J Forensic Sci, Nov. 2002, Vol. 47, No. 6
Paper ID JFS2001406_476
Available online at: www.astm.org

TECHNICAL NOTE

Donna M. Grim,[1,2] *B. S.; Jay Siegel,*[2] *Ph.D.; and John Allison,*[1] *Ph.D.*

Does Ink Age Inside of a Pen Cartridge?*

ABSTRACT: In questioned document examination and ink dating, it has been assumed that the ink inside of a pen cartridge does not begin aging until the ink is dispensed onto paper. Positive ion laser desorption (LD) mass spectra were obtained of ink-on-paper samples containing methyl violet, from new and old pens. Mass spectral studies with methyl violet have established the mechanism for how the dye degrades over time, and have provided structural information concerning the dye's degradation products. This information was used as an indication of the relative age of ink on paper. The LD mass spectrum of the ink from a new pen was indicative of "new" ink, whereas the spectra of the ink found in some older pens may appear to be either new or old. The ink from most of the old pens studied appears not to have aged, supporting the common assumption, whereas other ink samples produced "aged" ink spectra, suggesting otherwise.

KEYWORDS: forensic science, questioned documents, methyl violet, ink aging, mass spectrometry, dye degradation

Pens have evolved from being mere writing implements. Pens can be, at one extreme, works of art—collector's items. At the other extreme, they are inexpensive advertisements. For most people, pens accumulate. If one purchases a "12 pack" of pens, there may be a substantial period before some of them come into daily use.

Suppose that a will has just been drawn up. The lawyer reaches for a random pen from a cup on her desk. It is a pen that the lawyer has had for more than a decade. Two years later, that client dies and the will is contested. Will existing methods (1–11) confirm that the will was signed two years ago, or will the selection of that particular pen yield analytical results that only show the will was prepared within the past 10 years.

It has been suggested that ink cartridges in pens should be considered as "closed" systems, in contrast to ink on a paper surface, which would be an "open" system (8). This is logical from the standpoint of the vehicle components of the ink, in that volatile molecules begin to evaporate when the ink is applied to the paper. While a good working hypothesis is that the ink drying process begins as soon as the ink is placed on the paper (8), it is not uncommon to find an older pen that either does not write anymore, or requires some attention ("scribbling") to get it to work again. Thus, some evaporation, at least at the tip, occurs. While overall, an ink cartridge in a pen may be considered as a closed system, its ends are open, and volatile components will evaporate slowly from them.

There are a number of processes that occur, which can be assumed to begin when the ink is applied to the paper. These not only include volatile component evaporation, but diffusion of components into the paper, away from the written line. However, the most obvious component of an ink is the visible dye. Laser desorption mass spectrometry (LDMS) has recently been reported as a useful tool for the molecular level analysis of dye molecules on paper (12,13). One of the most popular dyes used in blue and black inks, the cationic toner methyl violet, degrades over time on paper, following a demethylation mechanism. *From the dye perspective*, does aging begin when, and only when, the ink is applied to paper, or do common dye molecules age within pens? As the number of aging pens grows in the workplace, and as methods continue to be developed for the direct analysis of dye molecules on paper, this question becomes an important aspect of questioned document examination, and is briefly addressed here.

Experimental

Instrumentation

The PE Biosystems Voyager DE instrument (Framingham, MA) is equipped with a pulsed nitrogen laser (337 nm, 3 ns, 3 Hz) and a linear time-of-flight mass spectrometer. For the analysis of positive ions formed by LD, the sample plate 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 laser irradiation and ion acceleration. In these experiments, ink-on-paper samples were taped to a modified sample plate to achieve 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 $[Cs_nI_{(n-1)}]^+$ 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.

[1] Department of Chemistry, Michigan State University, East Lansing, MI.
[2] School of Criminal Justice, Michigan State University, East Lansing, MI.
* Presented at the American Academy of Forensic Science 53rd annual meeting, February 2001, Seattle, Washington.
Received 30 Nov. 2001; and in revised form 31 May 2002; accepted 31 May 2002; published 16 Oct. 2002.

Sample Preparation

Inks from a variety of commercially available ballpoint pens were analyzed, ranging from approximately 20 years old to recently purchased. Initially, each pen was used to draw straight lines across a 4 in^2 piece of paper (HammerMill Fore DP). Selected pens were disassembled, so that samples from inside of the ink cartridge could be obtained, using a metal probe. The metal pen tip was separated from the ink cartridge, which was then cut in half at the center of the cartridge. Samples were taken from the cartridge at the end closest to the pen's tip, the middle region, and the far end. Each sample was applied onto a paper substrate, using the metal probe tip. Positive ion LD mass spectra were obtained for the written samples and the smeared samples.

Results and Discussion

With respect to analyzing the dye component to determine the age of an ink, the difference between a "new" or fresh ink, and an "old" or aged ink, in terms of mass spectral data, has been established and reported in this Journal (12,13). Figure 1 shows the positive ion LD mass spectrum of ink on paper from a 20-year-old pen (pen #1 - Bic black pen). The most intense peak, at m/z 372, represents the cationic dye, crystal violet. The structure for crystal violet is also shown in Fig. 1 and consists of a cationic triphenyl methane center, with 6 methyl groups (—CH_3) attached to 3 nitrogen atoms. If crystal violet loses a —CH_3 group and it is replaced with a —H atom, it experiences a net mass change of −14 amu. The process is referred to as oxidative demethylation. In Fig. 1, a small peak is seen 14 mass units lower (m/z 358) than the base peak, representative of methyl violet, the pentamethylated homolog of crystal violet. Dyes are manufactured and sold as impure mixtures, with lower limits set for how much of the pure form of the dye must be present to maintain the desired properties the consumer is seeking. If one purchases either methyl violet or crystal violet, the substance obtained is essentially crystal violet. Thus, the mass spectrum shown in Fig. 1 is typical of what would be obtained for a new ink, and is characterized by a large peak at m/z 372, with a small or absent peak at m/z 358. This suggests that these dye molecules are stable in this pen, and have not "aged".

A variety of old pens were gathered which were known to be 5 to 20 years old. Positive ion LD mass spectra were obtained of the pen lines which were drawn using them. Pen #1, used to obtain the data in Fig. 1, was roughly 20 years old, and was known not to have been used for years. The positive ion LD mass spectra obtained from any point along the pen lines were consistent with the spectrum in Fig. 1, indicative of new ink. Other pens tested generated the same results, lending support to the assumption that ink (including the dye component) does not age inside of the pen. However, some of the old pens produced spectra indicative of old ink, which required a more in depth analysis.

A second old pen, pen #2 (manufacturer unknown, from the Henley Park Hotel, Washington, D.C.), yielded ink that clearly appears as "aged" ink. Figure 2 shows the positive ion LD mass spectra of the ink from pen #2, which were taken at various points along the length of a written line. As the dye degrades, the crystal violet dye molecules continue to demethylate. Evidence for this process appears in each of the mass spectra of Fig. 2. A significant increase in the intensity of the m/z 358 peak, and the appearance of a peak at m/z 344 are noted. The presence of the degradation products suggests that pen #2's ink has been aging in the pen.

All three spectra are similar, suggesting that the dye has degraded, but to what extent has it degraded, when compared with naturally aged ink-on-paper samples? The calculation of the average molecular weight of the dye and its degradation products from LD mass spectral data was recently proposed as an effective way to determine the extent of dye degradation (13). Furthermore, a controlled natural aging curve was created from ink library samples (Speckin Forensic Laboratories, Okemos, MI), which related the actual age of the ink to the average molecular weight of the dye computed from mass spectral data. From the mass spectral data in Fig. 2, the average molecular weight of the dye from each spectrum was approximately 363 amu. It is important to note that the small variations among the three spectra did not have a significant effect on the calculated average molecular weight. Compared with the natural aging of ink on paper, a dye with an average molecular weight of 363 corresponds to roughly 35-year-old ink on bond pa-

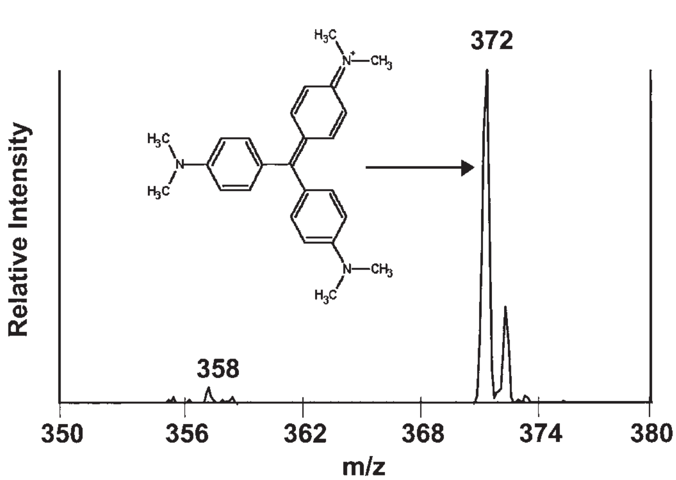

FIG. 1—*The positive ion LD mass spectrum of ink on paper from Pen #1.*

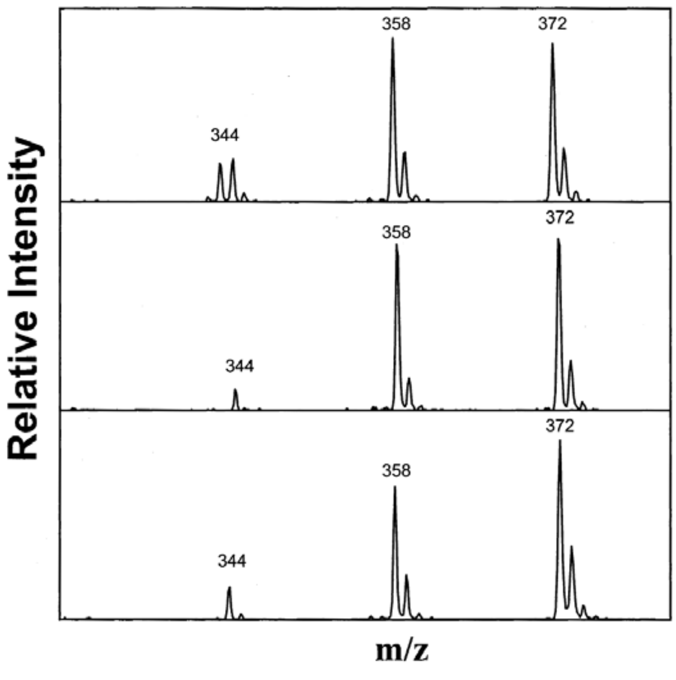

FIG. 2—*The positive ion LD mass spectra of ink along a written line from Pen #2.*

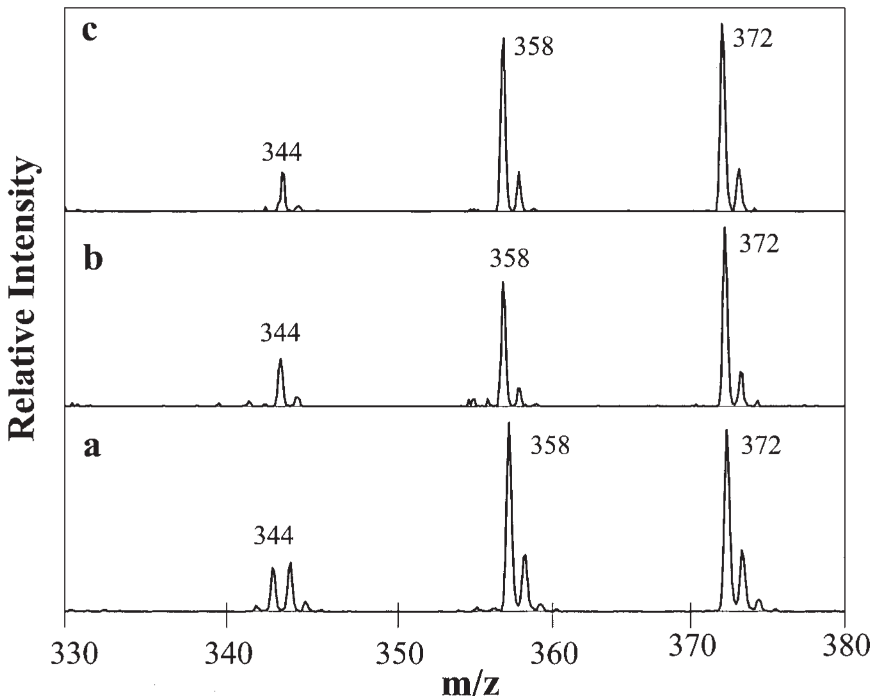

FIG. 3—*The positive ion LD mass spectra of ink within the cartridge of Pen #2:* a) *ink from pen tip;* b) *ink from middle of cartridge;* c) *ink from open end of cartridge.*

per. So, in this particular pen, one would conclude that the ink aged faster than if it had been on paper.

Considering that a pen cartridge holds enough ink to write a line approximately 3000 m long (14), the sample quantity of ink analyzed in the experiment is not a fair representation of the ink throughout the entire pen cartridge. The ink may only have degraded near the tip of the pen, since it is exposed to atmospheric gases and light, which may catalyze the demethylation process. Thus, pens which appeared to contain "aged dyes" were disassembled to investigate the issue further.

Ink from pen #1, taken from the region closest to the metal pen tip, the middle region of the cartridge, and the open, far end of the cartridge, generated LD mass spectra indicative of new ink (identical to that shown in Fig. 1). The ink appears to be in the same state throughout the entire ink cartridge. Figure 3 shows the positive ion LD mass spectra of ink from pen #2, taken from three regions inside of the ink cartridge. As in Fig. 2, the spectra in Fig. 3 are all very similar, and representative of a dye with an average molecular weight of 363 amu. The slight differences are small. The significance arises when trying to determine the relative age of a questioned document by dye analysis, when the pen used contained dye that, from a degradation standpoint, is already 35 years old.

A third pen (manufactured by Pierre Cardin), from which a written blue line produced "aged" positive ion LD mass spectra (not shown), was also disassembled. In this case, the pen cartridge was metal and capped. The spectra obtained from all three regions again suggested that the aging process occurs uniformly throughout the entire ink cartridge.

A second interpretation is that the ink in Pen #2 did not age at all, and the spectra shown in Fig. 2 represent the initial composition of the dyes in the pen. We believe that this is unlikely. Spectrum #2 suggests the presence of approximately equal amounts of methyl violet and crystal violet. Could this have been a mixture used in pen manufacturing 20 years ago? This seems improbable. Most of the older pens we have studied contained pure crystal violet, so the dye was available as is found in pens today. One would not have blended equal amounts of methyl violet and crystal violet to make a pen ink for two reasons. First, there would be no benefit from the visual standpoint. Second, even if one purchased a bottle of methyl violet and a bottle of crystal violet and mixed the two, the result would be crystal violet. The possibility certainly exists that Fig. 2 represents ink as provided by a manufacturer 20 years ago. However, the additional feature, the third peak at m/z 344, and the relative intensities of the three dye peaks, are consistent with a mixture that could be formed by degradation of crystal violet, following a simple kinetic mechanism of successive demethylation steps. We conclude that the ink had aged in the pen. If this is not the case, we still report that ink distributions that resemble "aged ink" have been found in a small number of old pens, and they are not found in any newer pens.

Conclusion

Laser desorption mass spectrometry is a sensitive tool for the analysis of the commonly used ink dye, methyl violet, and its degradation products. We have evaluated the ink in a collection of pens that were up to 20 years old. In most cases, the dye appears to be sufficiently stable in the ink cartridge and no degradation is observed. However, in some pens, substantial degradation appears to have occurred at a rate even higher than what would occur if the dye were on paper. The stability of dye in an ink depends on the ink formulation. As aging pens accumulate on and in desks, document examiners should be aware that "aged," degraded dyes may be found in old pens. From the standpoint of professionals who prepare documents such as wills, it is in the best interest of the client to always use a new pen when documents are signed.

The possibility that a dye can degrade in a pen need not negate the use of methods such as laser desorption MS for the analysis of inks to determine the age of a written line, since other methods are commonly used that evaluate solvent content. Thus, if one analytical method suggests that the dye on the paper is 40 years old, and a second method suggests that there is still substantial solvent remaining, then the evaluation could proceed with the information that the document was recently signed, with an old pen.

References

1. Brunelle RL, Pro MJ. A systematic approach to ink identification. J Official Anal Chem 1972;55:823–6.
2. Brunelle RL. Determining the relative age of ballpoint ink using a single-solvent extraction, mass-independent approach. J Forensic Sci 1989;34:1166–82.
3. Brunelle RL. Ink-dating—the state of the art. J Forensic Sci 1992;37: 113–24.
4. Brunelle RL. A sequential multiple approach to determining the relative age of writing inks. Int J Forensic Doc Examiners 1995;1:94–8.
5. Cantu AA, Prough RS. On the relative aging of ink—the solvent extraction technique. J Forensic Sci 1987;32:1151–74.
6. Cantu AA. Comments on the accelerated aging of ink. J Forensic Sci 1988;33:744–50.
7. Cantu AA. Analytical methods for detecting fraudulent documents. Anal Chem 1991;63:847–54.
8. Cantu AA. A sketch of analytical methods for documenting dating. Part II. The dynamic approach: Determining age independent analytical profiles. Int J Forensic Doc Examiners 1996;2:192–208.
9. Kikuchi Y. Estimation of the age of the writing in blue black ink (first report). Japanese Police Science Laboratory Report 1959;12:379–86.
10. Aginsky VN. Dating and characterizing writing, stamp pad and jet printer inks by gas chromatography/mass spectrometry. Int J Forensic Doc Examiners 1996;2:103–116.
11. Stewart LF. Ballpoint ink age determination by volatile component comparison—a preliminary study. J Forensic Sci 1985:30;405–11.
12. Grim DM, Siegel J, Allison J. Evaluation of desorption/ionization mass spectrometric methods in the forensic applications of the analysis of inks on paper. J Forensic Sci 2001;46:1411–20
13. Grim DM, Siegel J, Allison J. Evaluation of laser desorption mass spectrometry and UV accelerated aging of dyes on paper as tools for the determination of the age of a questioned document. J Forensic Sci 2002; 47:1–9.
14. Kunjappu JT. Molecular thinking in ink chemistry. Ink World 1999;5: 50–3.

Additional information and reprint requests:
John Allison, Ph.D.
335 Chemistry Building
Michigan State University
East Lansing, MI 48824-1322