ANALYSIS OF BLACK BALLPOINT PEN INK EXPOSED TO DIFFERENT LIGHT CONDITIONS

By

Amanda Jeanne Slebodnik

The light conditions to which a document is exposed are often unknown to the forensic scientist. It has been shown that the dyes in ink can degrade when exposed to light which can cause the relative abundance of dye components to change. This might cause an analyst to determine that two ink samples, one exposed and one not exposed to light, are from different sources when they were not. Though dye components in two ink samples from the same source may differ qualitatively, it has been shown that the rate at which they degrade is similar. Controlled light exposure to induce degradation and the subsequent comparison of degradation rates has been shown to be an effective method in comparing inks from blue ballpoint pens that have undergone different light conditions.

High-performance liquid chromatography was used to analyze thirty-two black ballpoint pens that were exposed to fluorescent light. The relative abundance of dye components was then plotted on a ternary diagram. Black ballpoint pen inks containing crystal violet dye degraded in the same manner as blue ballpoint pen inks containing the same dye. The method of controlled light exposure to induce the degradation of the dye components in black ballpoint pens was tested in two blind case studies containing a total of twenty ink sample pairs. The analyst was able to correctly conclude whether or not the ink samples could have come from the same pen for sixteen of the ink sample pairs.

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TABLE OF CONTENTS

TABLE OF CONTENTS, continued

LIST OF TABLES

LIST OF TABLES, continued

LIST OF TABLES, continued

LIST OF TABLES, continued

LIST OF FIGURES

LIST OF FIGURES, continued

Chapter 1: Introduction

Forensic Analysis of Ink

The analysis of documents for potential fraud is a practice that has been a part of the forensic community for decades. Documents examined range from tax returns, wills and medical documents to ransom and threatening notes. In questioned document cases, the analyst is sometimes asked to determine the identity of the writer, whether a document was backdated, a forgery made, additional information added to the document after its completion, or whether two documents could have been written with the same writing instrument. The examiner analyzes many different writing tools employed in the creation of these documents ranging from ballpoint pen ink, the most common, to fiber tip pens, inkjet printers, and even crayons.

The examination of these documents and subsequent conclusion can be made more difficult if the documents being analyzed have been stored under different light conditions. Differences in the conditions at which a document is stored can cause variation in the analytical results obtained. For example, storage under different light conditions may alter the optical properties and chemical composition of the inks.[1] This may cause problems in a case where the analyst is asked to compare two documents, one kept in a file folder and the other left on a desk exposed to fluorescent light. Another problem case might be a document with writing on both sides which has been stored on a desk; one side has continuously been exposed to light while the other has been shielded from it. In these cases, even if the pens used to write the documents were the same, the difference in light condition can cause the inks to look different under analysis.

In a recent study, blue ballpoint pen ink on documents stored under different light conditions was analyzed using HPLC with diode array and a proposal was made on how to compare inks stored under these conditions.[2] The scope of this thesis examines black ballpoint pen ink to assess its reaction to different light conditions, and a method is proposed to analyze the black ballpoint pen ink. The accuracy of this method, using HPLC as the sole analytical instrument, is assessed using a blind case study.

The Problem to be Studied

The analysis of ballpoint pen ink on paper by HPLC is a reliable method in determining whether two ink samples could have come from the same source when the samples have endured the same conditions.[3,4] It has been found, however, that when some ballpoint pen inks are exposed to light, the dyes within them degrade and change in presence and intensity. This happens when crystal violet successively losses methyl groups. Crystal violet (CV) decomposes into methyl violet (MV), which subsequently decomposes into tetramethylpararosaniline (TPR). This change could cause two samples of ink which have been exposed to different light conditions to look different even if they originated from the same source. In this respect, the HPLC method of evaluating inks alone is insufficient.

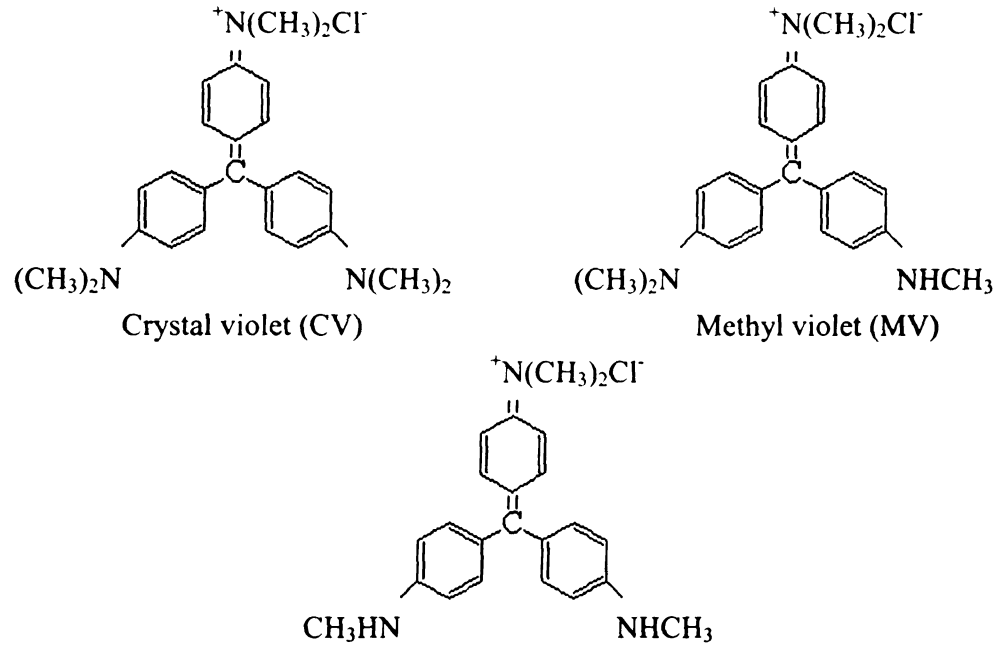


Figure 1.1 Molecular structures of CV, MV, and TPR.

When the forensic scientist receives evidence, it is often unknown to what light conditions this evidence has been exposed. For example, it could have been in a file folder completely unexposed to light, on a desk in an office where the lights are turned on and off, or consistently exposed to light in a room where the lights are always on. Also, the type of lighting to which the evidence was exposed could affect the rate at which the dye degraded. This factor is also unknown. At this point, the scientist has no idea what kind of degradation the dyes in the ink have undergone. If the pens are analyzed using HPLC, the forensic scientist might see that there are several peaks differing in intensity or presence in the 500 nm range. This is the area of the violet dyes found in ink. The differences in this area do not necessarily mean that the inks are from different sources.

These peaks could just be different due to the changes undergone when the dye degrades. Thus, the scientist might conclude a false negative.

Andrasko discovered that a solution to this problem in blue ballpoint ink was to purposely expose the sample ink to a light source and analyze the degradation of the dye from that point on at timed intervals. The rate of the degradation of the ink is then plotted on a ternary diagram and compared to the other samples. If the rates are similar it is possible that the inks came from the same source.[5]

There are two questions asked and answered in this study along this line of research: Can this same method be used for black ballpoint pens? And can the rate of degradation of the dye alone be used to discriminate the inks allowing HPLC the capability of a reliable ink comparison? The discriminatory power of a single wavelength comparison will be determined by analyzing a representative sample of black ballpoint pen inks and undergoing a blind case study.

Purpose of the Study

As differences in light exposure may cause the dyes in inks to degrade differently, it is possible that the forensic scientist could determine a false negative when comparing ink samples. In this study, a method to determine whether or not black ballpoint pen ink exposed to different light conditions could be from the same pen will be tried and tested using HPLC as the only analytical instrument.

This study can benefit the scientific community in several ways. First, this study will provide a method capable of appropriately analyzing ink samples exposed to different light conditions in order to avoid false negatives. Second, the method for ink analysis presented by Andrasko will be tested using a blind case study which will

determine whether the method is reliable. Third, data gained from HPLC analysis is objective and not subject to interpretation allowing this method to be less subjective than other methods. Finally, laboratories that do not have access to HPLC with diode array will have a reliable method to successfully complete ink analysis using only HPLC.

Hypothesis

It is predicted that black ballpoint pens exposed to different light conditions will exhibit different relative percentages of violet dyes and the purposeful exposure of black ballpoint pen ink to light and plotting of the information gained from this exposure using ternary diagrams will determine whether or not two inks could have come from the same black ballpoint pen. This is supported by the work of Andrasko who determined that this analysis can be accomplished in blue ballpoint pens.[6] It is also hypothesized that HPLC without diode array will prove a sufficient analytical instrument to discriminate between different black ballpoint pen inks.

Methodology

This study primarily consists of research using HPLC to separate dye components, Turbochrome Software to determine the component peak areas, and ternary diagramming to display the data obtained.

This research was conducted at the Allegheny County Coroner's Office- Division of Laboratories in Pittsburgh, Pennsylvania, using a Perkin Elmer HPLC and Turbochrome software.

The degradation of black ballpoint pen inks was analyzed during exposure to fluorescent (580 nm when at six feet, 545 nm when at 8.25 cm), long wave ultraviolet (365 nm), short wave ultraviolet light (254 nm) and the differences in reactions were

compared; additionally, one set of samples was unexposed to any light source. The inks were also exposed to light and then put into darkness to investigate the reaction of the dye to a sudden halt in exposure.

The HPLC method used to analyze the dye composition was that which was found suitable for blue ballpoint pen ink in previous studies.[7] In this method, a linear gradient of an 80:20 water: acetonitrile mixture to 100% acetonitrile at room temperature was used. The internal reproducibility of the HPLC method was explored by repeating sample analysis on the same sample five times. Turbochrome software then made it possible to record the component peak areas of the dyes and their relative quantities were compared.

The changes in dye composition were graphed using a ternary diagramming program made available on the Internet by Daniel Marshall at the Department of Earth Sciences, Carleton University, Ottawa Canada (www.sfu.ca/marshall/ternplot.htm). Additional graphing to compare specific areas was done using Microsoft Excel 2002. Images in this thesis are presented in color.

Finally, ten blind case studies were made available to the analyst in which two ink samples, same or different source, had been exposed to light conditions unknown to the analyst. The inks were then analyzed using the methods previously described and the accuracy of the method to determine whether or not the inks could have come from the same source was tested.

Chapter 2: Chromatography and the Analysis of Inks

Chromatography

Chromatography is a family of techniques by which components in a mixture are separated from one another. They can be used to separate the components of mixtures of many substances including, but not limited to, amino acids, proteins, lipids, drugs, nonhydrocarbon gases and dyes. There are many types of chromatography that are used in the separation of mixtures of these substances, however; this description will focus on the separation of dyes using high performance liquid chromatography.

In HPLC, the sample is injected into the instrument and progresses through a stationary phase column via a liquid mobile phase. The various components of the sample then separate from each other during their travel through the column due to their size, shape, charge, and affinity for the stationary or liquid phase. The separated components are then detected using a UV/VIS detector and their retention times and relative quantities are sent as data to the computer. When analyzing inks, HPLC is preferable to gas chromatography (GC) because it allows analysis at a specific wavelength of light which is useful when studying materials that are colored. Also, HPLC does not vaporize the sample, as in gas chromatography, but the sample remains intact and can be collected after analysis.

Ballpoint pen inks can be differentiated using HPLC because each batch of pen ink has a different composition of ink dyes and resins. This is due to the different manufacturing processes.

The Composition of Inks in Ballpoint Pens

Ballpoint pens were first introduced to America in 1945. Their popularity grew rapidly due to the ease of use versus the nib pen (fountain pen). In a ballpoint pen, a ball is inserted into an housing at the tip of the pen that allows it to roll freely. As it rolls it picks up a viscous ink from an adjacent ink chamber and deposits it on the paper. The ink chamber can last for weeks to months depending on frequency of use and can sometimes be removed and replaced with a new ink chamber into the same housing for a lesser cost than replacing the entire pen.[8]

Ballpoint pen inks consist primarily of coloring materials and solvent. The coloring materials, usually soluble dyes, give the ink its color and the solvent works as a carrier to transport the ink to paper. Crystal violet dye and its decomposition products, methyl violet and tetramethylpararosaniline, are often present in black ballpoint pens. The rest of the ingredients can include fatty acids, resinous materials, surface active agents, and corrosion control ingredients.

The formula of the ink in ballpoint pens is largely dependent upon the climate of the region to which the pen is to be shipped and the specific requirements of the customer. However, the "recycling" of excess ink batches can also play a role. These factors result in different ink formulas for various pens even if they are all black ballpoint pens.[9]

The difference between the climate in which the ink is manufactured and that in which the ink is used can have a significant effect on the efficiency of the ink in a ballpoint pen.[10] Many companies make their inks thicker so that they can be thinned out to meet the requirements of different climates. Pens that are used in arid climates must

have more plasticizers than those used in humid climates or the ink may dry out faster. Consequently, a black Bic Round Stic pen shipped to Nevada may have a different composition than one shipped to Florida.

The specific requirements of the customer also dictate the formula of the ink. If the customer requests a higher grade ink, more dye is added to the formula. The color of the ink or combination of dyes is determined by the customer. Often, a mixture of several dyes in different quantities will be incorporated into the same ink formula to produce a specific color.[11]

There are also times when an excess of ink is produced by the manufacturer. This can happen when the manufacturer overestimates the quantity of ink needed to fulfill a customer's order or if the manufacturer makes an error in the formulation of the ink and it no longer meets the specifications of the customer. When this occurs, the excess ink is often mixed with a similarly formulated ink as long as it meets the manufacturer's quality control standards. This results in a slightly different formula than the one initially intended by the manufacturer.[12]

All of the above situations result in many different ink formulations created for a single type of pen. These differences in formulation allow each individual formulation of black ballpoint pen ink to be more descriptive, as there is not a standard formulation used for all black ballpoint pens, and provide a point of analysis for forensic scientists.

Summary

Chromatography is useful in separating individual components of a sample. The formulation of ink in ballpoint pens varies even among those of the same brand and type, allowing different components and different concentrations of those components. HPLC,

among other forms of chromatography, can be used to separate and quantify these components and the analyst can use this information in comparison against another ink to determine if both inks could have come from the same pen.

Chapter 3: Review of Literature

Analysis of Inks

Since the introduction of the ballpoint pen and its subsequent rise in popularity, examiners have discovered many suitable methods to analyze them. Originally inks were analyzed using physical methods such as visual examination under various wavelengths of light ranging from ultraviolet to infrared, photography using specific filters, and reflective spectrophotometry. These methods were used because the courts would not accept the removal of small portions of a document that was physical evidence, and these methods allowed the document analyzed to remain intact. They were also advantageous because they could easily be demonstrated and presented in the courtroom. Though these tests could often differentiate between different inks of the same type, the photography and reflective spectophotometry methods had one disadvantage. Inks are most often dark blue or black and since these tests depend on the differences of light absorption properties in different inks, they were often difficult since most of the light was absorbed.[13]

Once courts started allowing the removal of small portions of a document in evidence, chemical methods were used. In these methods, one or two plugs of paper containing a sample of the ink in question were removed from the document using the blunted end of a hypodermic needle. The ink on these plugs was then differentiated depending on their color reaction to different chemicals indicating the presence of specific metallic salts and their reaction with acids, bases, oxidizing and reducing agents. These tests differentiated between different types of ink; however, were often unable to distinguish two inks of the same type.[14]

When physical and chemical methods failed to discriminate between two inks, a new method was proposed. In 1952, Somerford and Souder studied the analysis of writing inks using paper chromatography.[15] They found that when an ink was diluted in water and allowed to travel along a strip of filter paper, the various dye components in that ink were separated into bands of color along the length of the filter paper. These bands could then be compared to the bands formed when another ink was subjected to the same analysis. If the bands were different colors or at different distances along the filter paper, it was concluded that the inks were not the same. However, if the inks did have the same chromatogram, they were then mixed, subjected to the same analysis and compared to the previous individual chromatograms. If all three chromatograms were the same, the inks were considered to be of the same composition. The chromatograms were also subjected to ultraviolet light so that the components of the inks that were not visible to the eye might be seen via fluoresence.[16]

That same year, Brackett and Bradford also studied the analysis of inks using paper chromatography.[17] In their study, they expanded on Somerford's and Souder's research by determining the best solvent systems to use and developing a microscale method so that a minimum of the document was changed. They also created a series of observations and tests that should be performed on the chromatogram to make the analysis more discriminatory. They found that their technique was successful analyzing inks as old as twelve years. Brackett and Bradford concluded that though paper chromatography was useful to gain information about inks otherwise not available, the process was tedious and had to be performed with great care.[18]

A more efficient method of ink analysis incorporating thin-layer chromatography (TLC) was developed by Tholl.[19] He felt that paper chromatography required the use of too much sample and was too coarse a medium to differentiate between different dye components in small amounts of extracted ink. In TLC, ink extracted from microplugs taken from documents is placed at the bottom of a stationary phase consisting of powdered material adhered to a glass plate. The plate is then vertically placed in a mobile phase (solvent system) which travels up the TLC plate moving the components of the sample varying distances. In Tholl's study, he experimented with various solvent systems, development techniques, and developing plates to determine the most efficient analysis of different kinds of inks.[20] Tholl also developed a system of evaluation for a developed TLC plate. By performing the steps involved in the evaluation, the document examiner had many points by which to compare the different ink samples.[21] Thin-layer chromatography became widely accepted and is still commonly used today for ink analysis.

Kuranz later modified the TLC methods established by Tholl. In one study, Kuranz removed areas of the silica gel or cellulose layers from the TLC plate that were nearest to the spotted sample. This allowed a channeling effect of the eluent which resulted in improved separation.[22] In another study, Kuranz created a method in which the ink sample was transferred to the TLC plate by placing the microplug from the document directly on the TLC plate. The ink was then dissolved from the paper directly onto to the TLC plate using small amounts of solvent. This technique required as little as one microplug of sample resulting in minimal document damage.[23]

After TLC was introduced as a method for analysis of inks, many other techniques were found to be suitable in forensic ink analysis. Analysts developed many methods including proton-induced X-ray emission, gas-liquid chromatography, Fourier-transform infrared spectroscopy, high-performance thin layer chromatography, X-ray microanalysis, and various capillary electrophoresis techniques.

Colwell and Karger first determined that HPLC was a suitable method for ink analysis in 1977.[24] They felt that paper chromatography was inefficient and required large sample sizes, and that thin layer chromatography lacked discriminatory power when dyes were similar. Therefore, they chose HPLC as a potential method for ink analysis due to its speed, reproducibility, separation ability, and quantitative superiority to thin layer chromatography. Also, HPLC used an ultraviolet detector that could be used to examine components of the pen which were not visible by using spray reagents or fluorescence.[25]

Colwell and Karger found that there were three basic ways to differentiate between inks: presence of particular dyes, relative amounts of dyes, and composition or type of vehicle. By analyzing the samples at 580 nm, the blue dye components were detected. Inks could be differentiated very quickly if they had different dye composition. The difficulty arose when inks had the same dye composition, but in different relative amounts. Colwell and Karger determined that inks could be discriminated using a comparison of relative peak heights of the dye components.[26]

A.H. Lyter III later concurred with Colwell and Karger in similar research involving the use of HPLC for forensic ink discrimination.[27] In that study, ten different

inks were analyzed using both qualitative and quantitative methods, and differences were detected in all ten of the sample inks.

Another study using HPLC analysis of inks was conducted by A.A. Kher, E.V. Green, and M.I. Mulholland. In this study, eight blue and seven black inks were analyzed at several different wavelengths allowing examination of all components of the inks, visible and non-visible. A flow chart was created using the retention times of the peaks at different wavelengths to discriminate among the inks. This flowchart was successful in discriminating between pens from different manufacturers, but not necessarily between pens from the same manufacturer.[28]

Both Colwell and Karger and Lyter used relative amounts of dye components to differentiate between different inks. However, Colwell and Karger mentioned that small discrepancies in comparing relative amounts of dye components could be due to slight decomposition in one of the cases.[29] This observation, though very briefly mentioned, introduced an uncertainty in the accuracy of the comparison. In a presentation given at the 168th meeting of the American Chemical Society, Richard L. Brunelle and A.A. Cantu also discussed the issue of decomposition of ink components while presenting information about ink analysis.[30] They discussed why inks often could not be identified accurately. Frequently, the standard ink library was not up-to-date and did not contain information for a specific ink. Also, Brunelle and Cantu noted that sometimes ink characteristics changed due to extreme exposure to light and could not be accurately matched against an ink in the standard library.[31]

The studies above documented an acceptance of HPLC as an effective analytical tool in discriminating among different inks. However, they also raised a question as to

the accuracy of comparing inks that have undergone different amounts of light exposure. Was the discrepancy in relative amounts of dye components due to decomposition of one sample of the same ink or to an actual difference between two separate inks?

Analysis of Inks Exposed to Light Using High Performance Liquid Chromatography

The changes in dye composition due to light exposure were examined by Andrasko. In this study, Andrasko sought to determine a method to compare inks that had been exposed to different light conditions.[32] Inks exposed to different conditions degrade in different ways; therefore, documents undergoing different light exposure might be at different stages of decomposition causing their relative dye concentrations to differ even if they are from the same pen. Because forensic examiners usually have no knowledge of the light conditions the samples have been exposed to, it is important to explore this problem.

Blue ballpoint pen inks stored under different light conditions were analyzed over time and the rate of their decomposition was graphed. Though inks might initially have different relative dye amounts due to different exposure, Andrasko determined that the rate at which they degraded was the same if they originated from the same pen. Thus, it was possible to compare two blue ballpoint pen samples of unknown light exposure and determine whether or not they could have come from the same source. Andrasko's method was tested on real casework.[33]

Summary

High performance liquid chromatography has proven to be useful in the forensic comparison of ink samples due to its efficiency, reproducibility, and provision for

quantification. The examination of relative amounts of dye components in ink samples has been especially helpful in differentiation of ink samples. However, differences in decomposition states of the dyes due to light exposure can cause a false negative result.

A method for comparing inks by their rates of dye degradation was proposed and used to graph several different dyes undergoing decomposition. The method worked well for differentiating between different inks; however, comparison of two inks of unknown origin was only tested using real casework. Since, the true origin of the pens in the real casework will never be known it was not a sufficient test of the method proposed.

Chapter 4: Analysis and Comparison of Black Ballpoint Pen Inks by Controlled Exposure to Light

Though a method for comparison of blue ballpoint pen inks exposed to different light conditions has been proposed, it is yet to be determined whether this same method might be applicable to black ballpoint pen inks. Black ballpoint pens often contain crystal violet and its degradation products, the same dyes that are found in blue ballpoint pens. It is therefore logical to hypothesize that black ballpoint pen inks might be analyzed in the same manner as blue ballpoint pen inks. However, to ensure that various other components in black ballpoint pen inks do not interfere with the analysis, experimentation and a case study were performed.

There were three points of interest on which this study focused. First, whether black ballpoint pen inks degrade in the same manner as the inks in blue ballpoint pens making them suitable to undergo the same analysis was investigated. Second, the most effective light source used to intentionally degrade the inks was considered. Third, a blind case study was undergone to examine if the method proposed to compare black ballpoint pen inks exposed to different light conditions was accurate.

Pens Examined

Thirty-two black ballpoint pens were examined in this study and are listed in Table 4.1.

Number of Pen	Manufacturer	Type
1	Zebra	Stainless Steel Comfort Grip
2	Saga	Comfort Rubberized Barrel
3	Eversharp	Stick-tite Security
4	Pentel	RSVP Comfort Grip
5	Papermate	Erasermate
6	Bic	Cristal Grip
7	Office Depot	
8	Bic	Round Stic Grip
9	Bic	Round Stic
10	Papermate	Stick pen
11	Papermate	Flexi-Grip Ultra
12	Pilot	Easy Touch
13	Sanford	Sure Grip
14	Papermate	Easy Touch
15	Bic	Atlantis
16	Papermate	Write Bros
17	Pentel	Razzle Dazzle
18	Sanford	Tri-Grip
19	Papermate	Comfortmate
20	Sanford	X-tend
21	Scripto	GIGA
22	RoseArt	Great Grips
23	Pilot	GX 300
24	Sanford	Sidetrac
25	Pilot	Renegade
26	Bic	3bic
27	Bic	Cristal
28	Bic	Clear Clics
29	Papermate	Dynagrip+
30	Pilot	The Better Retractable
31	Zebra	Jimnie retractable
32	Zebra	Jimnie ballpoint

Table 4.1: List of black ballpoint pens.

Two of the thirty-two pens contained dyes other than crystal violet, methyl violet, and tetramethylpararosanaline and were not used in this research. This leaves a total of thirty black ballpoint pens that were considered in this analysis. These pens were taken

from eleven different manufacturers. Each pen was a different type though not necessarily from a different company. For example, the Bic Cristal Grip was used in comparison with the Bic Round Stic. The use of pens from the same manufacturer was allowable for this study because, as discussed in Chapter 2, the ink composition varies significantly even among lot numbers in the manufacture of the same type of pen. Thus, the use of different types of pens from the same manufacturer still allowed the difference in ink composition necessary for this study.

The ink samples were taken in the form of 1.5 cm long lines drawn on white, long grain, sub. 20 copy paper by IMPACT$_{TM}$. No other types of paper were used in this analysis.

Extraction and HPLC Analysis of the Dyes Present

Before undergoing analysis of these inks, a suitable method for extraction and HPLC analysis was determined.

Extraction of the dyes was done using a method already in place in the Michigan State University Forensic Sciences Graduate Program. This method was chosen because it was very simple and used a minimal amount of solvent. The 1.5 cm long sample of ink was cut from the copy paper, subsequently cut into smaller pieces, and placed in a micro-volume insert in a screw cap vial. Thirty microliters of HPLC grade methanol from Fisher were then added to the pieces of ink stained paper. The entire vial was then placed in a Cole-Parmer 8854 sonicator and sonicated for thirty minutes. This sonication allowed the dyes from the ink to dissolve. The entire vial, paper included, was then placed in an autosampler caddy in the HPLC for analysis. Ten microliter aliquots were taken for analysis.

The chromatographic analysis of the dyes was performed using high-performance liquid chromatography. The method used in this study was based on that used by Andrasko in her study mentioned in Chapter 3.[34] All analyses were run using a Perkin Elmer Series 200 Autosampler and Pump. A Perkin Elmer Series 785A UV/VIS Detector equipped with a tungsten lamp was used in detection of the dyes. HPLC separations were accomplished using a 30 cm μ Bondapak$_{TM}$ C18 column from Waters. A guard column was used at all times to help keep the column clean.

The mobile phase program used involved two mobile phases. Solvent A was an 80:20 mixture of deionized water and acetonitrile (Fisher OPTIMA), respectively, containing 10mM $KClO_4$ (Fisher) adjusted to a pH of 3 using hydrochloric acid (Fisher). Solvent B was acetonitrile (Fisher OPTIMA). For the mobile phase program, an 80:20 mixture of Solvent A: Solvent B was run for one minute during a pre-run. For the next twenty minutes, a linear gradient of Solvent A to Solvent B was programmed ending in a five minute hold using only Solvent B. The program ended with an 80:20 mixture of Solvent A: Solvent B for five minutes.

Since a diode array detector was not available, the tungsten lamp was set to detect at 540 nm, the wavelength at which CV, MV, and TPR absorb light.

Once analysis of the inks began, it became apparent that there was a possible carryover problem. The extraction of the dye from the ink on the paper produced a high concentration of the dye in the methanol, which resulted in the dye adhering to the injector needle and port and contaminating the next sample. This was easily corrected by adding additional flush cycles to each run. Each flush cycle had a volume of 700μL and a total of twelve cycles were used for each sample. The flush solvent consisted of a

60:20:20 mixture of acetonitrile (Fisher OPTIMA): isopropanol (Fisher HPLC grade): deionized water with an additional 10mL of phosphoric acid (Fisher). This eliminated the carry over of dye from one sample to the next.

Use of Ternary Diagrams

The data obtained from analysis was then organized using ternary diagrams. Each of the dyes (crystal violet, methyl violet, and tetramethylpararosaniline) was detected at different times along the chromatogram making them easy to identify. The area of each peak was recorded and the sum of those areas totaled. The area of each peak was then calculated as a percent of the sum of the areas (Table 4.2).

Pen	Area of CV peak	Area of MV peak	Area of TPR peak	Total
11	601837.2	171562.0	14143.6	787542.8

% CV	% MV	% TPR
(601837.2/787542.8) x 100 = 76.4	(171562.0/787542.8) x 100 = 21.8	(787542.8/787542.8) x 100 = 1.8

Table 4.2: Sample calculation for Pen 11, determining the relative abundance of dye components

This calculation was performed for each of the thirty pens that contained CV, MV, and TPR each time they underwent analysis.

The relative percentages of CV, MV and TPR were then plotted on a ternary diagram. A ternary diagram is a triangular graph that has three axes and allows the analyst to plot a single point representing three numbers whose total equals one hundred.

A single point representing the relative percentages of CV, MV, and TPR was determined for each time an ink was sampled as it underwent degradation due to light exposure and that point was plotted on a ternary diagram specific to that pen.

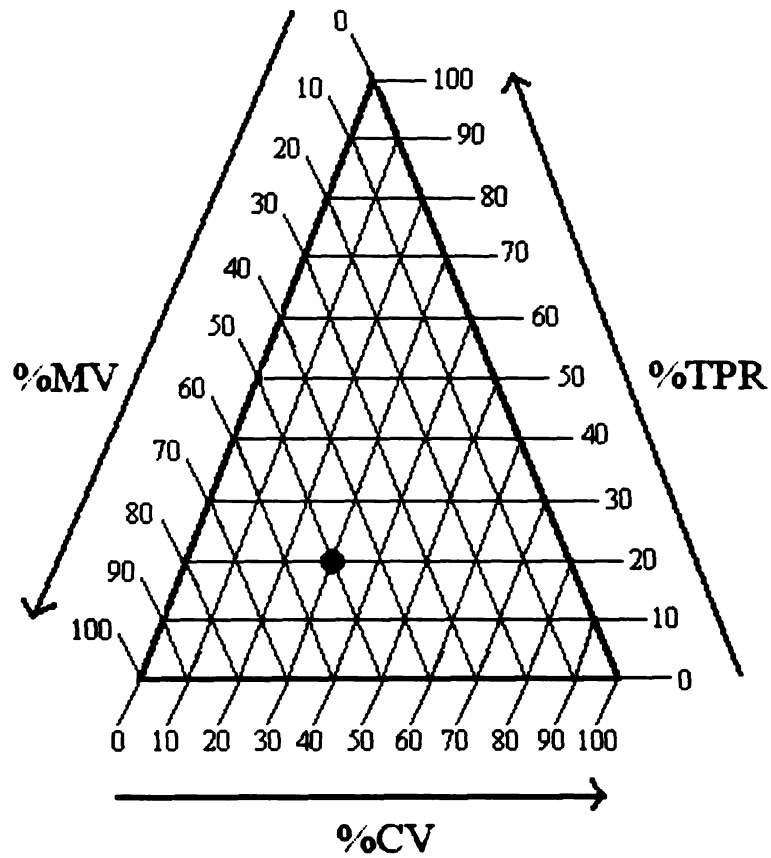


Figure 4.1: Example of a ternary diagram. The dot represents 30% CV, 50% MV, and 20% TPR.

The Degradation of the Dyes in Black Ballpoint Pen Ink During Exposure to Light

In real life scenarios, documents are most often exposed to fluorescent or lamp light in an office or home setting. Consequently, fluorescent light was chosen as the light source used in determining the reaction of black ballpoint pen ink to light. Whether the

dyes in black ballpoint pen ink degraded in the same manner as that of blue ballpoint pen ink was also explored.

All thirty-two samples, two of which were found not to contain crystal violet, divided into two groups of ten and one group of twelve, were exposed to fluorescent light (580nm) from a distance of about six feet, the approximate distance from the ceiling to any ordinary work table or desk. This was done to simulate possible real-life positioning of a document. Analysis was done on each sample using HPLC initially every other day and then decreasing in time to every other week as the degradation of the ink slowed. The first twenty pens were exposed to fluorescent light for approximately seven months. It was discovered that degradation of the ink became extremely slow after a few months and, consequently, the last twelve inks were only exposed to fluorescent light for four months. A blank paper sample was analyzed with every set of samples.

Ink samples from each of the pens were also kept in a drawer and exposed to no light. These samples were analyzed at the same time intervals as those that were exposed to light. This was done to ensure that the dyes were degrading due to the exposure to light and not merely to the aging of the ink.

The relative percentages of CV, MV, and TPR were calculated and plotted on a ternary diagram for each pen in both light and darkness. The ternary diagrams for the light exposed ink samples showed a trend of decreasing CV as MV and TPR increased (Figure 4.2). This trend is typically that which is observed in the degradation of blue ballpoint pen inks. The ternary diagrams for the inks that were not exposed to light showed no significant degradation. Thus, it was determined that black ballpoint pens

were suitable for analysis in the same manner as blue ballpoint pens. A summary of the results can be found in Appendices I and II.

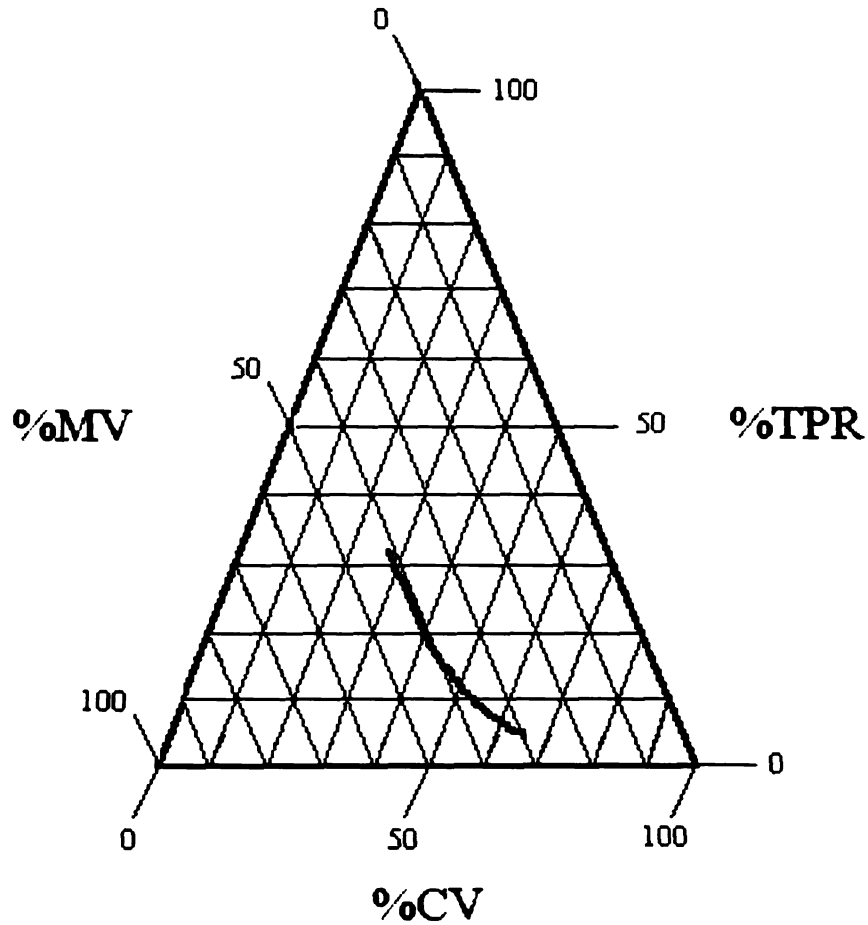


Figure 4.2: Ternary diagram of Pen 26 under fluorescent light exposure at six feet.

The Degradation of Dyes in Black Ballpoint Pen Ink During Exposure to Different Types of Light

Having now established that black ballpoint pen inks reacted to fluorescent light in the same manner as blue ballpoint pen inks, making them suitable for comparison analysis using a light exposure method, it was then necessary to determine which light

source would be most effective in degrading the ink. To determine this, black ballpoint pen inks were exposed to fluorescent light, long wave ultraviolet light, and short wave ultraviolet light. In the interest of time and conserving resources available to the analyst, four black ballpoint pen inks were analyzed in this procedure.

The samples were first exposed to fluorescent light (545nm) at 8.25 cm and sampled at 0, 1, 2, 4, 6, and 8 hours. The sampling was done at shorter intervals than the study mentioned earlier due to the proximity of the light source. The samples were then extracted and analyzed using HPLC and the appropriate calculation for determination of relative abundance of CV, MV, and TPR were performed. These numbers were then plotted on a ternary diagram.

Next, samples from the same pens were exposed to long wave UV light (365nm) at 20.25 cm. They were sampled at 0, 0.5, 1, 2, 3, and 4 hours. The sampling was done at different time intervals than that of the fluorescent light due to the strength of the light source. Again, the samples were extracted and then analyzed using HPLC, appropriate calculations performed, and the data plotted on a ternary diagram.

Last, samples from the same pens were exposed to short wave UV light (254nm) at 20.25 cm, and samples were taken at the same time intervals as those exposed to long wave UV light. The analysis, calculations, and plotting were again performed.

This resulted in twelve separate ternary diagrams, each documenting the degradation of one pen under a specific light source. The placement of the data points on the ternary diagram was typical of the trend observed earlier in the degradation of CV, MV, and TPR. For each pen, the data from each individual light source was compared and their ternary diagrams overlain. This resulted in four ternary diagrams, each with

three trendlines: one representing the degradation of the ink under fluorescent light, one representing the degradation of the ink under long wave UV light, and one representing the degradation of ink under short wave UV light.

The trendlines on each diagram were compared to determine the light source that would degrade the ink the most, thus giving the most information about how the ink degrades. As shown in Figure 4.3, it is clear that the fluorescent light source degraded the sample to the farthest point. However, the samples were exposed to florescent light for twice the amount of time as under short wave UV or long wave UV. Thus it is necessary to compare the speed of degradation of the dye at the same time intervals under all three light sources. As shown in Table 4.3, at 0, 1, 2, and 4 hours, time intervals common in all three light exposures, the fluorescent light has had the most effect on the pen samples. The faster decrease in CV and increase in MV and TPR evidence this.

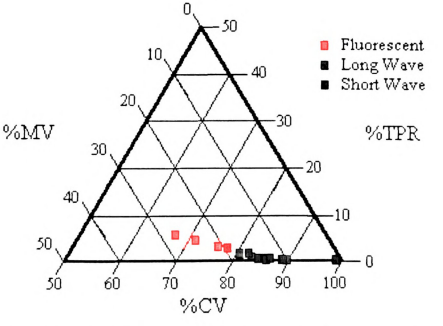


Figure 4.3: Degradation of ink from Pen 8 under fluorescent, long wave UV, and short wave UV light.

Hour	Fluorescent			Long wave UV			Short wave UV		
	%CV	%MV	%TPR	%CV	%MV	%TPR	%CV	%MV	%TPR
0	98.7	1.0	0.3	98.7	1.0	0.3	98.7	1.0	0.3
1	85.3	14.0	0.7	88.7	10.9	0.4	86.5	12.9	0.6
2	80.9	17.8	1.3	86.1	13.5	0.4	82.3	16.1	1.6
4	75.9	20.8	3.3	83.1	16.1	0.8	78.0	19.3	2.8

Table 4.3: Comparison of relative percentages of CV, MV, and TPR in ink from Pen 8 at 0, 1, 2, and 4 hours of exposure to fluorescent, short wave UV, and long wave UV light.

Therefore, it was determined that fluorescent light exposure at 8.25 cm gives the maximum amount of degradation in the shortest amount of time, making it the best source to use in exposing the pens to light. A summary of the results from all of the pens used in this experiment can be found in Appendix III.

It should, however, be noted that while the fluorescent light degraded the pen inks further in a shorter amount of time than the long or short wave UV light sources, the pen degrades in the same manner and proportions under each light source. Thus, the trendlines representing the degradation of the ink under fluorescent, long wave UV, and short wave UV lie almost on top of each other.

The Use of Blind Case Studies to Determine the Accuracy of the Light Exposure Method

Once it was determined that exposing black ballpoint pen ink to light and analyzing its dyes' degradation trend was possible, it became necessary to determine whether or not this information could aid forensic analysts in document examination. As discussed in Andrasko's article and in Chapter 3 of this study, the degradation of the dyes in blue ballpoint pen ink was thought to have forensic value.[35] By comparing the

trendlines of the degradation of the dyes in two blue ballpoint pen ink samples it is possible to determine whether or not they could have come from the same blue ballpoint pen. It was hypothesized that this same comparison could be made in black ballpoint pen ink due to its similarity in degradation to that of the blue ballpoint pen. A blind case study was implemented to test this hypthothesis. The analyst had no knowledge as to the origins of the ink samples used in this study until all comparisons had been completed and all conclusions made.

The thirty black ballpoint pens used in earlier experiments were given to a supervisor. This supervisor was given instructions to create ten simulated cases. In each case, the supervisor was asked to make two black ballpoint pen ink samples. They could be created from the same or different pens, resulting in the use of as few as ten and as many as twenty different black ballpoint pens. The samples were then exposed to the light conditions of the supervisor's choice: constant fluorescent light, fluctuating fluorescent light and darkness, and constant darkness. The decision of what pens to use and what light conditions to expose the samples to were withheld from the analyst. This was done because in a "real-life" case, the analyst usually does not know the source of the samples or the conditions to which they have been exposed. Any document containing an ink sample could have been kept in a file folder, left on a desk, or a combination of both since it was created and the analyst has no knowledge of these conditions.

The samples were exposed to their various light conditions for two weeks and were then analyzed. During analysis the samples were purposely exposed to fluorescent light at 8.25 cm, the light conditions deemed to present the most information, as

explained above. They were analyzed at 0, 1, 2, 4, and 6 hours using the HPLC analysis described earlier and graphed on ternary diagrams. A single cutting was taken from each sample at each of the time intervals.

This resulted in twenty different ternary diagrams, each with five points plotted, one for each time interval. A polynomial trendline was then drawn through the points plotted. Each case contained two ternary diagrams that were overlain and their trendlines were compared.

A second blind case study was then set up in the same manner as the previous study except that the ink samples were analyzed five times at each sampling instead of once. In the previous study, when only a single sample was taken at each time interval, it was impossible to know if the data from that sampling was accurate. By taking five samples at each interval, the analyst ensured that the data was reproducible and thus accurate. Owing to the high degree of reproducibility within each sampling, no statistical analyses were performed. During this study, different pens and light conditions were used in the comparison cases and subject to the decision of the supervisor who implemented the previous study. The ternary diagrams from all twenty cases can be found in Appendix IV.

As described in the Andrasko article[36], initial comparison eliminated a few of the cases from originating from the same pen. They were eliminated on the basis that their trendlines were too different to possibly overlap at any point during degradation. Figure 4.4 contains an example of this.

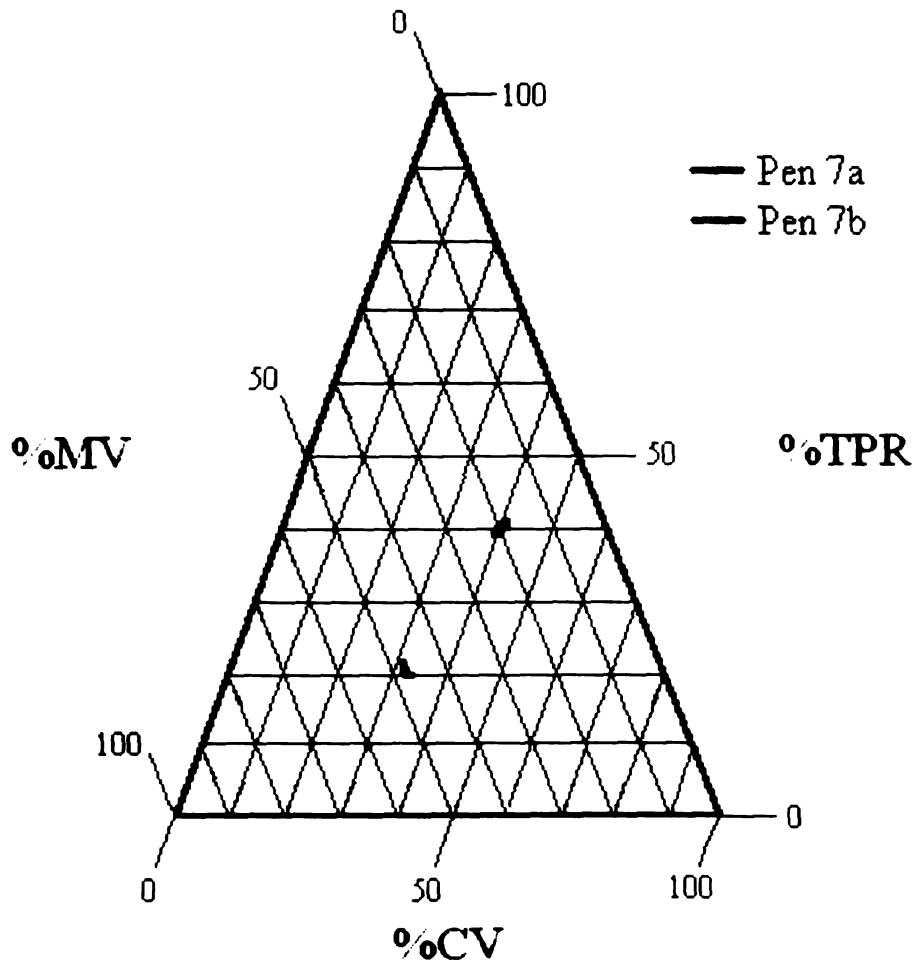


Figure 4.4: Comparison of the degradation of the inks in Pen 7a and 7b due to fluorescent light exposure.

In other cases, the conclusion as to whether or not the ink samples could have come from the same pen was not as clear. There were two main factors that required further analysis to be done. First, in some cases the trendlines did not overlap, but they were arranged on the diagram so that if one of the dyes had continued to degrade, it might have coincided with the second dye degradation trend (Figure 4.5). Second, in some of the cases, the trendlines were very similar, but did not directly overlap. It was not certain whether this difference was due to error or the fact that the ink samples came from

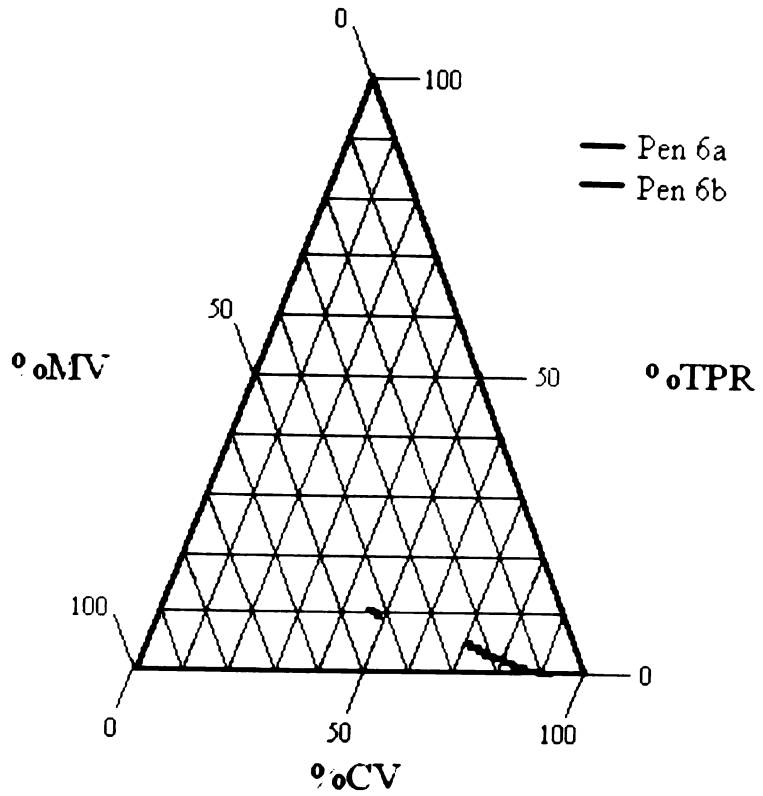


Figure 4.5: Comparison of the degradation of the inks in Case 6 due to fluorescent light exposure.

different sources (Figure 4.6). Both of these factors made it necessary to continue analysis and look at other factors present in the chromatograms.

In order to account for the first factor mentioned above, a short experiment was done to determine whether samples previously exposed to light and then put into darkness could be re-exposed to light to extend their degradation. Four inks were exposed to light for six days and then put into darkness. Samples were taken when the inks were first put on the paper, after six days exposure, after six days of darkness, and after ten days of darkness. It was determined that minimal if any degradation took place during the time the inks were in darkness (Table 4.4). The data from all pens involved in this experiment can be found in Appendix V.

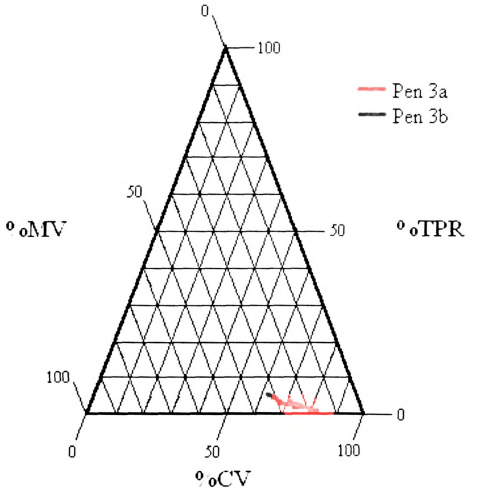


Figure 4.6: Comparison of the degradation of the ink in Case 3 due to fluorescent light exposure.

	Unexposed	Six Days Light Exposure	Six Days Darkness	Ten Days Darkness
%CV	92.5	79.9	79.9	80.3
%MV	7.0	17.2	17.1	16.9
%TPR	0.5	2.9	3.0	2.8

Table 4.4: Relative abundance of CV, MV, and TPR present in the ink in Pen 21 before, during, and after light exposure.

Due to the results above, several samples from the case studies were submitted to further light exposure to determine if their degradation lines would overlap. The samples

were kept completely in darkness since the time of the analysis and thus were subjected to minimal degradation. They were taken from darkness and purposely exposed to fluorescent light at 8.25 cm. They were then sampled and analyzed at 2, 4, 6, and 8 hours which were their 8^{th}, 10^{th}, 12^{th}, and 14^{th} hours of exposure, respectively. The results were graphed on the ternary diagrams used in the graphing of the initial analysis, extending the degradation trendlines and presenting more information.

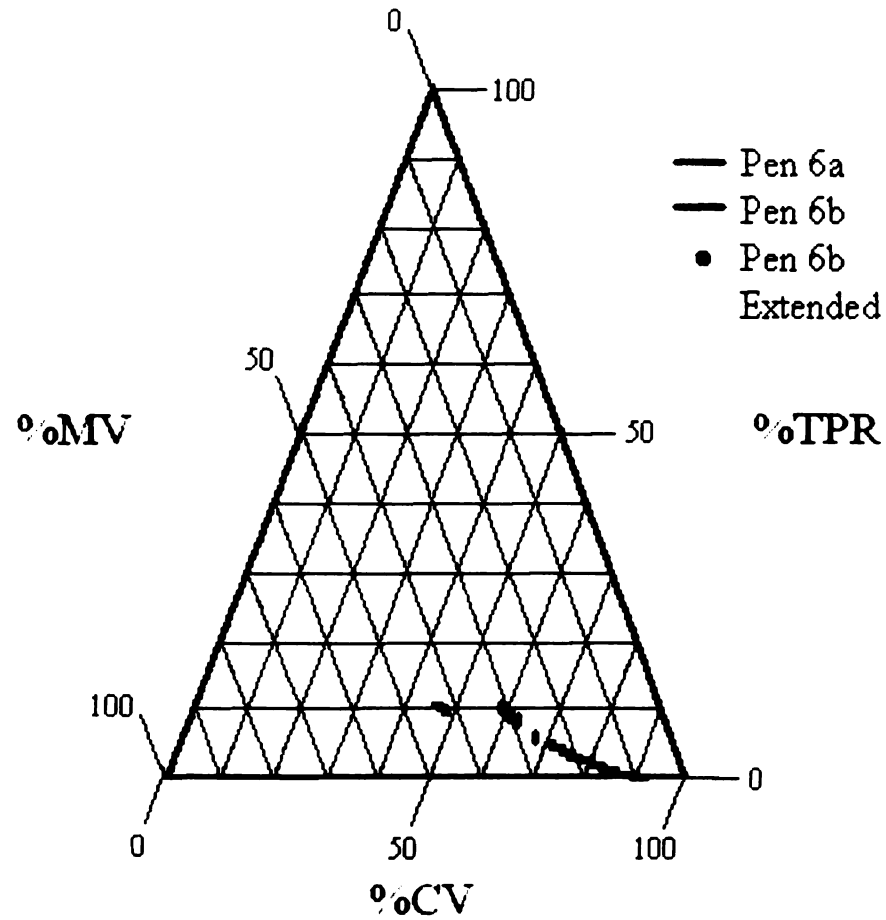


Figure 4.7: Comparison of the degradation of inks in Case 6 due to exposure to fluorescent light for an additional eight hours.

The exposure to darkness in between analyses seemed to have no effect on the degradation of the dyes in the ink sample. This further degradation allowed judgements

to be made on some of the cases as to whether or not the ink samples could have come from the same pen; however, some of the cases still contained trendlines that were very similar, though not completely overlain. Appendix IV can be referenced for information on all the cases that used extended light exposure.

It must be remembered that though much data can be obtained from the degradation of these dyes, these are still all black ballpoint pens. It must then be expected that the degradation of the dyes could be very similar. It was necessary to look at factors other than the decomposition of CV into MV and TPR. Each dye had several peaks that eluted before CV, MV, and TPR. Two distinct patterns of minor peaks were apparent throughout the ten case studies. One involved a pattern of as many as six peaks and the other a pattern of three peaks. By comparing the pattern of minor peaks present in two inks, one may eliminate the possibility that two of the ink samples came from the same pen. If one ink sample shows the pattern of six minor peaks and another shows the pattern of three peaks, it can immediately be concluded that they are not from the same source.

In addition to the pattern of minor peaks, another comparison was necessary because some inks, such as the ones shown above in Figure 4.6, had similar degradation rates, and also had similar patterns of minor peaks. Andrasko plotted the relative percentage of TPR against the sum of the area under all of the minor peaks and found that plotting this data resulted in a linear relationship between the two components. As the relative percentage of TPR to CV and MV increased, so did the sum of the area under the minor peaks. This data could then also be used to compare two ink samples. If the points belonged to the same straight line, it could be concluded that the ink samples could have

come from the same source.[37] When this was done on inks in this study, it was found that the linear relationship was often skewed by error. As shown in Figure 4.8, the relationship between the relative percentage of TPR and the sum of the area of the minor peaks was often not clearly linear.

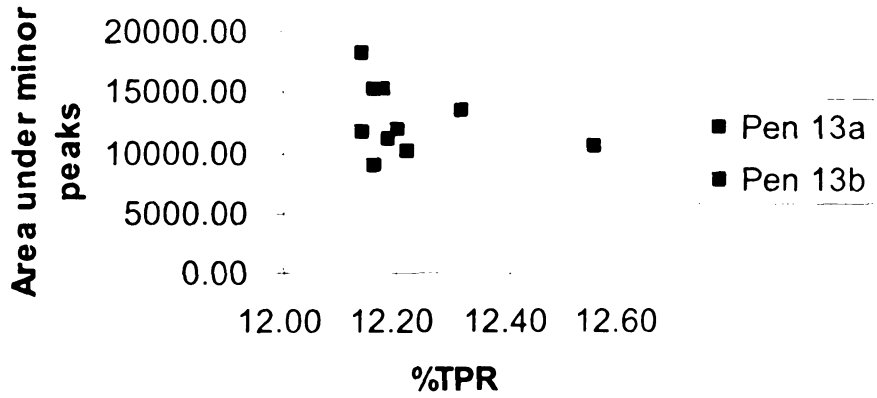


Figure 4.8: Plot of the sum of the area under the minor peaks versus the percent of TPR present in the inks in Case 13.

As a result of this, the area of the TPR peak was plotted against the sum of the area of the minor peaks (Figure 4.9). This plot produced a much clearer linear relationship and was henceforth used as the plotting technique for the data gained from the minor products. Only minor peaks which were present in both inks were used in comparison. Graphs of all twenty cases can be found in Appendix VI.

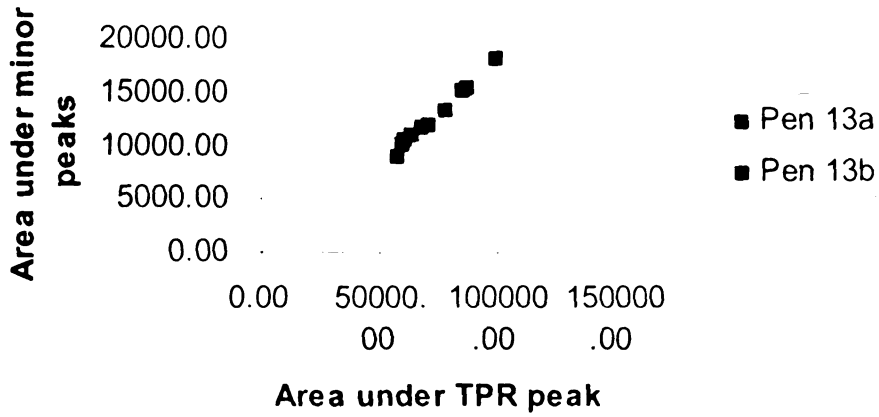


Figure 4.9: Plot of the sum of the area under the minor peaks versus the area under the TPR peak in the inks in Case 13.

In summary, ternary diagrams containing the trendlines depicting the degradation of CV, MV, and TPR, the pattern of minor products, and an XY plot of the sum of the area under all of the minor peaks versus the area under the TPR peak were all used in the comparison analysis of twenty blind case studies.

Overall Results

When thirty of the thirty-two black ballpoint pens studied were exposed to light they degraded in the same manner as blue ballpoint pens. The two that did not degrade in the same manner contained different dyes than the crystal violet, methyl violet, and tetramethylpararosaniline found in the other pens.

Each case from both blind case studies was evaluated separately using the three comparisons listed above: ternary diagrams containing the trendlines depicting the degradation of CV, MV, and TPR, the pattern of minor peaks, and an XY plot of the sum of the area under all of the minor peaks versus the area under the TPR peak. Once this data was collected, an overall conclusion was made as to whether or not the two inks in

each case could have originated from the same pen. These conclusions were then compared to the known origins of the inks. In the first case study, there were nine correct conclusions and one false exclusion. In the second case study there were seven correct conclusions and three false inclusions (Table 4.5). Over all twenty cases, 80% of the conclusions were correct. A table containing all of the pens used in the case studies can be found in Appendix VII.

	Correct Conclusions	False Positives	False Negatives
Case Study 1	9	0	1
Case Study 2	7	3	0

Table 4.5: Summary of Conclusions

Summary

When forensic document examiners receive a sample of ink as evidence to be analyzed, they are often unsure of what conditions the ink has undergone before it reached the laboratory. Andrasko has shown that blue ballpoint pen ink degrades upon exposure to light.[38] This degradation could cause the relative abundance of dyes present to be different than if it was not exposed to light leading to a misrepresentation of the composition of the ink ingredients. Consequently, a false conclusion could be made. This study investigated whether black ballpoint pen ink degrades in the same manner when the same dye is used.

HPLC was used to analyze ink from thirty black ballpoint pens containing crystal violet dye that were exposed to light, and the relative amounts of the dyes present were

plotted on ternary diagrams. All thirty black ballpoint pens containing crystal violet dye degraded in the same manner in light as the blue ballpoint pens. The amount of crystal violet steadily decreased while the amount of methyl violet and tetramethylpararosaniline increased.

After exposing the ballpoint pen inks to fluorescent light at 8.25cm, long wave UV light at 20.25cm, and short wave UV light at 20.25cm, fluorescent light at 8.25cm was chosen as the light source able to produce the most degradation of the ink thus giving the largest amount of information.

Two blind case studies were performed containing a total of twenty cases. In each case two inks of unknown origin and previous exposure were compared using ternary diagrams containing trendlines representing the degradation of each ink, the pattern of minor peaks, and a plot of the sum of the area under the minor peaks versus the area under the TPR peak. Whether or not the two inks originated from the same pen was correctly concluded in sixteen of the twenty cases.

Chapter 5: Conclusions and Discussion

Conclusions

The first conclusion made was that only black ballpoint pens containing the dye crystal violet could be used. Two of the thirty-two black ballpoint pens had unidentified dyes that were not found at the same retention time as crystal violet. These unidentified dyes underwent little or no degradation and were thus not suitable for tracking the degradation rate of the dye present.

As the black ballpoint pens containing crystal violet were exposed to light and analyzed, it was concluded that the crystal violet contained in the black ballpoint pen degraded in the same manner as that of the blue ballpoint pen. In all thirty pens studied, the amount of crystal violet decreased while methyl violet and tetramethylpararosaniline increased. Since the degradation of the dye could be analyzed, it was then concluded that black ballpoint pens were suitable to use in testing Andrasko's controlled light exposure method of comparing inks.

Also, it was construed that fluorescent light exposure at 8.25cm was preferable to short or long wave UV light at 20.25cm for inducing degradation of the dyes. All four inks that were exposed to the three types of light underwent further degradation using the fluorescent light at 8.25cm than short or long wave UV light at 20.25cm during the same amount of time. The more the ink degrades, the more information there is available about the degradation rate. Thus, fluorescent light was chosen as the light source to be used for the rest of the study.

In the midst of the first case study in which the light exposure method was being tested, it was concluded that if ink previously exposed to light is put into darkness it can

be stored in this manner and re-exposed to light with no change in the rate of degradation. The degradation in the dark slows so much that it is not noticeable during the short time period of this study. Any variation in relative abundance of dye components is so small it could be attributed to the error incurred by only taking one sample at each time of analysis. This allowed further analysis to be done on inks that were not initially degraded as much as was necessary.

Upon conducting two blind case studies in which a total of twenty pairs of ink samples were analyzed using the light exposure method, it was concluded that the method was fairly successful at determining whether or not the inks came from the same pen. In sixteen of the twenty cases, the correct origination was determined.

Discussion

When a scientist seeks data from an analysis performed it is favorable to know or even control exactly what conditions your subject has endured in order to take those factors into account throughout analysis. In forensic science this is not always possible. In this study, it was proven that the dye in black ballpoint pen ink degrades upon exposure to light. Since the forensic scientist is often unaware of what light exposure a sample has undergone this information is useful because the degradation of the dye could cause drastic quantitative differences between inks that have been exposed to light and those that have not. For example, the relative abundance of CV, MV, and TPR in Pen 13 at no light exposure is 90.7%, 9.1%, and 0.2%, respectively. After roughly two weeks of exposure to fluorescent light at an average desk height, the relative abundance of CV, MV, and TPR changes to 55.9%, 31.9%, and 12.2%, respectively. At no exposure the TPR peak is virtually unnoticeable, but it is quite prominent after only two weeks left on

a desk. If asked to compare ink from the underside of the paper (unexposed to light) to ink on the exposed side, the analyst might say they could be from different pens due to the severe qualitative differences in the dye component peaks. Merely being aware that this situation could occur is useful to the analyst.

Analyzing the degradation of inks exposed to light and comparing the data gained aids the scientist in discriminating between black ballpoint pen inks; however there are weaknesses in this method. The extraction technique in this study was often not efficient enough to extract extremely small amounts of ink and other extraction techniques were not possible due to lack of proper equipment in the laboratory. Consequently, inks that degraded rapidly could not be analyzed for the same amount of light exposure time as other inks.

Analysis was also most likely complicated due to similarities among black ballpoint pen ink recipes. For example, in this study there were four cases in which the two inks being compared were from different pens made by the same manufacturer. Of those four cases, in two cases it was incorrectly concluded that the inks could have come from the same pen. In these cases, the ternary diagrams, pattern of minor peaks, and plot of the area under the minor peaks versus the area under the TPR peak were all very similar. However, they were not from the same pen. Also, in case 18 the inks were from different pens from different manufacturers, but their comparisons by the factors listed above were all very similar. Thus, it was incorrectly concluded that they could have come from the same pen. These examples demonstrate that though there are a wide variety of black ballpoint pen ink recipes, there are many that are very similar. The slight variations in these recipes make it very difficult for the forensic scientist to discriminate between

pens. Another drawback to this method is that after all the data is collected, the analyst must make the final conclusion as to the origin of the inks. In forensic cases it is preferable to have an objective method that requires little interpretation by the analyst. If there is little subjective interpretation, there is less to be debated in court. This method lacks specific allowable ranges within which data points must fall for two inks to be considered to have possibly come from the same pen. Without these objective standards to follow, the analyst must make their own decision allowing subjectivity to enter into the analysis. However, though this analysis contains an element of subjectivity, it requires less interpretation than other methods such as handwriting analysis.

Though it has its weaknesses, the controlled light exposure method has proven to contain potential for forensic use in comparison of inks in black ballpoint pens. It is especially important to note that the entire analysis was done using HPLC without diode array. This method of analysis will be especially useful for those laboratories that do not have access to HPLC with diode array.

Future Research

There are several areas in which further research may prove beneficial to the scientific community: increasing the number of inks studied, altering the method developed to improve efficiency and minimal destruction of the evidence, exploring the significance of this study to other ink using products, utilizing other instruments such as capillary electrophoresis, and understanding the chemistry of the degradation of the dyes.

In this study thirty black ballpoint pens were analyzed and twenty comparisons were made using those thirty pens. A study using more pens and case comparisons to test the accuracy of determining whether or not two inks could have come from the same pen

by purposely exposing ink to light is necessary. The use of more pens and comparisons would offer better statistics as to the accuracy of the method and whether it could be used on actual evidence.

The method used in this study to analyze inks is fairly time consuming. The entire process takes at least seven hours just to collect the data. During that time period, the analyst has some free time in which they can perform other tasks, but the overall method requires almost an entire work day and can possibly lead into the next day. In a typical forensic laboratory, backlogs are high and efficiency is a subject that must be addressed. A study in which the ink is aged closer to the light source or with a stronger light source might prove useful in expediting the entire process.

The extraction process might also be improved to ensure the extraction of the dyes from highly degraded ink samples. After six months of exposure to fluorescent light at desk level, many of the inks analyzed released very little dye when extracted using the current method. These small amounts of dye were not easily detected by the HPLC leading to little or no useful data being obtained. As some documents that an analyst in a working laboratory might receive could have been exposed to light for any amount of time, the analyst can expect to receive samples that are highly degraded. An improvement of the extraction method should be explored in order to remove a suitable amount of ink from any sample.

In the current study, a 1.5cm line of ink was completely consumed in analysis during each sampling. Remembering that there were five samplings at every hour and at least five samplings over six hours of analysis, this amounts to a minimum of 37.5cm of ink used. This amount of ink removed from a real piece of case evidence could prove to

be extremely destructive. The method must be altered in order to make it less destructive and practical to use in everyday forensic analysis. This might be done by testing the lower limits of the HPLC to determine the minimum amount of ink necessary for analysis. If less ink is used there is less document damage.

There are many other writing tools which use ink and could possibly benefit from the proposed method. In this age, many documents created are never written in pen, but are produced directly on a computer. The ink in ink jet printers might be analyzed to determine if the dyes present undergo a degradation that can be analyzed. Also fiber tip pens and non-ballpoint pens could also be looked at to determine the value of the current method in their analysis.

Analysis using capillary electrophoresis may prove beneficial due to the small sample size required. This would allow the analysis of ink that has been greatly degraded and also reduce the amount of damage done to the evidence.

Lastly, it would be very useful to understand the chemistry that is taking place during the degradation of the dyes. For example, many of the pens had dye formulas that start at similar relative percentages, but then have very different rates of degradation. In these cases, an exploration as to the chemistry of the interaction of the dye components with the other components of the ink such as the resins and binders could prove useful. It is possible that the composition of the rest of the ink plays a role in the rate at which the dye decays. These other components might then be analyzed to determine their various quantities and whether or not they degrade when exposed to light. Due to the viscosity adjustments necessary for ink to be shipped to different parts of the country and world, it might also be interesting to analyze pens with ink from the same batch that has been

altered in viscosity to make it usable in many different climates. It would be beneficial to see whether the dyes in these inks degrade differently and whether or not that is due to the viscosity adjustment. This information might provide yet another method of comparison between different pen inks allowing the forensic scientist a more complete analysis.

These improvements to the current method and exploration of different applications of that method would certainly provide a more thorough and complete analysis and comparison of questioned documents in forensic analysis.

APPENDICES

Appendix I

Data: relative abundance of CV, MV, and TPR after fluorescent light exposure at six feet

Pens 5 and 15 contained a dye other than crystal violet. No data was obtained for these pens.

Date of Analysis	%CV	%MV	%TPR
12/03/01	35.63	45.21	19.16
12/05/01	34.17	46.93	18.89
12/10/01	32.78	46.59	20.64
12/12/01	32.69	46.39	20.91
12/17/01	30.67	47.55	21.78
12/19/01	31.22	47.27	21.51
12/27/01	28.90	47.02	24.08
01/02/02	29.81	47.05	23.13
01/14/02	28.97	46.72	24.31
01/16/02	28.58	46.68	24.74
01/22/02	27.08	48.20	24.71
01/28/02	26.93	47.30	25.77
02/05/02	28.83	46.86	24.32
02/12/02	26.74	46.94	26.32
02/18/02	26.18	47.48	26.35
02/25/02	26.43	45.34	28.23
03/04/02	26.15	47.60	26.25
03/11/02	26.47	45.89	27.63
03/18/02	26.74	46.04	27.22
03/25/02	24.73	44.57	30.70
04/01/02	26.66	45.91	27.44
04/08/02	24.79	47.14	28.07
04/15/02	23.87	47.70	28.43
04/22/02	22.23	46.98	30.80
04/29/02	23.66	46.02	30.33
05/07/02	25.24	42.89	31.86
05/13/02	21.65	44.77	33.58
05/22/02	20.87	46.84	32.29
05/28/02	23.62	46.33	30.04
06/03/02	23.94	45.02	31.04
06/10/02	21.87	45.76	32.37
06/17/02	22.11	45.19	32.70
06/24/02	23.36	45.87	30.77

Appendix Table 1.1: Relative abundance of CV, MV, and TPR in Pen 1 after exposure to fluorescent light at six feet.

Date of Analysis	%CV	%MV	%TPR
12/03/01	88.42	11.13	0.45
12/05/01	73.52	22.46	4.01
12/10/01	58.48	31.19	10.33
12/12/01	51.86	34.40	13.74
12/17/01	43.82	37.23	18.94
12/19/01	41.04	37.84	21.11
12/27/01	38.53	37.54	23.93
01/02/02	36.39	38.38	25.24
01/14/02	32.62	40.18	27.21
01/16/02	33.07	37.76	29.17
01/22/02	30.37	38.14	31.49
01/28/02	31.77	36.66	31.56
02/05/02	29.07	39.74	31.20
02/12/02	28.47	38.31	33.22
02/18/02	27.62	37.68	34.69
02/25/02	26.64	40.82	32.55
03/04/02	25.79	39.74	34.47
03/11/02	28.57	38.47	32.96
03/18/02	24.86	41.71	33.43
03/25/02	26.25	37.69	36.06
04/01/02	31.39	40.49	28.11
04/08/02	27.67	39.46	32.87
04/15/02	29.37	36.61	34.02
04/22/02	26.40	38.80	34.81
04/29/02	29.96	40.11	29.93
05/07/02	28.00	38.47	33.53
05/13/02	24.67	39.08	36.25
05/22/02	24.05	43.48	32.47
05/28/02	28.54	38.29	33.16
06/03/02	24.78	39.76	35.46
06/10/02	25.14	40.47	34.39
06/17/02	22.39	40.85	36.75
06/24/02	23.27	37.84	38.89

Appendix Table 1.2: Relative abundance of CV, MV, and TPR in Pen 2 after exposure to fluorescent light at six feet.

Date of Analysis	%CV	%MV	%TPR
12/03/01	99.36	0.56	0.08
12/05/01	60.31	33.96	5.73
12/10/01	57.15	35.55	7.30
12/12/01	56.59	36.02	7.40
12/17/01	53.22	37.33	9.44
12/19/01	54.67	36.69	8.64
12/27/01	52.89	37.07	10.04
01/02/02	51.76	38.02	10.22
01/14/02	49.14	38.82	12.04
01/16/02	49.15	39.07	11.79
01/22/02	48.41	39.43	12.16
01/28/02	47.39	38.61	13.99
02/05/02	44.70	40.58	14.71
02/12/02	45.57	40.71	13.73
02/18/02	45.86	40.98	13.16
02/25/02	44.91	40.52	14.57
03/04/02	42.94	41.77	15.29
03/11/02	42.97	41.83	15.20
03/18/02	42.91	40.94	16.14
03/25/02	41.64	41.98	16.38
04/01/02	40.04	41.35	18.61
04/08/02	40.13	41.99	17.88
04/15/02	38.37	41.42	20.21
04/22/02	37.07	42.37	20.57
04/29/02	36.01	41.94	22.05
05/07/02	35.75	41.13	23.12
05/13/02	34.32	41.35	24.34
05/22/02	35.05	44.05	20.91
05/28/02	35.95	43.00	21.05
06/03/02	35.79	41.43	22.77
06/10/02	34.05	41.83	24.11
06/17/02	33.04	42.08	24.88
06/24/02	32.15	41.43	26.42

Appendix Table 1.3: Relative abundance of CV, MV, and TPR in Pen 3 after exposure to fluorescent light at six feet.

Date of Analysis	%CV	%MV	%TPR
12/03/01	39.89	50.78	9.33
12/05/01	39.38	50.39	10.23
12/10/01	37.07	51.21	11.73
12/12/01	37.01	50.98	12.00
12/17/01	35.19	51.32	13.49
12/19/01	34.09	51.32	14.60
12/27/01	33.62	50.60	15.79
01/02/02	32.43	51.27	16.30
01/14/02	30.84	51.15	18.01
01/16/02	31.54	51.42	17.03
01/22/02	29.83	50.90	19.27
01/28/02	28.76	51.41	19.83
02/05/02	28.64	50.99	20.38
02/12/02	28.52	50.72	20.75
02/18/02	27.41	51.26	21.33
02/25/02	31.59	47.22	21.18
03/04/02	27.72	50.26	22.02
03/11/02	26.99	49.97	23.04
03/18/02	25.76	50.09	24.16
03/25/02	25.75	50.69	23.57
04/01/02	25.60	50.59	23.81
04/08/02	27.00	45.15	27.85
04/15/02	26.41	50.23	23.36
04/22/02	23.61	49.54	26.85
04/29/02	25.23	49.05	25.73
05/07/02	23.59	49.35	27.07
05/13/02	23.60	49.11	27.30
05/22/02	25.25	49.65	25.10
05/28/02	23.38	48.87	27.74
06/03/02	24.76	48.65	26.59
06/10/02	22.92	49.22	27.86
06/17/02	21.81	48.70	29.49
06/24/02	21.93	48.66	29.40

Appendix Table 1.4: Relative abundance of CV, MV, and TPR in Pen 4 after exposure to fluorescent light at six feet.

Date of Analysis	%CV	%MV	%TPR
12/04/01	86.43	12.49	1.08
12/06/01	79.04	18.36	2.60
12/11/01	68.83	25.43	5.74
12/13/01	63.93	28.50	7.57
12/18/01	58.07	31.48	10.45
12/20/01	56.37	32.38	11.26
12/28/01	51.29	34.12	14.59
01/03/02	46.79	35.62	17.58
01/15/02	45.65	35.72	18.63
01/17/02	43.33	36.41	20.26
01/23/02	40.92	37.34	21.74
01/29/02	39.38	37.57	23.05
02/04/02	36.05	38.19	25.76
02/11/02	33.92	37.21	28.87
02/18/02	36.92	39.51	23.57
02/26/02	33.28	37.35	29.37
03/05/02	33.04	38.75	28.22
03/12/02	33.02	39.75	27.22
03/19/02	31.69	37.98	30.33
03/26/02	29.50	39.34	31.17
04/02/02	32.99	37.98	29.04
04/09/02	30.94	40.75	28.31
04/16/02	33.49	39.16	27.35
04/23/02	28.43	37.78	33.79
04/30/02	24.32	39.72	35.96
05/07/02	32.49	36.49	31.01
05/14/02	28.21	45.15	26.64
05/23/02	27.75	36.97	35.28
05/29/02	27.60	36.69	35.70
06/04/02	28.32	40.27	31.41
06/11/02	27.36	36.48	36.16
06/18/02	24.28	39.37	36.35
06/25/02	25.24	37.76	37.01

Appendix Table 1.5: Relative abundance of CV, MV, and TPR in Pen 6 after exposure to fluorescent light at six feet.

Date of Analysis	%CV	%MV	%TPR
12/04/01	55.31	36.33	8.36
12/06/01	58.05	34.81	7.14
12/11/01	54.90	37.27	7.83
12/13/01	50.25	39.54	10.21
12/18/01	51.89	38.74	9.37
12/20/01	49.44	37.94	12.62
12/28/01	49.50	39.56	10.95
01/03/02	48.74	39.19	12.07
01/15/02	48.88	38.24	12.88
01/17/02	47.75	39.29	12.96
01/23/02	46.71	39.64	13.65
01/29/02	44.73	42.01	13.25
02/04/02	42.63	41.19	16.18
02/11/02	42.49	42.44	15.07
02/18/02	41.59	41.36	17.05
02/26/02	42.87	38.98	18.15
03/05/02	37.48	44.01	18.52
03/12/02	39.73	41.10	19.17
03/19/02	39.63	41.19	19.18
03/26/02	39.65	42.08	18.28
04/02/02	38.44	44.08	17.48
04/09/02	37.97	43.42	18.61
04/16/02	35.86	40.99	23.16
04/23/02	39.19	33.23	27.58
04/30/02	37.10	41.29	21.61
05/07/02	36.80	39.95	23.26
05/14/02	32.62	43.23	24.15
05/23/02	33.90	42.81	23.29
05/29/02	32.35	42.39	25.26
06/04/02	31.53	41.90	26.57
06/11/02	30.54	41.04	28.42
06/18/02	31.29	41.82	26.89
06/25/02	32.13	41.46	26.42

Appendix Table 1.6: Relative abundance of CV, MV, and TPR in Pen 7 after exposure to fluorescent light at six feet.

Date of Analysis	%CV	%MV	%TPR
12/04/01	82.12	16.12	1.76
12/06/01	72.55	22.94	4.51
12/11/01	59.96	30.41	9.63
12/13/01	58.84	31.09	10.06
12/18/01	52.23	33.12	14.65
12/20/01	51.07	34.01	14.92
12/28/01	45.92	35.85	18.23
01/03/02	43.74	35.84	20.42
01/15/02	36.22	38.12	25.65
01/17/02	39.37	37.48	23.15
01/23/02	36.50	37.20	26.29
01/29/02	37.36	37.06	25.57
02/04/02	34.92	37.56	27.52
02/11/02	32.99	40.05	26.96
02/18/02	33.80	37.20	29.00
02/26/02	34.66	37.92	27.42
03/05/02	33.60	37.22	29.18
03/12/02	31.25	39.78	28.97
03/19/02	35.26	39.27	25.47
03/26/02	32.33	37.28	30.39
04/02/02	33.13	36.74	30.13
04/09/02	36.87	33.32	29.81
04/16/02	30.93	41.93	27.14
04/23/02	25.75	42.34	31.90
04/30/02	25.17	38.73	36.10
05/07/02	23.84	44.07	32.10
05/14/02	21.50	43.61	34.89
05/23/02	23.36	40.40	36.24
05/29/02	29.25	39.55	31.20
06/04/02	24.06	37.58	38.35
06/11/02	27.18	34.39	38.43
06/18/02	28.94	38.51	32.54
06/25/02	20.82	44.03	35.15

Appendix Table 1.7: Relative abundance of CV, MV, and TPR in Pen 8 after exposure to fluorescent light at six feet.

Date of Analysis	%CV	%MV	%TPR
12/04/01	86.40	12.79	0.80
12/06/01	78.49	18.93	2.58
12/11/01	66.38	27.66	5.96
12/13/01	73.55	22.13	4.32
12/18/01	61.50	30.31	8.20
12/20/01	60.18	30.28	9.54
12/28/01	54.79	32.69	12.51
01/03/02	51.97	34.04	13.98
01/15/02	45.67	35.15	19.18
01/17/02	46.82	35.85	17.34
01/23/02	45.10	35.25	19.65
01/29/02	44.98	37.31	17.71
02/04/02	34.48	39.21	26.30
02/11/02	35.85	36.98	27.17
02/18/02	39.23	34.76	26.01
02/26/02	34.26	38.51	27.23
03/05/02	35.10	37.77	27.13
03/12/02	34.32	38.53	27.15
03/19/02	31.93	38.85	29.22
03/26/02	36.17	37.31	26.52
04/02/02	31.37	36.13	32.50
04/09/02	33.44	39.12	27.44
04/16/02	33.52	38.70	27.78
04/23/02	32.11	40.74	27.15
04/30/02	27.11	35.95	36.94
05/07/02	26.21	39.15	34.64
05/14/02	26.85	40.64	32.51
05/23/02	30.60	35.34	34.06
05/29/02	20.89	37.74	41.36
06/04/02	31.12	38.76	30.12
06/11/02	16.80	39.70	43.50
06/18/02	17.89	46.37	35.74
06/25/02	36.56	31.70	31.74

Appendix Table 1.8: Relative abundance of CV, MV, and TPR in Pen 9 after exposure to fluorescent light at six feet.

Date of Analysis	%CV	%MV	%TPR
12/04/01	70.47	26.41	3.12
12/06/01	61.53	31.39	7.08
12/11/01	51.13	37.16	11.71
12/13/01	46.80	40.77	12.43
12/18/01	40.03	39.30	20.66
12/20/01	37.58	41.59	20.83
12/28/01	36.12	40.44	23.44
01/03/02	32.63	42.31	25.06
01/15/02	28.28	41.41	30.32
01/17/02	28.34	41.62	30.05
01/23/02	25.28	41.09	33.63
01/29/02	23.66	38.79	37.55
02/04/02	25.57	38.03	36.40
02/11/02	24.62	36.76	38.62
02/18/02	14.49	41.46	44.04
02/26/02	19.29	29.26	51.45
03/05/02	14.69	41.27	44.04
03/12/02	22.79	38.77	38.44
03/19/02	17.76	35.18	47.06
03/26/02	19.75	38.05	42.20
04/02/02	30.13	41.09	28.78
04/09/02	18.86	42.69	38.44
04/16/02	20.08	46.90	33.02
04/23/02	12.13	44.81	43.06
04/30/02	25.06	40.39	34.56
05/07/02	18.94	40.94	40.12
05/14/02	29.73	35.73	34.54
05/23/02	17.33	47.71	34.96
05/29/02	20.37	53.29	26.34
06/04/02	22.84	42.14	35.02
06/11/02	22.92	35.03	42.05
06/18/02	18.75	42.43	38.82
06/25/02	23.20	41.54	35.26

Appendix Table 1.9: Relative abundance of CV, MV, and TPR in Pen 10 after exposure to fluorescent light at six feet.

Date of Analysis	%CV	%MV	%TPR
02/04/02	76.42	21.78	1.80
02/06/02	69.93	26.93	3.14
02/11/02	58.69	33.18	8.13
02/13/02	56.65	34.51	8.84
02/19/02	49.12	37.34	13.54
02/27/02	43.64	39.33	17.03
03/06/02	39.72	39.89	20.39
03/13/02	35.18	40.20	24.62
03/20/02	35.71	39.82	24.47
03/27/02	35.01	37.47	27.52
04/03/02	30.84	36.31	32.86
04/10/02	32.46	39.67	27.87
04/17/02	33.67	38.30	28.04
04/24/02	33.40	39.62	26.98
05/01/02	30.92	39.35	29.73
05/08/02	31.34	41.01	27.65
05/15/02	32.49	39.85	27.66
05/20/02	28.64	35.86	35.50
05/30/02	28.68	46.12	25.21
06/05/02	24.66	38.40	36.94
06/12/02	24.96	35.46	39.58
06/19/02	27.30	36.86	35.84
06/26/02	22.46	41.81	35.73
07/02/02	16.74	45.02	38.24
07/10/02	27.07	34.16	38.77
07/18/02	51.41	32.03	16.55
07/24/02	29.35	40.68	29.97
07/31/02	27.84	43.46	28.71
08/07/02	37.70	36.66	25.64
08/14/02	23.13	39.78	37.09
08/21/02	24.98	31.45	43.58
09/03/02	23.03	35.59	41.37

Appendix Table 1.10: Relative abundance of CV, MV, and TPR in Pen 11 after exposure to fluorescent light at six feet.

Date of Analysis	%CV	%MV	%TPR
02/04/02	35.46	47.87	16.67
02/06/02	34.80	48.44	16.76
02/11/02	32.51	48.74	18.75
02/13/02	32.64	48.29	19.07
02/19/02	32.44	47.89	19.67
02/27/02	30.57	48.64	20.79
03/06/02	29.40	48.74	21.86
03/13/02	28.41	49.17	22.42
03/20/02	27.66	48.99	23.35
03/27/02	28.18	49.01	22.81
04/03/02	26.33	48.68	24.98
04/10/02	26.73	48.44	24.83
04/17/02	25.62	50.07	24.31
04/24/02	26.68	47.56	25.77
05/01/02	24.71	48.66	26.63
05/08/02	23.59	48.76	27.66
05/15/02	22.54	48.10	29.36
05/20/02	21.91	48.31	29.78
05/30/02	20.92	50.15	28.94
06/05/02	22.85	48.03	29.12
06/12/02	21.70	47.85	30.45
06/19/02	20.95	49.09	29.96
06/26/02	23.40	47.80	28.81
07/02/02	21.56	47.81	30.63
07/10/02	22.00	47.34	30.66
07/18/02	21.29	47.76	30.95
07/24/02	19.30	47.72	32.98
07/31/02	18.92	47.78	33.29
08/07/02	24.90	46.54	28.56
08/14/02	18.89	47.14	33.96
08/21/02	18.78	46.76	34.45
09/03/02	17.50	49.15	33.35
09/18/02	17.36	46.73	35.91
10/02/02	16.93	47.78	35.29

Appendix Table 1.11: Relative abundance of CV, MV, and TPR in Pen 12 after exposure to fluorescent light at six feet.

Date of Analysis	%CV	%MV	%TPR
02/04/02	90.67	9.10	0.23
02/06/02	79.42	17.74	2.84
02/11/02	65.50	27.44	7.06
02/13/02	63.32	28.57	8.11
02/19/02	55.93	31.92	12.15
02/27/02	49.14	34.60	16.27
03/06/02	46.49	34.85	18.66
03/13/02	45.82	36.78	17.40
03/20/02	41.38	36.41	22.22
03/27/02	40.87	37.39	21.74
04/03/02	39.43	37.11	23.47
04/10/02	39.65	37.55	22.80
04/17/02	37.26	37.46	25.27
04/24/02	36.35	39.01	24.64
05/01/02	34.06	38.42	27.52
05/08/02	33.96	39.00	27.04
05/15/02	33.59	38.68	27.73
05/20/02	32.70	38.22	29.08
05/30/02	32.80	37.60	29.60
06/05/02	23.65	45.47	30.88
06/12/02	27.94	39.58	32.48
06/19/02	29.67	39.48	30.85
06/26/02	26.72	39.41	33.87
07/02/02	27.93	38.63	33.44
07/10/02	24.21	39.79	36.00
07/18/02	21.84	40.72	37.44
07/24/02	25.39	40.02	34.59
07/31/02	24.21	38.32	37.47
08/07/02	23.43	38.47	38.09
08/14/02	23.61	39.63	36.75
08/21/02	19.12	39.28	41.61
09/03/02	16.61	41.79	41.60
09/18/02	26.56	35.07	38.37

Appendix Table 1.12: Relative abundance of CV, MV, and TPR in Pen 13 after exposure to fluorescent light at six feet.

Date of Analysis	%CV	%MV	%TPR
02/04/02	34.51	46.05	19.43
02/06/02	33.77	45.86	20.37
02/11/02	31.63	46.51	21.85
02/13/02	32.46	46.47	21.07
02/19/02	31.26	46.56	22.18
02/27/02	30.47	46.55	22.98
03/06/02	29.49	47.71	22.80
03/13/02	29.40	47.24	23.36
03/20/02	29.33	46.38	24.29
03/27/02	27.45	46.40	26.15
04/03/02	27.20	46.52	26.29
04/10/02	26.06	46.53	27.41
04/17/02	25.57	47.27	27.16
04/24/02	25.84	45.29	28.87
05/01/02	26.51	46.29	27.20
05/08/02	24.20	46.91	28.89
05/15/02	25.63	45.55	28.83
05/20/02	26.00	44.55	29.44
05/30/02	23.42	45.54	31.04
06/05/02	23.98	45.49	30.53
06/12/02	23.58	46.23	30.19
06/19/02	22.12	45.79	32.09
06/26/02	21.26	45.65	33.10
07/02/02	21.62	46.33	32.05
07/10/02	21.08	45.48	33.44
07/18/02	22.15	45.00	32.85
07/24/02	22.16	44.24	33.60
07/31/02	21.50	43.80	34.70
08/07/02	21.35	43.28	35.37
08/14/02	20.70	44.09	35.21
08/21/02	32.79	59.41	7.81
09/03/02	19.58	45.02	35.40
09/18/02	20.02	44.70	35.27
10/02/02	20.33	42.60	37.07

Appendix Table 1.13: Relative abundance of CV, MV, and TPR in Pen 14 after exposure to fluorescent light at six feet.

Date of Analysis	%CV	%MV	%TPR
02/05/02	75.39	22.68	1.94
02/07/02	70.60	26.68	2.73
02/12/02	61.99	31.27	6.73
02/14/02	60.64	32.53	6.83
02/20/02	54.71	35.29	10.01
02/28/02	48.26	36.44	15.30
03/07/02	43.42	39.72	16.86
03/14/02	41.02	39.89	19.09
03/21/02	39.52	38.91	21.57
03/28/02	37.00	39.72	23.29
04/04/02	34.69	38.40	26.91
04/11/02	31.64	41.02	27.34
04/18/02	32.01	39.35	28.64
04/25/02	26.09	39.96	33.95
05/01/02	29.15	38.03	32.83
05/09/02	32.88	38.69	28.43
05/16/02	27.90	40.57	31.53
05/21/02	31.02	36.74	32.23
05/30/02	24.91	40.01	35.08
06/06/02	24.21	43.41	32.39
06/12/02	29.24	35.25	35.51
06/19/02	27.88	43.15	28.96
06/26/02	26.42	41.06	32.52
07/02/02	24.88	37.52	37.61
07/10/02	27.32	42.28	30.39
07/18/02	15.94	47.19	36.87
07/24/02	23.85	35.94	40.21
07/31/02	29.82	40.25	29.93
08/07/02	13.10	37.99	48.92
08/14/02	13.80	49.04	37.16
08/21/02	21.10	40.18	38.72
09/03/02	18.15	38.90	42.95

Appendix Table 1.14: Relative abundance of CV, MV, and TPR in Pen 16 after exposure to fluorescent light at six feet.

Date of Analysis	%CV	%MV	%TPR
02/05/02	38.38	51.88	9.74
02/07/02	37.79	51.47	10.75
02/12/02	36.48	52.11	11.41
02/14/02	35.98	52.15	11.87
02/20/02	34.82	52.10	13.08
02/28/02	33.98	51.62	14.41
03/07/02	31.79	51.99	16.22
03/14/02	31.06	52.02	16.92
03/21/02	30.10	51.58	18.32
03/28/02	31.20	51.38	17.42
04/04/02	29.81	51.37	18.82
04/11/02	29.65	51.75	18.60
04/18/02	28.83	50.85	20.32
04/25/02	28.57	51.29	20.15
05/01/02	27.84	50.48	21.68
05/09/02	27.06	49.85	23.08
05/16/02	26.51	50.04	23.45
05/21/02	26.13	50.33	23.54
05/30/02	25.22	49.57	25.20
06/06/02	25.14	49.93	24.92
06/12/02	24.21	50.06	25.73
06/19/02	25.52	49.09	25.39
06/26/02	24.58	48.76	26.66
07/02/02	23.96	49.12	26.92
07/10/02	23.06	48.49	28.45
07/18/02	21.52	49.21	29.28
07/24/02	20.74	45.19	34.07
07/31/02	23.07	48.24	28.68
08/07/02	22.43	48.61	28.96
08/14/02	22.42	47.58	30.00
08/21/02	20.89	47.72	31.39
09/03/02	21.41	47.77	30.82

Appendix Table 1.15: Relative abundance of CV, MV, and TPR in Pen 17 after exposure to fluorescent light at six feet.

Date of Analysis	%CV	%MV	%TPR
02/05/02	47.18	40.23	12.59
02/07/02	47.92	40.26	11.82
02/12/02	46.96	40.28	12.76
02/14/02	47.09	39.79	13.13
02/20/02	47.10	40.69	12.21
02/28/02	45.82	40.80	13.38
03/07/02	45.09	41.24	13.67
03/14/02	45.01	40.83	14.16
03/21/02	44.27	41.11	14.61
03/28/02	44.23	41.66	14.11
04/04/02	44.27	40.99	14.74
04/11/02	44.83	41.85	13.32
04/18/02	41.17	41.98	16.86
04/25/02	43.64	40.60	15.77
05/01/02	43.26	41.90	14.84
05/09/02	42.70	41.39	15.90
05/16/02	41.37	40.44	18.19
05/21/02	43.06	40.92	16.02
05/30/02	41.05	42.20	16.75
06/06/02	41.66	41.21	17.13
06/12/02	41.98	41.45	16.57
06/19/02	32.83	47.89	19.29
06/26/02	40.88	41.72	17.40
07/02/02	39.23	41.99	18.78
07/10/02	39.28	41.82	18.90
07/18/02	39.56	41.71	18.73
07/24/02	39.61	42.08	18.31
07/31/02	39.32	42.50	18.17
08/07/02	38.63	42.46	18.91
08/14/02	37.57	42.70	19.73
08/21/02	38.84	41.75	19.41
09/03/02	38.81	42.24	18.95

Appendix Table 1.16: Relative abundance of CV, MV, and TPR in Pen 18 after exposure to fluorescent light at six feet.

Date of Analysis	%CV	%MV	%TPR
02/05/02	76.12	21.86	2.03
02/07/02	71.61	25.64	2.75
02/12/02	62.54	30.78	6.68
02/14/02	61.19	31.62	7.19
02/20/02	55.47	34.94	9.59
02/28/02	49.77	37.63	12.60
03/07/02	46.92	37.85	15.23
03/14/02	42.78	39.72	17.49
03/21/02	40.25	40.05	19.70
03/28/02	41.87	38.38	19.74
04/04/02	41.15	38.54	20.31
04/11/02	41.41	38.77	19.82
04/18/02	38.30	39.46	22.24
04/25/02	37.68	38.66	23.66
05/01/02	37.05	39.51	23.44
05/09/02	37.80	38.99	23.20
05/16/02	35.43	40.03	24.53
05/21/02	35.77	39.23	25.01
05/30/02	35.70	39.56	24.74
06/06/02	39.77	37.75	22.48
06/12/02	30.00	39.79	30.21
06/19/02	30.99	39.66	29.35
06/26/02	29.95	38.19	31.86
07/02/02	28.89	41.07	30.04
07/10/02	29.58	41.48	28.94
07/18/02	24.72	53.23	22.05
07/24/02	26.25	41.54	32.21
07/31/02	27.67	40.54	31.78
08/07/02	23.67	40.69	35.63
08/14/02	26.39	41.46	32.14
08/21/02	26.88	40.35	32.77
09/03/02	24.59	39.84	35.56

Appendix Table 1.17: Relative abundance of CV, MV, and TPR in Pen 19 after exposure to fluorescent light at six feet.

Date of Analysis	%CV	%MV	%TPR
02/05/02	78.37	20.11	1.52
02/07/02	71.59	25.77	2.64
02/12/02	59.05	32.39	8.56
02/14/02	56.67	33.37	9.96
02/20/02	51.27	36.36	12.37
02/28/02	43.72	37.97	18.31
03/07/02	39.40	38.19	22.41
03/14/02	37.28	38.79	23.93
03/21/02	34.99	40.55	24.47
03/28/02	32.65	38.85	28.49
04/04/02	33.12	39.98	26.90
04/11/02	32.32	38.54	29.15
04/18/02	31.20	39.45	29.35
04/25/02	32.70	39.14	28.16
05/01/02	29.32	38.78	31.90
05/09/02	28.33	38.83	32.84
05/16/02	27.17	40.81	32.02
05/21/02	29.25	41.07	29.68
05/30/02	26.52	40.01	33.47
06/06/02	25.51	39.89	34.59
06/12/02	23.54	39.41	37.04
06/19/02	24.94	38.78	36.28
06/26/02	23.53	38.75	37.72
07/02/02	16.26	58.82	24.91
07/10/02	24.03	36.87	39.10
07/18/02	24.00	36.37	39.63
07/24/02	22.91	40.77	36.32
07/31/02	22.46	35.75	41.79
08/07/02	31.58	36.95	31.48
08/14/02	20.92	41.35	37.73
08/21/02	20.11	39.23	40.65
09/03/02	16.72	43.08	40.20
09/18/02	14.51	42.00	43.49
10/02/02	29.12	33.51	37.37

Appendix Table 1.18: Relative abundance of CV, MV, and TPR in Pen 20 after exposure to fluorescent light at six feet.

Date of Analysis	%CV	%MV	%TPR
09/10/02	78.37	20.11	1.52
09/12/02	71.59	25.77	2.64
09/17/02	59.05	32.39	8.56
09/19/02	56.67	33.37	9.96
09/24/02	51.27	36.36	12.37
10/02/02	43.72	37.97	18.31
10/09/02	39.40	38.19	22.41
10/15/02	37.28	38.79	23.93
10/24/02	34.99	40.55	24.47
11/06/02	32.65	38.85	28.49
11/14/02	33.12	39.98	26.90
11/20/02	32.32	38.54	29.15
11/26/02	31.20	39.45	29.35
12/04/02	32.70	39.14	28.16
12/11/02	29.32	38.78	31.90
12/18/02	28.33	38.83	32.84
01/03/03	27.17	40.81	32.02
01/08/03	29.25	41.07	29.68
01/15/03	26.52	40.01	33.47

Appendix Table 1.19: Relative abundance of CV, MV, and TPR in Pen 21 after exposure to fluorescent light at six feet.

Date of Analysis	%CV	%MV	%TPR
09/10/02	60.11	34.70	5.20
09/12/02	58.14	35.48	6.38
09/17/02	57.52	35.02	7.47
09/19/02	55.63	36.79	7.58
09/24/02	56.07	36.13	7.80
10/02/02	52.57	38.13	9.30
10/09/02	50.17	39.04	10.79
10/15/02	49.57	40.14	10.29
10/24/02	51.33	38.83	9.84
11/06/02	43.67	41.40	14.93
11/14/02	47.24	40.75	12.00
11/20/02	43.85	40.78	15.37
11/26/02	47.25	40.29	12.46
12/04/02	46.73	40.19	13.08
12/11/02	47.75	39.63	12.62
12/18/02	48.23	39.22	12.55
01/03/03	47.04	39.53	13.43
01/08/03	40.63	41.44	17.93
01/15/03	43.08	40.64	16.27

Appendix Table 1.20: Relative abundance of CV, MV, and TPR in Pen 22 after exposure to fluorescent light at six feet.

Date of Analysis	%CV	%MV	%TPR
09/10/02	36.25	47.49	16.26
09/12/02	35.12	48.03	16.85
09/17/02	33.56	48.25	18.19
09/19/02	33.00	48.20	18.81
09/24/02	32.04	48.57	19.39
10/02/02	30.63	49.02	20.35
10/09/02	29.39	49.64	20.97
10/15/02	29.61	49.49	20.90
10/24/02	28.82	49.07	22.11
11/06/02	27.34	50.35	22.31
11/14/02	24.57	54.90	20.52
11/20/02	24.93	55.13	19.94
11/26/02	24.55	54.73	20.72
12/04/02	23.50	55.27	21.23
12/11/02	25.29	54.64	20.07
12/18/02	23.95	55.46	20.59
01/03/03	23.89	55.28	20.83
01/08/03	23.24	55.65	21.11
01/15/03	23.79	55.28	20.93

Appendix Table 1.21: Relative abundance of CV, MV, and TPR in Pen 23 after exposure to fluorescent light at six feet

Date of Analysis	%CV	%MV	%TPR
09/10/02	51.45	40.47	8.08
09/12/02	47.94	41.92	10.15
09/17/02	45.87	42.48	11.65
09/19/02	46.15	42.76	11.09
09/24/02	45.36	42.40	12.25
10/02/02	42.99	43.31	13.70
10/09/02	41.49	44.06	14.45
10/15/02	40.95	44.34	14.70
10/24/02	41.55	44.75	13.70
11/06/02	40.72	44.45	14.83
11/14/02	40.20	43.63	16.17
11/20/02	39.04	45.16	15.80
11/26/02	40.71	44.43	14.86
12/04/02	39.29	44.09	16.62
12/11/02	39.45	44.16	16.39
12/18/02	38.99	44.48	16.53
01/03/03	38.01	45.25	16.73
01/08/03	36.58	44.69	18.72
01/15/03	37.75	44.35	17.91

Appendix Table 1.22: Relative abundance of CV, MV, and TPR in Pen 24 after exposure to fluorescent light at six feet

Date of Analysis	%CV	%MV	%TPR
09/10/02	34.22	48.35	17.43
09/12/02	34.21	50.36	15.43
09/17/02	31.89	49.11	19.00
09/19/02	31.80	48.52	19.69
09/24/02	31.40	48.29	20.31
10/02/02	29.17	49.61	21.22
10/09/02	28.89	49.25	21.85
10/15/02	28.40	49.67	21.93
10/24/02	27.74	49.75	22.51
11/06/02	25.82	50.74	23.44
11/14/02	22.93	55.46	21.61
11/20/02	23.33	55.13	21.54
11/26/02	23.00	55.96	21.04
12/04/02	22.90	55.76	21.34
12/11/02	21.95	56.22	21.83
12/18/02	22.27	56.11	21.62
01/03/03	22.75	55.92	21.33
01/08/03	21.57	55.83	22.60
01/15/03	22.08	55.79	22.13

Appendix Table 1.23: Relative abundance of CV, MV, and TPR in Pen 25 after exposure to fluorescent light at six feet

Date of Analysis	%CV	%MV	%TPR
09/10/02	65.51	29.61	4.88
09/12/02	60.63	32.94	6.43
09/17/02	51.41	37.30	11.29
09/19/02	47.87	38.68	13.45
09/24/02	43.01	39.75	17.24
10/02/02	36.63	41.63	21.74
10/09/02	35.94	41.64	22.41
10/15/02	33.32	41.48	25.20
10/24/02	34.12	41.32	24.56
11/06/02	30.69	41.92	27.39
11/14/02	30.89	40.31	28.80
11/20/02	30.76	40.87	28.37
11/26/02	29.42	40.96	29.62
12/04/02	30.10	39.66	30.24
12/11/02	29.92	39.68	30.41
12/18/02	29.93	40.61	29.46
01/03/03	28.64	39.25	32.12
01/08/03	33.02	39.28	27.71
01/15/03	27.74	40.43	31.82

Appendix Table 1.24: Relative abundance of CV, MV, and TPR in Pen 26 after exposure to fluorescent light at six feet

Date of Analysis	%CV	%MV	%TPR
09/10/02	84.48	14.69	0.83
09/12/02	77.72	19.66	2.62
09/17/02	65.54	28.05	6.41
09/19/02	61.97	30.03	8.01
09/24/02	56.88	32.32	10.80
10/02/02	48.22	35.43	16.35
10/09/02	45.37	37.18	17.45
10/15/02	41.79	37.81	20.39
10/24/02	39.47	38.59	21.94
11/06/02	39.03	38.68	22.29
11/14/02	37.16	36.97	25.87
11/20/02	35.58	37.93	26.48
11/26/02	37.46	38.47	24.07
12/04/02	31.64	36.84	31.53
12/11/02	33.71	36.84	29.45
12/18/02	32.02	38.69	29.29
01/03/03	31.42	38.56	30.02
01/08/03	33.58	40.53	25.89
01/15/03	34.93	33.48	31.59

Appendix Table 1.25: Relative abundance of CV, MV, and TPR in Pen 27 after exposure to fluorescent light at six feet

Date of Analysis	%CV	%MV	%TPR
09/10/02	86.76	12.54	0.70
09/12/02	79.77	18.73	1.50
09/17/02	68.81	25.68	5.51
09/19/02	66.87	26.99	6.14
09/24/02	59.11	31.21	9.68
10/02/02	50.44	35.21	14.35
10/09/02	49.18	35.34	15.48
10/15/02	45.08	36.67	18.25
10/24/02	41.65	36.69	21.65
11/06/02	34.78	39.06	26.16
11/14/02	43.02	36.24	20.74
11/20/02	38.09	37.30	24.61
11/26/02	36.98	36.46	26.56
12/04/02	34.85	42.19	22.96
12/11/02	33.46	38.11	28.43
12/18/02	34.04	37.26	28.70
01/03/03	30.86	38.72	30.41
01/08/03	41.56	33.84	24.59
01/15/03	36.68	36.23	27.10

Appendix Table 1.26: Relative abundance of CV, MV, and TPR in Pen 28 after exposure to fluorescent light at six feet

Date of Analysis	%CV	%MV	%TPR
09/10/02	77.91	20.54	1.55
09/12/02	76.08	22.06	1.87
09/17/02	71.42	25.74	2.84
09/19/02	69.56	26.22	4.22
09/24/02	65.61	28.59	5.80
10/02/02	61.95	30.64	7.40
10/09/02	60.72	31.16	8.11
10/15/02	59.27	31.78	8.95
10/24/02	55.12	33.64	11.24
11/06/02	51.82	34.96	13.22
11/14/02	51.68	34.59	13.73
11/20/02	50.80	34.91	14.29
11/26/02	50.98	34.85	14.16
12/04/02	51.73	34.64	13.63
12/11/02	49.48	35.42	15.10
12/18/02	51.24	34.98	13.78
01/03/03	46.45	35.99	17.57
01/08/03	45.37	36.79	17.84
01/15/03	47.33	36.06	16.61

Appendix Table 1.27: Relative abundance of CV, MV, and TPR in Pen 29 after exposure to fluorescent light at six feet

Date of Analysis	%CV	%MV	%TPR
09/10/02	34.61	47.72	17.67
09/12/02	35.04	47.72	17.24
09/17/02	32.83	48.19	18.98
09/19/02	32.64	48.18	19.19
09/24/02	32.42	47.93	19.65
10/02/02	29.86	49.30	20.84
10/09/02	29.54	49.24	21.22
10/15/02	27.65	52.80	19.54
10/24/02	25.86	54.07	20.06
11/06/02	27.49	49.75	22.76
11/14/02	24.94	53.40	21.66
11/20/02	25.08	54.03	20.89
11/26/02	26.28	53.44	20.29
12/04/02	25.08	53.74	21.19
12/11/02	25.05	53.89	21.06
12/18/02	24.31	54.15	21.54
01/03/03	24.10	54.20	21.70
01/08/03	23.43	54.17	22.40
01/15/03	23.75	54.69	21.57

Appendix Table 1.28: Relative abundance of CV, MV, and TPR in Pen 30 after exposure to fluorescent light at six feet

Date of Analysis	%CV	%MV	%TPR
09/10/02	35.36	45.20	19.44
09/12/02	34.38	46.07	19.55
09/17/02	33.38	46.67	19.95
09/19/02	33.92	45.97	20.11
09/24/02	32.51	46.39	21.10
10/02/02	32.16	46.11	21.73
10/09/02	30.70	46.42	22.88
10/15/02	29.60	45.78	24.62
10/24/02	28.81	45.67	25.51
11/06/02	28.32	44.77	26.92
11/14/02	26.21	46.14	27.65
11/20/02	25.39	47.10	27.51
11/26/02	28.43	45.73	25.84
12/04/02	24.23	46.00	29.77
12/11/02	25.18	46.11	28.71
12/18/02	27.55	45.67	26.78
01/03/03	26.16	45.45	28.40
01/08/03	24.77	46.95	28.29
01/15/03	25.77	45.92	28.31

Appendix Table 1.29: Relative abundance of CV, MV, and TPR in Pen 31 after exposure to fluorescent light at six feet

Date of Analysis	%CV	%MV	%TPR
09/10/02	31.61	46.72	21.67
09/12/02	31.30	46.63	22.08
09/17/02	30.19	47.03	22.78
09/19/02	30.21	47.01	22.78
09/24/02	28.88	46.96	24.16
10/02/02	29.44	46.15	24.40
10/09/02	27.86	47.27	24.86
10/15/02	28.12	46.04	25.85
10/24/02	26.39	47.46	26.15
11/06/02	26.74	47.00	26.26
11/14/02	27.58	46.28	26.15
11/20/02	24.22	47.27	28.51
11/26/02	27.15	47.09	25.76
12/04/02	24.05	47.28	28.66
12/11/02	24.73	46.44	28.84
12/18/02	25.24	46.42	28.33
01/03/03	24.64	46.68	28.68
01/08/03	24.97	46.33	28.70
01/15/03	24.14	46.34	29.51

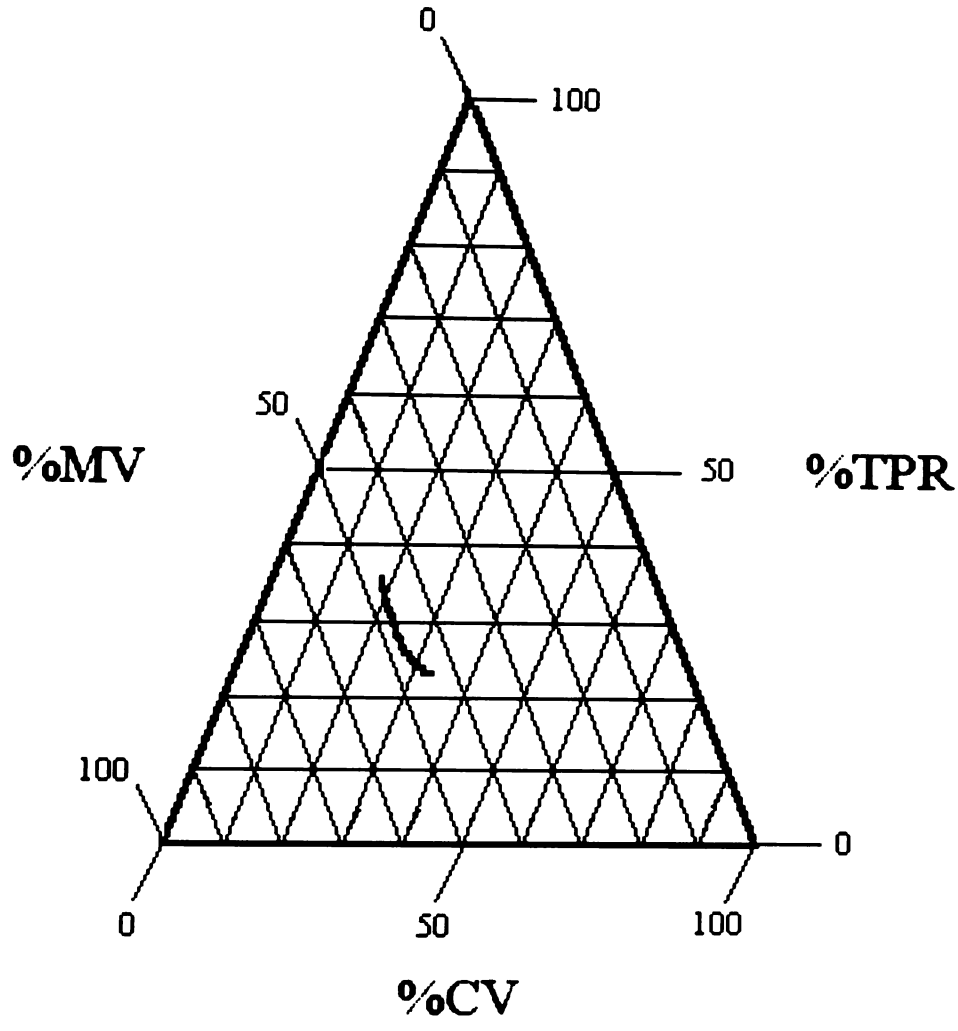
Appendix Table 1.30: Relative abundance of CV, MV, and TPR in Pen 32 after exposure to fluorescent light at six feet

Appendix II

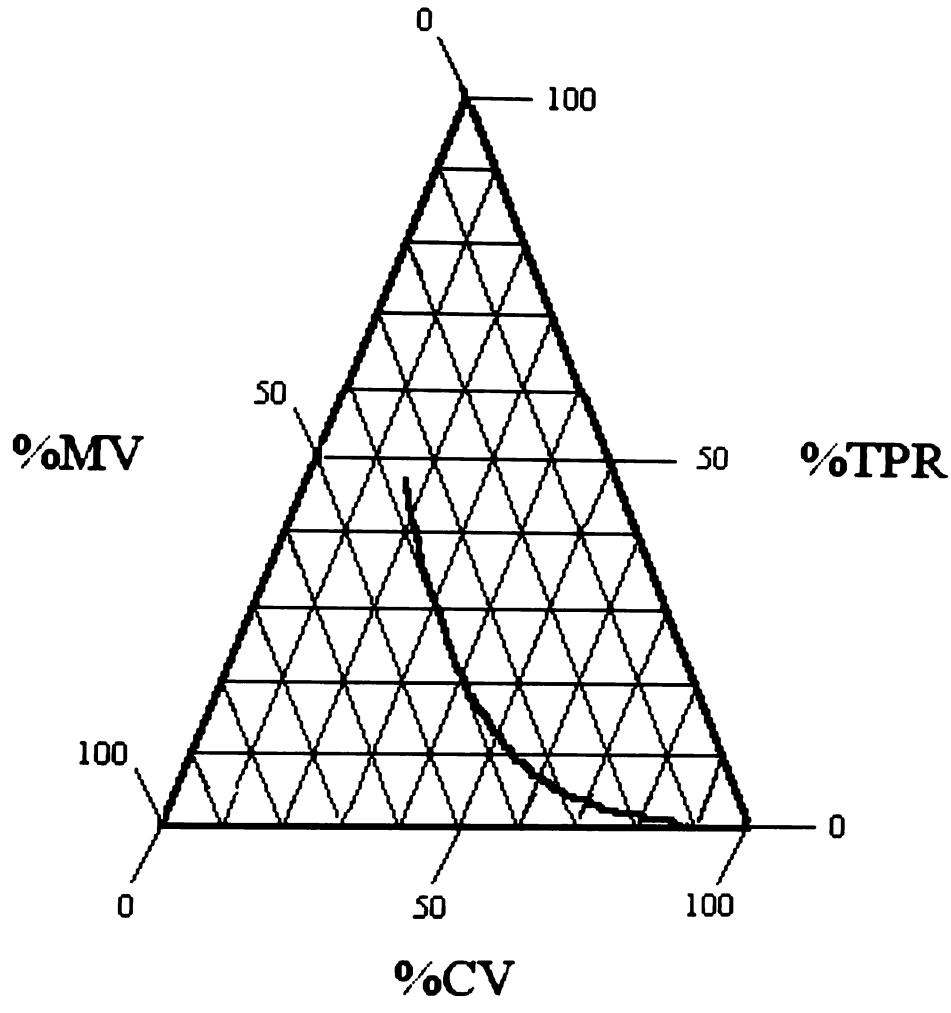
Data: ternary diagrams depicting the degradation of the dye components

upon exposure to fluorescent light at six feet

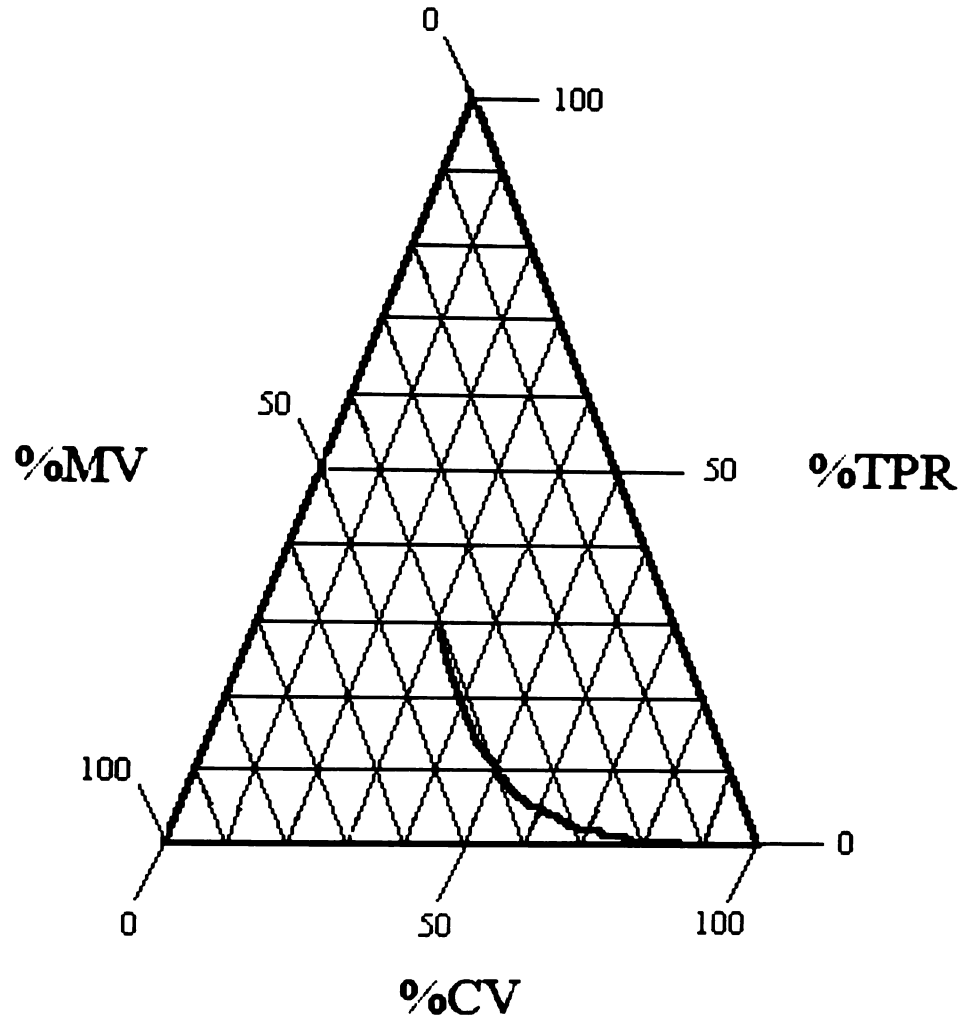
Pens 5 and 15 contained a dye other than crystal violet. No data was obtained for these pens.



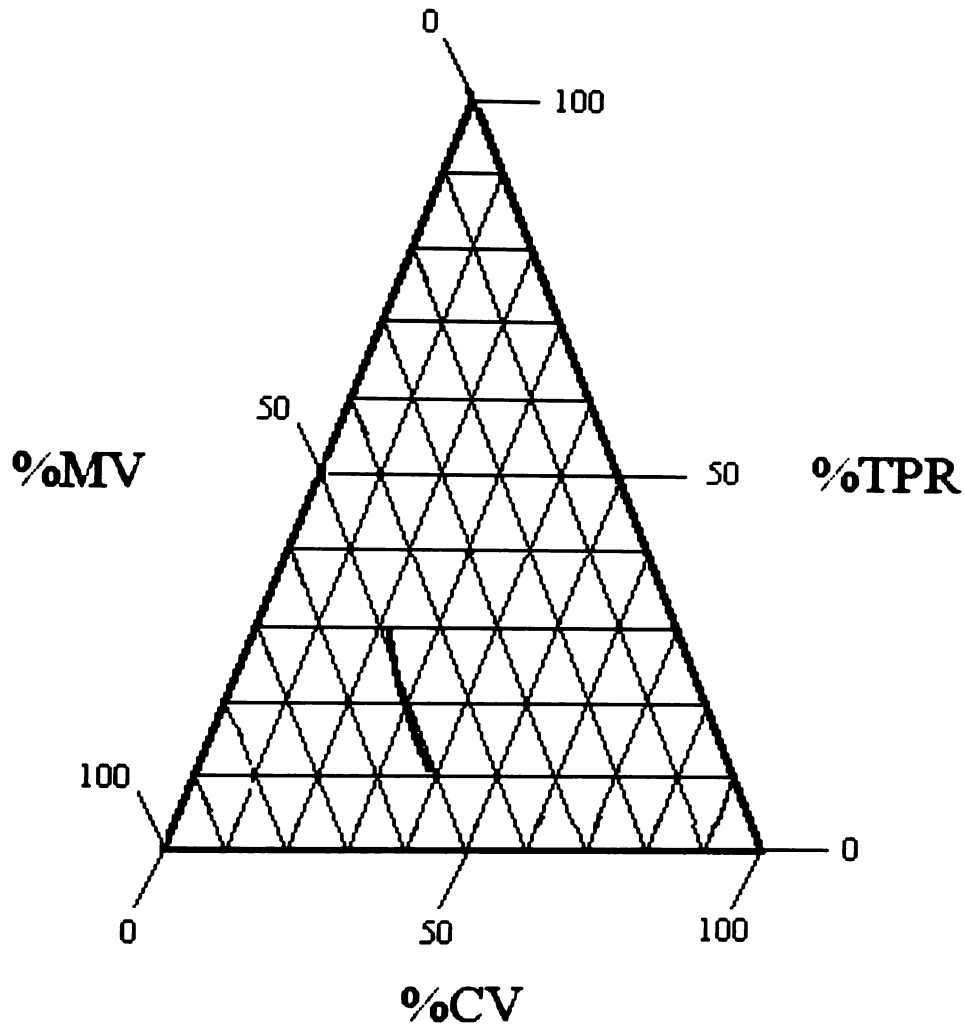
Appendix Figure 2.1: The degradation of the dye components in Pen 1 upon exposure to fluorescent light at six feet.



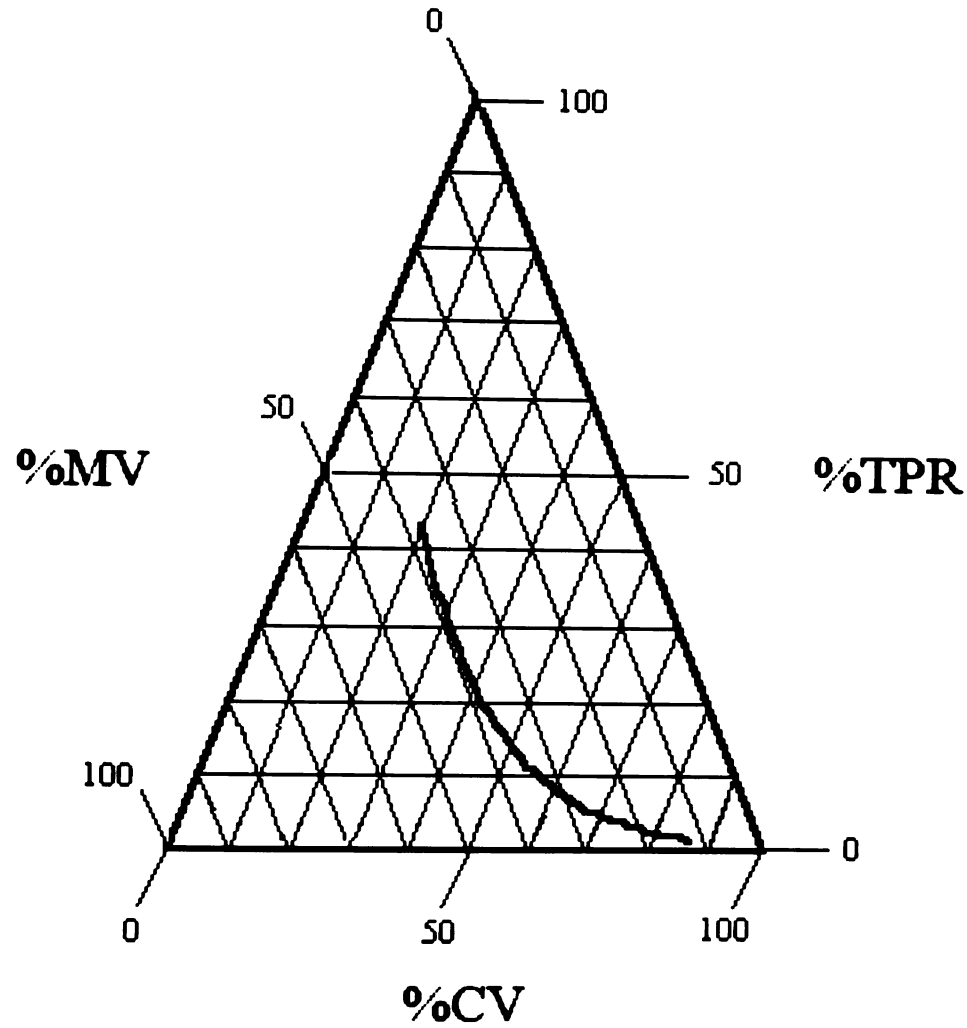
Appendix Figure 2.2: The degradation of the dye components in Pen 2 upon exposure to fluorescent light at six feet.



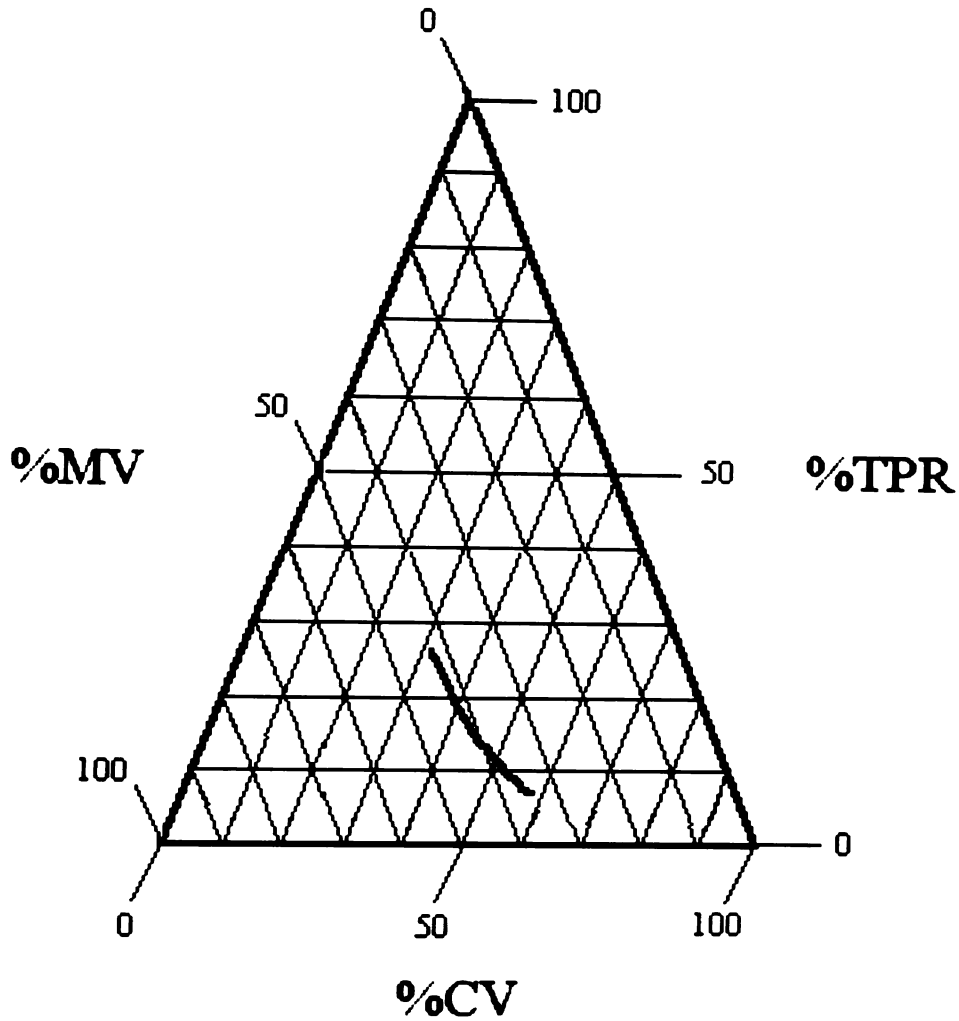
Appendix Figure 2.3: The degradation of the dye components in Pen 3 upon exposure to fluorescent light at six feet.



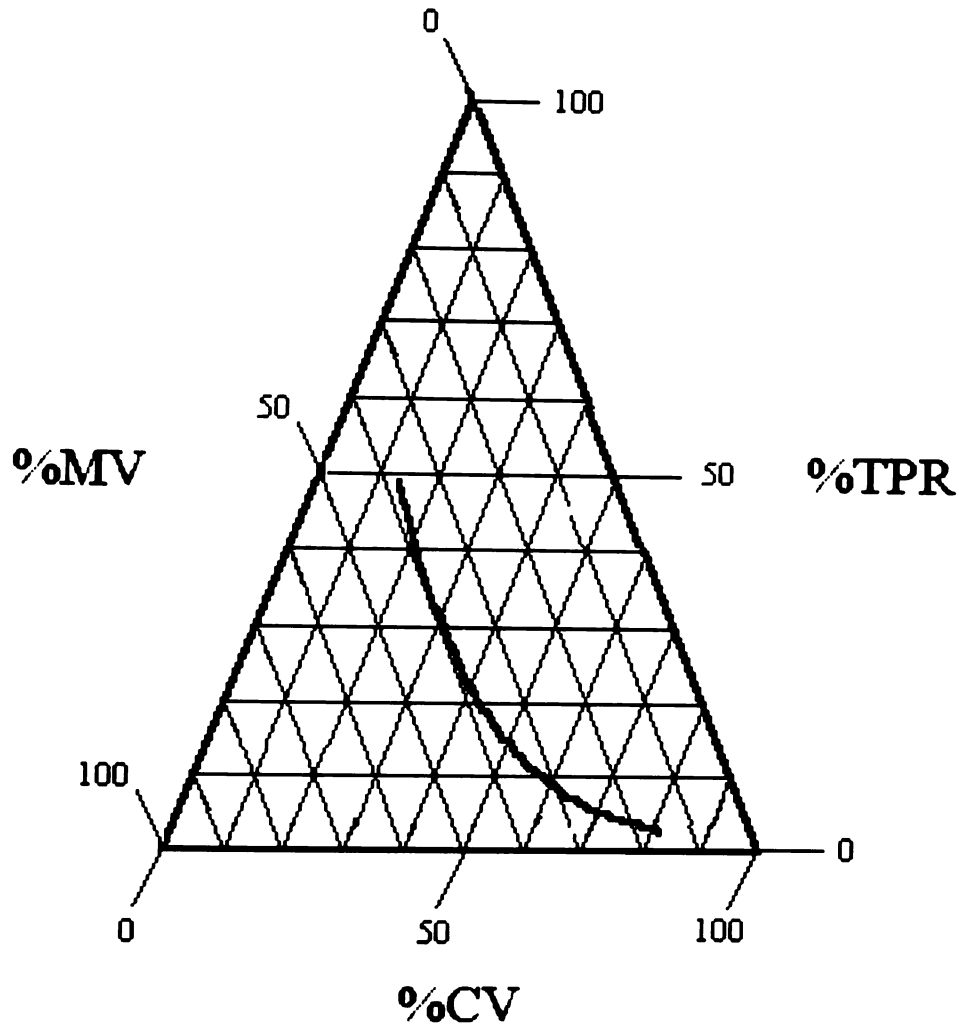
Appendix Figure 2.4: The degradation of the dye components in Pen 4 upon exposure to fluorescent light at six feet.



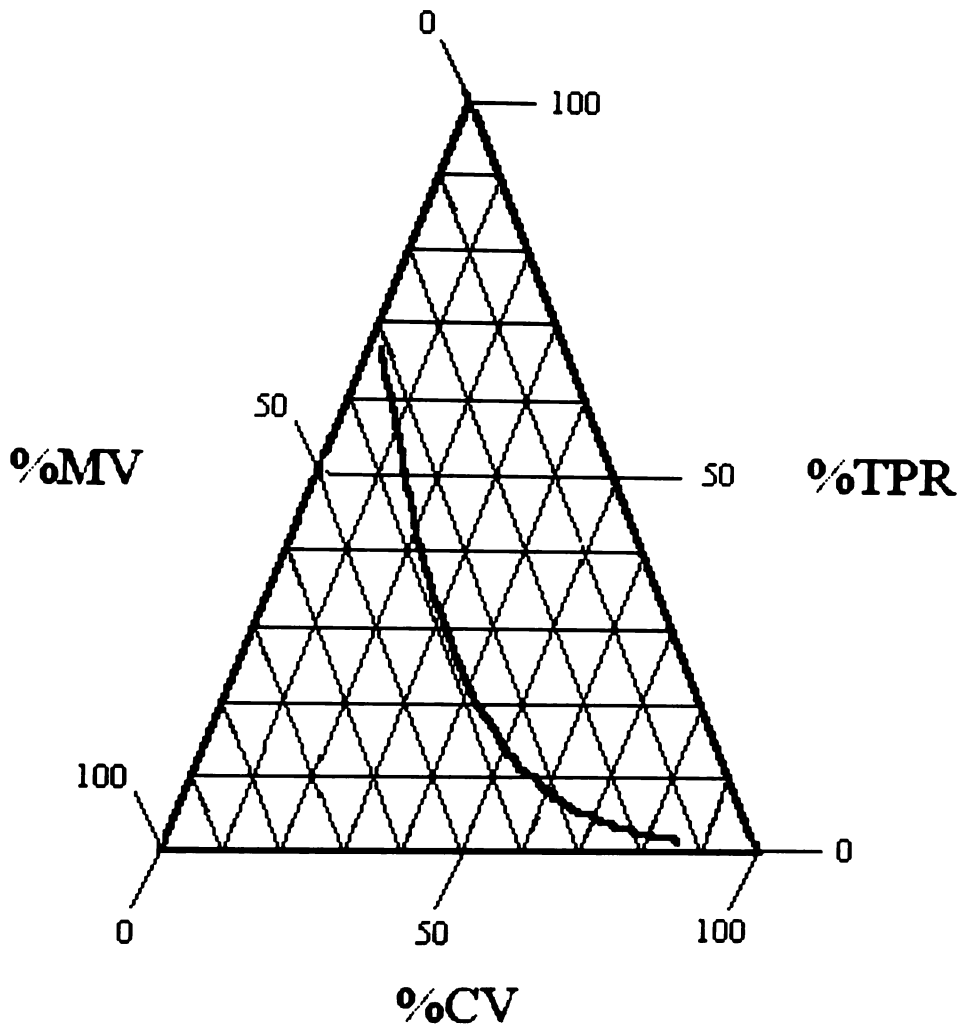
Appendix Figure 2.5: The degradation of the dye components in Pen 6 upon exposure to fluorescent light at six feet.



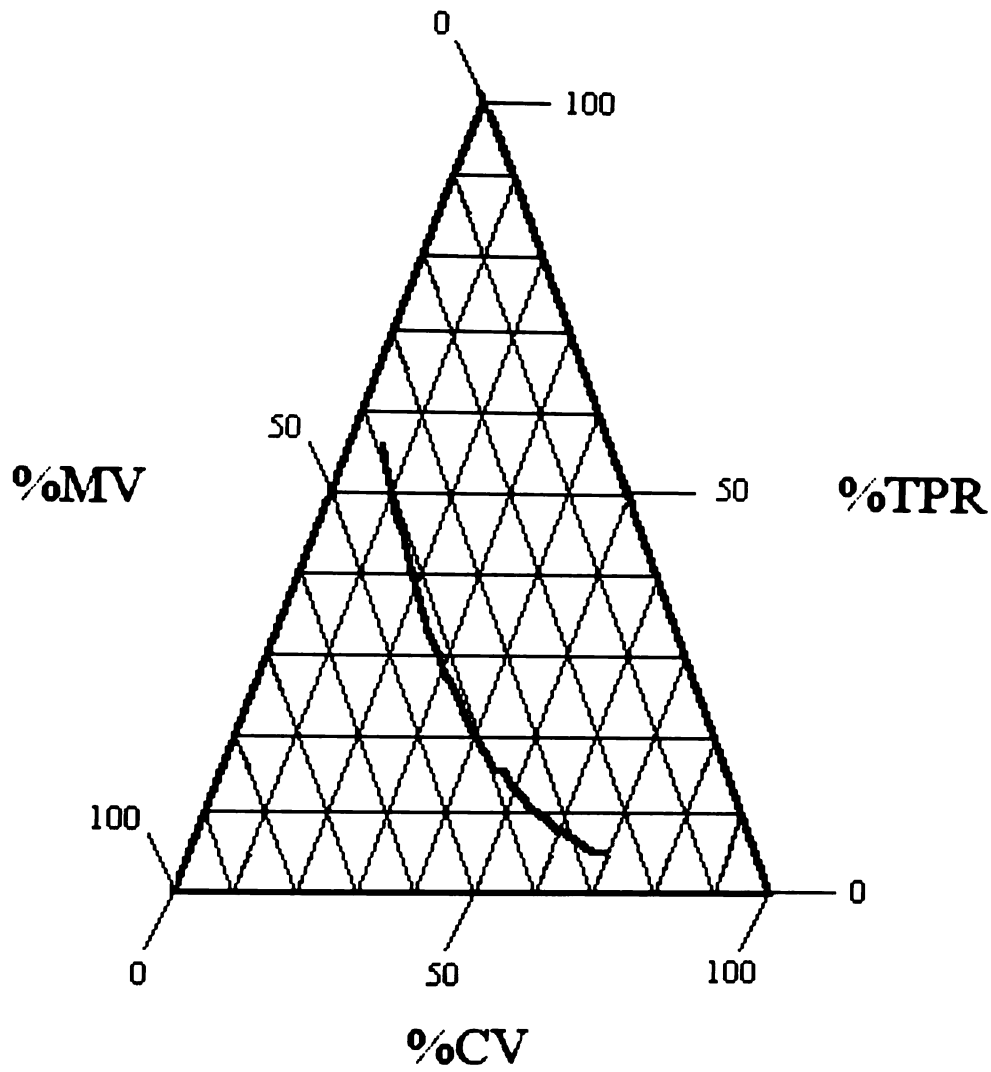
Appendix Figure 2.6: The degradation of the dye components in Pen 7 upon exposure to fluorescent light at six feet.



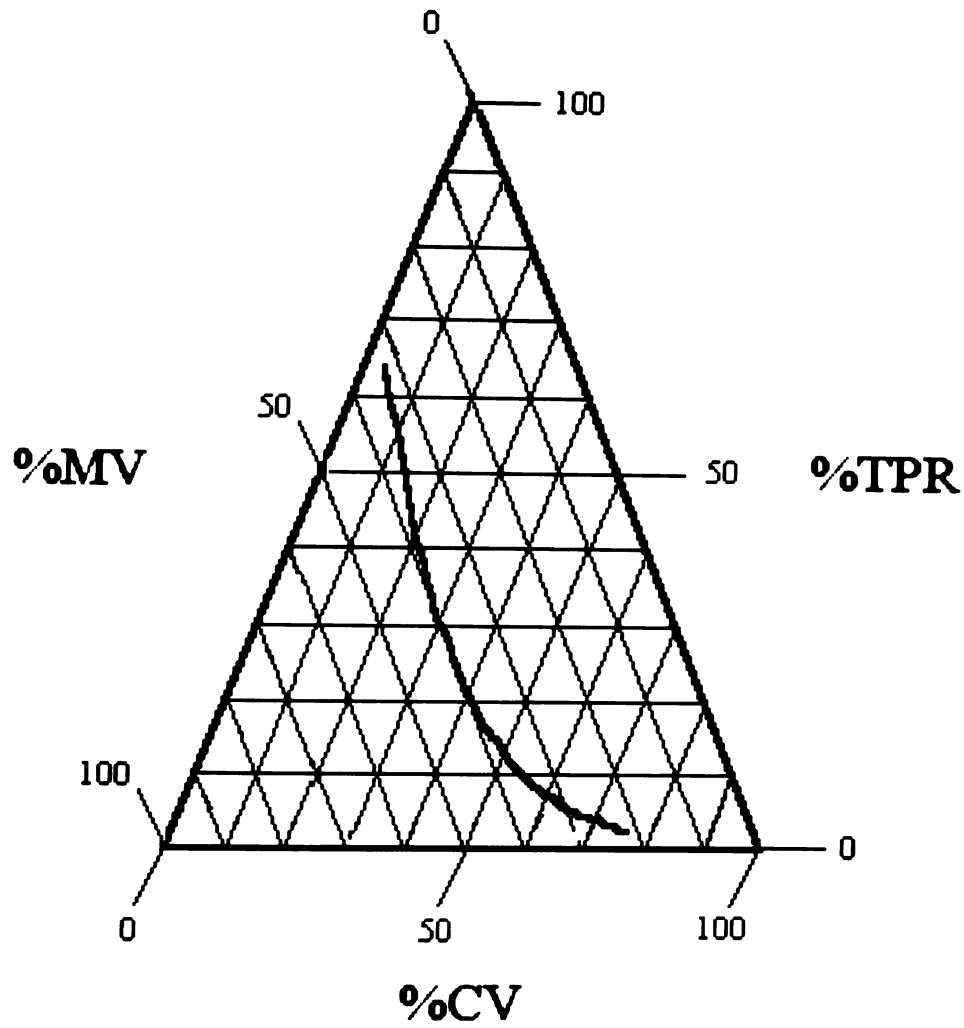
Appendix Figure 2.7: The degradation of the dye components in Pen 8 upon exposure to fluorescent light at six feet.



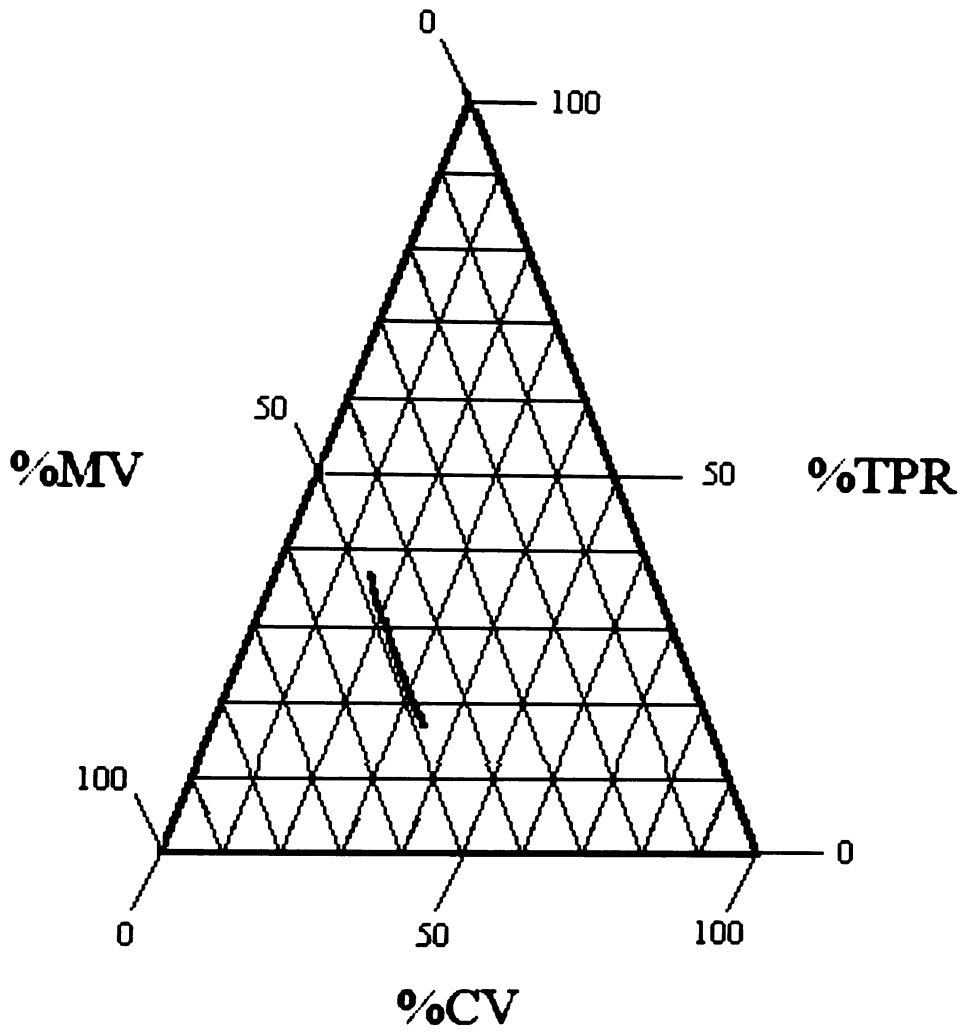
Appendix Figure 2.8: The degradation of the dye components in Pen 9 upon exposure to fluorescent light at six feet.



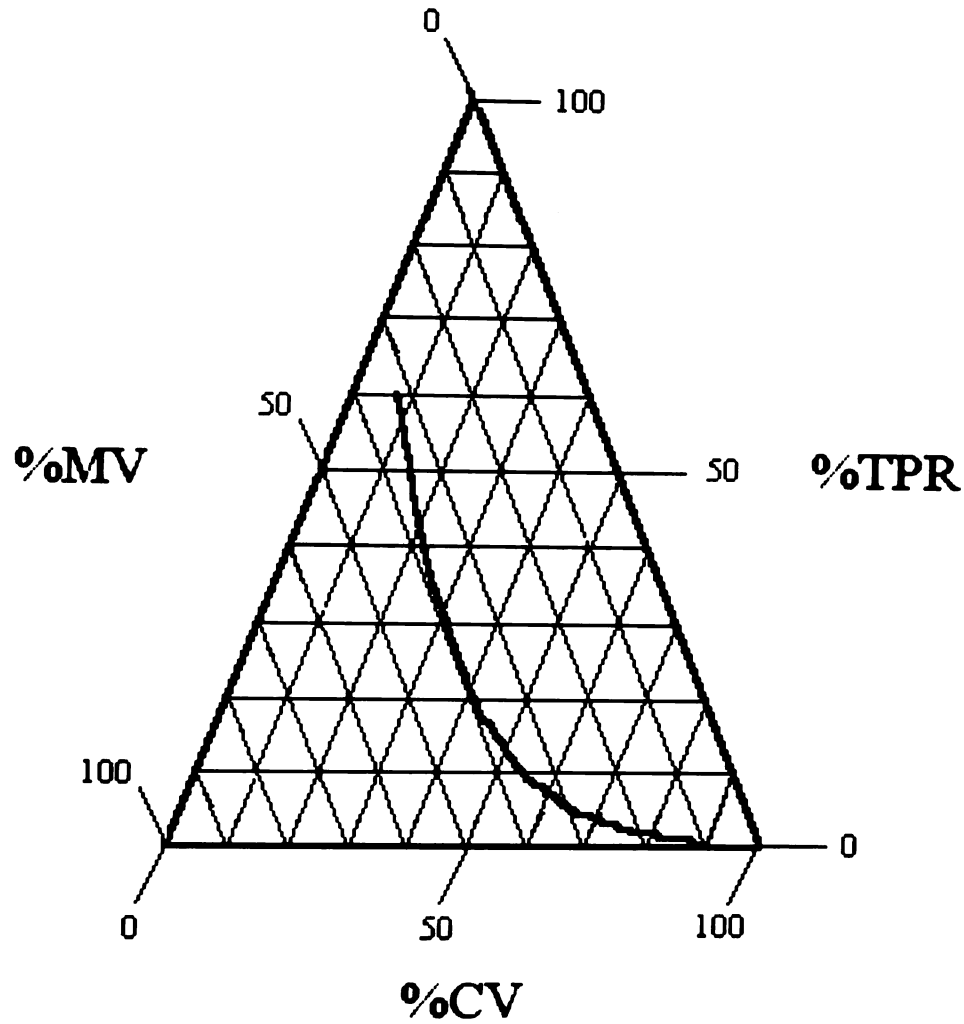
Appendix Figure 2.9: The degradation of the dye components in Pen 10 upon exposure to fluorescent light at six feet.



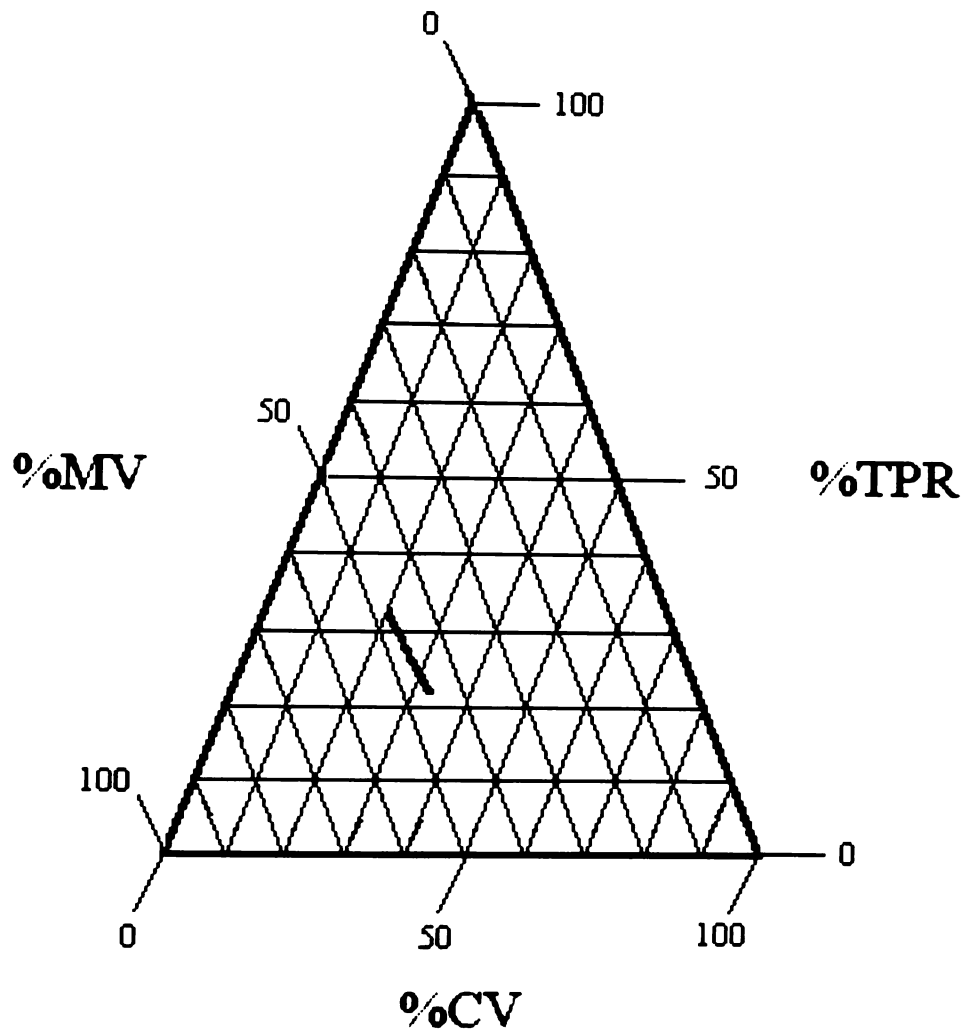
Appendix Figure 2.10: The degradation of the dye components in Pen 11 upon exposure to fluorescent light at six feet.



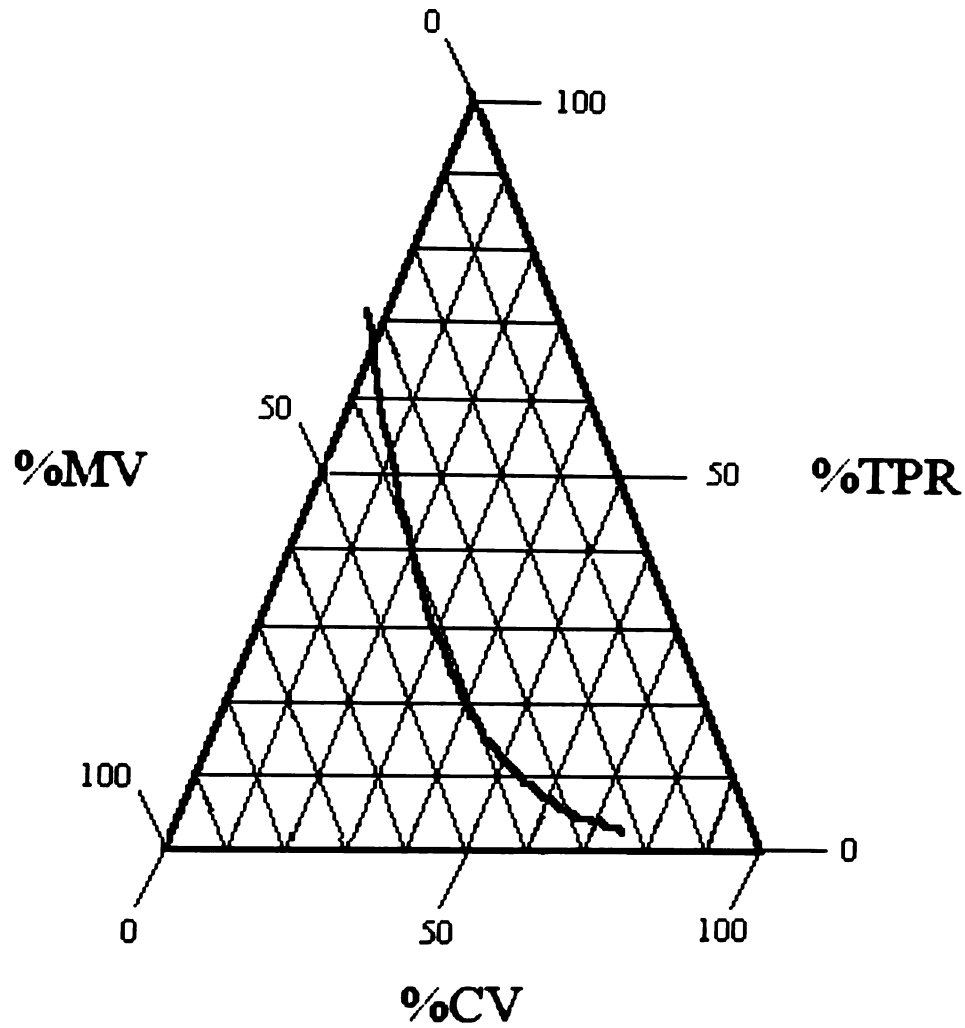
Appendix Figure 2.11: The degradation of the dye components in Pen 12 upon exposure to fluorescent light at six feet.



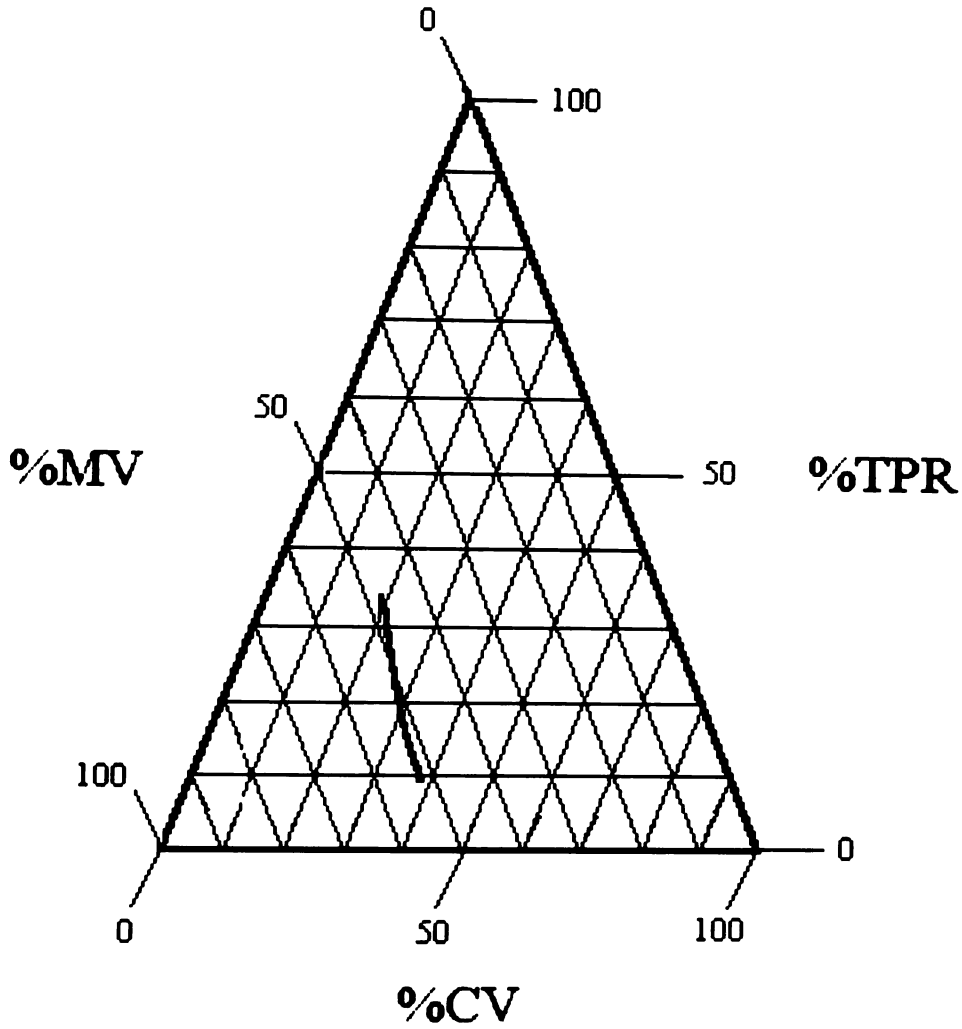
Appendix Figure 2.12: The degradation of the dye components in Pen 13 upon exposure to fluorescent light at six feet.



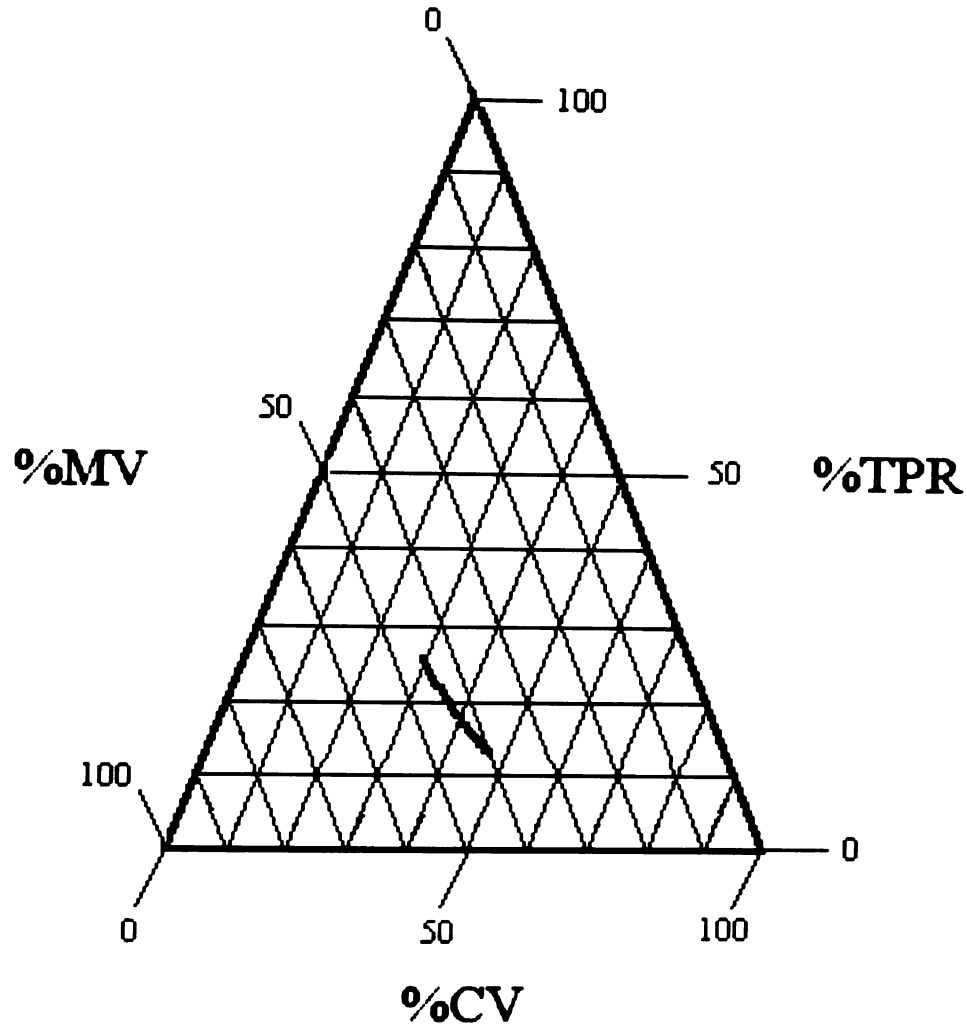
Appendix Figure 2.13: The degradation of the dye components in Pen 14 upon exposure to fluorescent light at six feet.



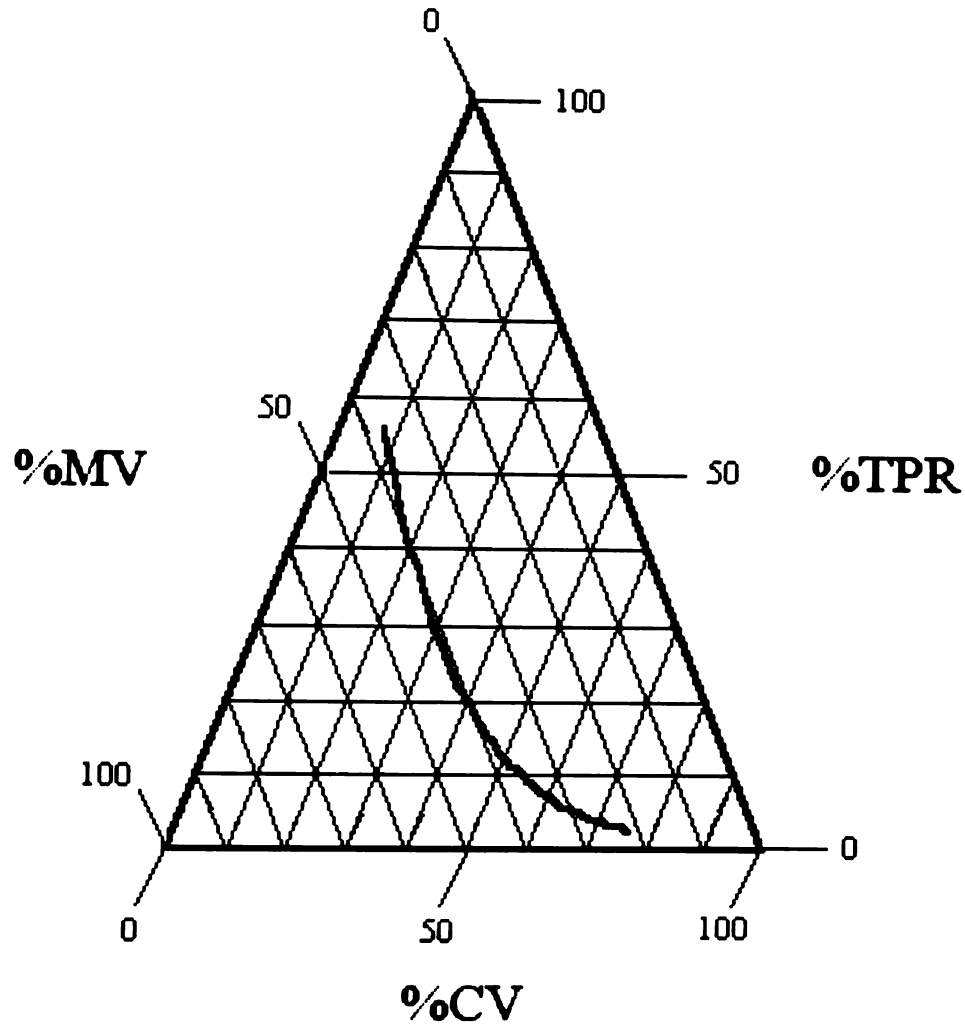
Appendix Figure 2.14: The degradation of the dye components in Pen 16 upon exposure to fluorescent light at six feet.



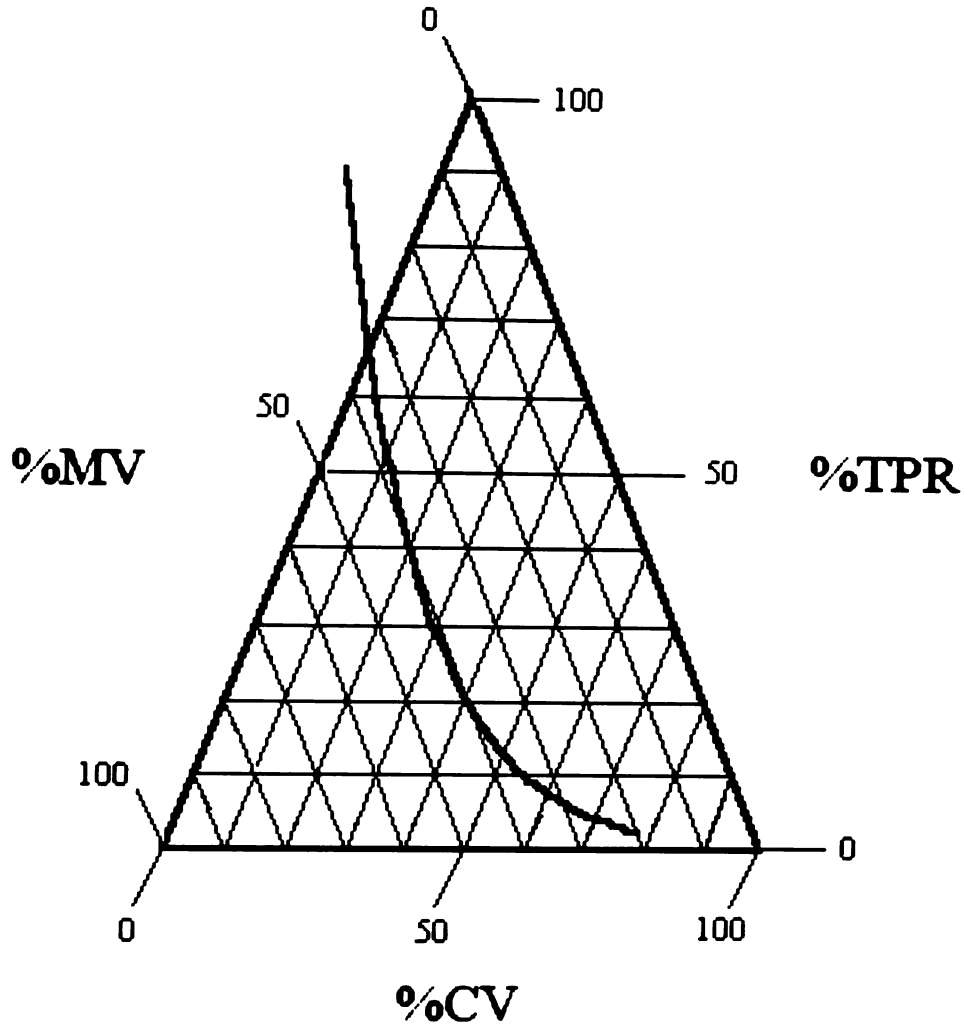
Appendix Figure 2.15: The degradation of the dye components in Pen 17 upon exposure to fluorescent light at six feet.



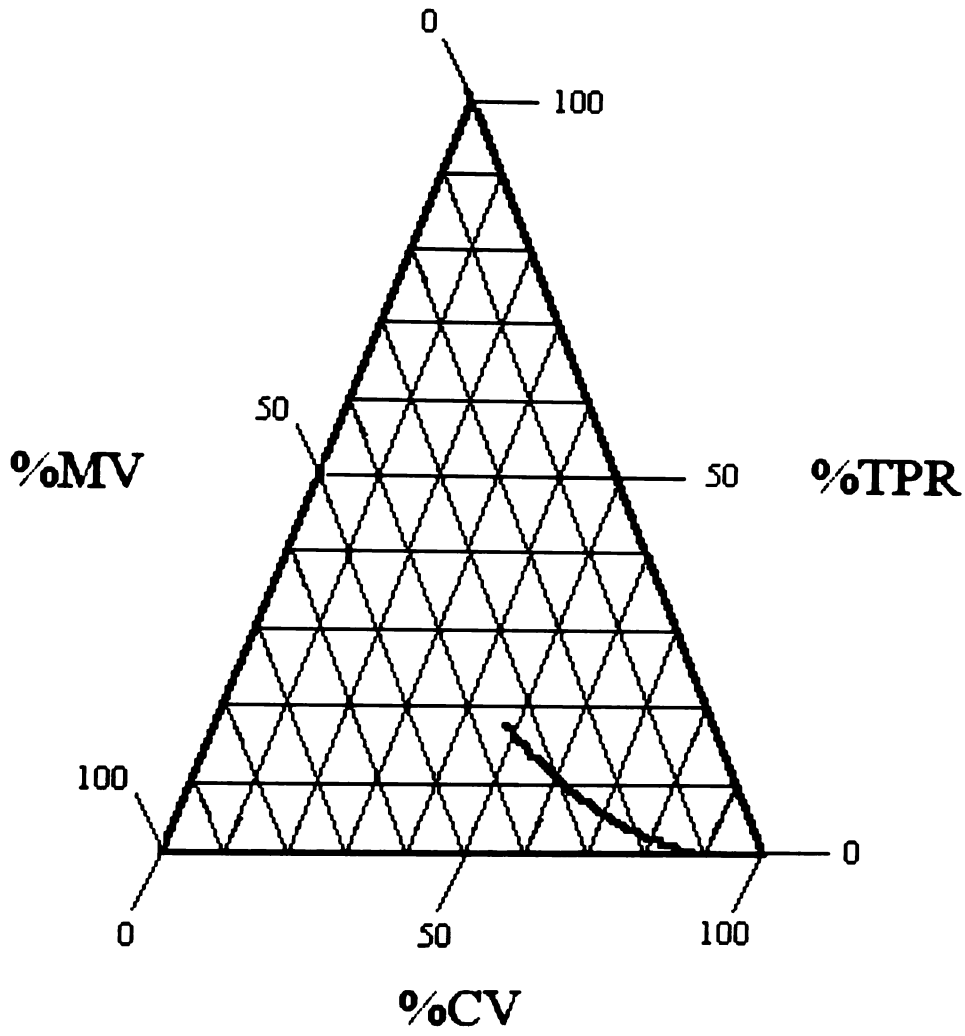
Appendix Figure 2.16: The degradation of the dye components in Pen 18 upon exposure to fluorescent light at six feet.



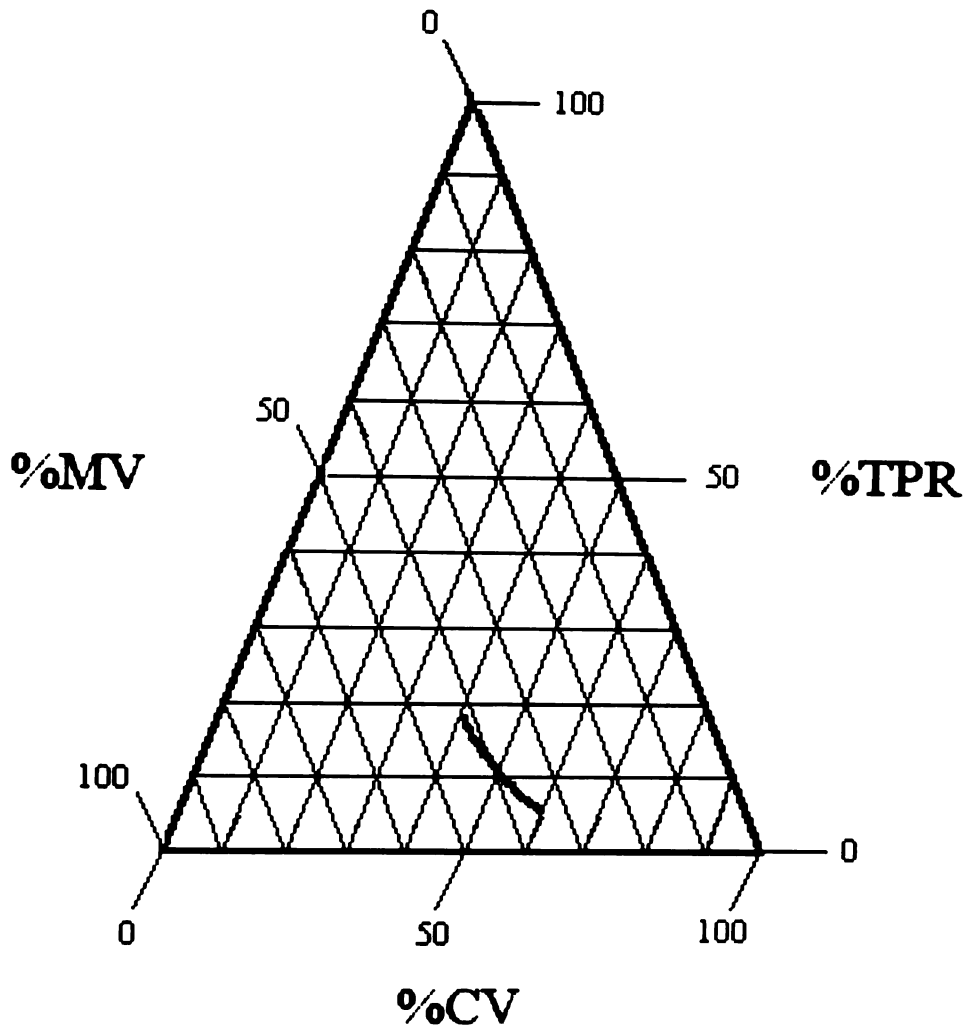
Appendix Figure 2.17: The degradation of the dye components in Pen 19 upon exposure to fluorescent light at six feet.



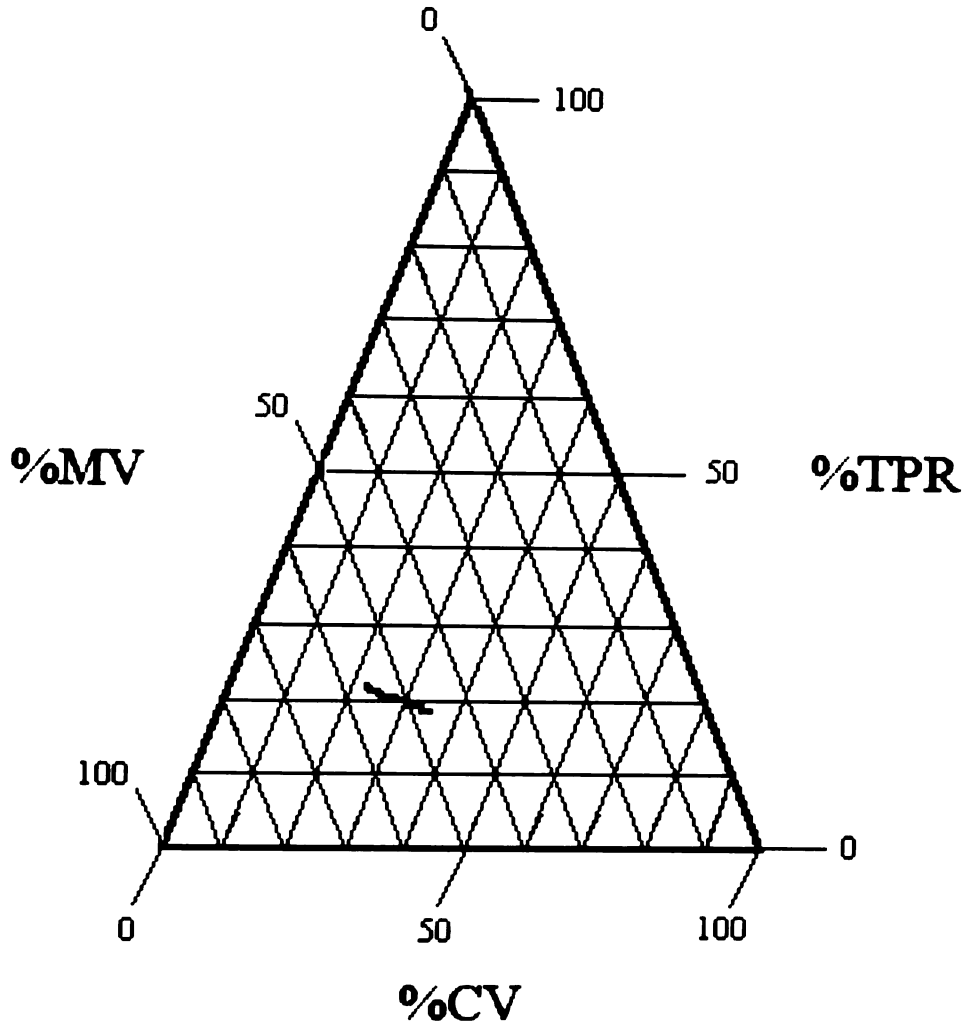
Appendix Figure 2.18: The degradation of the dye components in Pen 20 upon exposure to fluorescent light at six feet.



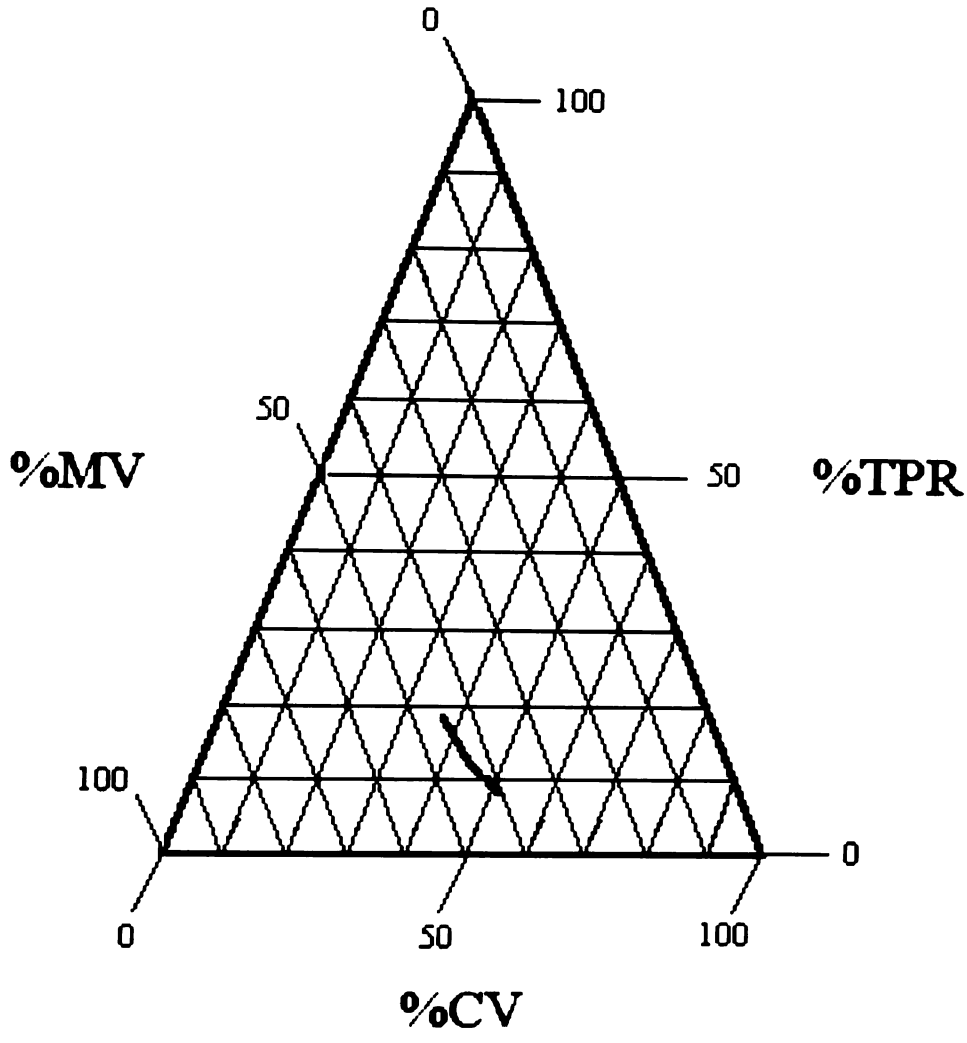
Appendix Figure 2.19: The degradation of the dye components in Pen 21 upon exposure to fluorescent light at six feet.



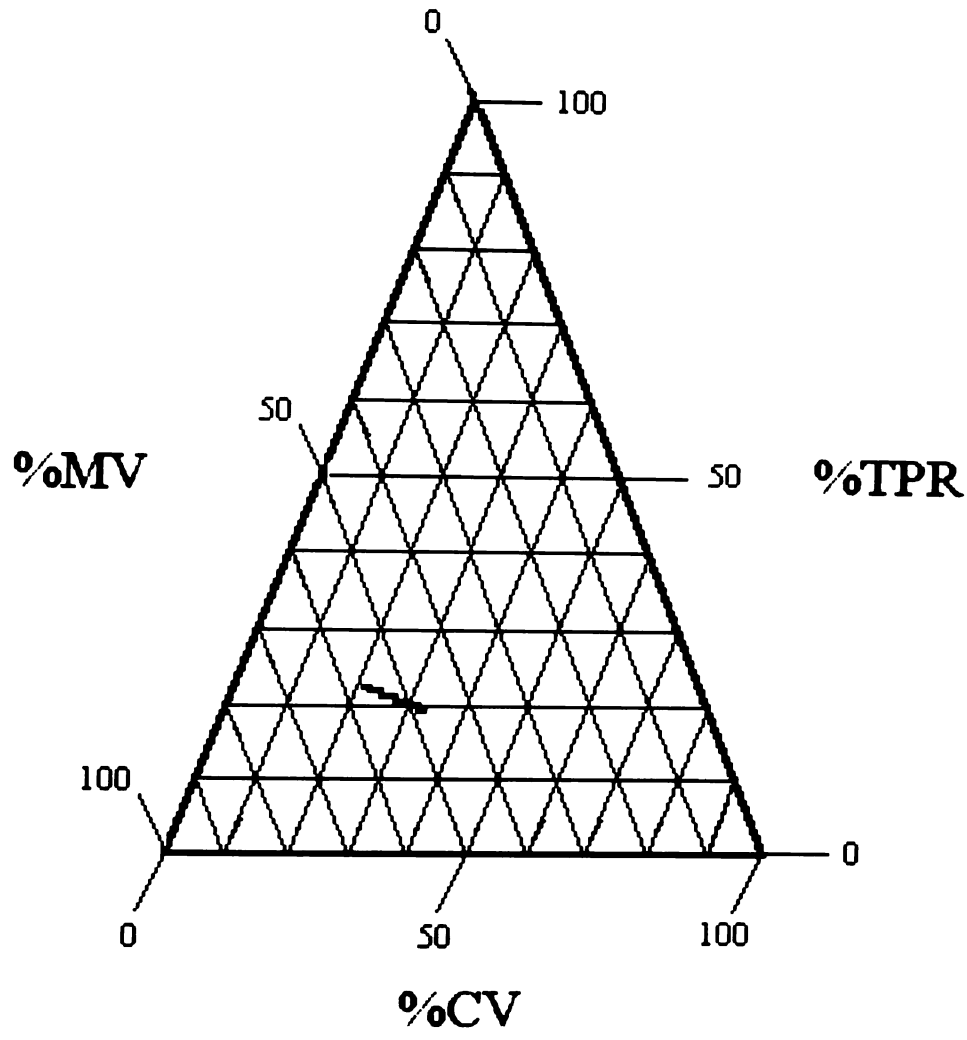
Appendix Figure 2.20: The degradation of the dye components in Pen 22 upon exposure to fluorescent light at six feet.



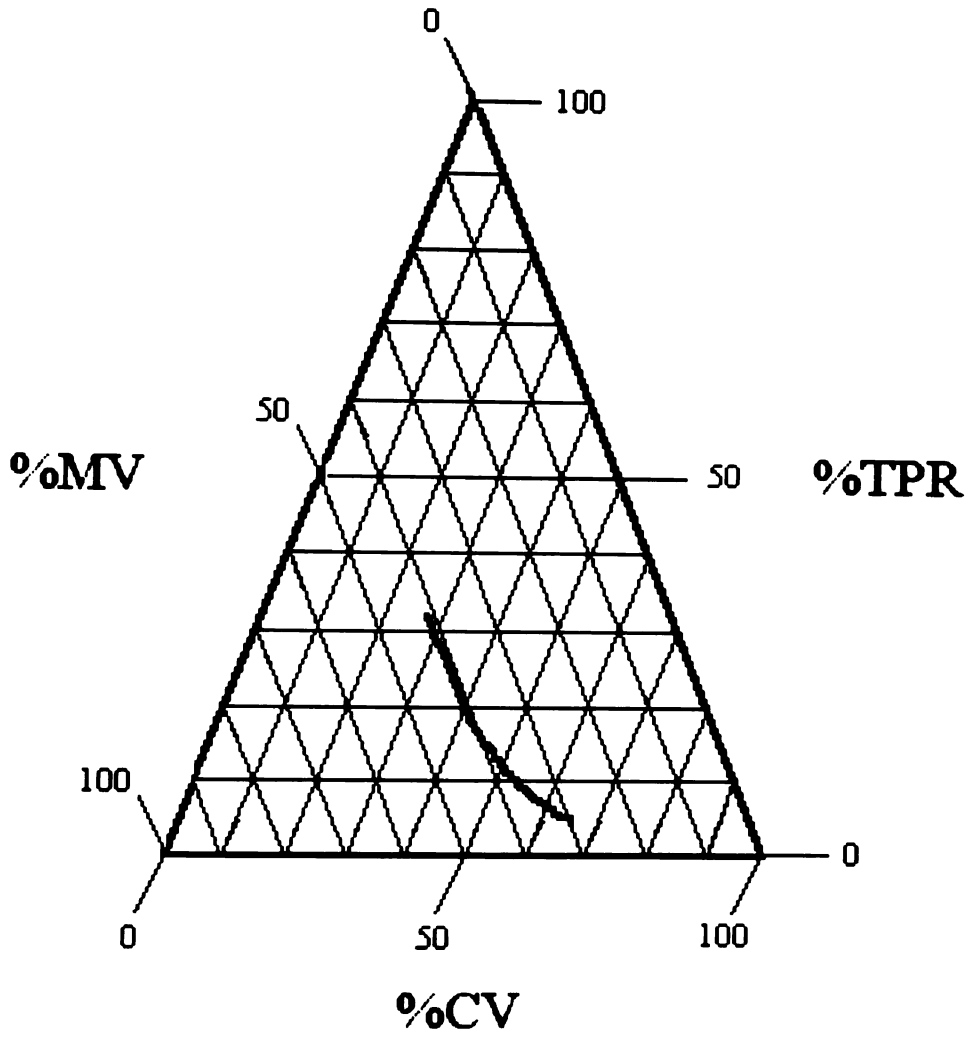
Appendix Figure 2.21: The degradation of the dye components in Pen 23 upon exposure to fluorescent light at six feet.



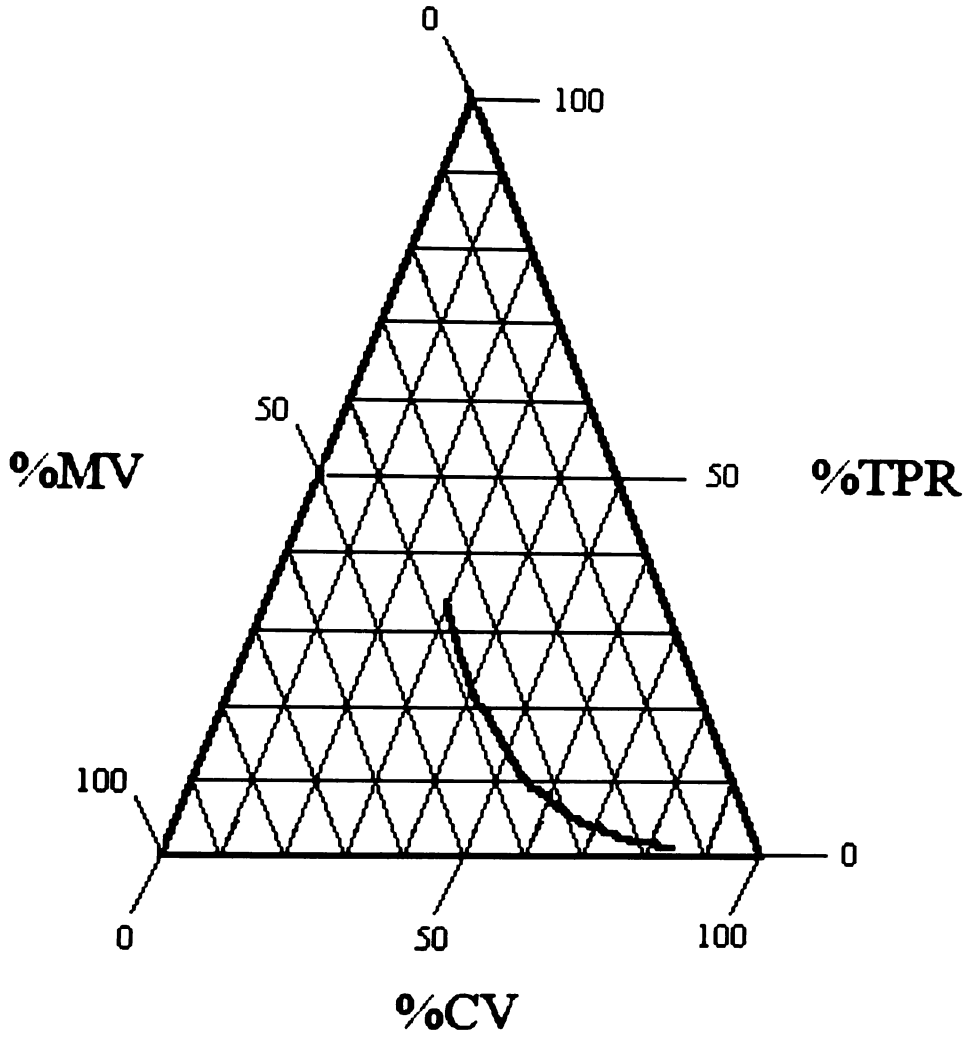
Appendix Figure 2.22: The degradation of the dye components in Pen 24 upon exposure to fluorescent light at six feet.



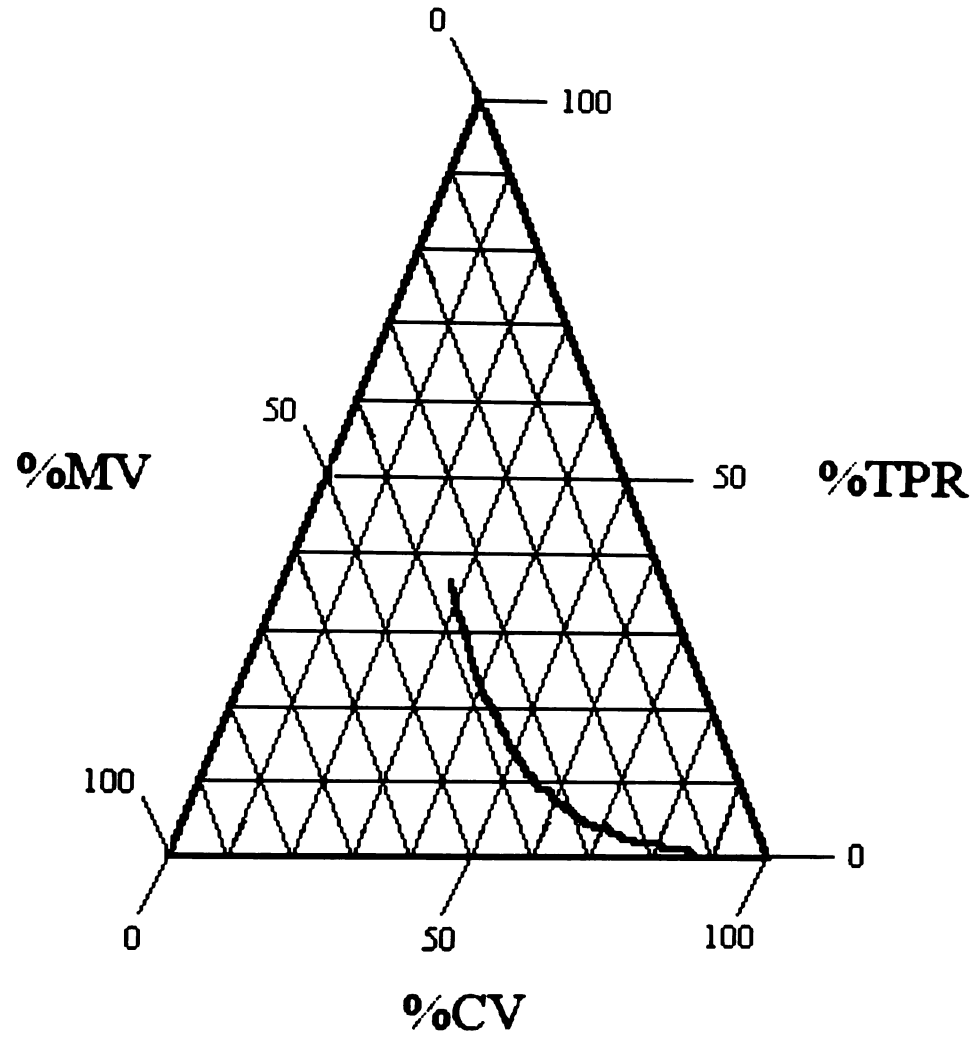
Appendix Figure 2.23: The degradation of the dye components in Pen 25 upon exposure to fluorescent light at six feet.



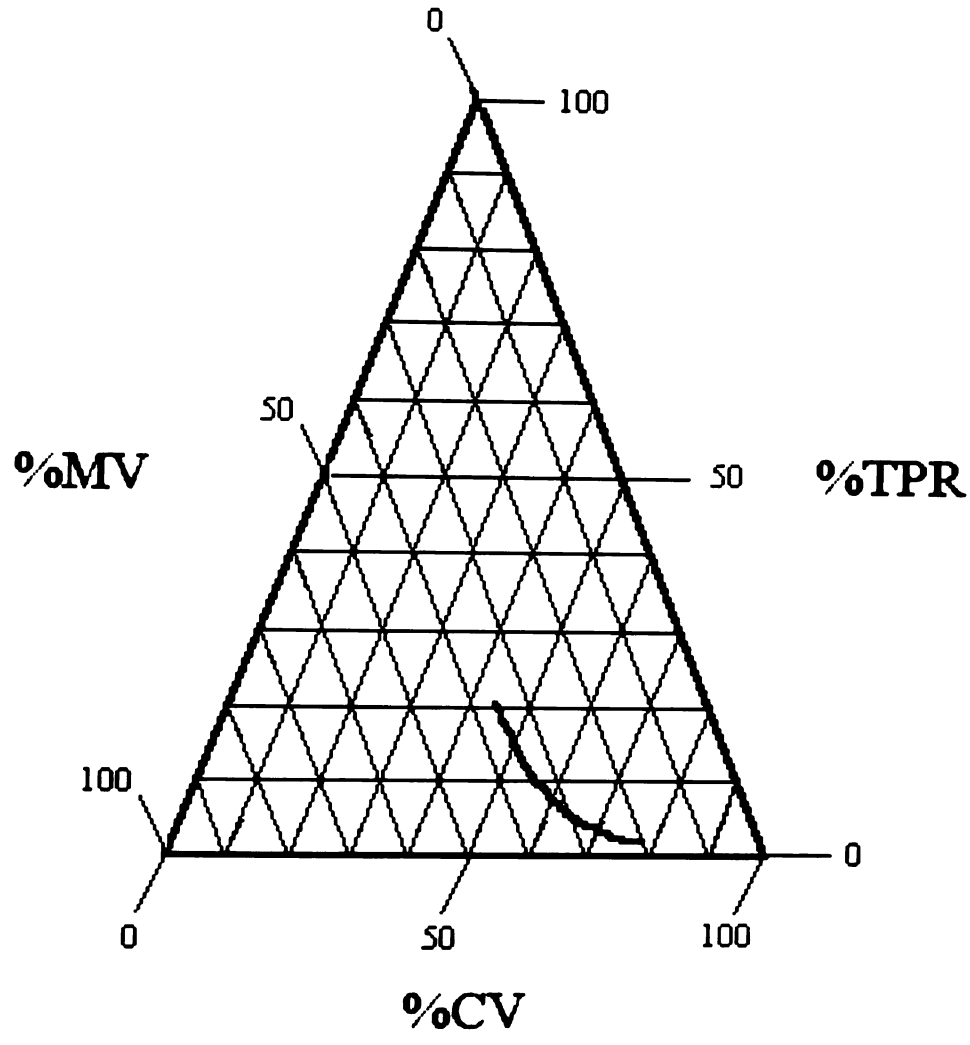
Appendix Figure 2.24: The degradation of the dye components in Pen 26 upon exposure to fluorescent light at six feet.



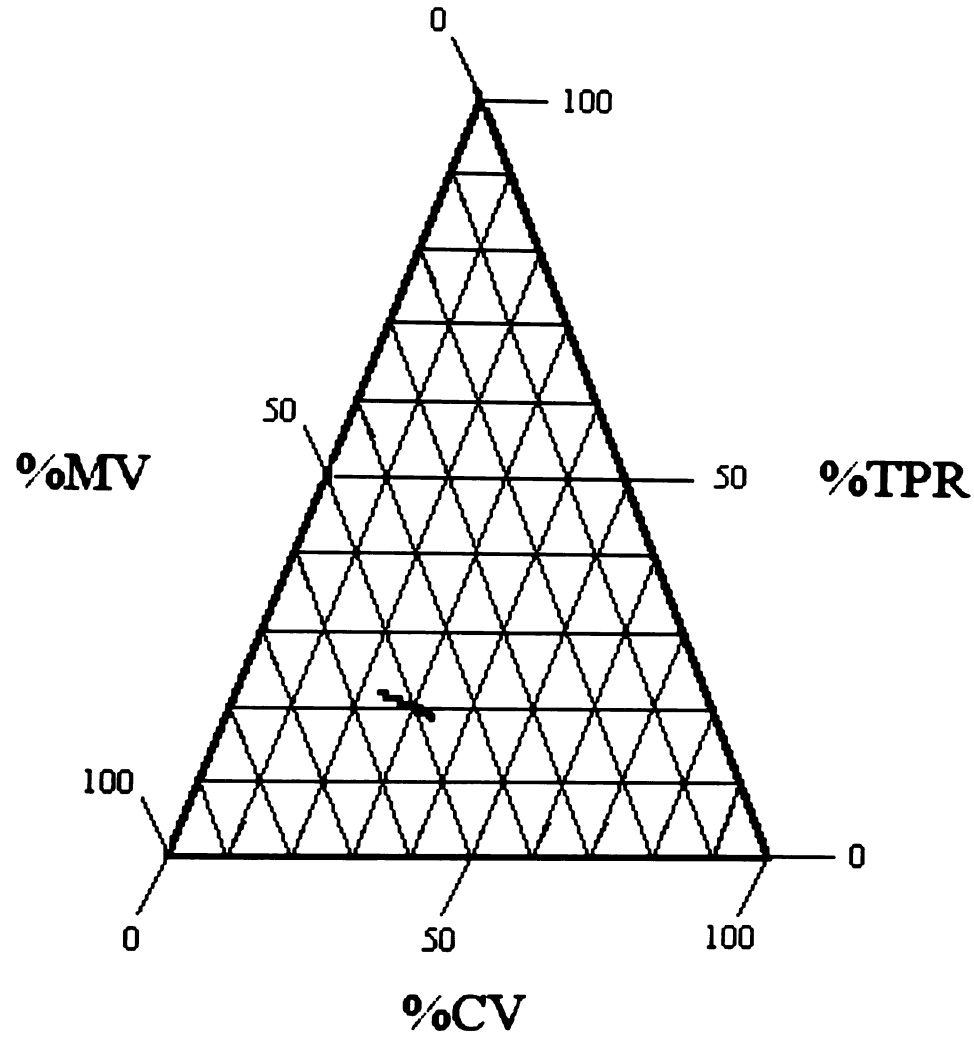
Appendix Figure 2.25: The degradation of the dye components in Pen 27 upon exposure to fluorescent light at six feet.



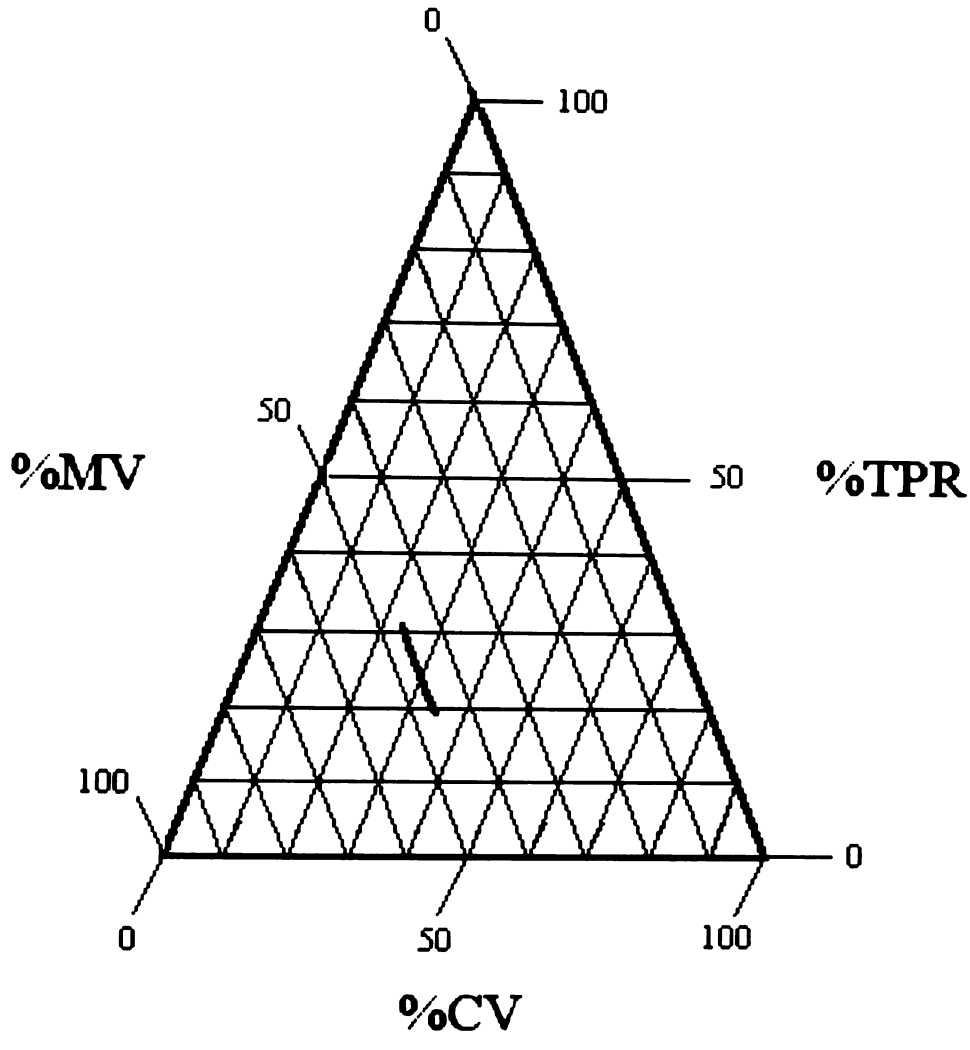
Appendix Figure 2.26: The degradation of the dye components in Pen 28 upon exposure to fluorescent light at six feet.



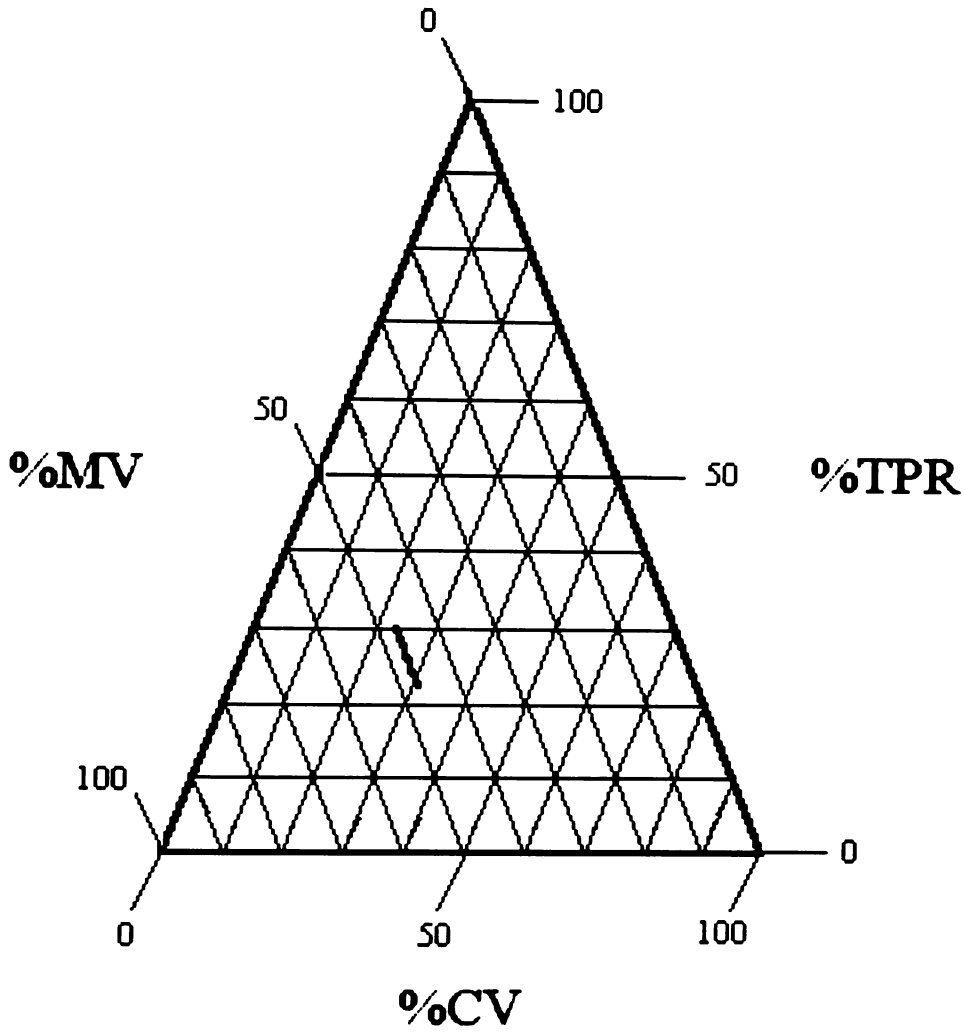
Appendix Figure 2.27: The degradation of the dye components in Pen 29 upon exposure to fluorescent light at six feet.



Appendix Figure 2.28: The degradation of the dye components in Pen 30 upon exposure to fluorescent light at six feet.



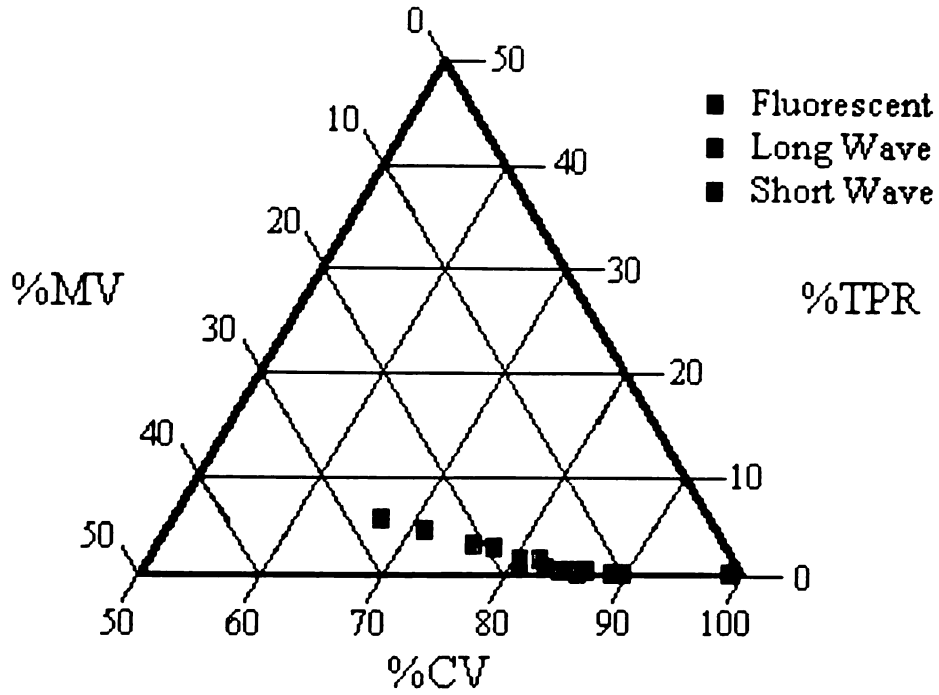
Appendix Figure 2.29: The degradation of the dye components in Pen 31 upon exposure to fluorescent light at six feet.



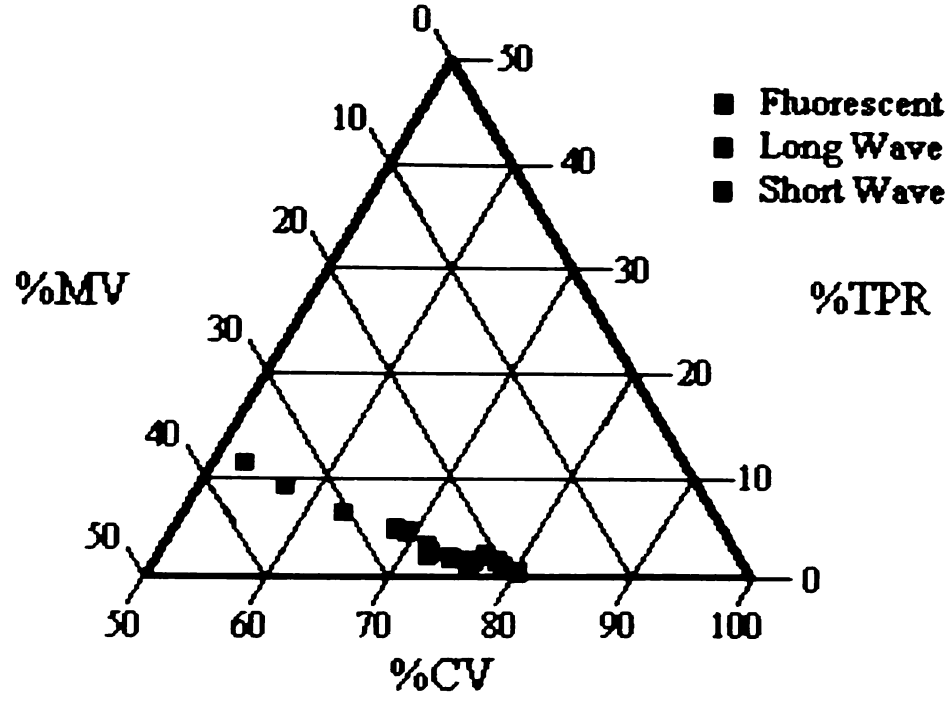
Appendix Figure 2.30: The degradation of the dye components in Pen 32 upon exposure to fluorescent light at six feet.

Appendix III

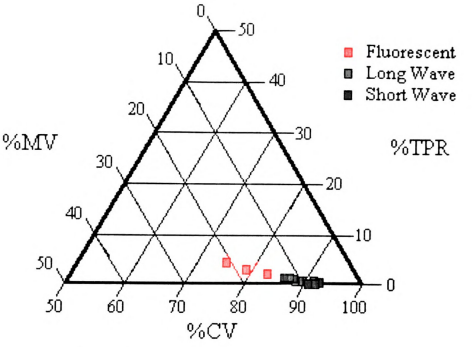
Data: Comparison of degradation of ink under fluorescent, long wave ultraviolet, and short wave ultraviolet light.



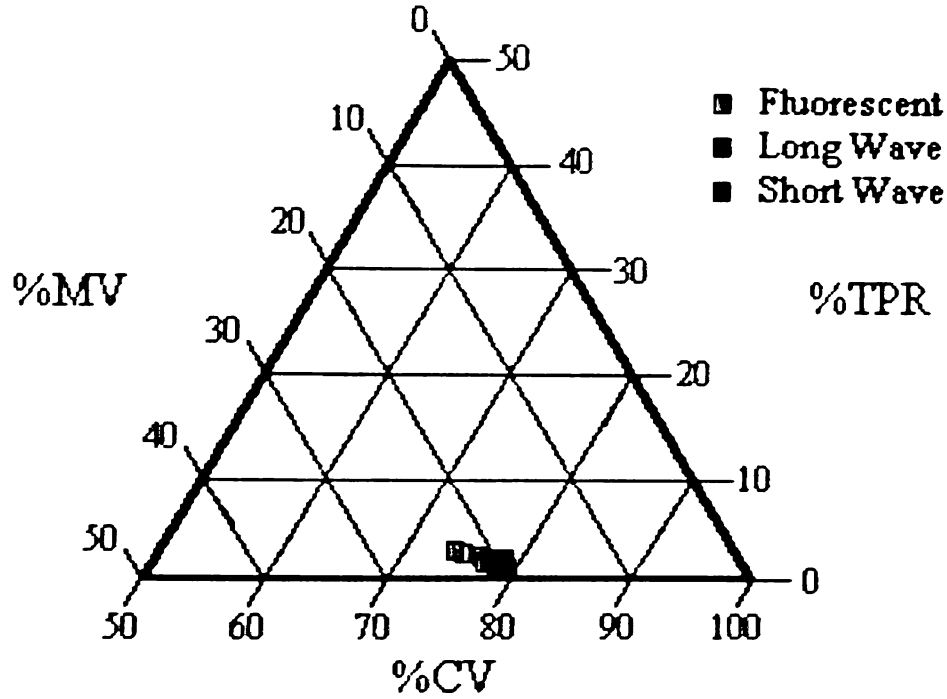
Appendix Figure 3.1: Degradation of ink from Pen 8 under fluorescent, long wave ultraviolet, and short wave ultraviolet light.



Appendix Figure 3.2: Degradation of ink from Pen 20 under fluorescent, long wave ultraviolet, and short wave ultraviolet light.



Appendix Figure 3.3: Degradation of ink from Pen 21 under fluorescent, long wave ultraviolet, and short wave ultraviolet light.



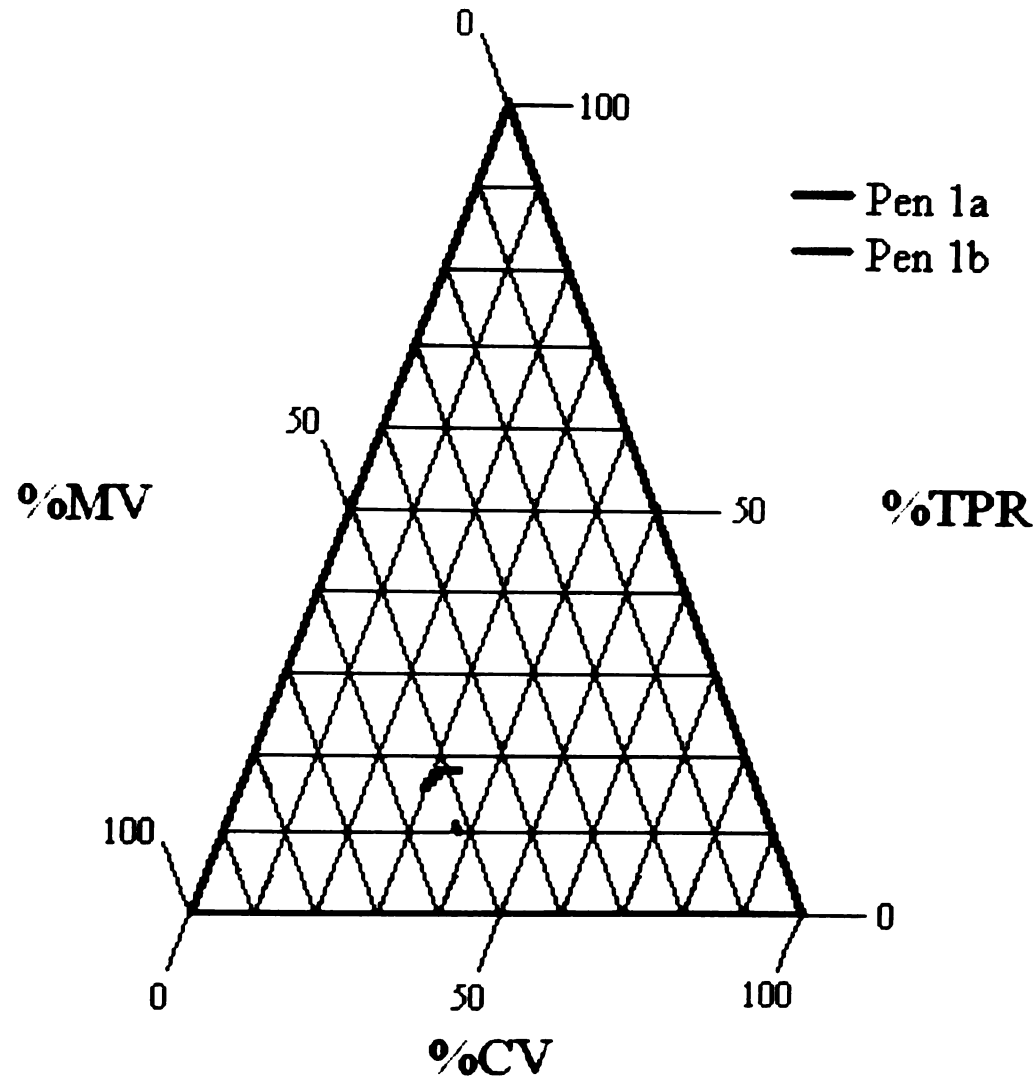
Appendix Figure 3.4: Degradation of ink from Pen 29 under fluorescent, long wave ultraviolet, and short wave ultraviolet light.

Appendix IV

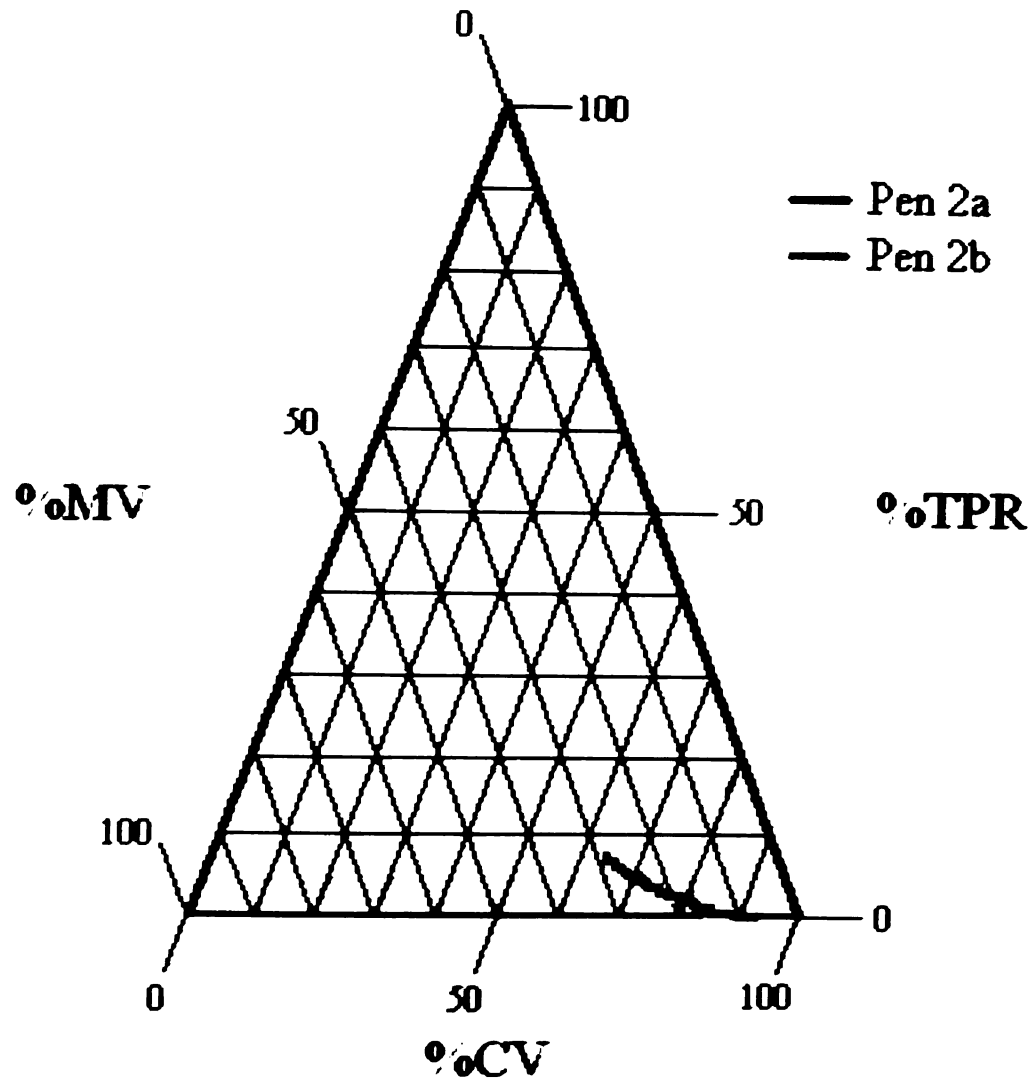
Data: Ternary diagrams containing data from all twenty cases,

including extended exposure to light.

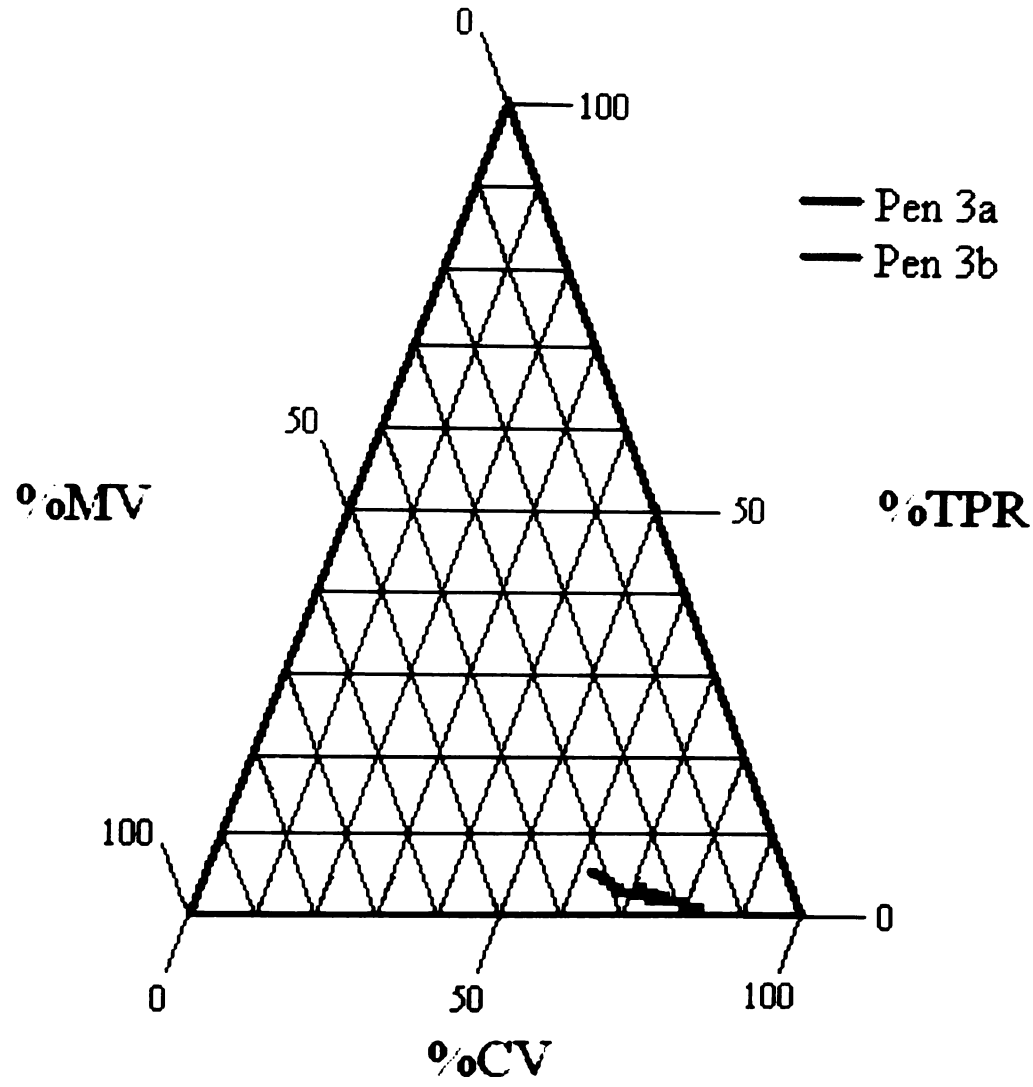
Diagrams that do not have two discernible trendlines contain collinear data.



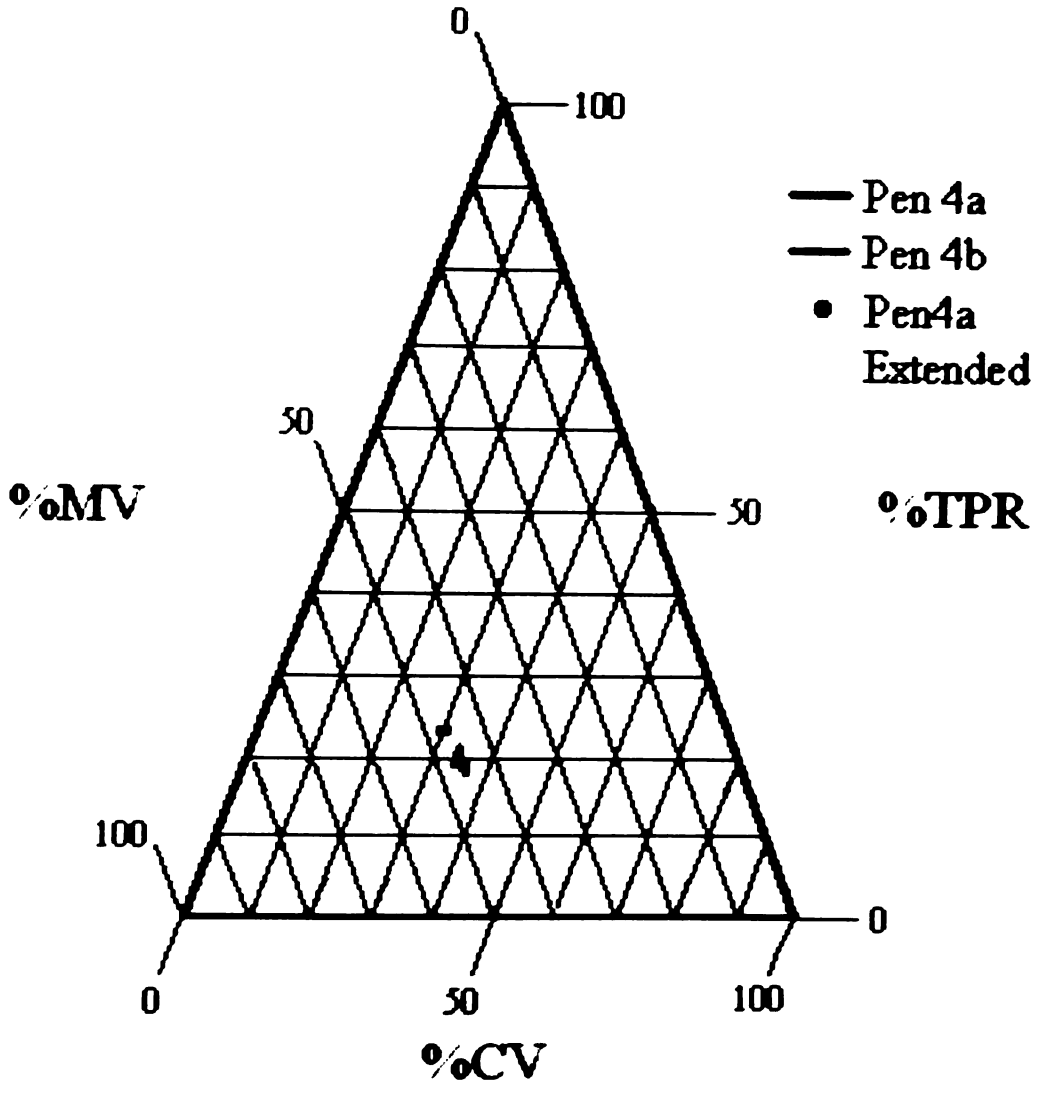
Appendix Figure 4.1: Comparison of the degradation of the inks in Pen 1a and 1b due to fluorescent light exposure.



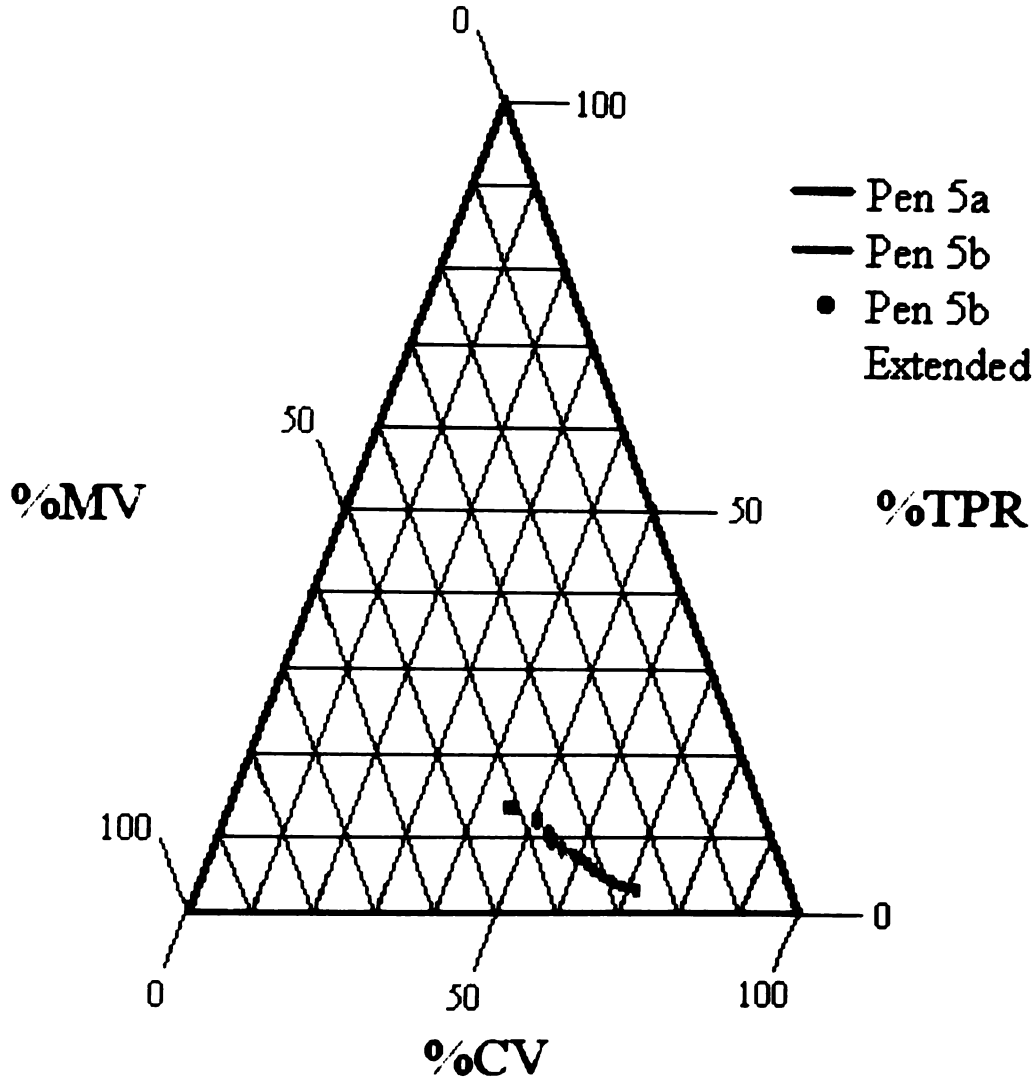
Appendix Figure 4.2: Comparison of the degradation of the inks in Pen 2a and 2b due to fluorescent light exposure.



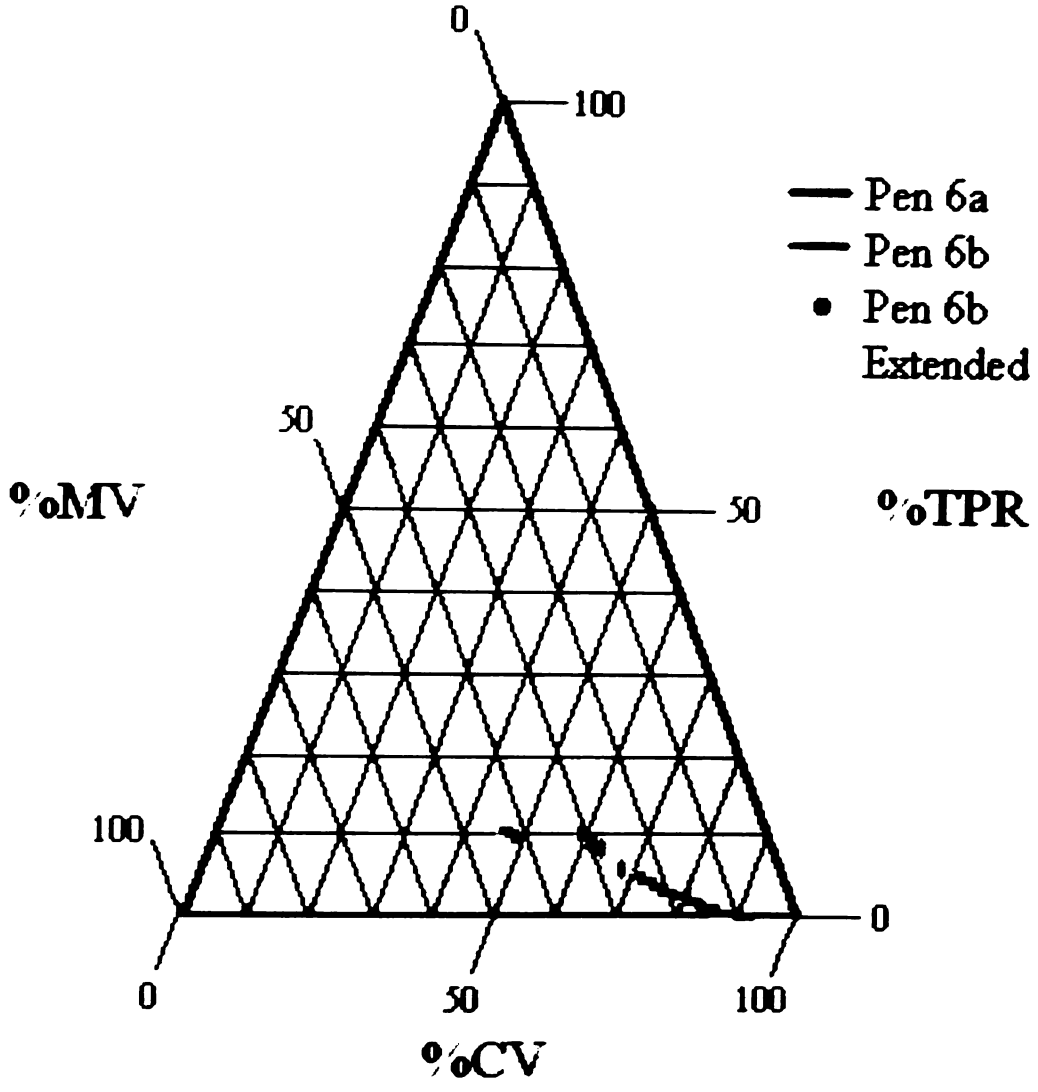
Appendix Figure 4.3: Comparison of the degradation of the inks in Pen 3a and 3b due to fluorescent light exposure.



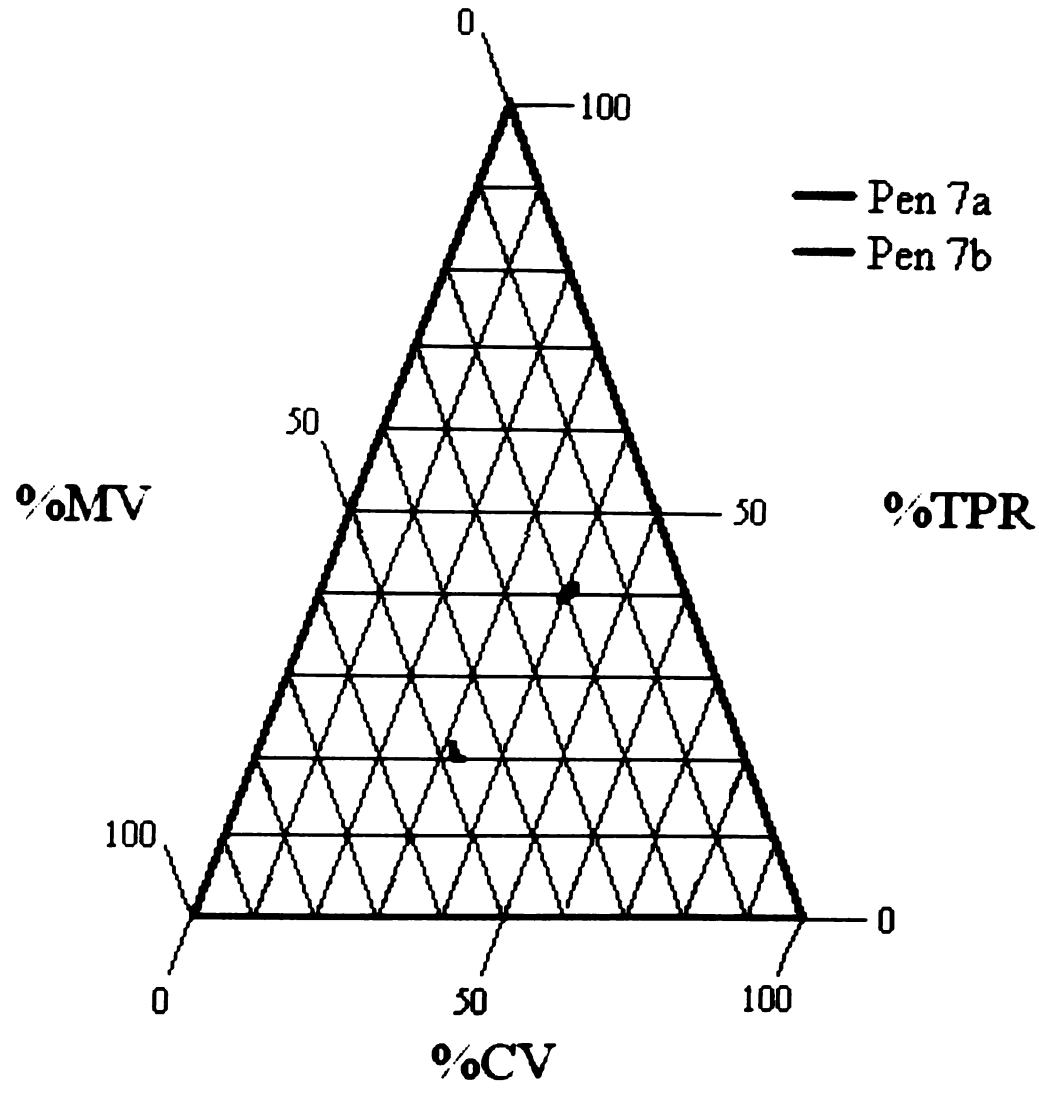
Appendix Figure 4.4: Comparison of the degradation of the inks in Pen 4a and 4b due to fluorescent light exposure.



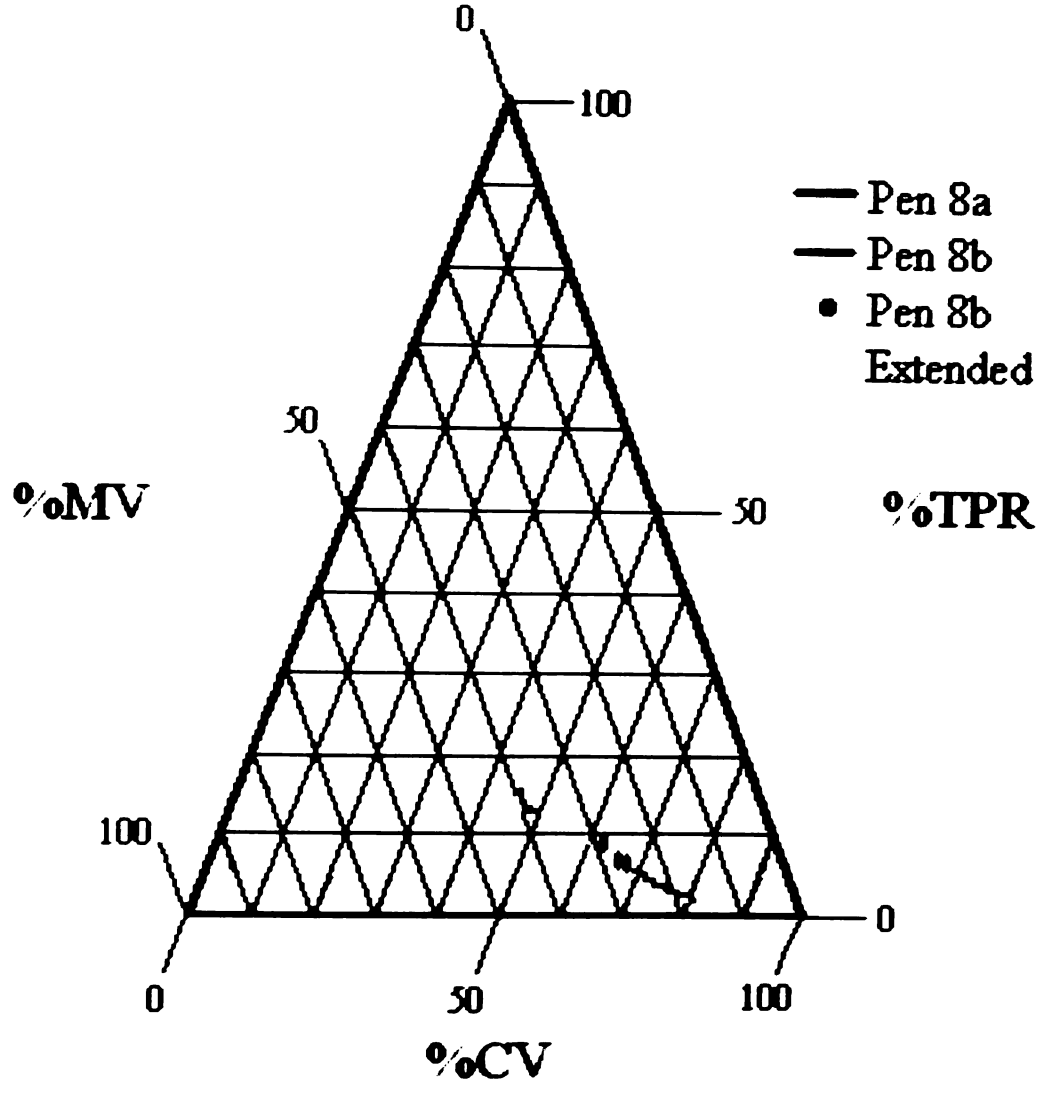
Appendix Figure 4.5: Comparison of the degradation of the inks in Pen 5a and 5b due to fluorescent light exposure.



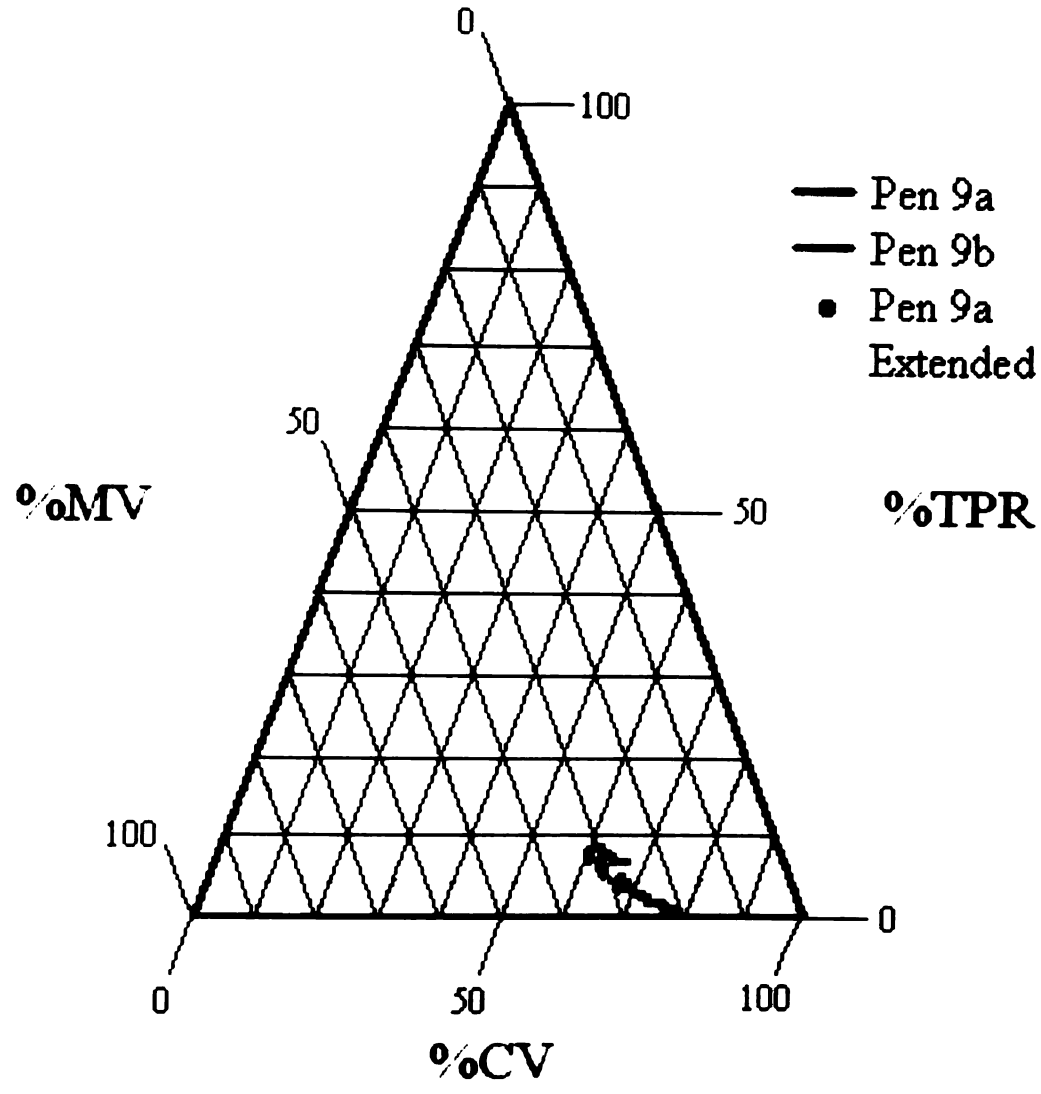
Appendix Figure 4.6: Comparison of the degradation of the inks in Pen 6a and 6b due to fluorescent light exposure.



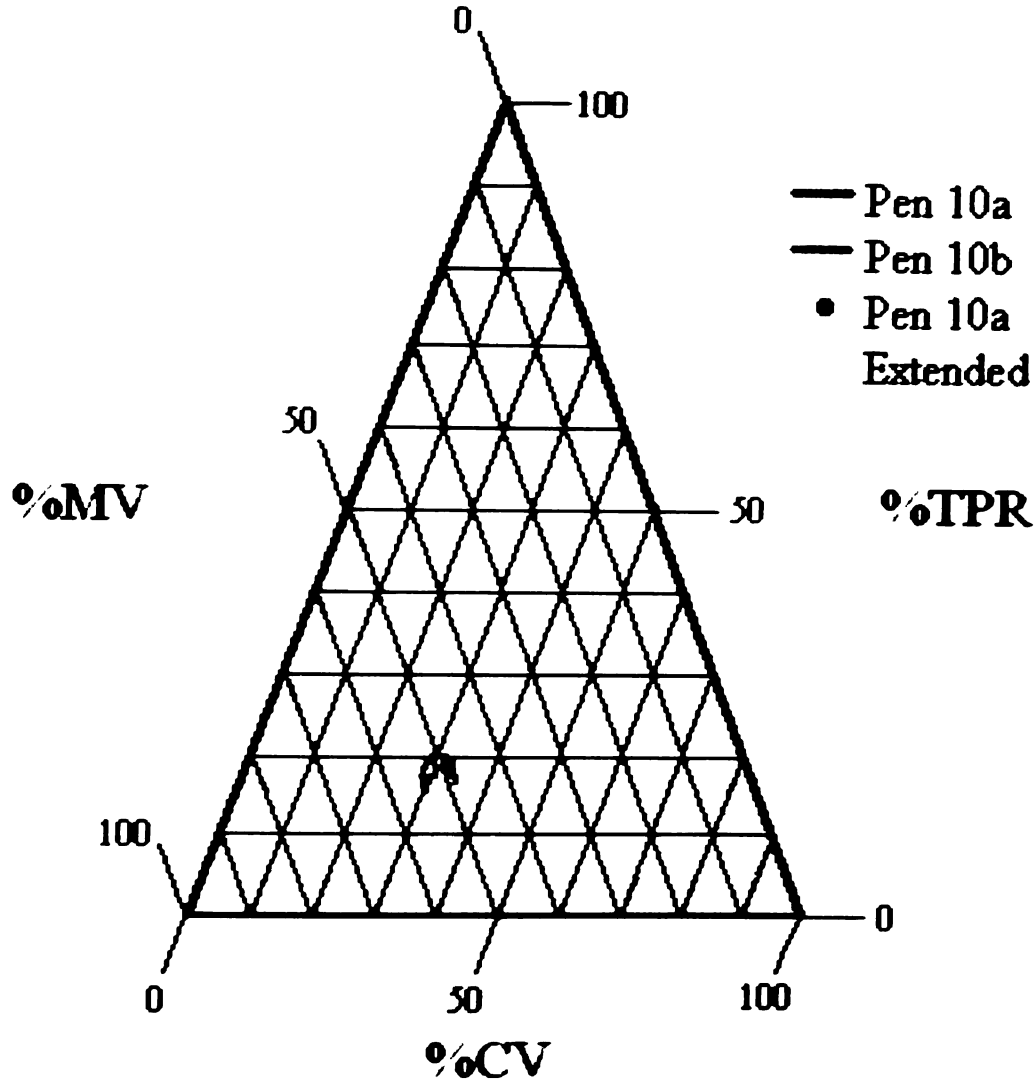
Appendix Figure 4.7: Comparison of the degradation of the inks in Pen 7a and 7b due to fluorescent light exposure.



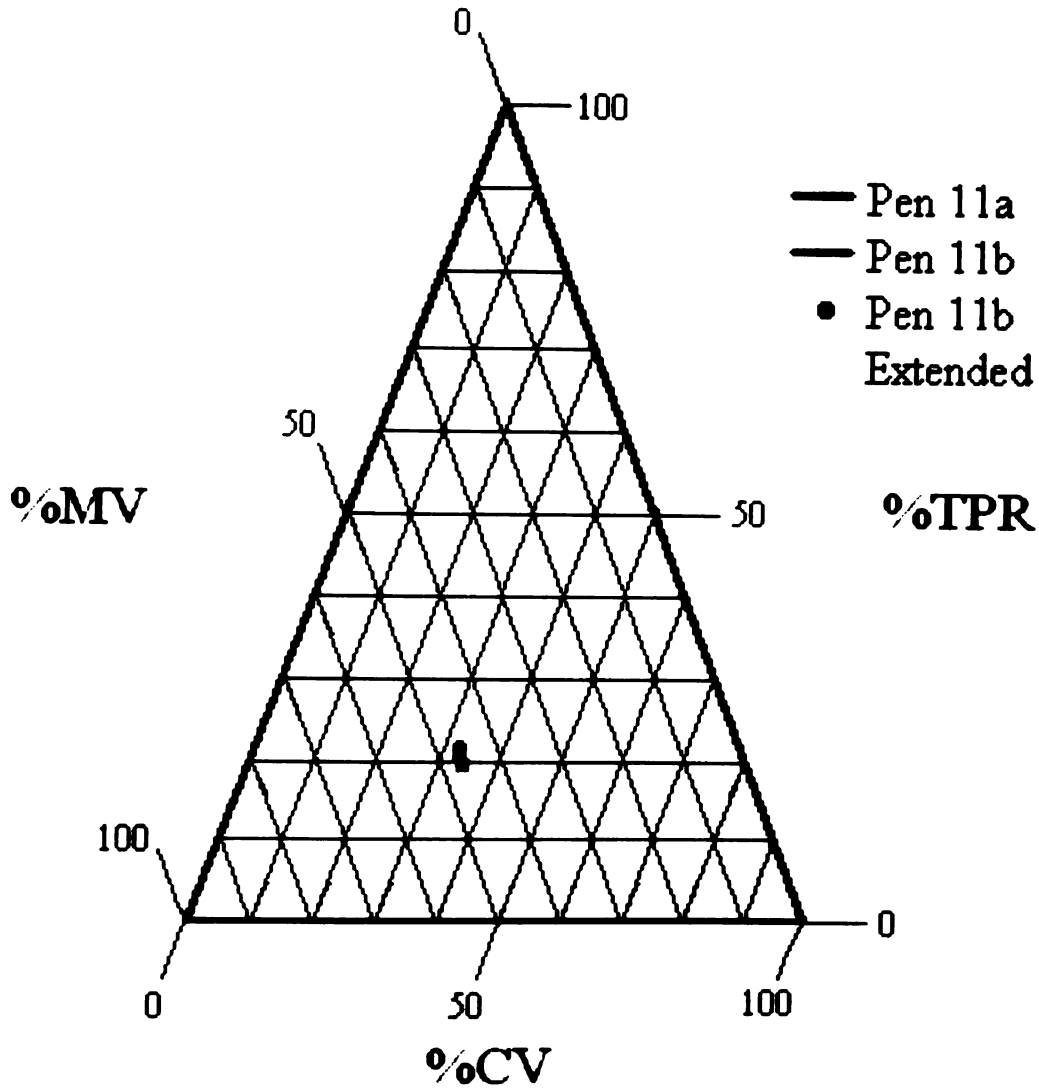
Appendix Figure 4.8: Comparison of the degradation of the inks in Pen 8a and 8b due to fluorescent light exposure.



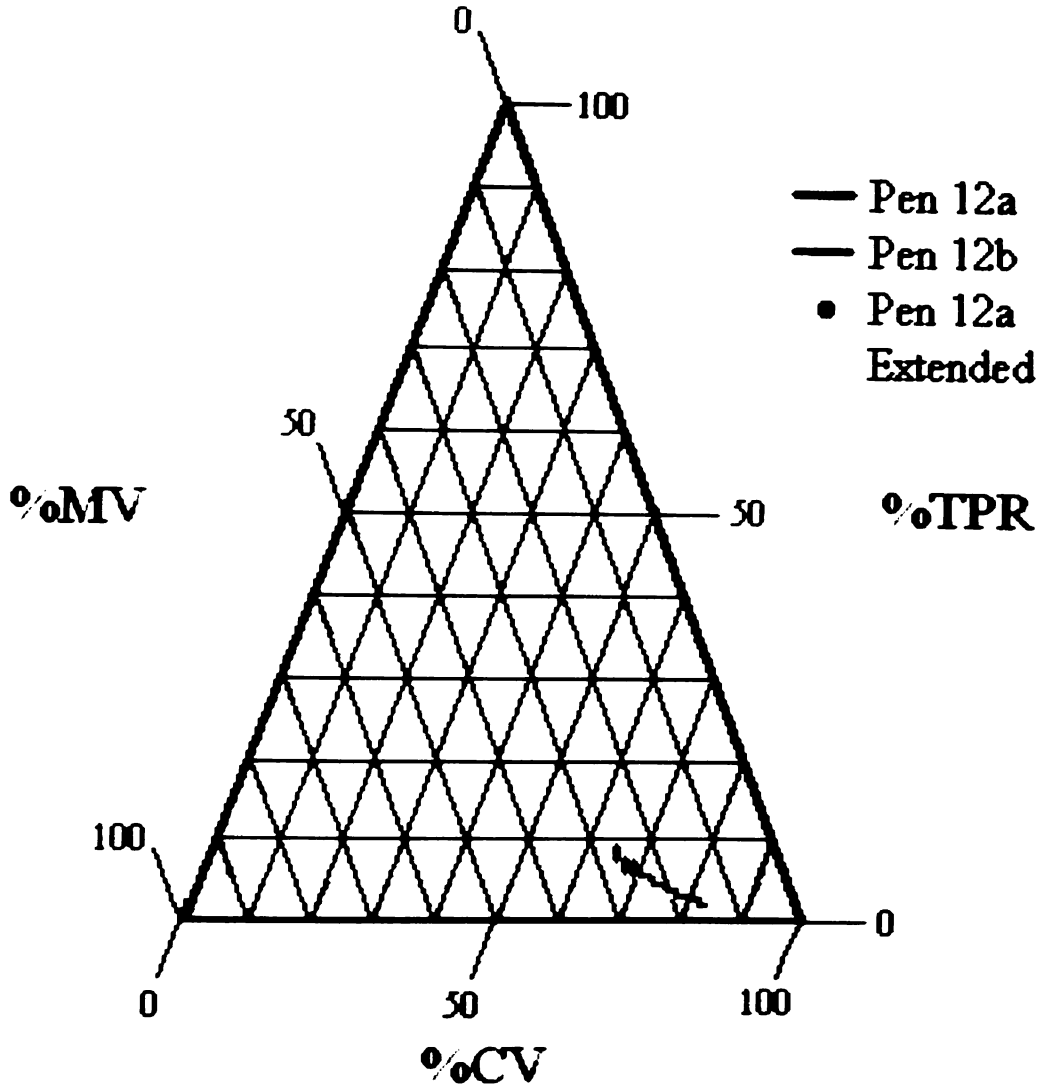
Appendix Figure 4.9: Comparison of the degradation of the inks in Pen 9a and 9b due to fluorescent light exposure.



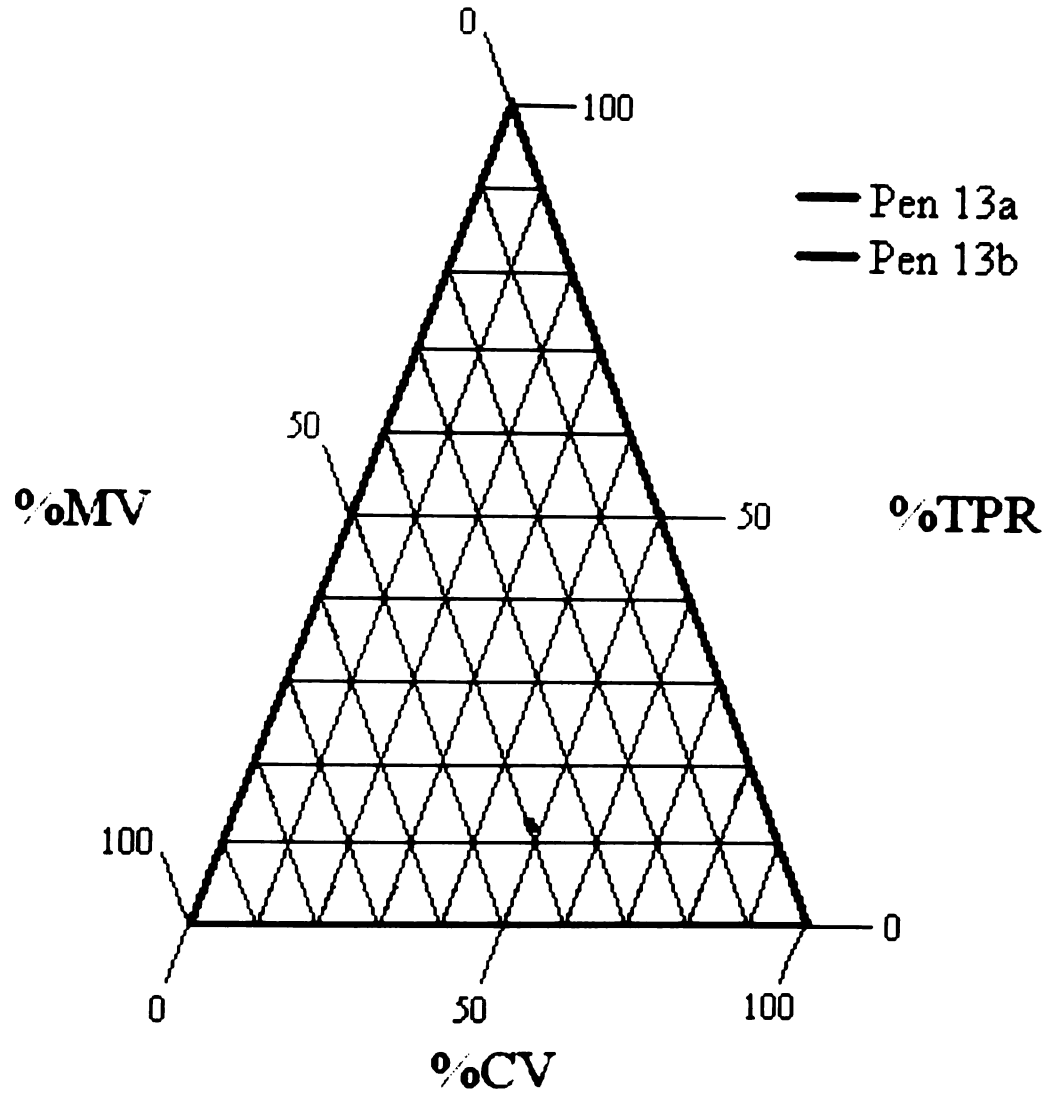
Appendix Figure 4.10: Comparison of the degradation of the inks in Pen 10a and 10b due to fluorescent light exposure.



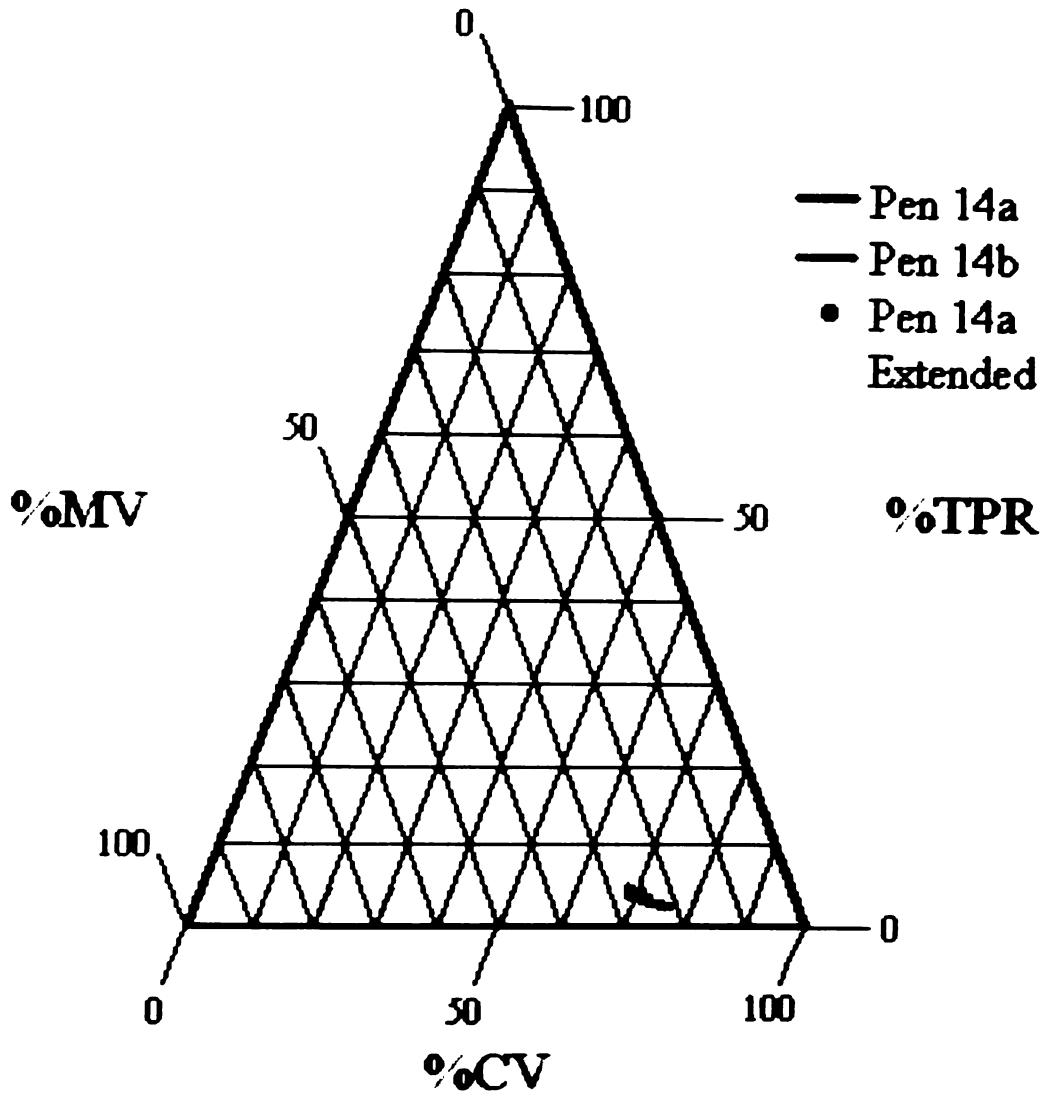
Appendix Figure 4.11: Comparison of the degradation of the inks in Pen 11a and 11b due to fluorescent light exposure.



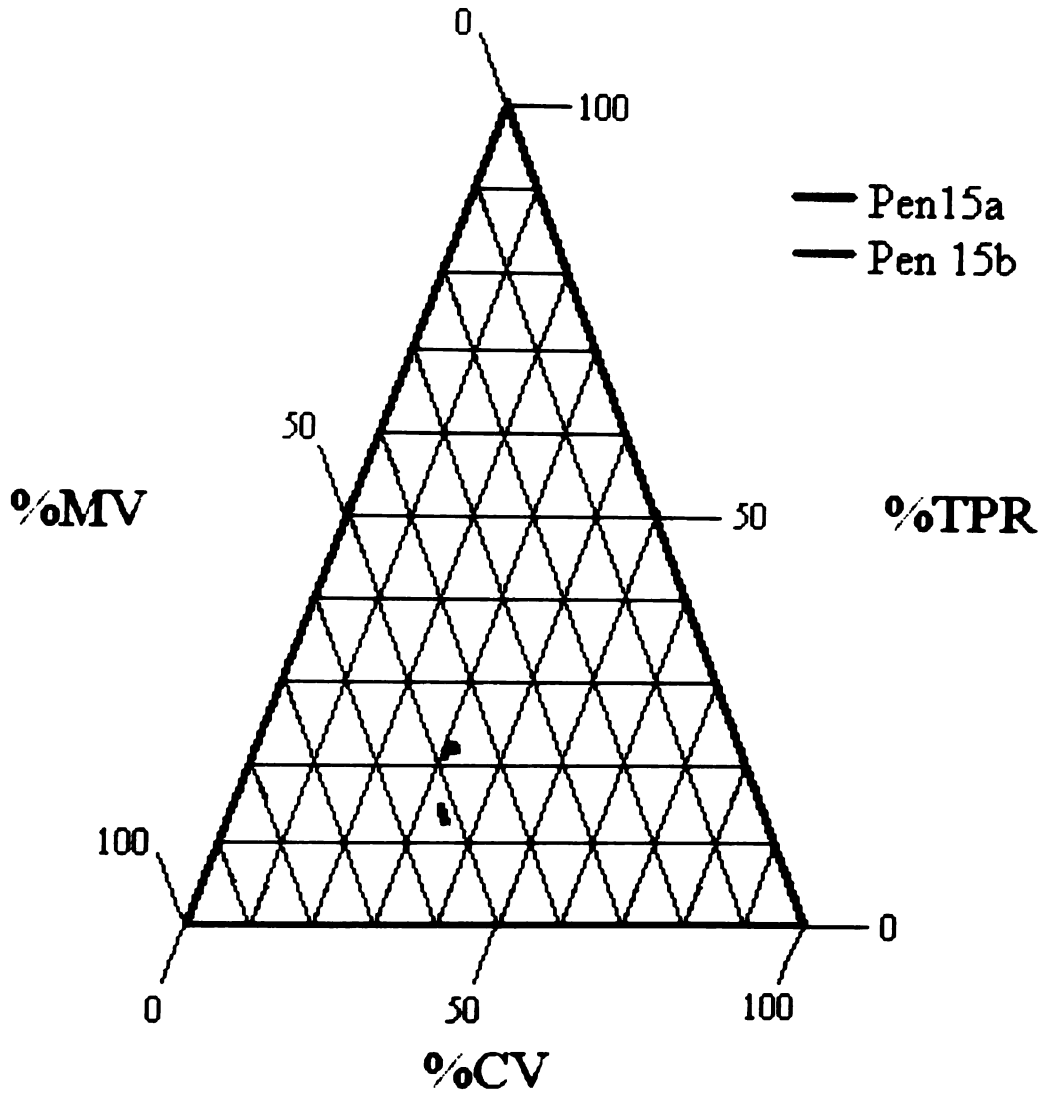
Appendix Figure 4.12: Comparison of the degradation of the inks in Pen 12a and 12b due to fluorescent light exposure.



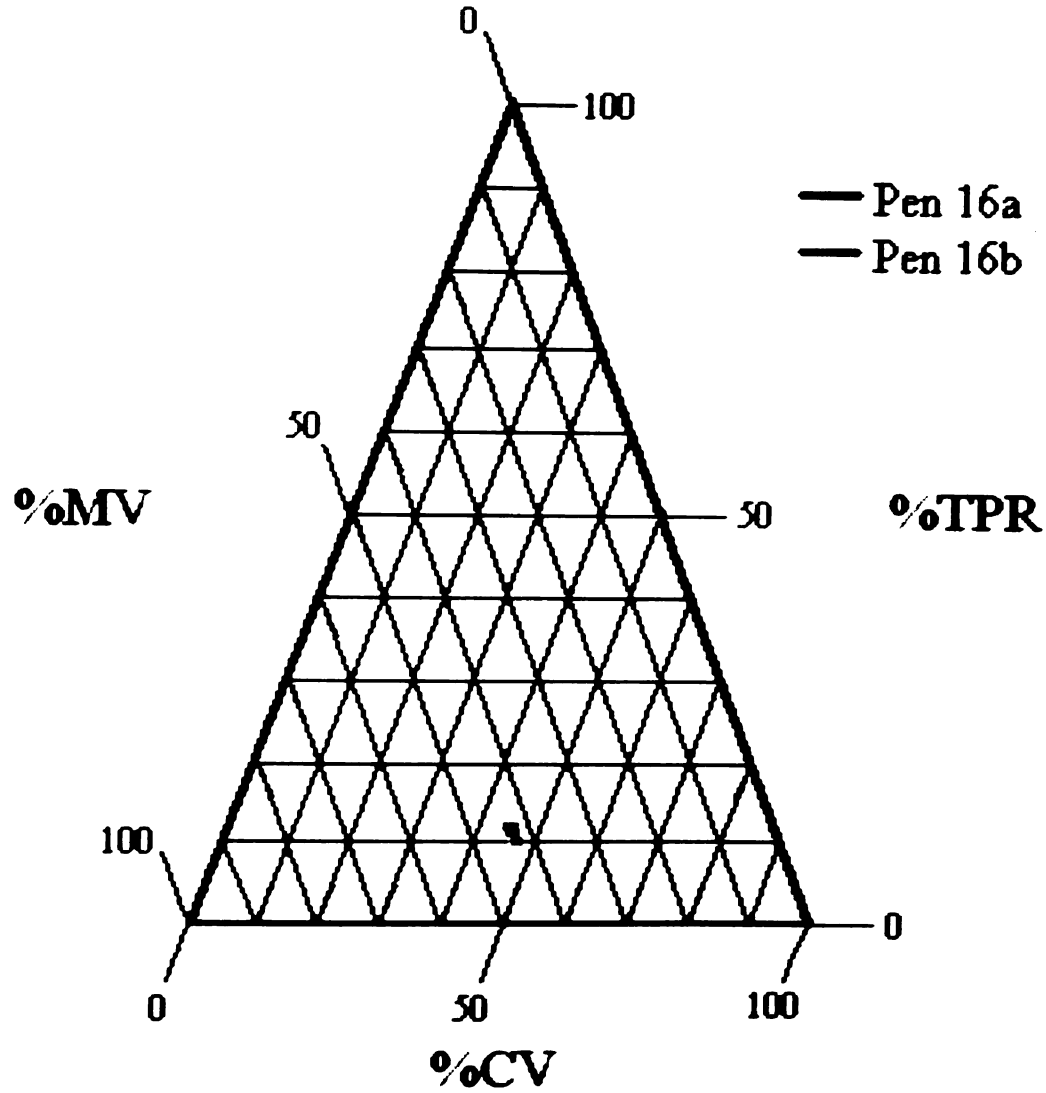
Appendix Figure 4.13: Comparison of the degradation of the inks in Pen 13a and 13b due to fluorescent light exposure.



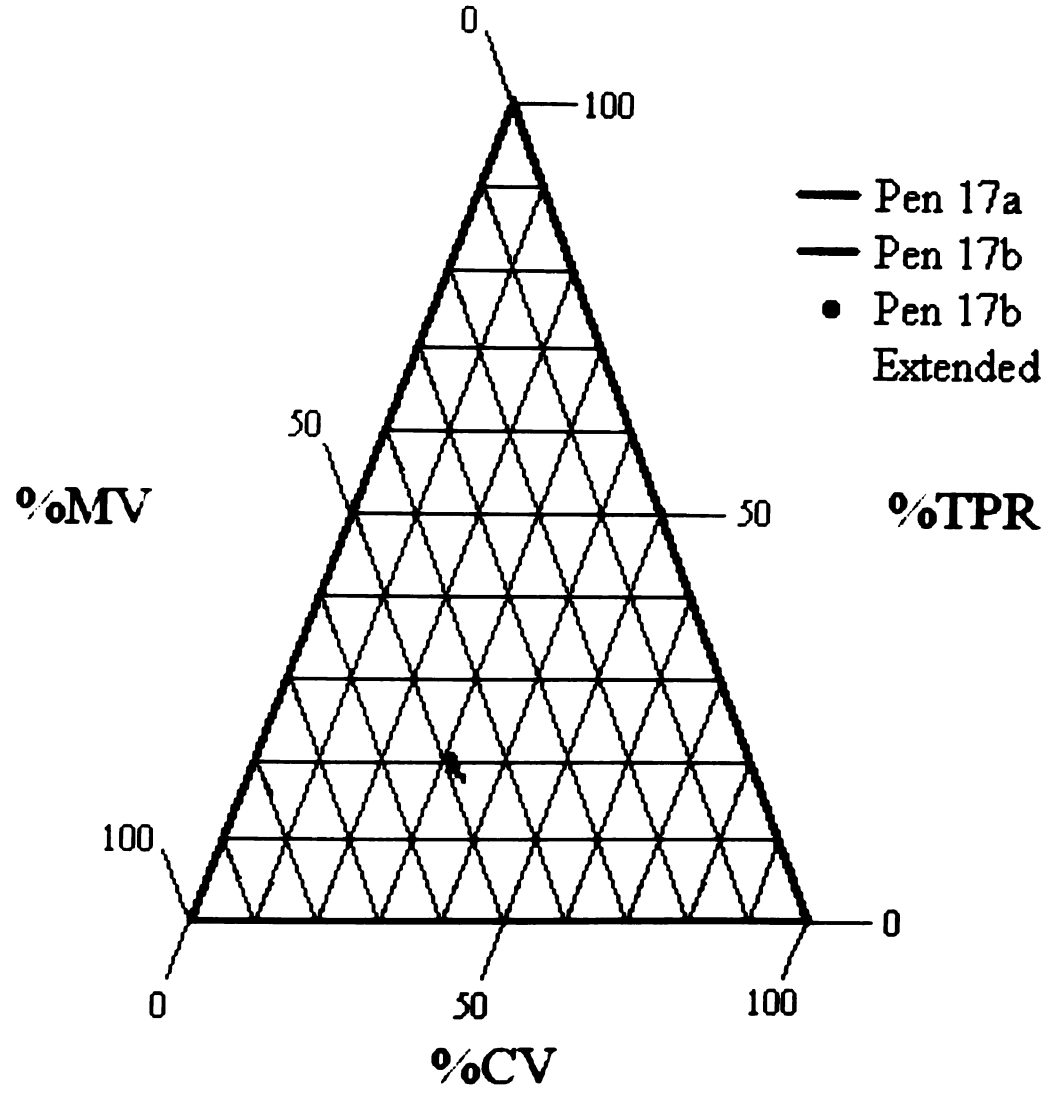
Appendix Figure 4.14: Comparison of the degradation of the inks in Pen 14a and 14b due to fluorescent light exposure.



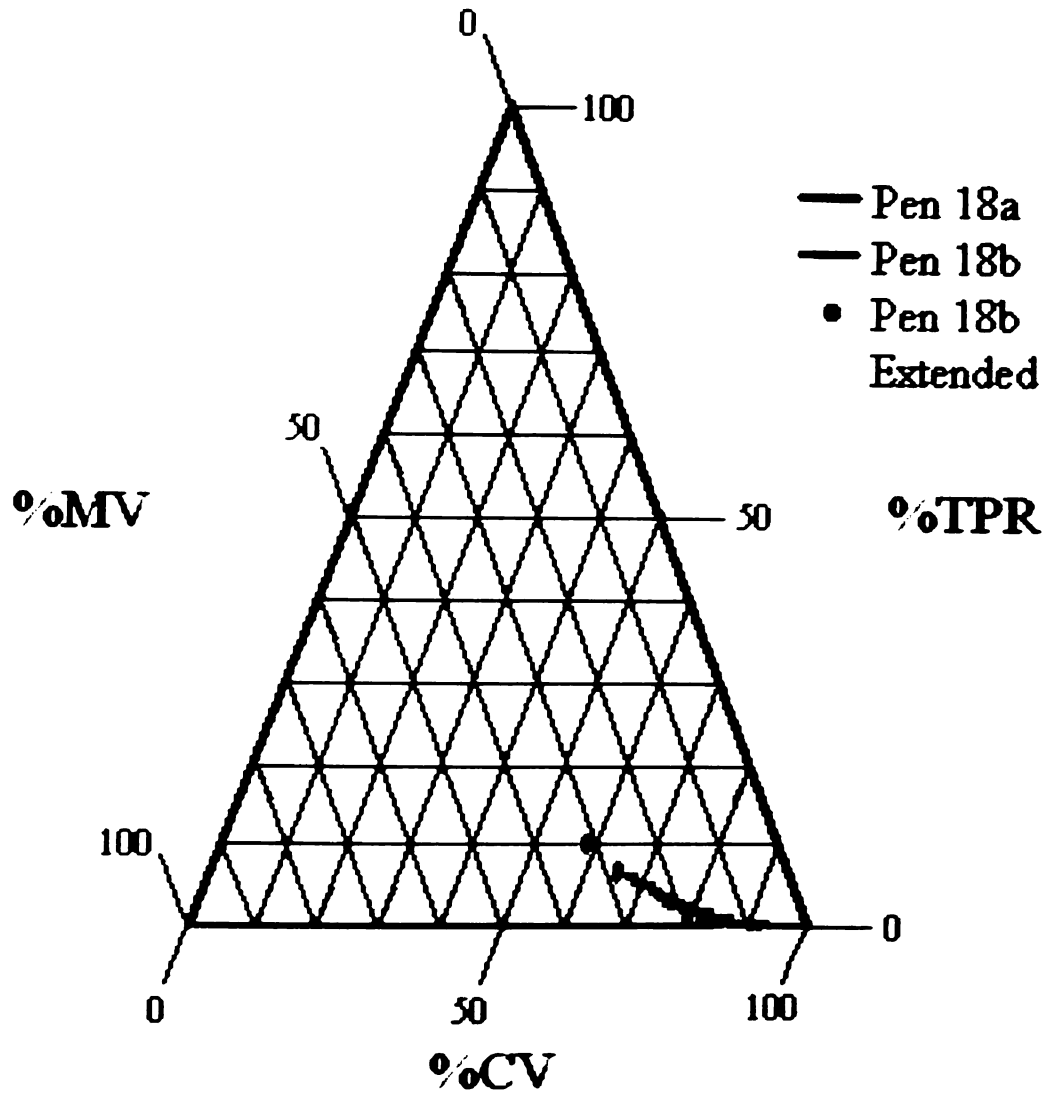
Appendix Figure 4.15: Comparison of the degradation of the inks in Pen 15a and 15b due to fluorescent light exposure.



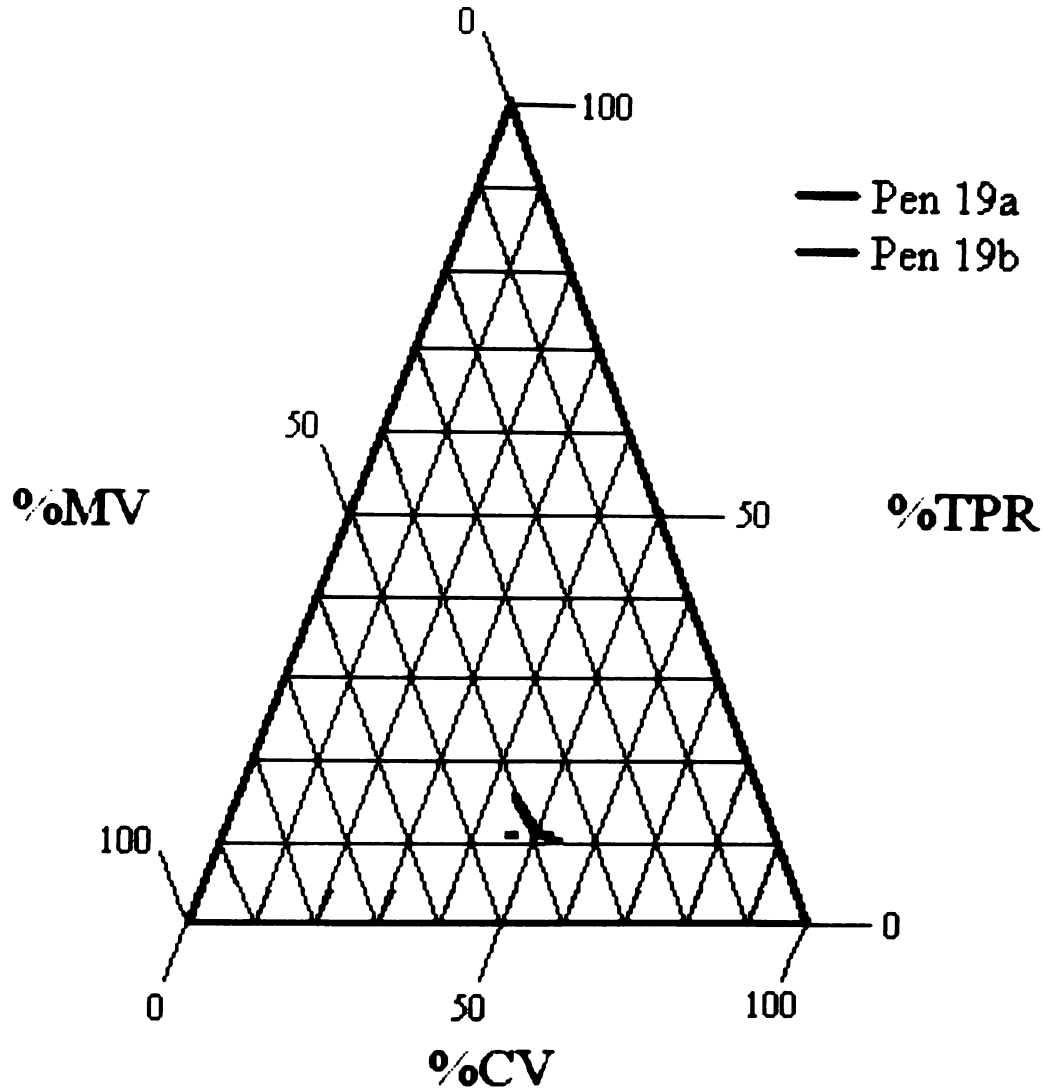
Appendix Figure 4.16: Comparison of the degradation of the inks in Pen 16a and 16b due to fluorescent light exposure.



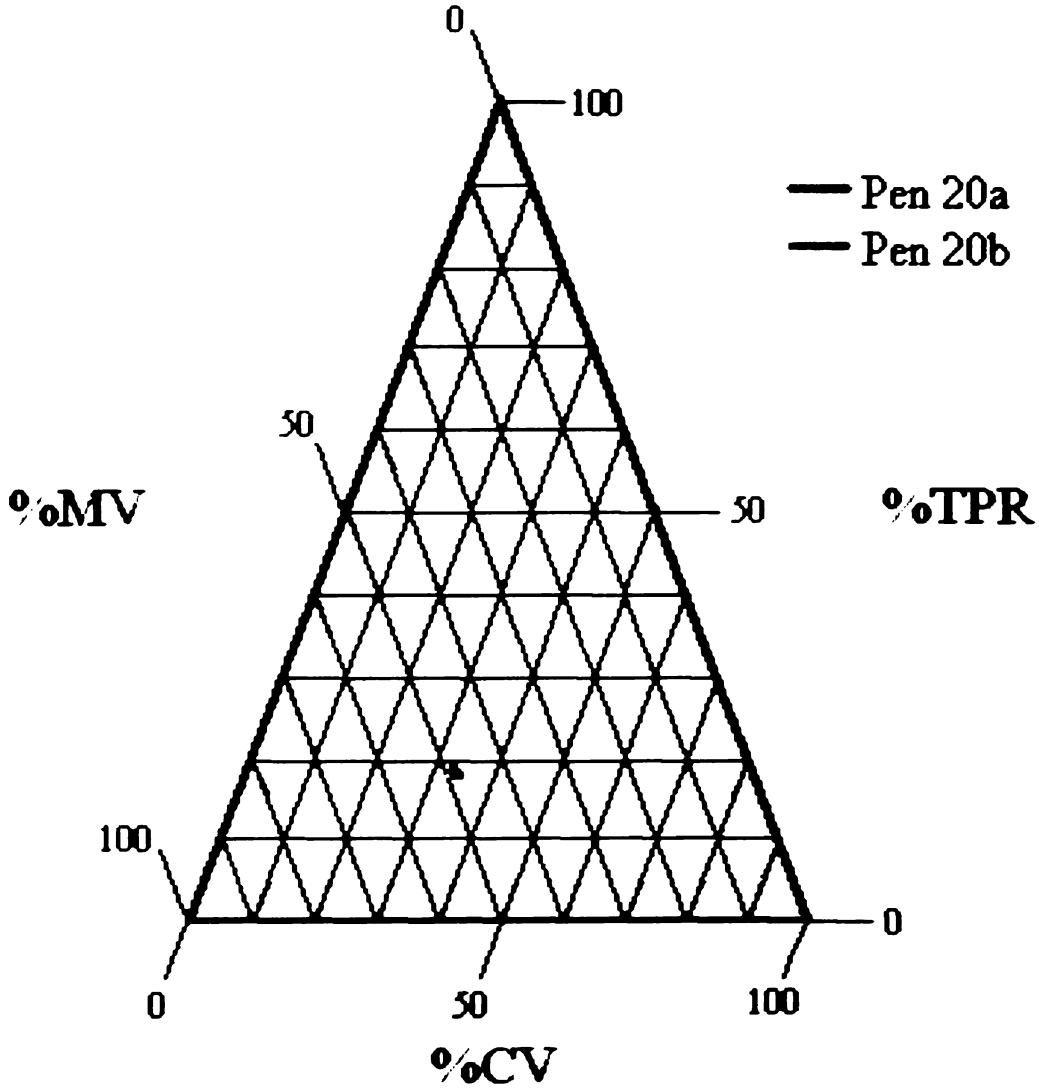
Appendix Figure 4.17: Comparison of the degradation of the inks in Pen 17a and 17b due to fluorescent light exposure.



Appendix Figure 4.18: Comparison of the degradation of the inks in Pen 18a and 18b due to fluorescent light exposure.



Appendix Figure 4.19: Comparison of the degradation of the inks in Pen 19a and 19b due to fluorescent light exposure.



Appendix Figure 4.20: Comparison of the degradation of the inks in Pen 20a and 20b due to fluorescent light exposure.

Appendix V

Data: Relative abundance of CV, MV, and TPR present in black ballpoint pen ink before, during, and after fluorescent light exposure.

	Unexposed	Six Days Light Exposure	Six Days Darkness	Ten Days Darkness
%CV	98.66	69.14	70.54	69.60
%MV	0.99	25.08	25.12	24.91
%TPR	0.35	5.78	4.34	5.49

Appendix Table 5.1: Relative abundance of CV, MV, and TPR present in the ink in Pen 8 before, during, and after light exposure.

	Unexposed	Six Days Light Exposure	Six Days Darkness	Ten Days Darkness
%CV	80.29	62.80	62.24	61.54
%MV	18.87	30.16	30.71	30.79
%TPR	0.84	7.04	7.05	7.67

Appendix Table 5.2: Relative abundance of CV, MV, and TPR present in the ink in Pen 20 before, during, and after light exposure.

	Unexposed	Six Days Light Exposure	Six Days Darkness	Ten Days Darkness
%CV	92.5	79.9	79.9	80.3
%MV	7.0	17.2	17.1	16.9
%TPR	0.5	2.9	3.0	2.8

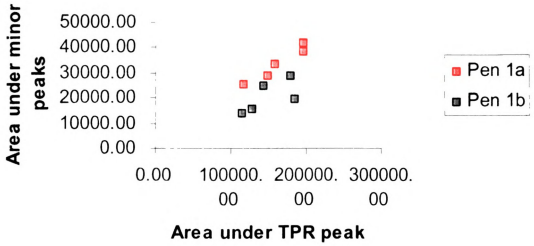
Appendix Table 5.3: Relative abundance of CV, MV, and TPR present in the ink in Pen 21 before, during, and after light exposure.

	Unexposed	Six Days Light Exposure	Six Days Darkness	Ten Days Darkness
%CV	78.87	74.87	75.37	75.22
%MV	19.31	22.26	22.79	22.06
%TPR	1.81	2.87	1.84	2.73

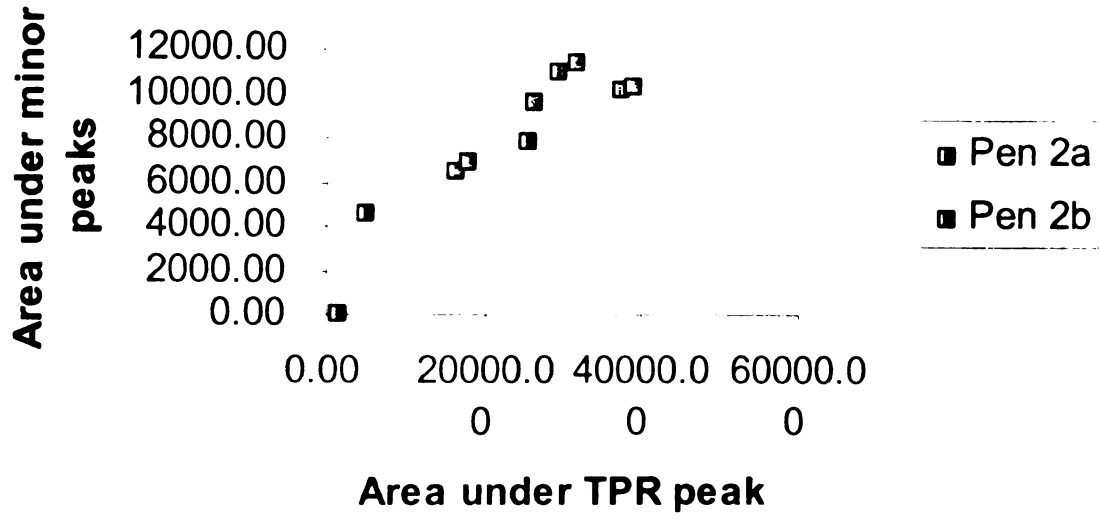
Appendix Table 5.4: Relative abundance of CV, MV, and TPR present in the ink in Pen 29 before, during, and after light exposure.

Appendix VI

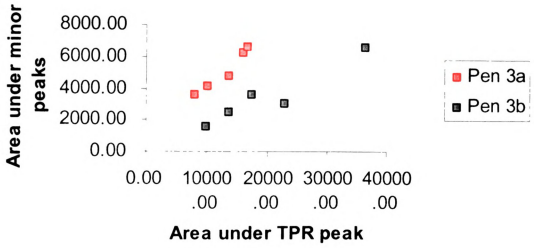
Data: Plots of the sum of the area under the minor peaks versus the area under the TPR peak in all twenty cases.



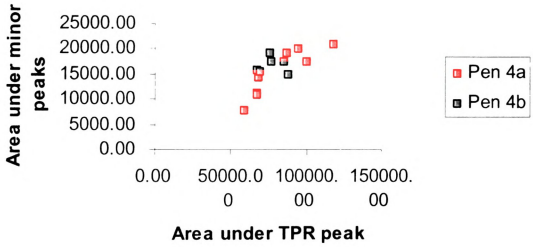
Appendix Figure 6.1: Plot of the sum of the area under the minor peaks versus the area under the TPR peak in the inks in Case 1.



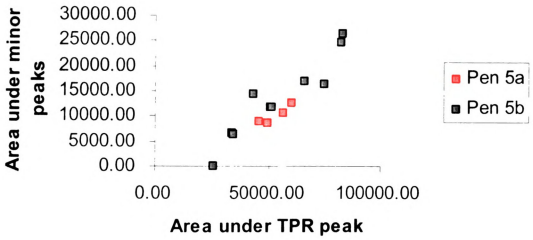
Appendix Figure 6.2: Plot of the sum of the area under the minor peaks versus the area under the TPR peak in the inks in Case 2.



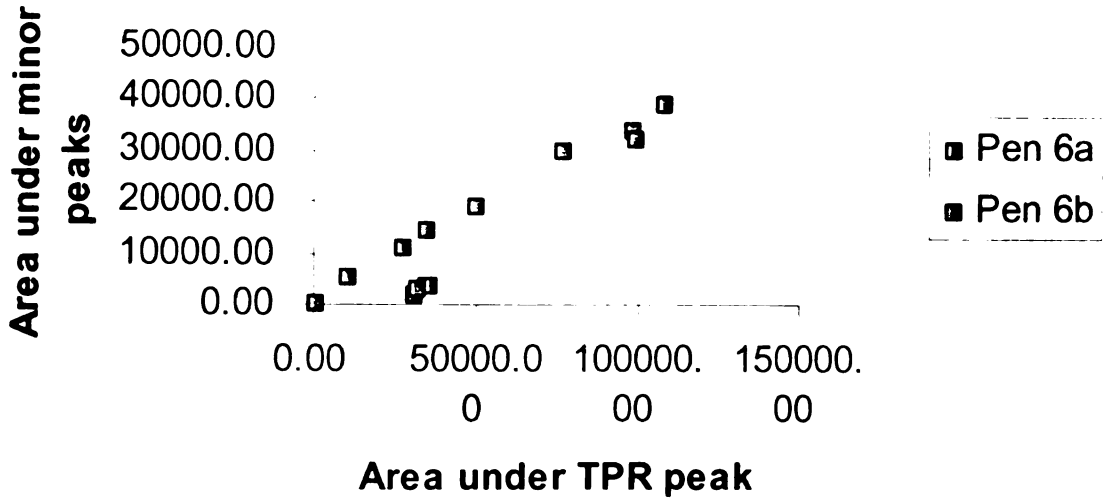
Appendix Figure 6.3: Plot of the sum of the area under the minor peaks versus the area under the TPR peak in the inks in Case 3.



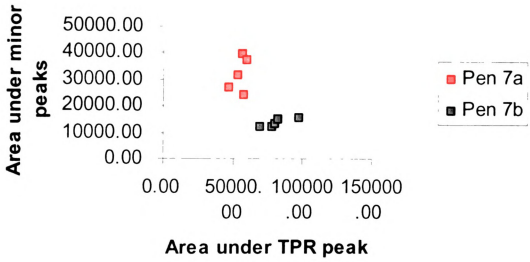
Appendix Figure 6.4: Plot of the sum of the area under the minor peaks versus the area under the TPR peak in the inks in Case 4.



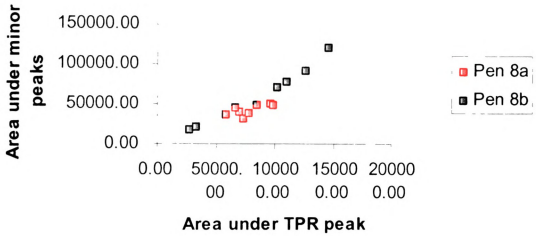
Appendix Figure 6.5: Plot of the sum of the area under the minor peaks versus the area under the TPR peak in the inks in Case 5.



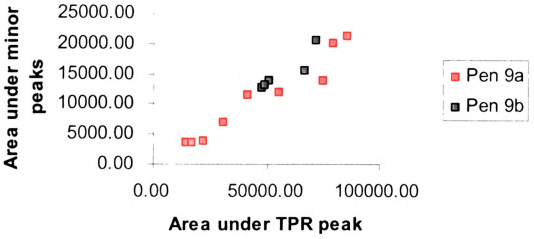
Appendix Figure 6.6: Plot of the sum of the area under the minor peaks versus the area under the TPR peak in the inks in Case 6.



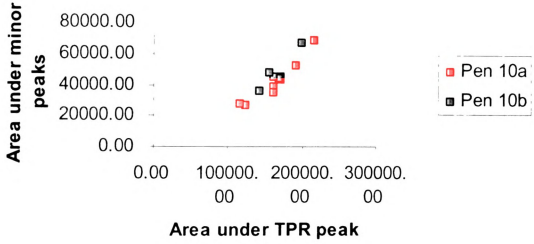
Appendix Figure 6.7: Plot of the sum of the area under the minor peaks versus the area under the TPR peak in the inks in Case 7.



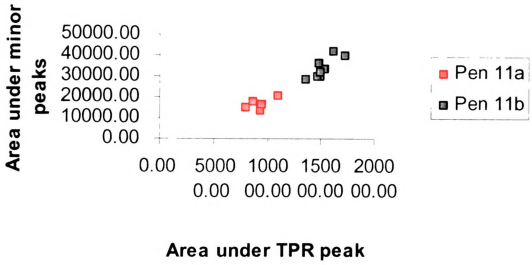
Appendix Figure 6.8: Plot of the sum of the area under the minor peaks versus the area under the TPR peak in the inks in Case 8.



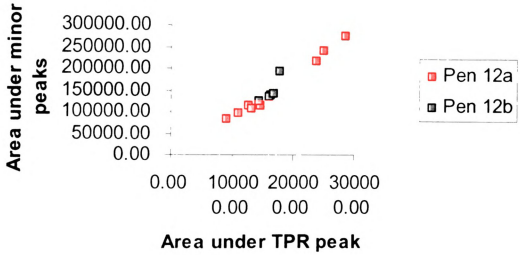
Appendix Figure 6.9: Plot of the sum of the area under the minor peaks versus the area under the TPR peak in the inks in Case 9.



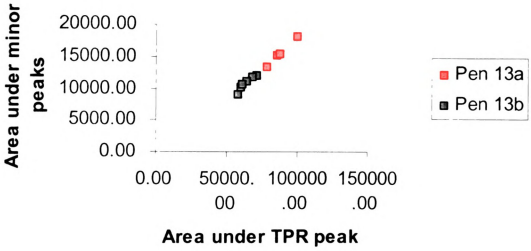
Appendix Figure 6.10: Plot of the sum of the area under the minor peaks versus the area under the TPR peak in the inks in Case 10.



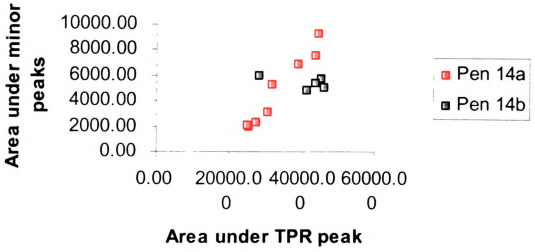
Appendix Figure 6.11: Plot of the sum of the area under the minor peaks versus the area under the TPR peak in the inks in Case 11.



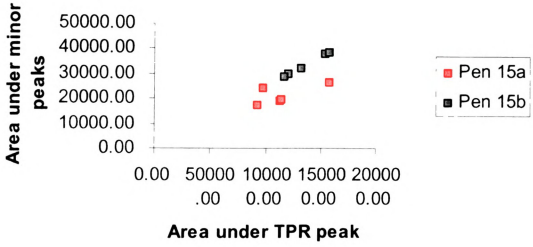
Appendix Figure 6.12: Plot of the sum of the area under the minor peaks versus the area under the TPR peak in the inks in Case 12.



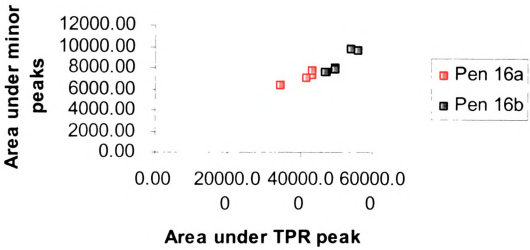
Appendix Figure 6.13: Plot of the sum of the area under the minor peaks versus the area under the TPR peak in the inks in Case 13.



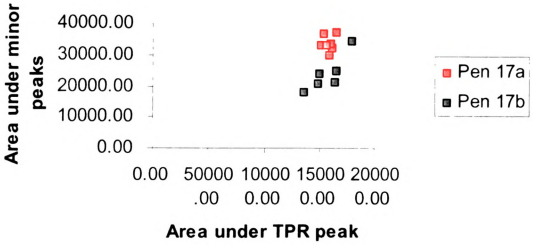
Appendix Figure 6.14: Plot of the sum of the area under the minor peaks versus the area under the TPR peak in the inks in Case 14.



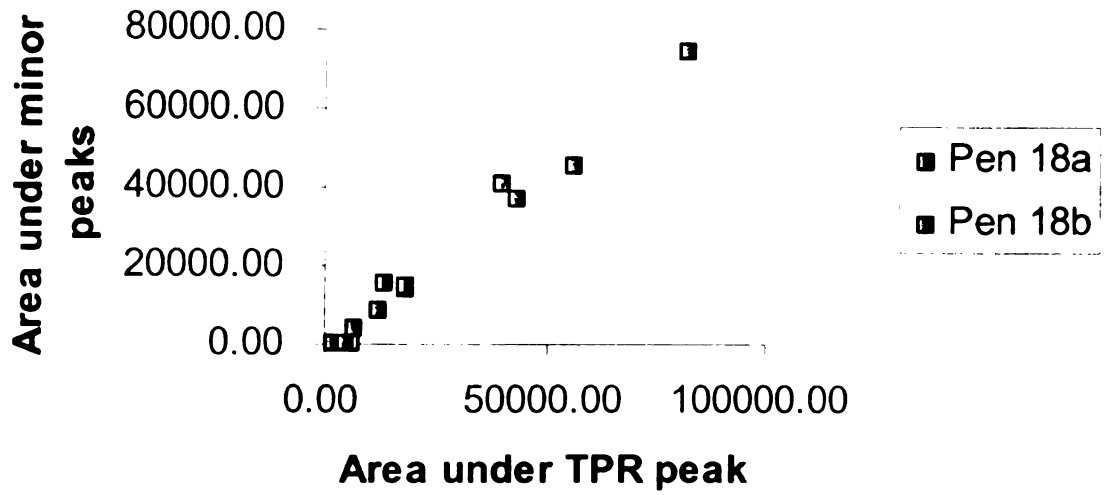
Appendix Figure 6.15: Plot of the sum of the area under the minor peaks versus the area under the TPR peak in the inks in Case 15.



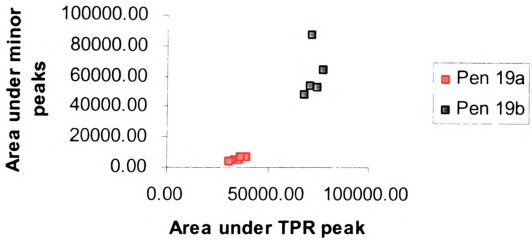
Appendix Figure 6.16: Plot of the sum of the area under the minor peaks versus the area under the TPR peak in the inks in Case 16.



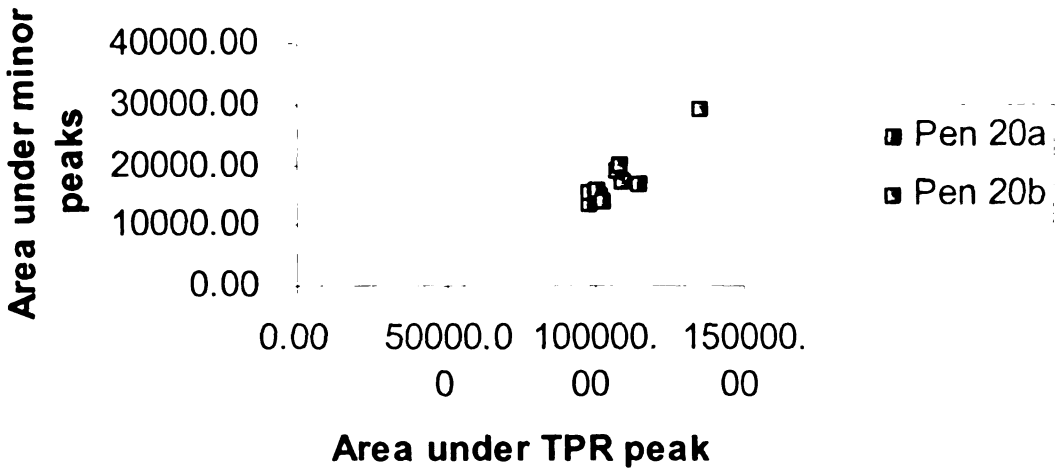
Appendix Figure 6.17: Plot of the sum of the area under the minor peaks versus the area under the TPR peak in the inks in Case 17.



Appendix Figure 6.18: Plot of the sum of the area under the minor peaks versus the area under the TPR peak in the inks in Case 18.



Appendix Figure 6.19: Plot of the sum of the area under the minor peaks versus the area under the TPR peak in the inks in Case 19.



Appendix Figure 6.20: Plot of the sum of the area under the minor peaks versus the area under the TPR peak in the inks in Case 20.

Appendix VII

Case Studies

Case	Pen A	Pen B	Pen A Light Conditions	Pen B Light Conditions	Analyst's Conclusion	Result
1	25	17	Mixture Light/Dark	Constant Dark	Different	Correct
2	2	2	Constant Dark	Mixture Light/Dark	Same	Correct
3	9	16	Mixture Light/Dark	Constant Dark	Different	Correct
4	31	32	Constant Dark	Constant Light	Different	Correct
5	18	26	Constant Light	Constant Dark	Different	Correct
6	24	13	Mixture Light/Dark	Constant Dark	Different	Correct
7	8	1	Constant Light	Mixture Light/Dark	Different	Correct
8	26	13	Constant Light	Mixture Light/Dark	Different	Correct
9	19	6	Constant Dark	Constant Light	Different	Correct
10	23	23	Mixture Light/Dark	Constant Light	Different	False Negative
11	1	31	Constant Dark	Mixture Light/Dark	Same	False Positive
12	21	21	Mixture Light/Dark	Constant Light	Same	Correct
13	18	18	Constant Dark	Constant Dark	Same	Correct
14	29	29	Mixture Light/Dark	Constant Light	Same	Correct
15	17	14	Constant Light	Constant Light	Different	Correct
16	24	24	Mixture Light/Dark	Mixture Light/Dark	Same	Correct
17	23	25	Constant Light	Constant Dark	Same	False Positive
18	13	28	Constant Dark	Constant Dark	Same	False Positive
19	24	26	Mixture Light/Dark	Mixture Light/Dark	Different	Correct
20	30	30	Constant Dark	Constant Dark	Same	Correct

Appendix Table 7.1: Pens in case studies, their light conditions, and results of analysis.

Notes

Chapter 1: Introduction

[1] Andrasko, J. 2001. HPLC analysis of ballpoint pen inks stored at different light conditions. *Journal of Forensic Sciences* 46(1):21-30.

[2] Ibid.

[3] Colwell, Jr., L.F. and B.L. Karger. 1977. Ball-point pen ink examination by high pressure liquid chromatography. *Journal of the Association of Official Analytical Chemists* 60(3):613-618.

[4] Kher, A.A., E.V. Green, and M.I. Mulholland. 2001. Evaluation of principal components analysis with high-performance liquid chromatography and photodiode array detection for the forensic differentiation of ballpoint pen inks. *Journal of Forensic Sciences* 46(4):878-883.

[5] Andrasko, J. 2001. HPLC analysis of ballpoint pen inks stored at different light conditions. *Journal of Forensic Sciences* 46(1):21-30.

[6] Ibid.

[7] Ibid.

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[8] Hilton, O. 1982. *Scientific Examination of Questioned Documents*. New York: Elsevier North Holland, Inc.

[9] Brunelle, R.L. and R.W. Reed. 1984. *Forensic Examination of Ink and Paper.* Springfield, IL: Charles C Thomas Publishing, Ltd.

[10] Ibid.

[11] Ibid.

[12] Ibid.

Chapter 3: Review of Literature

[13] Brackett, J.W. and L.W. Bradford. 1952. Comparison of ink writing on documents by means of paper chromatography. *Journal of Criminal Law, Criminology, and Police Science* 43(4):530-539.

[14] Brackett, J.W. and L.W. Bradford. 1952. Comparison of ink writing on documents by means of paper chromatography. *Journal of Criminal Law, Criminology, and Police Science* 43(4):530-539.

[15] Somerford, A.W. and W. Souder. 1952. Comparison of writing inks by paper chromatography. *Journal of Criminal Law, Criminology, and Police Science* 43(1):124-127.

[16] Ibid.

[17] Brackett, J.W. and L.W. Bradford. 1952. Comparison of ink writing on documents by means of paper chromatography. *Journal of Criminal Law, Criminology, and Police Science* 43(4):530-539.

[18] Ibid.

[19] Tholl, J. 1970. Applied thin layer chromatography in document examination. *Police* 11:6-10.

[20] Ibid.
[21] Tholl, J. 1966. The eastman chromatogram sheet for chromatography: review and experimentation. *Police* 10:6-10.
[22] Kuranz, R. 1974. Technique for separation of ink dyestuffs with similar Rf values. *Journal of Forensic Sciences* 19(4):852-855.
[23] Kuranz, R. 1986. Technique for transferring ink from a written line to thin layer chromatographic sheet. *Journal of Forensic Sciences* 31(2):655-657.
[24] Colwell, Jr., L.F. and B.L. Karger. 1977. Ball-point pen ink examination by high pressure liquid chromatography. *Journal of the Association of Official Analytical Chemists* 60(3):613-618.
[25] Ibid.
[26] Ibid.
[27] Lyter,III, A.H. 1982. Examination of ball pen ink by high pressure liquid chromatography. *Journal of Forensic Sciences* 27(1):154-160.
[28] Kher, A.A., E.V. Green, and M.I. Mulholland. 2001. Evaluation of principal components analysis with high-performance liquid chromatography and photodiode array detection for the forensic differentiation of ballpoint pen inks. *Journal of Forensic Sciences* 46(4):878-883.
[29] Colwell, Jr., L.F. and B.L. Karger. 1977. Ball-point pen ink examination by high pressure liquid chromatography. *Journal of the Association of Official Analytical Chemists* 60(3):613-618.
[30] Brunelle, R.L. and A.A. Cantu. 1975. Ink analysis – a weapon against crime by detection of fraud. *Forensic Science, American Chemical Symposium Series* 15:134-141.
[31] Ibid.
[32] Andrasko, J. 2001. HPLC analysis of ballpoint pen inks stored at different light conditions. *Journal of Forensic Sciences* 46(1):21-30.
[33] Ibid.

Chapter 4: Analysis and Comparison of Black Ballpoint Pen Inks by Controlled Exposure to Light

[34] Andrasko, J. 2001. HPLC analysis of ballpoint pen inks stored at different light conditions. *Journal of Forensic Sciences* 46(1):21-30.
[35] Ibid.
[36] Ibid.
[37] Ibid.
[38] Ibid.

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