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THE DATING OF WRITING INKS THROUGH 2-PHENOXYETHANOL USING GAS CHROMATOGRAPHY-MASS SPECTROMETRY, ADVANTAGES, INTERPRETATION, AND LIMITATIONS

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1. Introduction

1.1. Background information

To ensure understanding of the analytical chemistry techniques discussed in this paper, a short background of these techniques will be given before a discussion of ink analysis and ink dating. (More information about analytical techniques can be found in Advances in the Forensic Analysis and Dating of Writing Inks by Richard Brunelle and Kenneth Crawford (Charles C Thomas Publisher, LTD; Springfield, IL, 2003))

1.1.1. Thin Layer Chromatography

Chromatography is the name give to analytical chemistry techniques that involve separating components of a mixture. There are two phases to chromatography methods: a mobile phase and a stationary phase. The mobile phase can be a gas or a liquid while the stationary phase can be a liquid or solid. During the separation, the mobile phase moves past the stationary phase. The separation of a mixture is based on a component's interaction with each of the phases. Components that interact more with the mobile phase will move more quickly. Components that interact more with the stationary phase will be slowed.

Thin layer chromatography (TLC) utilizes a liquid mobile phase and a solid stationary phase. The stationary phase is a glass or plastic sheet coated with silica. The analysis begins with the extraction of a sample into a solvent. The extract (solvent with the sample) is applied to the TLC plate slowly (location of spot is called the origin). The solvent evaporates and leaves behind the sample. After all samples have been spotted on the plate, the plate is placed in a developing chamber with the liquid phase (a solution) filling the bottom of the container. The liquid phase is allowed to travel up the plate separating the sample as it progresses. After a given amount of time, the plate is then removed and allowed to dry. Finally the plate is viewed under various light sources (white light and UV light most often) to compare samples.

1.1.2. Densitometry

Often used in conjunction with TLC, a densitometer measures the optical density of an item (in this work the density of a spot of ink dyes). To obtain densitometry readings, the ink's dyes are extracted and spotted on a plate. The plate is then read by the densitometer. The densitometer creates an electronic image of the spot and the pixel readings are changed into densitometry measurements. The output of a densitometer is directly proportional to the amount of ink extracted in solution and placed on the TLC plate. When integrated (area under the peak determined), the peaks in the chromatogram give quantitative values for the concentration of the ink dyes.

1.1.3. Gas Chromatography-Mass Spectrometry

Gas chromatography-mass spectrometry (GC-MS) is a two-part technique used for many different chemical applications. Gas chromatography is a separation technique that uses a gas as the mobile phase. A basic gas chromatograph contains an injector, a column housed in an oven, and a detector. The sample is introduced into the instrument through the injector. The carrier gas mobile phase (often helium or nitrogen) carries tne sample onto the column. As the sample run progresses, the oven is heated, thus heating the column. The inside of the column is coated with the stationary phase which is made up of an inert substance that separates the sample. Different components of the sample will interact with the stationary phase of the column to different extents. Components that weakly interact with the column will travel quickly through it. However, components with strong interactions with the column will be slowed and take a longer time to travel through. The detector at the end of the column records the time at which the sample reached the end. The output is a chromatogram with components' intensities (or amount) plotted against the time it reached the detector.

A mass spectrometer is a common detector used for gas chromatography. The sample components leave the gas chromatograph's column and enter the mass spectrometer where they are broken into fragments (or pieces). The way a compound breaks apart (or fragments) in the mass spectrometer is unique and repeatable. These fragments are charged meaning that they respond to the changes in the voltage inside the instrument. Different voltages correspond to fragments of different masses. When a voltage is reached and a fragment with the corresponding mass is present, the fragment hits the detector. The number of fragments of that size is measured and recorded. The output (called a mass spectrum) is a graph that shows the mass of the fragments plotted against the number of fragments of each mass.

When these two instruments are combined, the mass spectrometer cycles for most of the time that the GC is running. For every time point in the chromatogram (the output of the gas chromatograph), there is a corresponding mass spectrum (the output of the mass spectrometer).

1.2. Current Ink Analysis and Ink Dating

Ink pens can be broken down into two general categories: ballpoint (the focus of this work) and non-ballpoint. Ballpoint ink contain three main components: vehicles (volatile components), dyes and/or pigments (coloring components), and resins and/or polymers (hardening components) [1]. Many different chemicals/molecules are available in each category to produce different ink formulations. A common vehicle used in ballpoint ink is 2-phenoxyethanol (PE). This chemical can be found in about 85% of ball point ink formulations [2]. The commonality of this component in inks makes it a good choice when designing procedures for ink testing as it can be widely applicable.

In many cases, one of the steps of the ink analysis is the identification of the ink. This is a multi-step process [3]. First the ink is analyzed visually and microscopically to determine its type (ballpoint vs. non-ballpoint) and color. Then samples of ink are removed, and the dyes are extracted. The extract is spotted on a TLC plate. Then the plate is placed into a chamber with a solution filling the bottom. The solution travels up the plate and separates the dye components. This plate is then compared to a library of similar plates to determine possible matches. After a list of possible matches is compiled, samples of known ink samples of these possible library matches are taken for comparison. The

questioned sample and the possible matches are then extracted and spotted on a high performance TLC plate. The plate is placed in the chamber with solution and the dye components are separated. Finally a comparison of the questioned sample to the possible matches is performed and the identity of the ink is commonly determined.

There are two general methods to dating ink: the static approach and the dynamic approach [4-5]. In the static approach, an ink is identified, often as described above, and the productions dates are determined by obtaining manufacturing information. This approach is useful in determining if a document was backdated, but typically the older the purported date of the document the more discriminating the test can be as more changes are made in formulations as time passes. Maintaining and monitoring the changes in the ink formulations and changes by manufacturers through contacts with ink companies, size of the known ink library, and surveying the market place for inks being sold is an important component to the usefulness of this test. (The static method can also be applied to other aspects of a document, for example watermarks in paper. However, this is beyond the scope of the presented work.)

For documents written in the past few years, the dynamic approach to ink dating is typically more useful. This type of dating is based on physical and chemical changes of the ink as it dries on the document. The most common characteristics that can be analyzed to determine age are: changes in the volatile components (vehicles) and changes in the extraction of the dye components [6]. The ink can be identified prior to dynamic age determination; however this step is not always necessary. The change in the extraction of dye components is used most often by this laboratory to date inks. For this method two extracting solvents are used: a weak solvent and a strong solvent [7]. The weak solvent only extracts a small amount of the dyes from the overall amount. Small amounts of the extract are removed at timed intervals throughout the extraction process and spotted on a TLC plate. The ink samples are then dried to remove excess weak solvent. The strong solvent then extracts the rest of the dye components, which is then spotted on a TLC plate. Using densitometry, the amount of dye components extracted by the weak solvent at each interval and the strong solvent is measured and recorded. Through calculations, the amount of dyes extracted is converted into a rate of extraction and a percent extraction. This procedure is followed (generally in triplicate) for all inks that are to be compared. The extraction values and calculated error rates for the tests for each sample are compared to determine the age of the ink.

From start to finish (ink id to calculations), the dynamic ink dating process mentioned above can take approximately an entire day or more depending on the number of samples being compared. A drawback of these ink dating methods includes the amount of sample required. For the process mentioned above, samples of ink (about 0.5 mm in diameter) are removed from the paper. However, this testing method has been shown to be reliable for both ballpoint and non-ballpoint inks.

1.3. Literature Review

In 1985, Stewart published a preliminary study of volatile ink components and their usefulness in aging ink [l]. Using GC, he analyzed ink samples and determined the peak areas of vehicles in the ink. When two vehicles were present, the areas of the two peaks were used to calculate a ratio. This was performed for several ink samples of different ages. A plot was then made for the ink that showed the ratio of the two peaks against the age of the ink. He found that some inks had reproducible aging curves for up to 1.5 years. By using the ratio of the two peaks, the procedure is mass independent, meaning that it is not necessary to remove equal amounts of ink. He noted that storage conditions of the paper can affect the drying process and should be taken into consideration. A downfall of this procedure is that two vehicles must be present in the ink in order to calculate the ratio.

Aginsky also described how a two step GC method and a densitometeric TLC method can be used to determine ink age [8]. Using samples up to fifteen years old The GC portion of the research

analyzed the volatile components while the TLC portion analyzed the resins. For this procedure only one vehicle is needed to be present in the ink. To study the volatile components, the developed method used a weak solvent to extract the volatile components and analyzed it by GC. Then, the ink sample was dried, extracted with a strong solvent, and analyzed by GC. The masses of volatile components extracted by each solvent were compared and used to calculate a percentage. In an application of this procedure, heated (artificially aged) samples were studied to determine a relative age (recent or old) of the original questioned sample. In the second part of the work, TLC was used to determine the age of the sample based on the resins in the ink. The sample was extracted and spotted on a high performance TLC plate. Calibration and aging curves were created using known dated ink samples spotted on plates. The plate was developed and analyzed by densitometry. The amounts of different types of resins were compared to determine the ink age.

Aginsky [6] discussed comparing the mass of volatile components to the amount of dyes in inks in order to determine the ink's age. After identifying the ink, the PE was extracted and analyzed by GC to determine its mass in the sample. The sample was then dried, the dyes extracted using a second solvent, and absorbance measurements were taken. The ratio between the mass of PE and the absorbance of the dyes was calculated and used to create an aging curve where the ratio was plotted against the age of the ink. The author discussed that if more than one vehicle is present, ratios between the first vehicle and absorbance, the second vehicle and absorbance, and the two vehicles to one another can also be calculated. These additional values could provide more reliable aging results. A downside to this proposed procedure is that 2 cm of an ink line is required; however, the author mentions other alternatives to absorbance measurements (including densitometry) that may minimize the amount of sample used.

In an effort to avoid damaging documents by removing samples, Brazeau and Gaudreau constructed a sampling cell that sits on top of a document [9]. The pair used a sampling technique known as headspace solid-phase microextraction (HS-SPME). For this procedure, the sampling cell is place on the document and heated. As the ink sample heats, the volatile components evaporate from the ink and absorb onto the SPME fiber. The fiber is then analyzed by GC-MS. The volatile components that they encountered most often were benzyl alcohol, PE, and 1-methyl-2- pyrrolidineone. Through the optimization of the procedure they report that they were able to detect ink solvents up to two years after the ink was placed on the paper.

1.4. Presented Research

This presentation reports the procedures and findings of an effort to design an ink dating technique using GC-MS analysis of 2-phenoxyethanol (PE). The samples and extraction procedures used are discussed as well as the application of the instrumentation to the work. The studies completed to date are described and results are discussed. Finally, future research of the project is mentioned.

2. Materials and Methods

2.1. Samples and Extraction

2.1.1. Ink Samples

Ballpoint ink pens of various colors were obtained from different manufacturers or purchased from the marketplace. The pens were then used to draw on blank paper to create "scribble sheets." Scribble sheets of samples used in this work were created in March 1995, November 2003, and January 2004. Scribble sheets have been used for a variety of applications in our laboratory, including ink identification and ink dating. In addition to the scribble sheets, several ink pens were used to keep a known dated writing collection that has been updated monthly starting in October of 2008. All ink samples (scribble sheets and the known dated writing collection) were stored at room temperature in a closed cabinet in what would typically be considered "normal office conditions".

2.1.2. Internal Standard Solution and Extraction

An internal standard solution of deuterated 2-phenoxyethanol (100 parts per million, ppm) in chloroform was purchased from Restek (Bellefonte, PA). This solution was diluted with chloroform (Mallinckrodt Baker, Inc., Phillipsburg, NJ) to create a solution of 1 ppm deuterated 2-phenoxyethanol in chloroform (denoted as dPE solution). These solutions were stored in a refrigerator.

For each extraction, three samples of an ink line were taken using a Harris Uni-Core, 0.5 mm (Electron Microscopy Sciences, Hatfield, PA). The samples of ink were placed into a conical vial and 5 µL of the dPE solution were added. The sample was then agitated lightly to ensure that all three samples of ink were immersed in the solution. The ink was allowed to extract for 10 minutes at room temperature. One µL of the extract was used for GC-MS analysis and 2 µL of extract were used for densitometry analysis (where applicable).

2.2. Instrumentation

2.2.1. Gas chromatography-Mass Spectrometry (GC-MS)
A Varian 3800 gas chromatograpi1 (GC; Palo Alto, CA) paired with a Varian 2100T ion trap mass spectrometer (MS) was used to analyze all extracts. The instrument was equipped with a CP-Select 624 CB column (60 m, 0.32 id, 1.8 df; Varian). For sample analysis, the injector of the GC was maintained at 245 °C with a constant flow of helium at 1 mL/min. The oven program consisted of a 5 minute hold at 100 °C followed by a ramp of 15 °C/min to 220 °C, and a final hold of 8 minutes (21 minutes total run time). The MS was operated in electron ionization (EI) mode scanning a mass range of 40-350 m/z after an initial filament delay of 10 minutes. Instrument software was used to calculate the concentration of PE in each sample using the 1.000 ppm dPE solution as an internal standard for comparison.

2.2.2. Densitometry
A Uniscan Video Densitometer (Analtech, Inc., Newark, DE) was used as a second analysis technique for some of the ink samples. After sample extraction and GC analysis, a 2 µL volumetric micropipette (Drummond Scientific Company, Broomall, PA) was used to spot the sample on a high performance thin layer chromatography plate (HPTLC, EMD Chemicals, Gibbstown, NJ) with replicate samples spotted in the same row. The plate was placed in the densitometer, and the number of lanes was set as one or five (see Section 3.2.3.) and the number of passes was set to 30. After setting the boundaries of the lane at the edge of the spots, the instrument began the scan. The instrument output included a chromatogram with the area of each sample peak labeled.

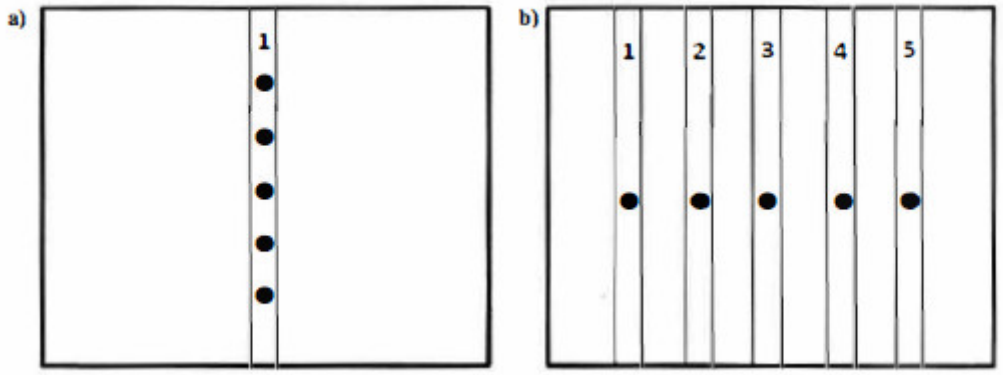
2.3. Studies

2.3.1. Determination of 2-Phenoxyethanol in Fully Aged Samples
To establish a baseline for the concentration of PE in fully aged inks, samples more than six years old were analyzed for PE concentration. Twenty one black inks from nine manufacturers, sixteen blue inks from nine manufacture1s, eleven red inks from six manufacturers, three green inks from two manufacturers, and three purple inks from three manufacturers were studied. The samples were taken from scribble sheets dated March 1995, November 2003, and January 2004. Each sample was extracted and analyzed by GC-MS as described above to determine the concentration of PE. The concentration obtained from each sample was then compiled and studied for trends in the data.

2.3.2. Determination of Scanning Parameters of Densitometer
To determine the most repeatable scanning method of the densitometer, a short study using one black ink and three blue inks from three different manufacturers was performed. For each ink, five separate vials of the sample were extracted and analyzed by the densitometer. Two different

densitometer scanning methods were investigated. First, the number of lanes was set to one with the five vials of the same ink in the lane (Figure 1a). Second, the number of lanes was set to five with one sample vial in each lane (Figure 1b).

Figure 1: a) schematic of plate scanned by densitometer with one lane of five vials; b) schematic of plate scanned by densitometer with five lanes of one vial each.



The densitometer scans were performed in triplicate for each method and the resulting peak areas were averaged and standard deviations and relative errors (Equation 1) were calculated. This was repeated for each of the four inks tested.

$$\left(\frac{Standard\ Deviation}{Average}\right) \cdot 100 = Relative\ Error \qquad \text{Equation 1}$$

2.3.3. Preliminary Studies to Overcome Mass Dependence

Theoretically, ink samples from the same pen, written at the same time on the same piece of paper should have the same amount of ?E. However, preliminary studies showed that this is not always the case. Part of the reason for this is likely due to the mass dependence of the procedure. (Mass dependence basically means that the mass of the sample affects the results.) In this work, the mass dependence means that if more ink is present on one of the sets of samples being compared, then that sample will have more PE than a sample of the same type with less ink. While great care has been taken throughout this research to remove samples of ink with the same amount of ink, the densitometer was investigated as a possible technique to overcome the mass dependence. It has been previously researched and reported by Brunelle, that with care, an examiner can take samples of ink within a few percent of the same rr.ass to one another.

Seven black inks from five manufacturers and three blue inks from three manufacturers from the known dated writing collection were studied. Inks were written in October 2008, November 2008, and September 2010. For each ink, five replicate ink samples were taken from close to the same location on the page and analyzed by GC-MS and the densitometer as described above. The GC-MS was used to determine the concentration of PE in the ink samples, and the densitometer was used to normalize the GC-MS results. The resulting values, in ppm, were used to assess the ability of the densitometer to overcome the mass dependence.

3. Results and Discussion

3.1. Determination of 2-Phenoxyethanol in Aged Samples

Previous publications indicate that ball point ink samples can take between six months and two years for the concentration of PE to cease changing at a detectable rate [1,8,9]. This lack of detectable changes is typically referred to as completely dry or aged. In this study for ink that were completely dry, ink samples more than six and a half years old were used to establish a baseline of PE concentration in aged samples as these samples are well beyond their drying stage. Table 1 shows a list of the inks studied and the concentration of PE in each determined by GC-MS analysis. The concentration of PE in the aged samples tested ranges from 0.148 ppm up to 1.589 ppm. The range of concentrations of PE can be attributed to the wide range of ink formulations on the market from various manufacturers.

The data in the table appear to indicate that, in general, colored ink (blue, red, green, and purple) have less PE in aged samples than do black inks (Table 1 inset). However at this point, this type of generalization should be avoided when reaching a conclusion about an ink as a range of values exist within each color. For example, PE concentrations of 0.237 ppm to 1.589 ppm were found for aged black inks. Generalizations concerning the concentrations of PE based on the manufacturer should also be avoided because PE concentrations can vary within a manufacturer. For example, aged black Zebra inks show a range of concentrations from 0.478 ppm to 1.589 ppm.

All completely aged ink samples tested gave concentrations of less than 1.6 ppm. Therefore, this value can be thought of as a cutoff (for this instrument and solution only). Concentrations of PE greater than 1.6 ppm indicate that the ink sample is not completely dry because only recent ink samples could still have an amount of PF this great present. On the other hand, an ink sample from a document with less than 1.6 ppm PE cannot be said to be fully aged. Some inks have low concentrations of PE in the formulation, and even new (recent) ink samples have been shown to have a low concentration (less than 1.6 ppm) of PE. For example, a black Bic ink six days old had a PE concentration of 0.594 ppm. Based on the data and results from this portion of the testing, it is clear that the determination of an elevated level of PE can be used to determine that an ink sample is more recent (typically in the last year). However, the opposite cannot be used to draw the conclusion that an ink MUST be more than a year old alone. It may be possible through ink identification and further testing, however this possibility is not the subject of this paper.

One must keep in mind that the concentrations given in Table 1 and the cut-off concentration of 1.6 ppm are based on the 1.000 ppm dPE solution used as the internal standard in this work. If a different internal standard (different compound or concentration) were used, then raw values for different concentrations of aged samples and a different cut-off concentration would be obtained. Therefore, each lab should establish a cut-off concentration for their instrument, known standard, and techniques for series of fully aged samples before any conclusions are drawn. Also, testing the internal standard solut1on should be periodically tested to determine if changes within the solution (for example, changes in concentration due to evaporation) are occurring and have the potential to affect the results. This can be done by testing a known sample at regular intervals and noting any differences in the results. Although the date of writing of each sample tested below is given, it is not significant since each sample is known to be completely aged and changes in PE are no longer detectable in testing performed in 2010.

Table 1: Concentration of PE in aged samples; inset: average concentration of PE in aged samples by color

	Manufacturer	Ink No.	Date	[PE] (ppm)
Black	Bic	B645	Mar 95	0.968
	Pilot	B647	Mar 95	0.762
	Bic	B652	Mar 95	0.577
	Zebra	B654	Mar 95	0.614
	Eversharp	B657	Mar 95	0.817
	Bic	B700	Nov 03	1.379
	Bic	B701	Jan 04	1.313
	Bic	B702	Jan 04	0.861
	Parker	B709	Jan 04	0.623
	Office Max	B710	Jan 04	0.237
	Pentel	B712	Nov 03	1.161
	Papermate	B713	Jan 04	1.456
	Papermate	B718	Jan 04	0.295
	Papermate	B719	Nov 03	1.450
	Sanford	B720	Jan 04	0.559
	Sanford	B721	Jan 04	0.599
	Pilot	B722	Jan 04	0.515
	Pilot	B723	Nov 03	0.460
	Zebra	B725	Nov 03	0.478
	Zebra	B726	Jan 04	0.652
	Zebra	B727	Jan 04	1.589
Red	Papermate	B755	Jan 04	0.585
	Papermate	B756	Jan 04	0.719
	Sanford	B758	Jan 04	0.387
	Papermate	B759	Nov 03	0.403
	Office Max	B760	Jan 04	0.150
	Zebra	B761	Jan 04	0.537
	Bic	B762	Jan 04	0.212
	Bic	B763	Jan 04	0.148
	Bic	B764	Jan 04	0.462
	Pentel	B765	Nov 03	0.406
	Pentel	B766	Jan 04	0.255
Blue	Fisher	B649	Mar 95	0.545
	Pentel	B661	Mar 95	0.339
	Staples	B728	Jan 04	0.204
	Pilot	B729	Jan 04	0.267
	Office Max	B730	Jan 04	0.271
	Zebra	B731	Jan 04	0.535
	Pentel	B733	Jan 04	0.182
	Pentel	B734	Nov 03	0.350
	Bic	B735	Jan 04	0.409
	Bic	B736	Jan 04	0.512
	Bic	B737	Jan 04	0.414
	Papermate	B741	Nov 03	0.161
	Papermate	B743	Jan 07	0.339
	Papermate	B744	Jan 04	0.531
	Papermate	B746	Jan 04	0.567
	Sanford	B748	Jan 04	0.512
Green	Pentel	B749	Jan 04	0.288
	Bic	B750	Jan 04	0.382
	Bic	B751	Jan 04	0.375
Purple	Pentel	B752	Nov 03	0.370
	Papermate	B753	Jan 04	0.529
	Sanford	B754	Jan 04	0.777

Color	Average [PE] ppm
Black	0.827
Blue	0.384
Red	0.388
Green	0.348
Purple	0.559

3.2. Determination of Scanning Parameters of Densitometer

Tables 1a and 1b show the average densitometer value for each set of vials for each of the four inks as well as the relative errors. Lower errors were achieved when the replicates were scanned in one lane. In other words, the triplicate densitometer readings were more similar when the vials of the same ink were scanned together in one lane of five.

Table 2: Average densitometer readings and relative error for triplicate scans when:
a) Vials of each ink are scanned together

Ink	Vial	Average	Relative Error
	1	747.0	0.5
Black	2	1050.8	0.3
Zebra	3	1256.3	0.7
B727	4	792.2	0.4
	5	854.0	0.7
	1	756.2	0.7
Blue	2	1048.0	0.1
Zebra	3	668.5	0.4
B731	4	821.2	0.9
	5	851.8	1.4
	1	412.5	1.8
Blue	2	277.8	1.2
Pentel	3	289.0	1.1
B734	4	252.7	3.0
	5	341.3	0.9
	1	804.3	2.4
Blue	2	1022.8	0.7
Bic	3	813.3	1.6
B737	4	904.8	1.9
	5	1004.2	0.6

b) Vials of each ink are scanned separately

Ink	Vial	Average	Relative Error
	1	697.7	2.1
Black	2	877.0	2.0
Zebra	3	459.2	1.2
B727	4	604.5	0.9
	5	761.8	1.6
	1	599.0	1.4
Blue	2	810.5	1.7
Zebra	3	934.3	1.1
B731	4	562.2	1.3
	5	661.7	1.3
	1	275.0	3.3
Blue	2	185.7	3.3
Pentel	3	216.2	2.1
B734	4	200.5	5.7
	5	187.3	2.1
	1	785.7	1.7
Blue	2	1065.7	1.7
Bic	3	878.8	1.8
B737	4	934.8	1.1
	5	1047.8	2.0

In addition, the spots on the TLC plate were visually examined to determine which had the most or least amount of ink. These results were then compared to the areas of the spots given by the densitometer. The goal was to determine if the spots that visually contained more ink corresponded to higher densitometer readings. (Note that this comparison was very qualitative. Only significant differences in the visual amount of ink were noted.) The densitometer values lined up with the visual results more often when the vials of the same ink were analyzed in one lane. These results are illustrated in Figure 2 (below) which shows a photograph of the spots scanned by the densitometer for ink 8731. In Figure 2, Vial 3 appears to have the least amount of ink extracted. In Table 2a, Vial 3 for ink 8731 showed the lowest densitometer average of the five vials. However, in Table 2b, Vial 3 for ink 8731 showed the highest densitometer average of the five vials. Based on these results, future studies involving the densitometer will be scanned with replicates in one lane.

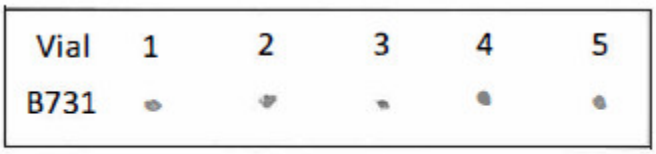


Figure 2: TLC plate spots scanned by densitometer for ink B731

3.3. Preliminary Studies to Overcome Mass Dependence

Mass dependence is a factor in achieving good repeatability. Repeatability is a measure of the closeness of the results of replicate samples. In other words, if a procedure is repeatable, then performing the same procedure with the same sample should give very similar results.

To minimize the affect of mass dependence on the repeatability, great care was taken to remove the same amount of ink from replicate samples making them as similar as possible. For some ink samples, this goal was achieved. For example, a black Bic ink written 11/14/08 extracted and analyzed five times. These samples showed good repeatability with a range of PE concentrations of 1.848 ppm to 2.019 ppm. Other samples tested in multiples did not show as reproducible results. The densitometer was used in conjunction with the GC-MS analysis as a means of overcoming the mass dependence. Overall, normalizing samples using the densitometer to calculate the amount of ink in a sample did not aid in the attempt to overcome mass dependence. In many cases the results showed to be more reproducible, but in some cases the results were not helpful in increasing reproducibility of samples known to be the same age. Further work will be performed to determine a more appropriate correlation between the GC-MS data and the densitometer data as well as investigate other methods of overcoming mass dependence.

3.4. Future Work

Establishing a technique that was reproducible and reliable to quantify PE and establishing a baseline for completely aged samples was a large first step. Future work to be completed includes optimization of the extraction procedure and the GC-MS program. Also, the testing of more ink samples will be performed to obtain a broader view of the available ink formulations and the concentrations of PE within them.

Further research will also be completed to determine a reliable method to overcome the mass dependence seen with this type of testing and improve repeatability of the procedure. Currently in this work, the analyst must take great care when removing ink samples in order to remove the same amount of ink for each extraction.

Also, work is being done to narrow down the time frame in which samples completely age. The goal is to find the time when the concentration of PE in an ink sample stops changing at a detectable rate. Further research may allow that if an ink formulation is known, then more conclusions could possibly be reached. If the formulation of an ink is known (the type of ink and the manufacturer), then it may be possible to determine that the ink is completely aged (instead of simply that it's new). For example, if a certain ink formulation is known to have high levels of PE, then low levels of PE when the sample is tested may show that the ink is old.

4. Conclusions

The use of gas chromatography-mass spectrometry shows promise for the use of aging ink samples. Fewer ink samples from the document are required for this GC-MS analysis than for traditional ink dating analyzing the dyes. The instrument and solutions used in our laboratory revealed that ink samples tested with greater than 1.6 ppm PE are recent samples that have not aged fully. Samples should be run in multiples (we suggest triplicate if at all possible) in order to take into account possible errors, anomalies in the testing process, and for a better confidence in results. Based on the current testing performed and results obtained, no conclusions should be drawn based on a single test run for a sample as to its age.

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