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Evaluation of Laser Desorption Mass Spectrometry and UV Accelerated Aging of Dyes on Paper as Tools for the Evaluation of a Questioned Document*

ABSTRACT: Laser desorption mass spectrometry (LDMS) may be used for the detection and identification of dyes found in inks. Naturally-aged and artificially-aged blue and black ballpoint pen inks containing the cationic dye methyl violet were analyzed on paper. The average molecular weight of the dye sample was calculated from LD mass spectral data and plotted versus time. The resulting aging curves demonstrate that, as dye degradation increases, the average molecular weight of the dye decreases. Typical variables involved in ink aging, such as the type of paper and ink formulation, were investigated. Results show that these variables influence the rate of dye degradation. Furthermore, UV accelerated aging has been developed and tested as an alternative to thermal approaches.

KEYWORDS: forensic science, questioned documents, methyl violet, accelerated aging, mass spectrometry, ink, dyes

A simple method for determining the relative age of an ink on a questioned document has eluded document examiners for nearly a century. As an ink sample on paper ages, solvents evaporate, resins polymerize, vehicle components diffuse into the paper, and dyes degrade. What aspect best reflects how long the ink has been on the paper? Current methods frequently involve, in some way, analysis of the solvent content of the ink remaining on the paper (1–13). For example, the remaining solvent content is reflected in the ease of extractability of the dyes from the document in question (2,5). While there are some inconsistencies as to the length of time that solvent remains in the ink-on-paper sample (6,8), the general consensus is that the ink is considered to have ceased aging once the solvent is essentially gone. Even after solvents evaporate, dye molecules obviously remain on a document for many decades.

The use of laser desorption mass spectrometry (LDMS) for the direct analysis of dyes and dye degradation products on paper is currently being investigated. This work complements the recent results from Andrasko, who performed an extensive study using high performance liquid chromatography to characterize the degradation of dyes found in ballpoint pen inks exposed to different light conditions (14,15). While gas chromatography - MS has commonly been employed to separate and detect the volatile components in an ink (13), LDMS may be used to detect the nonvolatile and thermally-labile components. The LD mass spectrometer in this laboratory is equipped with a nitrogen laser. Light from this pulsed UV laser can be used to efficiently desorb and ionize dye molecules from a document. It has recently been demonstrated that

LDMS can be used as a minimally invasive analytical tool to detect intact dye molecules and their degradation products, which are formed as the ink ages (16). High relative amounts of degradation products of dyes present in an ink, as determined from the LDMS mass spectrum, are indicative of an older ink. To determine how old a document is, an aging curve must first be established, frequently using an accelerated aging technique to age new ink to mimic old ink. Therefore, an investigation of UV aging as a means of artificially accelerating the age of ink dyes on paper was also undertaken. This is a departure from the usual thermal aging approaches that have been used extensively in the past for accelerated aging studies (6,13,17,18). It has been necessary to pursue an alternative direction, since the addition of heat fails to sufficiently accelerate the mechanism producing the dye degradation products that are detected by LDMS.

Materials and Methods

Sample Preparation

For the UV accelerated aging studies, ink from both blue and black Bic[®] ballpoint pens were analyzed directly on paper (Hammermill Fore DP). Straight lines were drawn across a 4 in² surface area. In these experiments, the laser could be focused directly on the pen line. Artificially-aged samples were prepared by irradiation with a UV-lamp (254 nm, 760 microwatts/cm²; UVP Inc., San Gabriel, CA, model UVGL-58) that was raised 6 cm above the sample. Samples were analyzed by LDMS at 15 min intervals.

Two natural aging studies were conducted. In the first study, two sets of samples, naturally aged under controlled conditions, were provided by Speckin Forensic Laboratories (Okemos, MI). The samples were written with the same pen ink (Bic[®]-STK BP black B-460 fine point ink, purchased 4/29/91) on both printer paper and bond paper. Thus, these samples were all written with the same pen, on the same paper, and stored under the same conditions. The

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second natural aging investigation was not controlled. The Chemistry Department at Michigan State University maintains records dating back before the 1900's. The chemistry building was constructed in 1965, therefore, it is known that these documents were stored under the same conditions for at least 36 years. According to our observations, the dye of interest, methyl violet, has been used in blue and black ink formulations since approximately 1950. Numerous samples on a variety of paper types were obtained and tested. This study contained samples affected by many more variables, including different ink formulations and different paper.

Sample Analysis

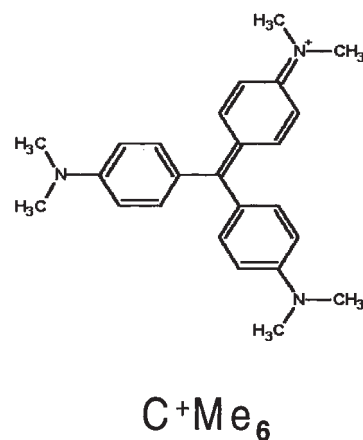
The PE Biosystems Voyager DE time-of-flight mass spectrometer (Framingham, MA) is equipped with a pulsed nitrogen laser (337 nm, 2 ns, 3 Hz) and a linear time-of-flight mass spectrometer. For the analysis of positive ions formed by LD, a sample plate (on which analytes are placed) was held at a voltage of 20,000 V, an intermediate acceleration grid in the ion source was held at 94.5% of the plate voltage, and a delay time of 150 ns was used between the laser irradiation pulse and ion acceleration. A typical sample plate consists of 100-wells, however, the manufacturer supplies a modified plate that can be used to analyze small polyacrylamide gels from gel electrophoresis experiments. In these experiments, ink-on-paper samples were taped to this modified sample plate, which allowed for a flat target. This target can then be moved and selected areas can be subjected to laser irradiation. The instrument was calibrated using a saturated solution of CsI pipetted directly onto paper. Laser desorption of CsI yields $[\text{Cs}_n\text{I}_{(n-1)}]^+$ ions, from the paper. Positive ion spectra were generated, employing the parameters cited above. Under these conditions, the full resolution of the instrument is realized, even though ions are being formed from a non-conducting surface (paper) instead of a traditional conducting metal surface.

Mass spectra from approximately 50 laser shots, at a single location, were accumulated and averaged to yield a single mass spectrum. Three averaged spectra were acquired per sample at different points, separated by several millimeters, along the pen line. The data from all of the spectra were used to compute the average molecular weight of the methyl violet dye present on the paper. The average molecular weight was computed, and graphed versus time. The standard deviation was also computed from all of the spectra taken for each sample, and appears on the graphs that are presented as an error bar for each point.

Results and Discussion

Methyl violet is of particular importance, since it is present in both blue and black inks dating back to 1950. During this time period, a historic change in ink formulations occurred, from an oil-based to a glycol-based vehicle (19). Since methyl violet is a cationic dye, it already carries a +1 charge. Consequently, the dye is easily detectable in a UV-LDMS experiment, since no energy or process is required to ionize the desorbed molecules.

Methyl violet (Fig. 1) is readily degradable through a number of pathways including demethylation. Compounds such as TiO_2 , used in the manufacturing of paper, are known to catalyze the degradation of triphenylmethane dyes (20). As the dye on paper "ages", each of the six methyl ($-\text{CH}_3$) groups in the aromatic amine substructures of this cation (C^+) will be replaced by hydrogen atoms ($-\text{H}$), resulting in a net loss of 14 atomic mass units. The structure in Fig. 1 is presented as having six methyl groups, with a mass-to-charge ratio (m/z) of 372 (C^+Me_6). This structure is referred to as



m/z	Structure
372	C^+Me_6
358	$\text{C}^+\text{Me}_5\text{H}$
344	$\text{C}^+\text{Me}_4\text{H}_2$
330	$\text{C}^+\text{Me}_3\text{H}_3$
316	$\text{C}^+\text{Me}_2\text{H}_4$
302	$\text{C}^+\text{Me}_1\text{H}_5$
288	C^+H_6

FIG. 1—The structure of Crystal Violet and its degradation products.

crystal violet. Methyl violet only has five methyl groups with an m/z value of 358, $\text{C}^+\text{Me}_5\text{H}$.

Dyes are manufactured and sold as impure mixtures. For example, basic fuchsin, the completely demethylated form of crystal violet (C^+H_6), is described as "a homologous mixture of dyes, and in any given lot any homolog may be dominant" (21). However, a lower limit is set on purity, so the dye can provide the consumer with the desired properties. In the case of basic fuchsin, 50% of the dye mixture must be basic fuchsin, with rosaniline, magenta I, and magenta II comprising the remainder of the mixture. When a positive ion LD mass spectrum is obtained of the substance that is sold as methyl violet, the base peak (most intense peak) appears at m/z 372, with a very small peak representing the pentamethylated molecule at m/z 358. As the molecule ages, peaks appear in the spectrum at m/z 358, 344, and 330. Oxidative demethylation continues until the molecule is completely reduced (m/z 288).

UV irradiation for accelerated aging of ink on paper is used in this study, rather than thermal approaches that have been almost exclusively used in the past. The reason why photochemical approaches for accelerated aging are being developed is that thermal methods are not effective for these studies. For this discussion, when methyl violet undergoes oxidative demethylation reactions, the other reactant molecule, that which provides the $-\text{H}$ atom replacing a $-\text{CH}_3$ group, may be an ink vehicle component (solvent). Consider Fig. 2. Ink has been freshly applied to paper. Both ink dye (C^+Me_6) and solvent ($\text{S}-\text{H}$) molecules are present. To accelerate the aging of this sample, thermal approaches are common. Accord-

average molecular weight for the dye at each time interval. Figure 5 shows the plot of the average molecular weight versus the time the document was irradiated in the UV accelerated aging study of Bic[®] black ballpoint pen ink on paper. The average molecular weight (MW_{avg}) was calculated by multiplying the normalized intensity of each peak by the nominal mass of that peak, summing all of the products, and dividing by the sum of the relative intensities of all of the peaks. This value was computed for each of the spectra acquired per sample, and all of the molecular weights were averaged. Scatter in the data is noted, however, a distinct trend is established in which, a decrease in the average molecular weight occurs over

time. The lower MW_{avg} limit for this experiment is 288 Daltons, which would occur if all of the C^+Me_6 were converted to C^+H_6 . We have not yet found any naturally aged samples in which degradation has been this extensive. Figure 5, shows that the average molecular weight falls to 361 Daltons following 450 mins of UV irradiation.

In order to relate the UV accelerated aging curve in Fig. 5 to aging which occurs naturally, a natural ink aging curve (Fig. 6) was constructed using a set of controlled ink library samples from Speckin Laboratories, Okemos, MI. The samples were written with the same pen, on the same paper, and stored under the same condi-

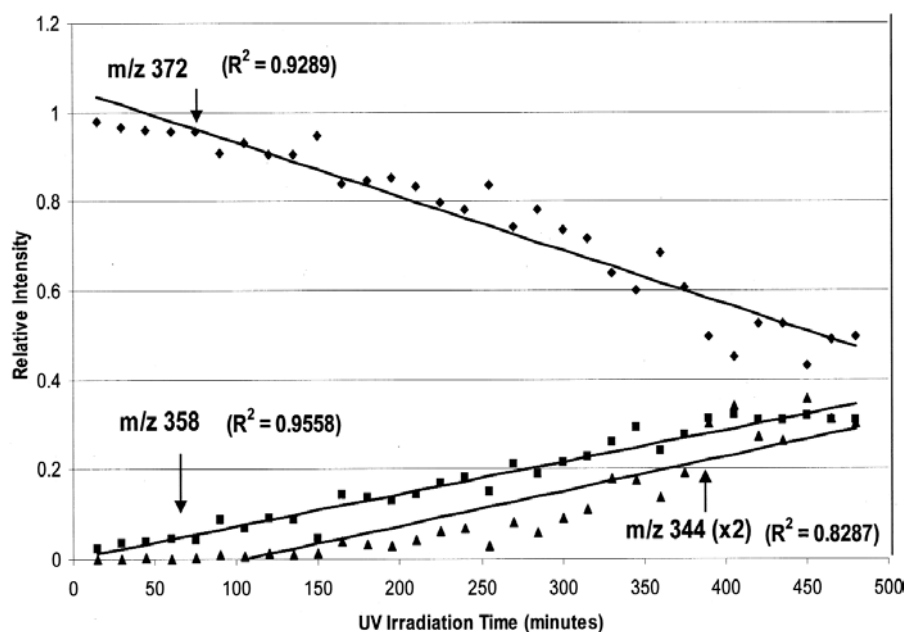


FIG. 4—UV accelerated aging study data for new Bic[®] black ballpoint pen ink on printer paper: a plot of the relative intensity of the m/z 372, 358, and 344 ($\times 2$) peaks versus UV irradiation time.

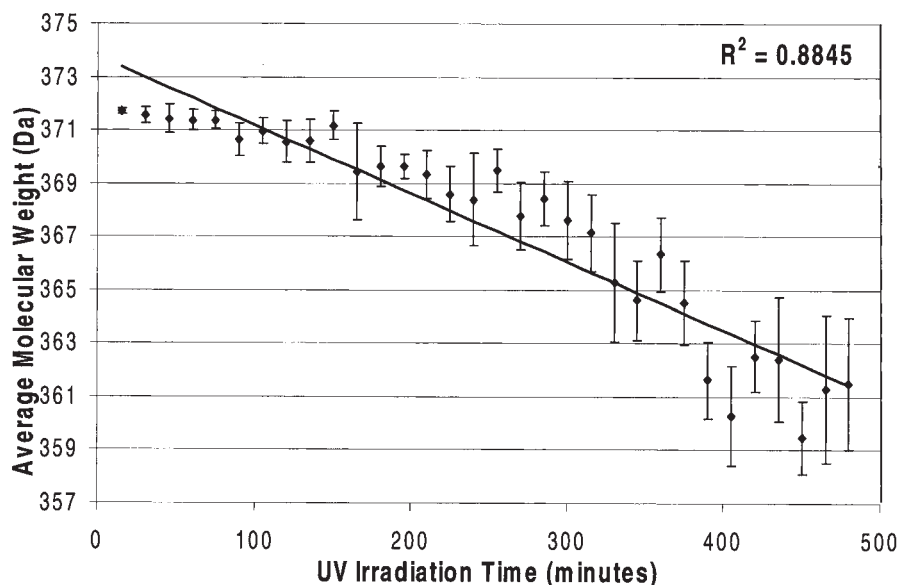


FIG. 5—UV accelerated aging study data for new Bic[®] black ballpoint pen ink on printer paper: a plot of the average molecular weight of the dye, methyl violet, versus minutes of UV irradiation.

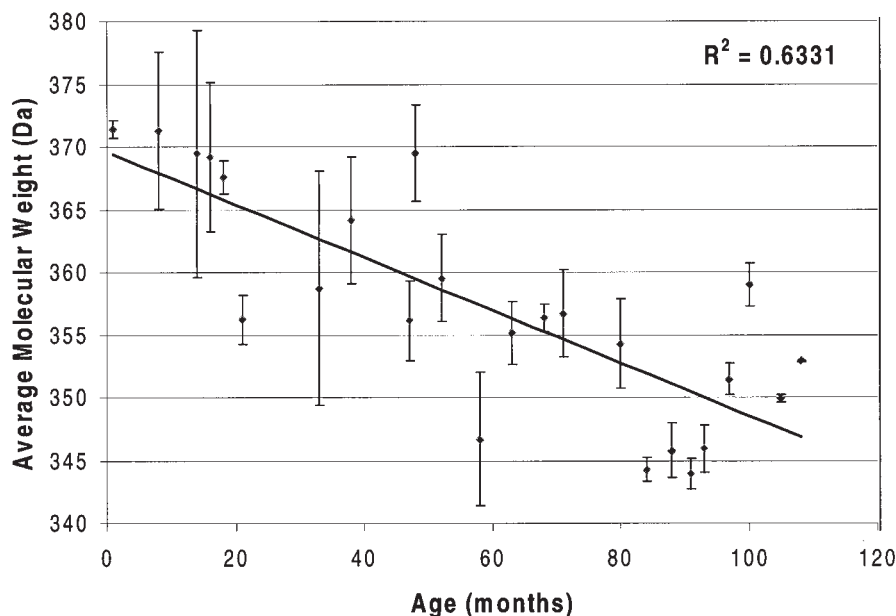


FIG. 6—Controlled, natural aging study data for Bic® black ballpoint pen ink on printer paper: a plot of the average molecular weight of the dye, methyl violet, versus the age of the document.

tions. Again, from LDMS spectra, the average molecular weights were computed. According to the UV accelerated aging curve prepared under the outlined experimental conditions, 500 min (8.3 h) of UV irradiation degraded methyl violet to an average molecular weight of approximately 360 Daltons. Referring to the straight line fit of the controlled natural aging data (Fig. 6), an average molecular weight of 360 Daltons is equivalent to 52 months of natural aging for this particular ink and paper. By combining the information in Figs. 5 and 6, it appears that 500 min of UV irradiation (at the conditions used here) would age a document by approximately 52 months (~ 1560 days). Therefore, in this particular study, for every hour of UV irradiation, the document was aged roughly 187 days. This compares favorably with the initial estimate of 182 days per hour determined from the initial data shown in Fig. 3.

UV accelerated aging is more complex to perform than thermal aging. The details of the UV-aging experimental set-up can influence the resulting aging curve. Although the exact correlation between natural aging and artificial (thermal) accelerated aging may still be unknown (6,13,17,18), a thermal aging technique is very straightforward. For instance, one source suggests that if a particular ink on a particular paper is heated to 100°C for 4 min, it will have aged by three months (6). UV aging is not as straight-forward and easy to control. The distance between the UV lamp and the sample, as well as the age of the light source in the lamp affect the flux of UV photons and consequently, the aging rate. Furthermore, the power of UV lamps may vary the longer the lamp is in use. The lamp was turned off at hourly intervals for 15 min throughout the experiment, to ensure that the sample was not being heated by the lamp to any appreciable extent. It was found that having the lamp 6 cm above the sample surface, allowing the sample to cool every hour for 15 min, and taking LDMS spectra at 15 min intervals, allows for generation of an acceptable aging curve. Others attempting to use this aging technique would therefore need to first develop their own aging curve, using their own defined experimental geometry and lamp. The accelerated aging rate of 180–190 days/hour is for this particular system, not to be considered as applicable in general.

Result #2—The rate of natural aging of methyl violet is dependent on many variables. Certainly, it would be ideal if the chemical degradation of methyl violet was insensitive to the common variables involved in ink aging (ink formulations, the type of paper, relative humidity, and environmental storage conditions). To determine whether dye aging is sensitive to some of these variables, naturally aged ink samples were obtained from the departmental archives. The samples gathered were written in both blue and black ink, and were therefore of different ink formulations, and were obviously not from the same pen. Also, the types of paper selected varied significantly. Positive ion LD mass spectra were obtained for more than 25 samples, that spanned a 50-year period. The average molecular weight of the dye was calculated as previously described, and then plotted versus age (Fig. 7). The graph shows differences from the aging curves of the artificial aging study (Fig. 5) and the controlled ink library study (Fig. 6). Substantial scatter is evident in the data, and it appears as though, after roughly 15 years, all of the samples produce very similar spectra. Therefore, this study suggests that the generally accepted theory that ink aging (from a solvent content standpoint) will asymptotically level off and eventually stop (6,8), may be true in the case of dye degradation as well. Another interesting observation is that the leveling off occurs at an average molecular weight of approximately 365 Daltons. It has already been demonstrated that UV accelerated aging can surpass this value (Fig. 5). What is even more surprising is that the natural aging ink library samples had degraded to lower average molecular weights (Fig. 6) than what is seen in Fig. 7. A series of experiments were designed to test some of the variables, which were thought to be causing the deviations (scatter) in the “real life” samples (Fig. 7). There is also interest in why the naturally aged samples appear to stop aging, while the accelerated aging and controlled ink library samples have aged to a greater extent and appear to be still aging significantly.

The type of paper influences both natural and accelerated aging of methyl violet. To test the influence of the paper on the degradation of methyl violet, an additional set of samples was provided by Speckin Laboratories. This set was written with the same pen and

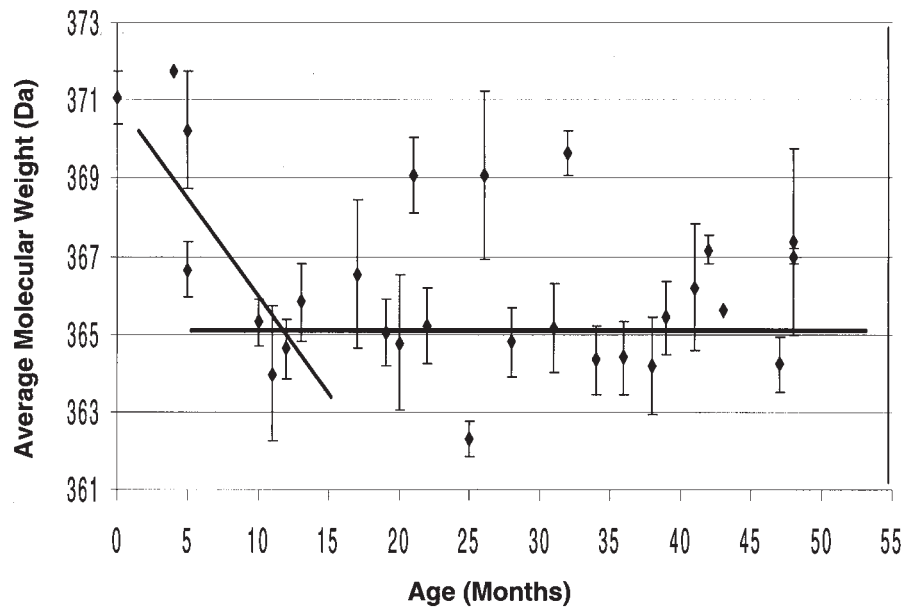


FIG. 7—Uncontrolled, natural aging study data for various inks on various types of paper: a plot of the average molecular weight of the dye, methyl violet, versus the age of the document.

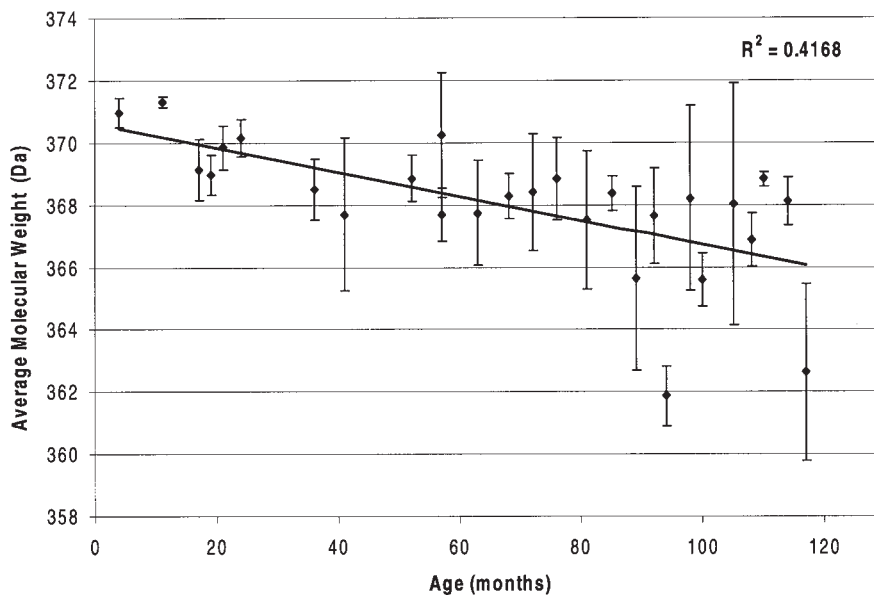


FIG. 8—Controlled, natural aging study data for Bic® black ballpoint pen ink on bond paper: a plot of the average molecular weight of the dye, methyl violet, versus the age of the document.

stored under identical conditions as the first set, however this second set was written on bond paper as opposed to printer paper. Positive ion LD mass spectra of the samples were obtained and a natural aging curve of the average molecular weight of methyl violet versus time was prepared (Fig. 8). While there is significant scatter in the data, the dye appears to be aging at a slower rate than that of the first set of ink library samples (Fig. 6). For instance in ten years, dye in the first set has degraded to an average molecular weight of 347 Daltons, while the second set, the dye has only degraded to 366 Daltons. In the data from Fig. 7, spectra from 10-year-old documents led to a dye MW_{avg} of 365 Daltons. Thus, natural aging as reflected by dye degradation products is paper-dependent. It is im-

portant to note that the artificial UV aging study performed in this laboratory was conducted on the same type of paper as the first set of ink library samples, which is the basis for our initial correlation that 1 h of UV irradiation is equivalent to 187 days of naturally aging. However, the studies were not performed with the same pen, but with the same company's ink. Most of the samples in documents selected for the study in Fig. 7 are "professional correspondence", mostly on letterhead paper.

Having established that the rate of natural degradation of the dye is paper-dependent, the decision was made to investigate whether accelerated aging is paper dependent from data generated from non-white paper. A legal pad, which consisted of tan paper with a

green design on each page, was used for this study. Ink was written on the different colors of the page, and artificially aged under the same conditions previously described. The results of this experiment (not shown), suggested that the artificial ink aging process on the colored and white papers proceeded at similar rates, and fall in the following order for degradation rates: (tan paper) > (green paper) > (white paper). The paper certainly influences the aging process.

Although the extents of dye degradation in samples 20–50 years old are similar, this does not necessarily suggest that degradation ceases to occur after 15 years. One explanation for the data in Fig. 7 is that, after 15 years on paper, dye molecules do not continue to react and form degradation products. There could be multiple explanations for the data. First, if the dye reacts with solvent molecules, the concentration of the solvent in the paper could be sufficiently small after 15 years that the reaction essentially ceases. Alternatively, the reaction may involve water, which could always be provided by the relative humidity of the environment in which the document is stored, but the dye molecules may become immobile over time. They may become permanently bound to the paper, trapped in hardened resins, and may be unable to diffuse to reactive molecules and form products. If these possibilities are correct, then old samples should not age if one were to subject them to UV accelerated aging. To test this, a 1958 sample from the naturally aged set was taken and exposed to UV irradiation. The results of this experiment are shown in Fig. 9. Initially, the average molecular weight of the 42-year-old sample was roughly 367 Daltons. Irradiating the sample with UV light decreased the average molecular weight to approximately 363 Daltons. It is obvious that the ink aging process continued. One interpretation is that methyl violet on documents that are more than 15 years old can and does continue to form degradation products, but more slowly than on documents created more recently. Certainly, in the past 50 years there have been considerable changes in both ink formulations and in paper chemistry. Ink chemists are learning how to create thinner films, with different vehicle systems. Older vehicles may form more of a non-reactive, protective coating on the dye molecules than do newer solvent systems. It would certainly not be surprising that a

document written 40 years ago with a pen that contained methyl violet in the ink would be a very different chemical system than one created recently.

Solvent molecules from the ink are not the only possible compounds that react with dye molecules to form degradation products. An additional experiment was conducted to test the solvent dependency of the dye degradation process. A new sample was aged in the oven at 100°C for 320 min, which is equivalent to 20 years of natural aging according to a thermal method of aging (6). The ink solvents should have evaporated. LDMS spectra of the sample were taken following this aging process. The spectra showed that the sample was still “new” from a dye degradation standpoint. This sample was then exposed to the UV accelerated aging experiment. If most of the solvent was gone, and the degradation of methyl violet was solvent-dependent, then no further aging would take place. The results of this experiment are shown in Fig. 10, and they clearly demonstrate that the aging process can still occur. In fact, the aging process continues at a rate similar to that observed in Fig. 4. This may suggest the —H donor that reacts with the dye molecules may not be a volatile ink component, but may be a component of the paper, another dye molecule, or absorbed water vapor. Clearly, the chemistry of dye molecules on paper is complex, and much work remains to determine the actual mechanisms through which degradation occurs.

Result #3—Methyl violet in blue ink degrades faster than in black ink. One other factor to consider when attempting to rationalize the scatter appearing in the uncontrolled natural aging study (Fig. 7) involves the influence of ink formulations. Certainly, one would expect the presence of different dye components, and as a result, changes in the vehicle, for different ink colors. In the data presented to this point, all of the experiments were conducted using Bic® black ballpoint pen ink. Additional accelerated UV aging studies using Bic® blue ballpoint pen ink were performed and the results are presented in Fig. 11. Comparing this data to that shown in Fig. 5, it appears as though components present in the blue ink cause it to degrade much more rapidly. At 250 min of UV irradiation, for example, it has already surpassed the extent of degradation observed for the black ink at 500 min of UV irradiation. Therefore,

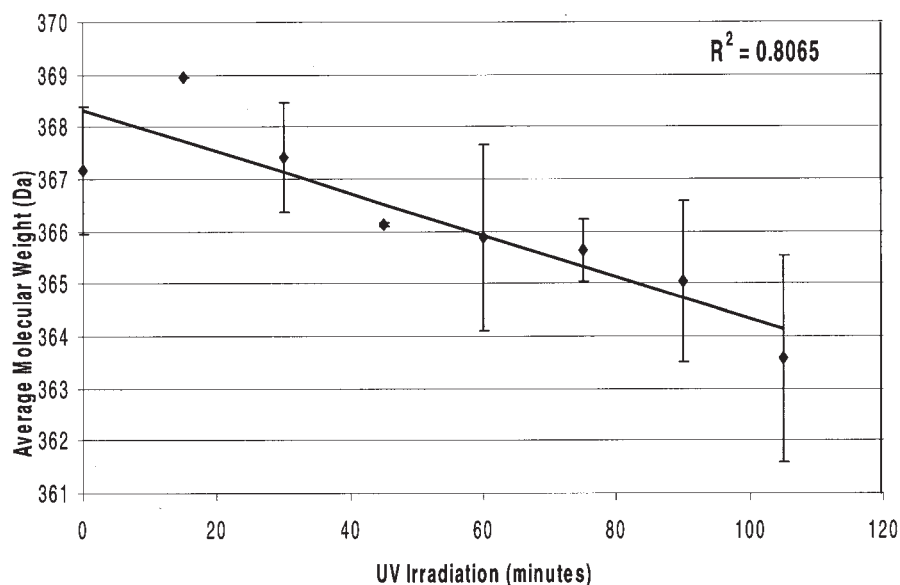


FIG. 9—UV accelerated aging study data for ink on a 1958 old document: a plot of the average molecular weight of the dye, methyl violet, versus minutes UV irradiation.

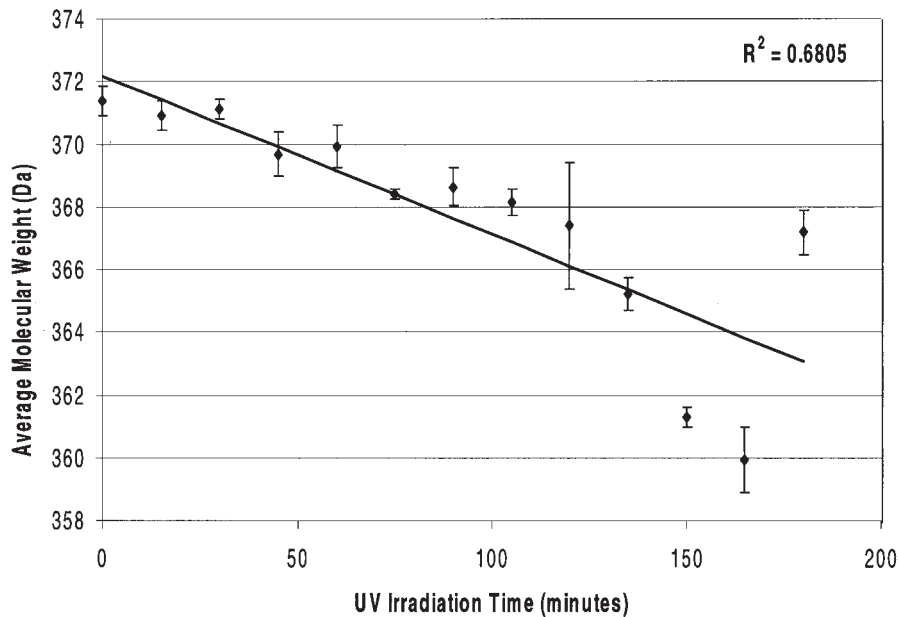


FIG. 10—UV accelerated aging study data for thermally aged 20-year-old ink on printer paper: a plot of the average molecular weight of the dye, methyl violet, versus minutes of UV irradiation.

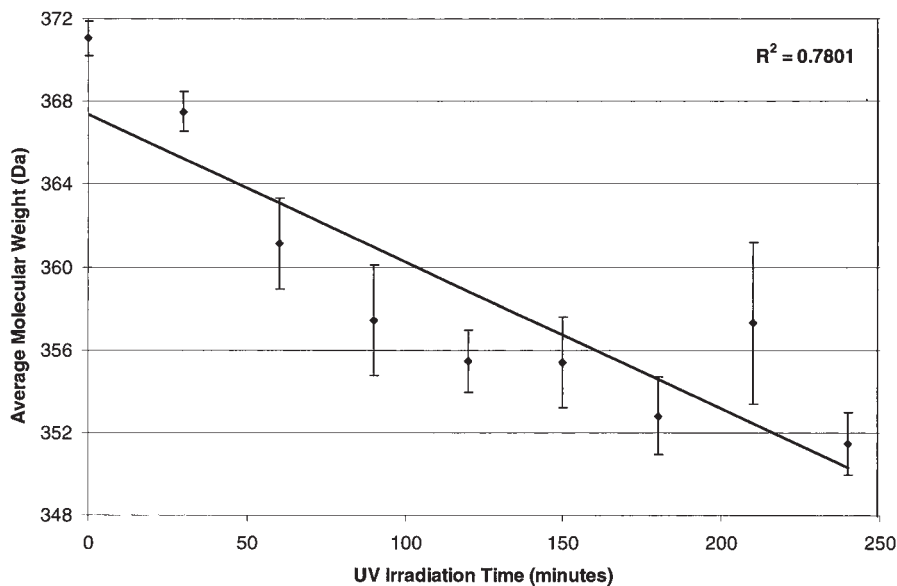


FIG. 11—UV accelerated aging study data for new Bic® blue ballpoint pen ink on printer paper: a plot of the average molecular weight of the dye, methyl violet, versus minutes of UV irradiation.

if there are components in blue ink, which are not commonly used in black ink, and they cause the methyl violet to degrade much faster, this would help explain the scatter present in the uncontrolled, naturally aged samples (Fig. 7).

Conclusion

It has been shown here that one of the most popular dyes in pen inks, methyl violet, degrades over time by the process of oxidative demethylation. Molecular information on the intact dye and its degradation products can be detected using laser desorption mass spectrometry. There are three advantages to the LDMS experiment.

Laser desorption is a relatively non-destructive method. For all of the data shown, there were no visible changes to the ink-on-paper samples used following laser irradiation. Second, the technique is very sensitive for ink dyes. LDMS can generate multiple spectra from ink on paper samples with very high signal-to-noise ratios, even from 50-year-old samples. (We estimate that the amount of dye irradiated by the laser spot used in this work is 10^{-10} moles.) Third, the laser can be easily moved to multiple points along a line, and a substantial number of measurements can be made quickly. This allows for deviations of ink along a line to be quickly and easily realized, while extraction-based methods are much more time-consuming.

Since LDMS is a sensitive analytical tool for the analysis of dyes on paper, it was logical to evaluate it as a tool for aging studies. The variations in the analysis of individual samples show that age determination using the method would be challenging. In these experiments, each spectrum obtained was the sum of 50 spectra, and multiple summed spectra were processed to produce the graphical data. Conservatively, more than 20,000 mass spectra were generated to yield the data presented here. Data variations are not inherent to the LDMS method, but are due to inter-sample variations. Comparison of Figs. 5 and 6 show that there is more spread in the data from natural aging studies than accelerated aging studies. Pens are inexpensive devices, and variations in the amount of ink deposited along a written line are common—a function of pressure and the instantaneous output from the pen tip. Over time, our results would suggest that these spatial variations lead to variations in degradation rates and product distributions that vary along a pen stroke. Data that resulted in points on the graphs with large spreads were evaluated separately. They clearly show that, for an aged sample, there are different extents of aging realized at various locations, even near each other on the written line. (In contrast, point-to-point variations are small for fresh ink samples.) As more points are sampled, averaged values more closely fit to the trend line.

If an ink library is being maintained, appropriate sampling methods are not obvious. If pen strokes from a single pen are recorded over time, how should each sample be created? Should it be the ink first out of the pen (mostly exposed to air, in the tip)? Should two meters be written before the sample is taken? With a method such as LDMS, where many measurements can be quickly made along a pen stroke, it seems clear that variations can be significant, but that averaged values can be more representative of age. This provides a format for not only considering LDMS-based methods, but ink sampling methods in general. Age determination remains a difficult experiment to perform to yield high temporal-resolution, unless substantial numbers of measurements can be made and averaged to yield a true representative value.

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