Exhibit 24

Declaration of Larry F. Stewart

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Ballpoint Pen Inks: The Quantitative Analysis of Ink Solvents on Paper by Solid-Phase Microextraction

ABSTRACT: We wish to describe further developments to a method previously reported on the detection of 2-phenoxyethanol in ink. The solid-phase microextraction (SPME) sampling technique, together with gas chromatography–mass spectrometry (GC-MS), has been used to quantify solvents in writing ink. In conventional approaches, the analysis of ink on documents requires some degree of destructive sampling. The methods commonly used remove ink samples from paper using a scalpel or a paper punch. To avoid document destruction, a sampling cell was constructed that allows solvents to be adsorbed directly onto the SPME fiber from the headspace above the document surface. Analytes (ink volatiles) are then desorbed from the SPME fiber on a gas chromatograph equipped with a mass selective detector (GC-MSD). With this method, it was possible to detect the presence of ink solvents on documents for a period lasting up to *c.* 2 years.

KEYWORDS: forensic science, questioned documents, ballpoint inks, solid-phase microextraction, SPME, gas chromatography, mass spectrometry, GC-MS

Establishing the approximate age of a document relative to its purported date of production is a question often raised during investigations. Excluding eyewitnesses, it is practically impossible to derive the exact time at which a document was prepared from physical or chemical evidence. There are generally two approaches that can be followed to estimate the age of a document from physical/chemical evidence (1,2).

The first is based on the evaluation of compositional or *static* characteristics of a document and how they relate to the purported date of the document. The dates of introduction or earliest availability of the paper used, the watermark, the ink from the writing instrument or printing devices, the printing technology used, as well as any additional physical or latent information that can be dated are compared with the date of the document. The earliest availability of all of the materials used must predate the date of the document. If the date of the document is earlier than the date of availability of any material used in its creation, then such an anachronism is consistent with the document having been backdated.

The second or *dynamic* approach is based on the evaluation of certain components of a document that change over time and how they relate to the purported date of a document. The state of some components of ink does not remain constant from the moment it is applied to a document. There have been a number of different methods reported in the literature for measuring the dynamic process of ink aging (3–7). To determine the solvent content of ink on a document, most techniques, if not all, require the removal of a small amount of ink from the paper, usually with a scalpel or a small hole-punch. The ink is extracted with a solvent and then analyzed by chromatographic and spectral analysis. These techniques are somewhat destructive and in some cases the analysis is rejected, due to the alteration of the original document. The development of a nondestructive technique for sampling ink would be beneficial.

The method presented here uses solid-phase microextraction (SPME) as the technique to monitor the evaporation of the ink's volatile components as the ink ages on a document. SPME is an adsorption/desorption technique that does not require the use of organic solvents to extract analytes (8–10). The adsorption procedure consists of exposing a SPME fiber coated with a thin film of a polymer having an affinity for the general class of compound being analyzed. Sampling can be conducted either in a liquid or gas phase (headspace). Our application involves sampling of the headspace over documents. In the desorption procedure, the SPME fiber is introduced into a conventional injection port of a gas chromatograph (GC) for analysis.

In our approach, we are attempting to determine whether the level of various volatiles present in ink that has been applied to paper can be quantified. To optimize the sampling method for this particular application, a number of experiments were designed to isolate the effects of various parameters on the SPME procedure. These experiments are described next.

Experimental

Selection of SPME Fiber

There are a number of sorbent materials that are used as coatings for SPME fibers. Selection of the appropriate fiber will depend on the analytes being considered (9,11). Most of the volatiles found in ballpoint pen ink are polar compounds having a high boiling point (~ 200–240°C). The volatiles being considered in this paper are 2-phenoxyethanol, benzyl alcohol, and 1-methyl-2-pyrrolidinone. An SPME fiber having a 65 μm polydimethylsiloxane/divinyl benzene film was used for our application.

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Chemicals, Materials, and Samples

Benzyl alcohol 99.8% anhydrous, 1-methyl-2-pyrrolidinone 99+% ACS reagent, and 2-phenoxyethanol 98% were purchased from Sigma-Aldrich Canada (Oakville, ON, Canada). Acetonitrile HPLC grade was purchased from Caledon (Georgetown, ON, Canada). Methanol HPLC grade was purchased from J. T. Baker (Phillipsburg, NJ). Fiber holder and SPME fiber assemblies from Supelco. Black ink from a ballpoint pen containing 2-phenoxy-ethanol in the ink formulation was purchased from a local office supplies store. A regular paper punch having a 7 mm cutting diameter was also purchased from the local office supplies store. A Harris micropunch having a 1.2 mm diameter was purchased from Whatman (Florham, NJ). Silylalized 2 mL samples vials were purchased from Supelco (Bellefonte, PA) and plain normal 2 mL vials were purchased from Chromatographic Specialties (Brockville, ON, Canada). The paper used was Buntin Read Photocopy Paper 10M P4, 75 g/m², long grain. A neodymium iron boron magnet 1 in. disk, 0.25 in. thick, was purchased from Edmund Scientific Company (Barrington, NJ).

Instrumentation

The headspace was analyzed with an Agilent 6890A GC equipped with a 5973N mass selective detector (MSD) equipped with electronic pressure control capability and a split/splitless injector (250°C). Samples were handled by a Multipurpose Combi Pal autosampler equipped with a multi-vial incubator with head-space and SPME capability. The GC/MS is from Agilent, and the auto-sampler from CTC analytics (Zwingen, Switzerland). The column used was a DB-5 (J&W Scientific, Folsom, CA) 30 m × 0.25 mm × 0.25 μm. The oven was programmed from 70°C (1.5 min hold) to 250°C (8 min postrun) at 25°C/min. The total cycle time was 21 min. Helium (99.995%) was used as a carrier gas (inlet pressure 9.8 psi) with a constant flow of 1.2 mL/min. Column and detection conditions were kept constant during and throughout the study. The system is controlled by the Agilent Chemstation version G1701A data system revision C.00.00, and the auto-sampler by the Cycle Composer software version 1.4.2.

Sampling Cell

A sampling cell was designed to allow the nondestructive sampling of ink volatiles from headspace above the surface of a document. The bottom of a vial was cut and a magnetic metal flange was fitted flush with the bottom edge of the vial (Figs. 1 and 2).
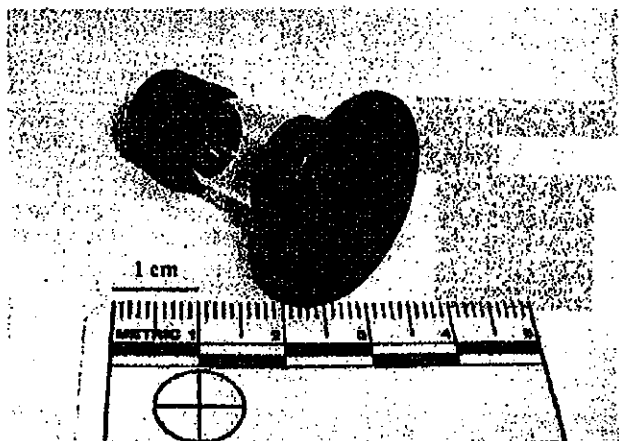

FIG. 1—Sampling cell.

Top View

Septum 07.00 mm
Glass vial 011.66 mm
Plastic cap 012.80 mm
Metal base ⌀14.26 mm
025.35 mm
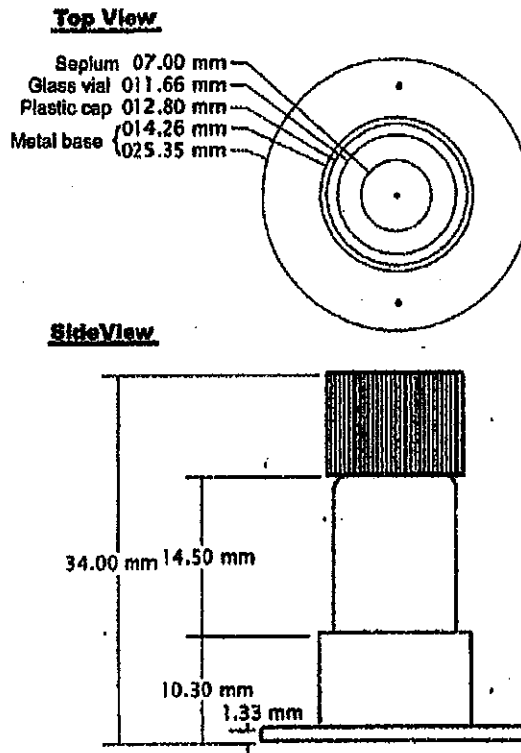
SideView

34.00 mm 14.50 mm

10.30 mm
1.33 mm

FIG. 2—Sampling cell design.

Placing a magnet below the document surface being sampled will secure the vial firmly in place for SPME extraction. Stainless-steel 416 was used to make the metal flange due to its high machinability. The 400 series stainless-steel is also relatively inert and is magnetic (12). Epoxy was used to bond the glass vial to the metal flange part. A heating jacket for the sampling cell was made from an aluminum bar stock; three holes were made into it to incorporate two heaters and a thermistance to monitor the temperature (Figs. 3 and 4). To control the temperature of the sampling cell, the instrument temperature controller from Valco Instrument (Houston, TX) was utilized with two pencil heaters and a thermocouple sensor.
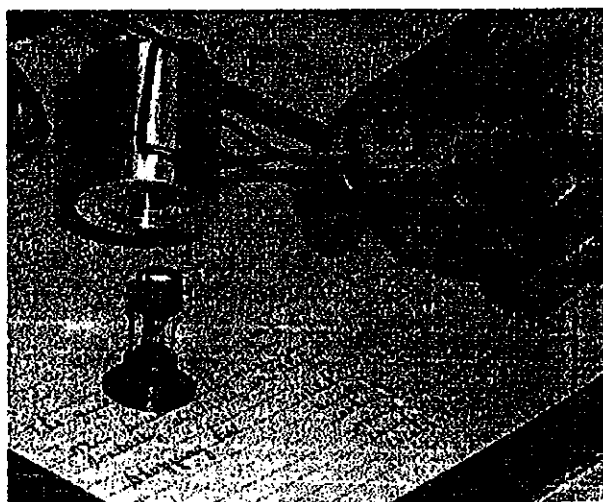

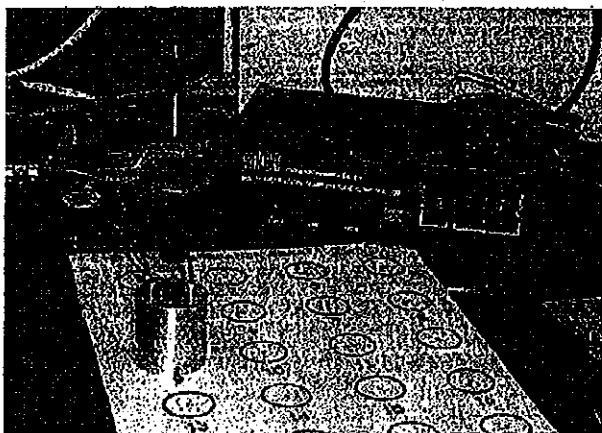FIG. 3—Heater about to be placed over the sampling cell on paper.

FIG. 4—*Controller, sampling cell, and solid-phase microextraction holder over calibration paper sheet.*

General Sample Preparation and Analysis

Small paper disks were cut from a sheet of plain photocopy paper ($8\frac{1}{2} \times 11$ in. 40 M) with either a Harris micropunch (plug size about 1.2 mm in diameter) or hole punch (office equipment large punch about 7 mm in diameter). The instrument used was previously cleaned with methanol, dried with Kimwipes. Blank paper disks (10) were also cut and discarded to ensure clean conditions. For a Harris micropunch, 20–30 disks were cut and discarded. Large paper disks from new plain photocopy paper were placed at the bottom of the closed vials using tweezers. Known amounts of 2-phenoxyethanol were taken from standard solutions and slowly transferred to a paper disk by contacting the needle of a microsyringe to the paper and monitoring the rate of absorption into the paper as to prevent any liquid loss. The syringe was washed five times before and after sampling with acetonitrile. The paper with the solution was allowed to air dry for 5 min. The vials were tightly sealed by hand and placed in the auto-sampler for headspace analysis by SPME.

All samples were prepared at a 21-min interval and then placed in the incubator. Twenty-one minutes is the instrument cycle time. In a separate experiment, a ballpoint pen containing 2-phenoxy-

ethanol was used to draw lines as evenly as possible on white photocopy paper. A hole punch was used to cut 7 mm paper disks. The disks were placed in a 2-mL auto-sampler vial for headspace analysis by SPME/GC/MS.

Optimization of Absorption Time

The absorption time is the amount of time the SPME fiber is left inside the vial for analyte adsorption. This time period was varied from 2.5 to 30 min. Ten nanograms of 2-phenoxyethanol was added to a 7 mm paper disk in a vial as described above. The sampling temperature was kept constant at 50° (Fig. 5).

Optimization of Sampling and Equilibrium Temperature Conditions

Ten nanograms of 2-phenoxyethanol was added to a 7 mm paper disk in a vial as described above. Samples were run in a similar way, keeping the absorption time constant and only varying the time at which the fiber was introduced into the vial. The results were plotted as intensity versus sampling time (Fig. 6). The process was repeated for different temperatures and graphed. In a second experiment, the same test was performed using the optimum temperature and varying the absorption time. The optimal sampling time was determined by plotting the intensity against absorption time (Fig. 7). By doing this, we can determine what is the shortest sampling time, and still giving high sensitivity. After optimizing both the absorption and equilibrium times for a given temperature, the experiment was repeated using different solvent concentrations in the vial and generating new intensity versus concentration (Fig. 8) data to determine the range of linearity of the method. 2-phenoxyethanol concentrations ranging from 1 to 150 ng were analyzed. After optimizing for 2-phenoxyethanol, the same procedure was applied for benzyl alcohol and 1-methyl-2-pyrrolidinone.

Calibration

There are a number of reported approaches of SPME calibration (13–15). Two types of calibration were conducted: one in which a known quantity of 2-phenoxyethanol was added directly into a
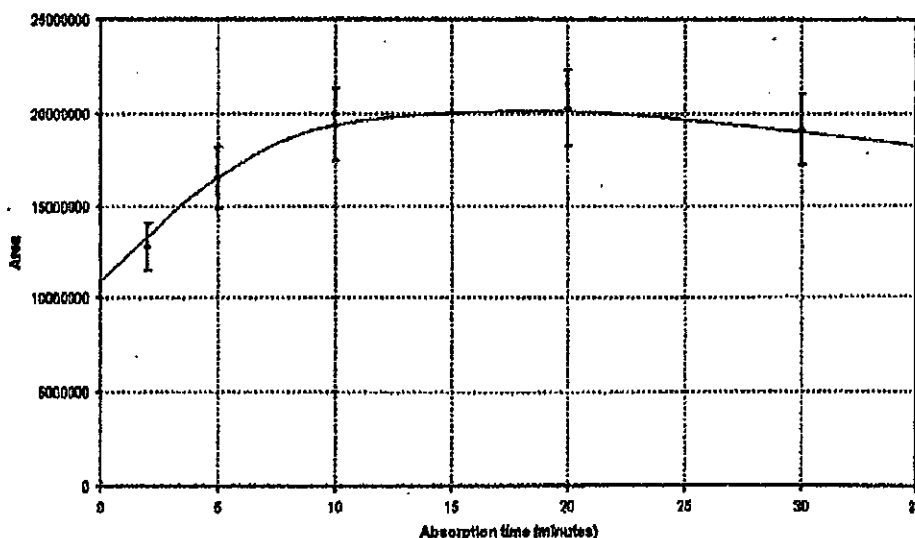

Optimization of extraction time

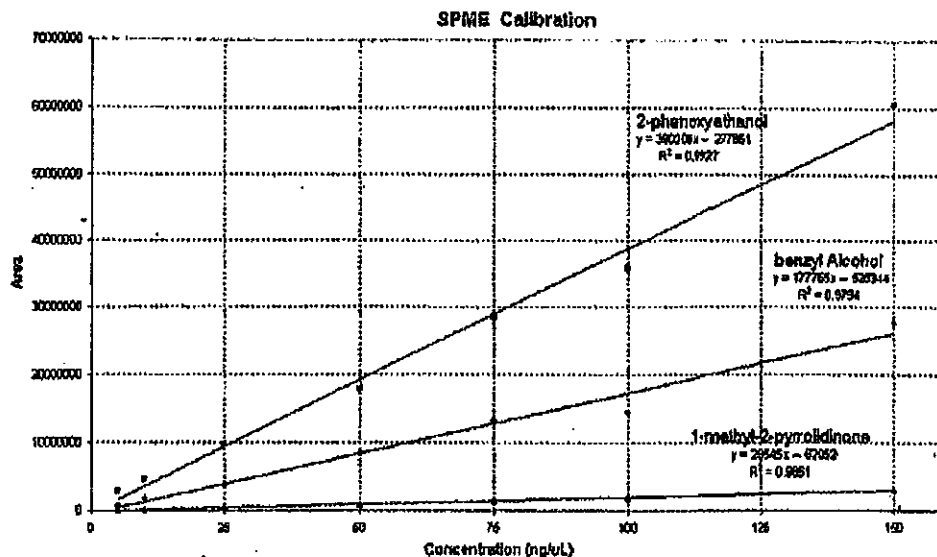FIG. 5—*Optimization of absorption time at 50°C (no equilibrium).*

FIG. 8—Calibration by solid-phase microextraction (SPME) for various solvents found in ballpoint pen ink (absorption time 7.5 min).

identified by GC-MS. Working in SIM mode for benzyl alcohol masses m/z 77, 79, 107, 108; for 1-methyl-2-pyrrolidinone m/z 71, 98, 99; and for 2-phenoxyethanol m/z 77, 94, 107, 138 are used to track and quantify benzyl alcohol, 1-methyl-2-pyrrolidinone, and 2-phenoxyethanol, respectively.

Using different columns under various conditions, it was difficult to obtain good peak separation between benzyl alcohol and 1-methyl-2-pyrrolidinone. However, in the SIM mode, they can be discriminated by monitoring mass 79 for benzyl alcohol and mass 99 for 1-methyl-2-pyrrolidinone. The signal response for these masses is good for the quantitation of each compound without having any interference.

Sampling for Headspace Equilibrium, Optimization, and Calibration Studies

The adsorption of analytes on the polymer film coating of the SPME fiber is a dynamic process that, at equilibrium, is directly related to the concentration of the analyte in the matrix; the thickness; porosity and volume of the SPME fiber; and the volume of the sampling cell. In our experiment, the equilibrium is affected by the various partitions between: matrix and vapor phase; vapor phase-SPME fiber; vapor-cell wall interactions; and the partition coefficient for the analyte between coating and sample matrix (16,17).

The first step was to determine the optimal absorption time. This is the time that the fiber is exposed to the headspace. The fiber is inserted at the beginning and exposed for a fixed period of time. The time of exposure was varied from 2.5 to 30 min. The maximum sensitivity was found with an exposure time of c. 15 min (Fig. 5). This step was performed to gain an approximate idea of how long the fiber should be exposed at 50°C. Later, we will see that the optimum temperature is 115°C.

The plot of area over time for different temperatures shows the same headspace-equilibrium profile. As can be seen in (Fig. 6), this is quite different from the profile for conventional headspace analysis over liquid (shown in dashed lines). When a liquid phase is present, there is an overabundant supply of analyte to the gas phase. In this experiment, the supply of analyte to the gas-phase from the paper surface is much more limited. Because of this, the interaction between analyte and paper, the effects of paper, vial

surface, and volume are also more significant. During initial sampling, values are high as the analyte are primarily adsorbed onto the SPME fiber in a nonequilibrium environment. As time passes, the value decrease as condensation of the analyte on the vial wall as well as equilibration of the distribution of the analyte in the entire gas phase occurs. The fact that the intensity increases with temperature further supports the effects of condensation. The values obtained tend to reach equilibrium after a period of c. 4 h. It was also noted that by increasing the temperature, and adding more sample into the vapor phase, however, the curve was still similarly showing a reduction with time. By increasing the temperature, sensitivity is increased but at a temperature above 125°C, there is leakage from the vial caps, and also some desorption from the fiber may start occurring. We found that the vial caps retain the gas phase well at a temperature of 115°C. Hence, the temperature was lowered to 115°C to obtain the best sensitivity.

A second optimization was performed at 115°C to determine the optimal absorption time. We found that there is no significant difference between 7.5 and 20 min; therefore, the shortest time was selected (Fig. 7).

Running samples from 1 to 150 ng generated a near-linear calibration curve. Running samples in triplicates reduced the error, bringing the R (correlation coefficient) from 0.96 to 0.99 for 2-phenoxyethanol (Fig. 8).

Effect of Paper Surface

For the same amount of solvent added to the vial, varying the paper surface area will have a proportional effect on the intensity. The greater the surface, the lower the intensity. The lowest intensity result was achieved for a paper surface completely covering the bottom of the vial (c. 11.5 mm in diameter). Hence, when working in headspace with very small amounts of analyte, it is critical that physical parameters such as paper surface, sampling cell as well as any other system component surfaces remain constant.

Glass Effects and Silation of Vials

It was shown that the glass vial could have chemically active sites. Samples were analyzed in both normal and silylolized vials.
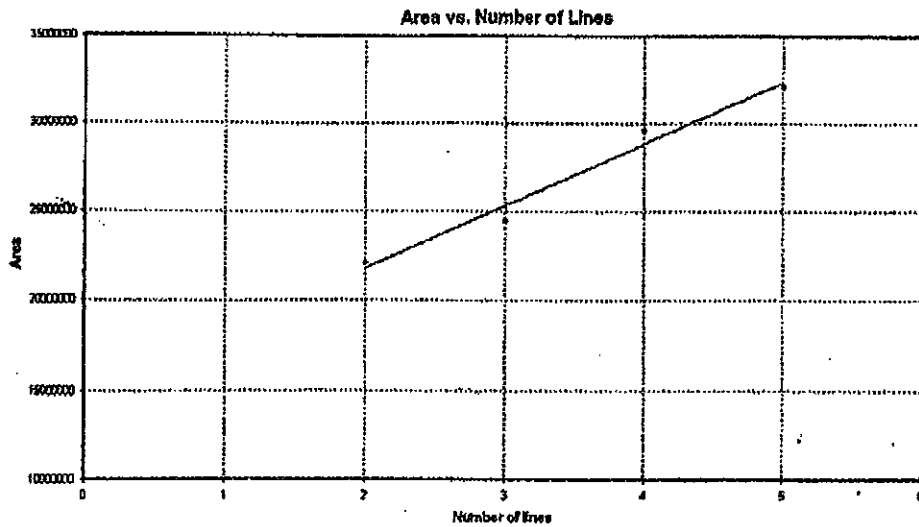
Area vs. Number of Lines

FIG. 9—*Linearity in relation of ink surface on paper.*

The change in conditions shows a small but significant increase in the average intensity for silylalyzed vials (*c.* 10% increase).

Nonequilibrium Sampling

Working at room temperature and at equilibrium, the presence of the three solvents placed on paper from fresh to about 2 months old can be detected. Samples containing solvents older than 2 months and of a similar surface area cannot be detected easily. This is more or less equivalent to the amount of solvent present in an ink that has been applied to paper for a period of less than 2 months preceding the analysis. The benefits of working at non-equilibrium are an increase in sensitivity and detection of samples that can range up to 2 years. The drawback is that the timing of the extraction is more critical as it can induce more error than working at equilibrium.

Contamination

It is important to run blank paper samples near the ink to confirm that no additional or other extraneous solvents are present. It is known that some of the solvents contained in ink may also be found in low quantities in other products such has hand creams, shampoo, etc.

Test with Ink

To determine whether the SPME technique had a linear response to the surface area of ink on paper, test sheets having in-
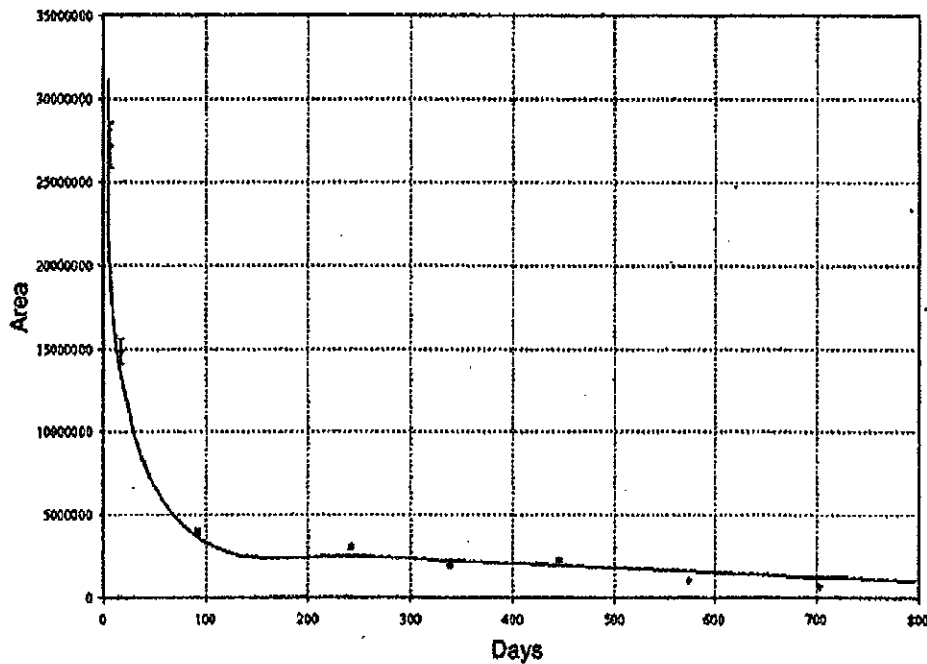
Ageing curve by SPME - black ballpoint pen ink

FIG. 10—*Aging curve of black ink.*

creasing number of ink lines were made, each having a length of about 4 mm. Figure 9 shows the response for two to five lines of ink on paper. As can readily be observed, volatility detection is directly proportional to the amount of surface sampled. The curve does not pass through or intercept the origin. This is due to area/density variation from line to line and also to a carry-over effect from the cell.

Nondestructive Surface Sampling Cell

The data obtained with the nondestructive sampling cell demonstrated the same linearity as the results obtained with closed incubated vials. A slight difference in intensity was noted. This was due to differences in paper surface area.

After developing the current method, the nondestructive sampling cell was used to measure 2-phenoxyethanol on sheets of paper bearing ink lines of known age varying from fresh to about 2 years. Although we were able to detect the presence of solvent over the entire period, the intensity of 2-phenoxyethanol detected becomes very faint after c. 1 year (see Fig. 10).

Conclusions

The results of this investigation show that the volatile components of ballpoint pen inks can be quantified by the analysis of the headspace above the paper surface using the SPME technique. By using the modified sampling cell described, this method allows the nondestructive analysis of ink volatiles on paper for the first time. The analysis requires minimum sample manipulation and can be repeated on different areas of a document. Our results are consistent with a similar study reported, where the method can be applied to detect whether inks are less than 6 months old (18). The effects of type of paper cannot be ignored especially if the results from analyses carried out on different papers need to be compared. Ideally, a calibration curve could be generated from the surface of any paper being investigated (using a reference ink or pure 2-phenoxyethanol, which would allow a more accurate interpretation of the data for a questioned ink). In the next phase of our research, we aim to develop a method in which the approximate age of an ink could be inferred from one or a series of SPME readings.

Additionally, this nondestructive approach can potentially be applied to a wide variety of other applications and material surfaces (walls, automotive parts, printed materials, toys, etc.) for sampling volatile compounds emanating from clear coats, paints, varnishes, conditioners, etc.

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Exhibit 25

Commentary on: Berger-Karin C, Hendricks U, Geyer-Lippmann J. Comparison of natural and artificial aging of ballpoint inks. J Forensic Sci 2008;53(4):989–92.

Sir,

We would like to comment on this study recently published in JFS. It is a short technical note proposing an artificial aging technique for the dating of ballpoint pen inks. This is a very difficult and controversial topic, and we are worried about the nature of this paper. The scientific content can be misleading and can actually be seriously questioned considering the following remarks:

- Two of the cited references are not relevant to the subject and were probably not read by the authors. In the cited papers, Aginsky (1) and Andermann and Neri (2) did not report about solvent evaporation but about dyes analysis. Aginsky did actually publish several papers about solvent evaporation that could have been cited instead (3–6).
- The data points on the figures are barely recognizable and the curve functions are not formulated. What the authors actually call a "very good correspondence" in Fig. 1 is unsubstantiated, as the curves do not have the same shape at all (only the decreasing-increasing tendencies are approximately the same). The scales for the y and x axes do not correspond between the compared figures. Moreover, the data point values, representing single measurements are considerably different and the curve fitting is obviously not good (i.e., the correlation coefficients R^2 are probably not approaching 1). It can also be noted that Figs. 1*a* and 2*b* are exactly the same representation (redundancy). The fact that each data point was represented by three correlated values (i.e., lozenge, square, and triangle) should have been explained by the authors, as they apparently yield the same information and add confusion to the figures.
- The SD measured on an ink standard (i.e., 0.06–0.07) represents an error that is not negligible in comparison with the apparent changes of phenoxyethanol in the figures. It is not specified if the SD can be extrapolated to all data points; however, it would be important to control that the error will not increase when the measured quantity decreases as was observed by Horwitz (7) in his evaluation of analytical methods.
- The authors analyzed 13 inks but showed results only for three selected inks (numbered 356, 359, and 364). The variations between the 13 different inks are probably considerable as was demonstrated in another work published in the same journal (8). This should be explained and discussed.
- The authors additionally proposed other compounds such as phthalic acid ester to help in the age determination of inks. However, they do not state precisely which aging phenomenon it follows (e.g., polymerization, evaporation, etc.). The graphical representation (Fig. 5a) does not help to understand what we are supposed to see (i.e., representation of the increase and then decrease of the peak area ratio of phthalic acid ester to phenoxyethanol). As ink 356 is a fast aging ink, the phenoxyethanol does not diminish significantly after 1 month anymore as explained earlier in the paper. So what is the meaning of such a curve? How would the curve look when only representing the phthalic acid ester peak area? The graphic representation is actually based on only six single measurements (no error measurements). The relevance of this curve can therefore be questioned, and except for

the maximum at about 400 days, the represented y-values correspond to at least two x-values (i.e., two possible age determinations): for example, a value of 0.1 ± 0.07 would correspond similarly to approximately 0, 30, 190, or 750 days! This cannot be valid. The accelerated aging curve (Fig. 5*b*) is again quite different from the natural aging (Fig. 5*a*). The values obtained are lower (and the scale is not the same for both figures).

The authors propose several ideas to differentiate fast aging and slow aging inks but their experimental data is not validly represented and/or discussed. These data are insufficient to draw any conclusions about any potential of the method for ink dating purposes. Bügler et al.'s (8) latest publication in the same journal offers, in contrast, a very valuable and informative publication on the subject. We are sorry to see this type of paper published while the influence of storage conditions on ink aging has not been addressed sufficiently in the literature. This lack of information on the subject must be filled before proposing such methods for practical caseworks. These are preliminary and unconvincing results from development research performed in a laboratory on controlled samples without due warnings about potential shortcomings. They cannot be used or even compared with results obtained in real situations on uncontrolled specimens of limited size, unknown composition, and undefined storage conditions. This can leave an undeserved feeling that these methods are ready for implementation when the task of ensuring their scientific validity is still far away (9). We would like to emphasize the ethical guidelines previously discussed by Brunelle and Cantu (10) in this journal and their warning that *forensic scientists should not attempt to examine actual criminal or civil cases until they have been tested.*

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Comparison of Natural and Artificial Aging of Ballpoint Inks

ABSTRACT: Solvent evaporation caused by aging from ballpoint inks was measured by gas chromatography/mass spectroscopy (GC/MS). The sample preparation was carried out with two different thermal desorption systems. The results are compared. Thirteen inks were classified with regard to their solvents, polymers, and additives. The variation of the aforementioned compounds caused by aging was monitored for naturally and artificially aged samples. In this paper, the results are compared and discussed with respect to forensic casework.

KEYWORDS: forensic science, age determination, artificial aging, ink, gas chromatography/mass spectroscopy, thermal desorption

In the last years the direct method of dating ink entries based on the analyses of the solvent evaporation from the writing has been a subject for several forensic investigations (1–6).

Recently Bügler et al. (6) published a method for age determinations of ballpoint inks by gas chromatography/mass spectroscopy (GC/MS) based on sample extraction by thermal desorption in two steps. It is postulated that the amount of phenoxyethanol (PE) in fresh pen strokes evaporates at a moderate temperature whereas the amount of PE which is included in the polymer matrix in older pen strokes needs a higher extraction temperature. The method is applicable if PE does not evaporate from the writing too fast.

The following paper describes a variation of the method.

Material and Methods

Equipment

For thermal desorption of the ink samples on paper two different thermal desorption units were used:

- Atas Desorption System Optic III with Linex Injector and cold trap, equipped with a CombiPAL autosampler, connected to a Thermoelectron GC/MS-system Trace GC/DSQ.
- Markes Desorption System Unity/Ultra TD with cold trap, connected to an Agilent 6890N GC/MS system.

In the Atas system the sample is placed directly into the liner where thermal desorption takes place. The gas is frozen out in a part of the column which is led through the cold trap cooled by liquid nitrogen. In the Markes system thermal desorption is carried out in glass tubes. The gas is gathered in a cold trap which is cooled by a peltier element.

The preconditioning of the glass tubes is performed by heating the tubes at 300°C for 30 min.

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For the monitoring of the instrument performance 1 μL of a solution of PE (Merck, purity >99%), 2-decanone, 2,3-dimethyl-naphtalin and n-pentadecan in acetone (Merck, purity >99.8%) on paper was analyzed using the same conditions under which the analyses of ballpoint inks were carried out.

Desorption of Ink Samples

Desorption Method—A piece of pen stroke on paper (length: 0.7–1.0 cm) was cut out and placed into the liner (Atas) or the thermal desorption tube (Markes). The sample was heated in three steps at 100°C (15 min), 140°C (15 min), and 200°C (10 min) and the desorption gas was collected in the cold trap at −80°C (Atas) or −15°C (Markes). After every thermodesorption step the sample was removed from the heating system. By heating the cold trap (300°C/min: Atas; 100°C/min: Markes) the desorption gas was given onto the column for analysis at the following conditions:

> Column: ZB5ms Guardian
> Carrier Gas: He, 1.2 mL/min
> Oven program: 100°C, 3 min; 100–200°C, 15°C/min; 200–320°C, 25°C/min; 320°C, 6 min

Integration of the signals was performed on chromatograms of the single ion mode.

Screening of Contents—In order to find criteria to differentiate between the inks, screenings of the volatile compounds were performed.

For the screening of the volatile contents of the ballpoint inks, ink samples on paper were put on glass pins which were placed into the glass tubes and heated at 240°C. The collection of the gas and the GC/MS-analyses followed the aforementioned conditions.

Accelerated Aging

For accelerated aging of ballpoint inks, samples were cut out (0.7–1.0 cm of the pen strokes) and put into an oven at 45°C.

FIG. 1—*(a) Validation of the two systems (Atas). (b) Validation of the two systems (Markes).*

FIG. 2—*(a) Fast aging ballpoint ink. (b) Slowly aging ballpoint ink (see also Fig. 1a).*

In a time range from 2 to 33 1/3 days the loss of the solvents and the variation of polymer compounds and plasticiziers was measured.

Results

Validation of the Systems

Naturally aged samples of the same ink were analyzed on the Atas and the Markes system. In all cases only single measurements were made.

The standard deviation was measured by analyzing samples of an ink standard with a natural age of 18–21 days once a week. The standard deviation of 10 measurements was 0.06–0.07.

The graphs for the variation of PE, measured at the three temperatures shows a very good correspondence for the two systems. So it is possible to control the reliability of the results of one system by the other (Fig. 1).

Natural Aging

The main compound which gives information about the aging of a ballpoint ink is PE which is used as a solvent in nearly all inks. The loss of PE was monitored for natural and artificial aging of inks in three thermal desorption steps at 100, 140, and 200°C. The amounts of outgassing PE at each temperature was brought into relation ratio to the total amount of PE measured in the three steps. These mass-independent results corresponded to those which were reported by Bügler et al. (6) for fast aging and slowly aging inks. The fast aging inks show a loss of PE within the first month while the slowly aging products lose the solvent during a time of 3 months or more (Figs. 2a and 2b).
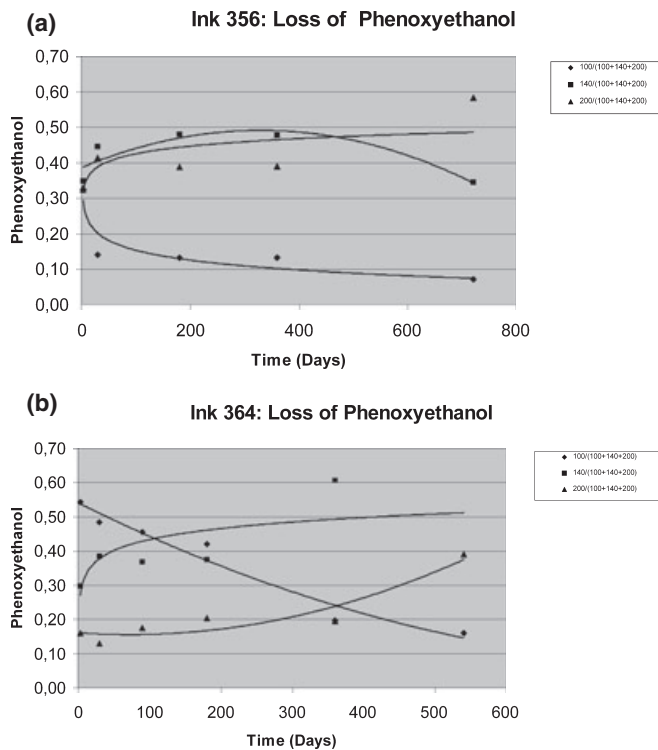
Accelerated Aging

The results obtained by analyses at the three temperatures for the samples from accelerated aging (Fig. 3) correspond to those of the naturally aged inks (Fig. 2b).

The loss of PE caused by accelerated aging of ink samples of defined natural ages is shown in Figs. 4a and 4b. Accelerating aging in three steps was carried out with ink samples with a natural age of 3 months (storage at 45°C for 3, 6, and 17 days) and 1 year (storage at 45°C for 3, 6, and 9 days). For writings of unknown age the amount of PE of the original sample and the variation of this amount by three steps of heating allow estimations of the original age of the writing.
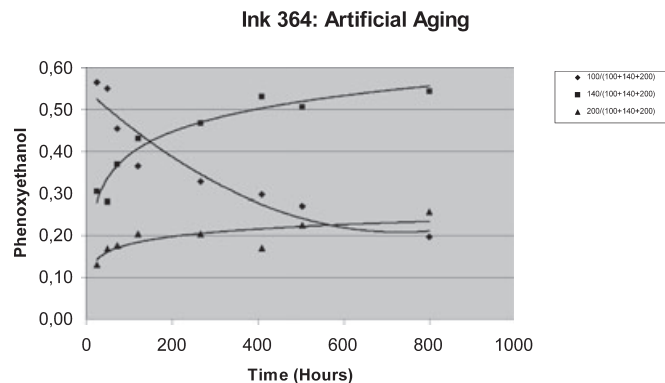

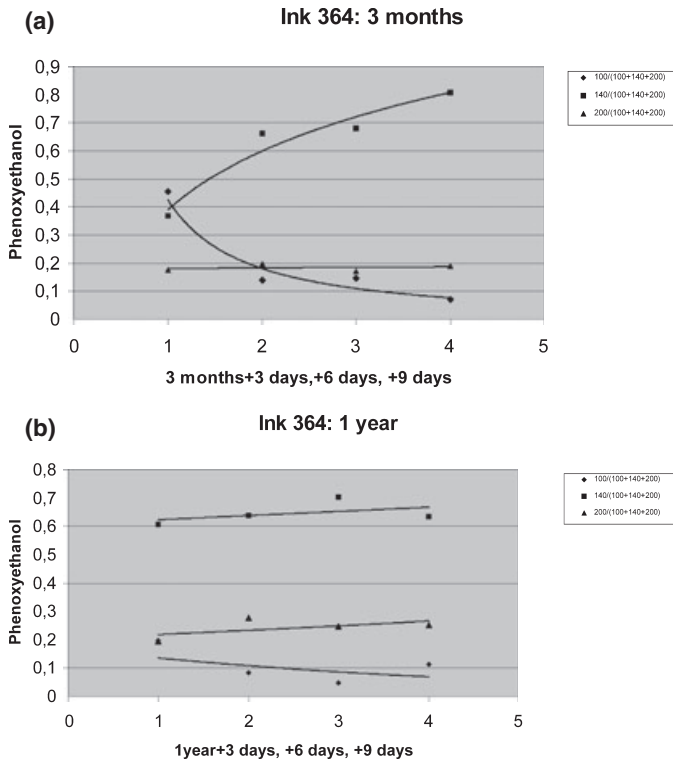FIG. 3—*Artificial aging of ink 364 at 45°C.*

(a)

(b)

FIG. 4—*(a) Artificial aging of a 3-month-old ink sample. (b) Artificial aging of a 1-year-old ink sample.*

(a)

(b)

FIG. 5—*(a) Fast aging ink 356—Natural aging: phthalic acid ester/phthalic acid ester + PE. (b) Fast aging ink 356—Artificial aging: phthalic acid ester/phthalic acid ester + PE.*

Estimations on the Age of Writings Based on other Compounds in Addition to Phenoxyethanol

For fast aging inks which contain large amounts of phenoxyethoxyethanol, phtalic acid esters, or phtalic anhydride, estimations about the age of questioned writings are possible based on the variation of these compounds by aging of the writing.

Seven of the ballpoint inks analyzed show characteristic graphs for the variation of phthalic anhydride or phthalic acid esters by aging of the pen strokes. This result, which is obtained for the naturally aged inks, corresponds to that of the artificially aged samples of the same inks (Figs. 5a and 5b).

For five inks which contain a huge amount of phenoxyethoxyethanol the decrease of this solvent at 140°C referred to the amount of PE allowed estimations on the age of the pen strokes (Fig. 6).

Discussion

As reported by several authors in the past (1–6), the loss of PE can be used as a reference to the age of a writing produced with ballpoint ink.

It is possible to differentiate between inks which lose most of the solvent very quickly (within 1 month) and inks which lose the biggest amount of the solvent within 3 months or more.

In our laboratory, these results could be verified by using thermodesorption GC/MS-chromatography with two GC/MS-systems with different thermal desorption systems. The sample preparation and the conditions of the analyses were the same, and the results obtained from the two systems, i.e., the amounts of PE detected at the three temperatures in relation to the whole amount of PE, showed a good correspondence.
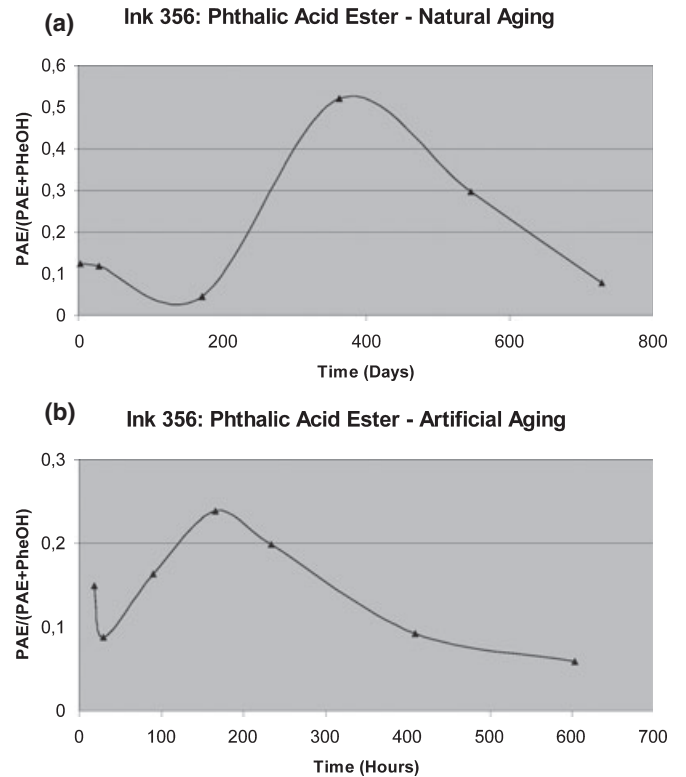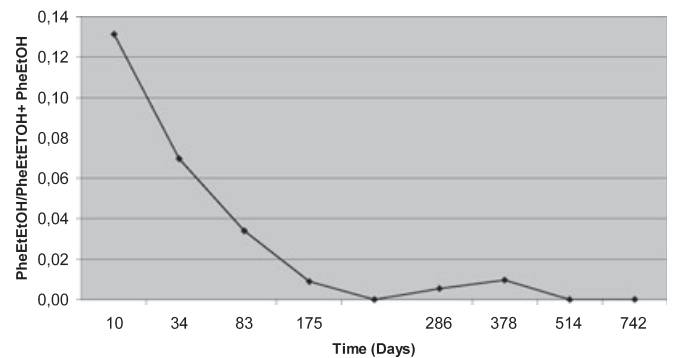

FIG. 6—*Ink 356—Decrease of phenoxyethoxyethanol.*

If either of the thermodesorption GC-MS methods is applied to forensic casework, the results may not give the necessary information to estimate the age of a questioned ink. This is possible if samples of the same ink are measured three or four times within a larger range of time (1–3 months). The storage time can be shortened by accelerated aging at 45°C (3–33 1/3 days). For this purpose, tests of accelerated aging at 45°C of fresh and naturally aged older samples were performed.

It was shown that the decrease of PE in slowly aging inks of artificially aged samples corresponds well to that of natural aging and allows conclusions on the original age of the questioned writing.

The results concerning the outgassing of PE cause some limitations to forensic case work if the samples delivered for analysis are of the fast aging type.

In that case the variation of other contents of the ink caused by aging can give more information. For seven inks which contained small amounts of plasticizers or phthalic anhydride as polymer a variation of these compounds was obvious which allowed further estimations on the age of the writing. Further studies will be carried out to support this result.

If the loss of phenoxyethoxyethanol in relation to the decrease of PE in inks which contain a huge amount of phenoxyethoxyethanol is monitored, a variation of phenoxyethoxyethanol can be noticed which gives additional information concerning the age of the ink.

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Exhibit 26

The dating of writing inks through 2-phenoxyethanol using gas chromatography-mass spectrometry, advantages, interpretation, and limitations

Patricia J. Giebink, Erich J. Speckin, Jason Harner

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.[1]

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

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[1]More information about analytical techniques can be found in <u>Advances in the Forensic Analysis and Dating of Writing Inks</u> by Richard Brunelle and Kenneth Crawford (Charles C Thomas Publisher, LTD; Springfield, IL, 2003)

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 the 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

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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 [1]. 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

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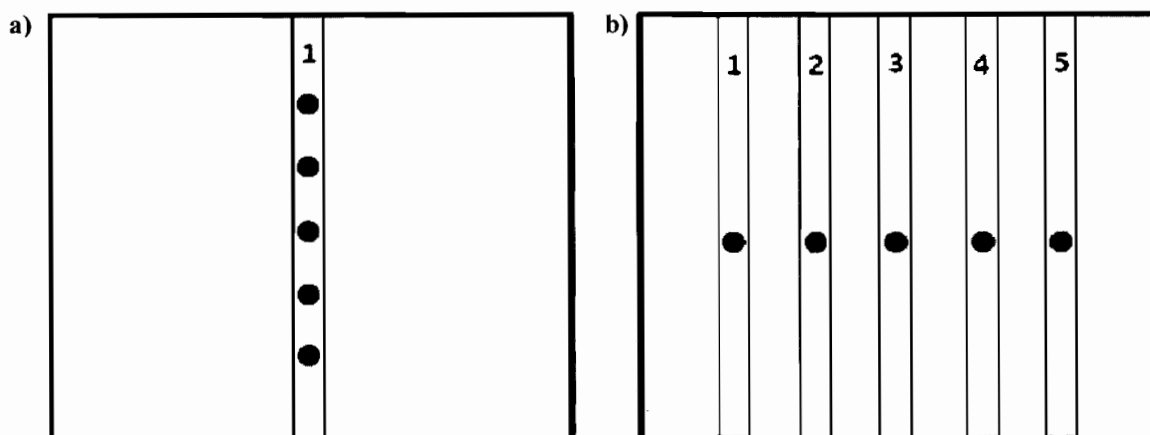
The densitometer scans were performed in triplicate for each method and the resulting peak areas were averaged and standard deviations and relative errors (Equation 1) were calculated. This was repeated for each of the four inks tested.

$$\left(\frac{Standard\ Deviation}{Average}\right) * 100 = Relative\ Error$$

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 PE. 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 mass 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 PE 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 solution 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

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

Color	Manufacturer	Ink No.	Date	[PE] (ppm)
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   **b) Vials of each ink are scanned separately**

Ink	Vial	Average	Relative Error	Ink	Vial	Average	Relative Error
	1	747.0	0.5		1	697.7	2.1
Black	2	1050.8	0.3	Black	2	877.0	2.0
Zebra	3	1256.3	0.7	Zebra	3	459.2	1.2
B727	4	792.2	0.4	B727	4	604.5	0.9
	5	854.0	0.7		5	761.8	1.6
	1	756.2	0.7		1	599.0	1.4
Blue	2	1048.0	0.1	Blue	2	810.5	1.7
Zebra	3	668.5	0.4	Zebra	3	934.3	1.1
B731	4	821.2	0.9	B731	4	562.2	1.3
	5	851.8	1.4		5	661.7	1.3
	1	412.5	1.8		1	275.0	3.3
Blue	2	277.8	1.2	Blue	2	185.7	3.3
Pentel	3	289.0	1.1	Pentel	3	216.2	2.1
B734	4	252.7	3.0	B734	4	200.5	5.7
	5	341.3	0.9		5	187.3	2.1
	1	804.3	2.4		1	785.7	1.7
Blue	2	1022.8	0.7	Blue	2	1065.7	1.7
Bic	3	813.3	1.6	Bic	3	878.8	1.8
B737	4	904.8	1.9	B737	4	934.8	1.1
	5	1004.2	0.6		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 B731. In Figure 2, Vial 3 appears to have the least amount of ink extracted. In Table 2a, Vial 3 for ink B731 showed the lowest densitometer average of the five vials. However, in Table 2b, Vial 3 for ink B731 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.
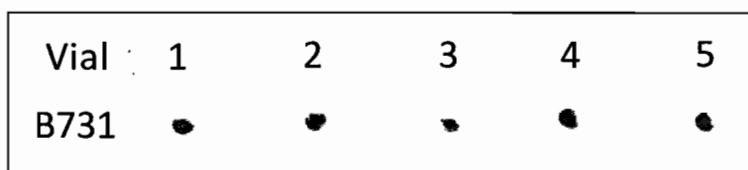

Figure 2: TLC plate spots scanned by densitometer for ink B731

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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Exhibit 27

Minimum requirements for application of ink dating methods based on solvent analysis in casework

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ABSTRACT

Several ink dating methods based on solvents analysis using gas chromatography/mass spectrometry (GC/MS) were proposed in the last decades. These methods follow the drying of solvents from ballpoint pen inks on paper and seem very promising. However, several questions arose over the last few years among questioned documents examiners regarding the transparency and reproducibility of the proposed techniques. These questions should be carefully studied for accurate and ethical application of this methodology in casework. Inspired by a real investigation involving ink dating, the present paper discusses this particular issue throughout four main topics: aging processes, dating methods, validation procedures and data interpretation. This work presents a wide picture of the ink dating field, warns about potential shortcomings and also proposes some solutions to avoid reporting errors in court.

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1. Introduction

Determining when an ink entry was produced on a document has always been a major issue in the examination of questioned documents. For this reason many scientists aimed at developing dating methods along the years [1–5]. There are three main approaches for ink dating on documents. The first approach is based on the analysis of ink stable components that are specific to a certain period in time. Production methods and compositions change and evolve with time following new industrial developments and processes. This approach is generally named in the literature 'static approach' because the measured parameters are almost invariable in time [2]. It allows the determination of the first possible date of existence for a given composition of ink and may thus highlight anachronisms. Knowledge of some major historical changes in ink manufacturing is available (e.g., introduction dates of the major classes of compounds and dates of major changes in formulation). However, most knowledge of changes is proprietary industrial information and not readily available. This is probably the reason why only the US Secret

Service (Washington, USA) and the LKA Bayern (Munich, Germany) reported having extensive ink samples and databases [6,7]. Additionally a program started in the mid 1970s in the USA, in collaboration with the ink manufacturers, for introducing annually modified tags to inks [2], but it covered only a fraction of the whole ink market. The second approach, addressed as the 'absolute dynamic approach' [3] is based on aging processes of ink on documents. It is assumed that ink does not age in the cartridge [8,9], but only after it is placed on paper where dyes fade, solvents diffuse and evaporate, and resins polymerise. Aging processes of ink follow complex pathways that are considerably influenced by several factors other than time, which may accelerate or slow down the aging. The influencing factors can be ordered in three main classes [4,10]: (i) initial composition of the ink (in the cartridge), (ii) physical and chemical properties of the substrate (paper composition, porosity and coatings) and (iii) storage conditions (temperature, light, air flux, humidity, neighbouring material, etc.). In practice, no information on these factors is generally available. This is why the determination of the absolute age of an ink entry remains truly difficult. Measured changes are reported as a function of time in order to establish an aging curve or a portion of it and the objective is therefore more the determination of a time range than a precise date. The time scale considered can significantly vary depending on the measured parameters. For example, while solvents disappear from the ink

very quickly, dyes degradation occurs more slowly. The third approach aims at determining the relative age of a document in comparison to others (i.e., to order them in chronological sequence) and is referred to as the 'relative dynamic approach' [3]. The comparison of the extent of ink aging may help reconstructing the sequence of apposition of ink entries on documents. This can only be applied for inks of the same formula stored under the same conditions on the same type of paper (e.g. diaries) [11]. That is, it applies to inks that only differ in the time they were placed on paper. The general evolution of the aging curve must be known [4]; for example if a decrease of the aging parameter is expected as a function of time, it is imperative to insure it will never increase whatever the conditions.

The most promising methods in the 1980s involved the analysis of sequential extraction of dyes using thin layer chromatography (TLC) [11–20]. It was based on the changes in the extractability of the ink supposedly caused by the hardening of the resins [10,21–24]. The use of this technique in caseworks was reported in the literature [18,25], but it was followed by a vigorous controversy among the scientific community about the limitations of this approach [5,26–42]. Several researchers tried reproducing the results obtained in previous studies and reported the methods to be unreliable [28,34–36], while other scientists debated about the necessity for inter-laboratory validation before their use in casework [4,27,31–33,38,41].

During the last decades interest has shifted to methods based on sequential extraction and analysis of ink volatile components by gas chromatography (GC) coupled with mass spectrometry (MS) or other detectors [17,18,34,44–58], which seemed more promising in terms of reproducibility. Although some forensic laboratories do already apply such ink dating methods in practice, several issues remain open including the inter-laboratory validation. Triggered by a recent ink dating case in Israel, this article aimed at clarifying the ink dating field for justice purposes and guiding scientists through validation of their methodologies, while highlighting practical limitations. It was earlier acknowledged that a central unsolved problem in the field of questioned documents examination is the unequivocal determination of their age [59]. Despite the significant progress in analytical techniques and several published propositions for ink dating, the field of document examiners is still divided about this issue, for reasons that will be clarified and discussed throughout this article. The purpose of this work is to give the status of the various ink dating methods that are based on the analysis of an ink's solvent components, show their limitations, and suggest methods to improve them. It is subdivided in four main sections as follows: Section 2: ink drying principles; Section 3: ink dating methods; Section 4: methods validation; Section 5: ink dating interpretation.

2. Ink drying principles

The dating methods considered in this article all focus on the analysis of solvents from ink strokes on paper. It was observed early that the amounts of solvents in the ink strokes decreased as a function of time [44], according to the following equation [50,51] for the relative peak area (RPA):

$$RPA = p_1 + p_2 \cdot e^{-(t/p_3)^{0.5}} + p_4 \cdot e^{-(t/p_5)^{0.5}} \qquad (1)$$

where p_1 is an additive constant, p_2 and p_4 provides the contribution of the first and second exponential, and p_3 and p_5 are time constants associated with the exponential. The ink drying processes were earlier described in the literature as two separated falling rate phases [51]. The first exponential represents the fast falling rate of drying (rapid solvent evaporation and diffusion into the paper) and the second exponential represents the slow falling
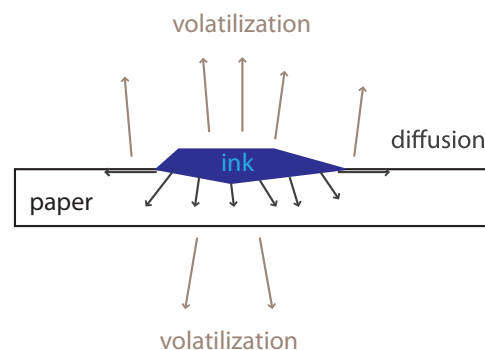

Fig. 1. Simultaneous ink drying processes on paper: the ballpoint pen solvent molecules volatilize (evaporate), diffuse (migrate and penetrate via absorption) and are adsorbed by the paper substrate. While grey arrows represent volatilization, black arrows represents diffusion, migration, penetration, absorption and adsorption.

rate of drying (slower evaporation and diffusion processes) [50,51]. Low amounts of solvents may even stay trapped in the ink matrix for years [17,45,52]. Based on previous researches, the following theoretical aging model can be formulated: several processes occur simultaneously when ink is placed on paper, such as evaporation of solvents in the ambient air, diffusion/absorption in the paper and adsorption by the paper substrate (Fig. 1). Volatilization occurs actually in the ink surface, in the paper surface near the ink and in the paper surface the opposite from the ink. Moreover the solvent molecules may diffuse into adjacent surfaces (for example in a stack of paper sheets) [51].

The compound phenoxyethanol is the most widespread solvent in ballpoint pen inks [57,60,61] and therefore most dating methods finally focused exclusively on the analysis of this specific substance (Fig. 2).

As explained above, ink aging pathways and rates are significantly influenced by a number of factors that may slow down or accelerate the phenomenon [42,61]. These parameters must therefore be extensively studied before a conclusion can be drawn on the absolute age of an ink entry.

2.1. Ink formulation

The influence of the initial ink composition on the aging rates of inks is very important [23,45,56]. Two aspects must be considered: the compounds (dyes, resins, solvents, and additives) and their relative amounts (initial solvent quantity in the ink formulation). Bügler et al. actually suggested that the type of resins influenced the aging rates as they observed the presence of acetophenone–formaldehyde–resin in 'slowly aging inks' [56]. It is therefore very important to have a precise knowledge of the ink market (for example through an ink database) in order to develop a method on selected representative inks.

2.2. Initial ink quantity

The initial quantity of solvents in an ink stroke also influences significantly the aging process (i.e., the drying of the ink). For example, it is dependent on the writing pressure (i.e., thickness of
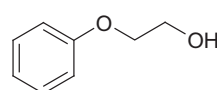
m.w.	138.2 g/mol
b.p.	247°C
viscosity at 25°C	21.5 cP

Fig. 2. Structure formula, molecular weight, boiling point and viscosity of the solvent phenoxyethanol.
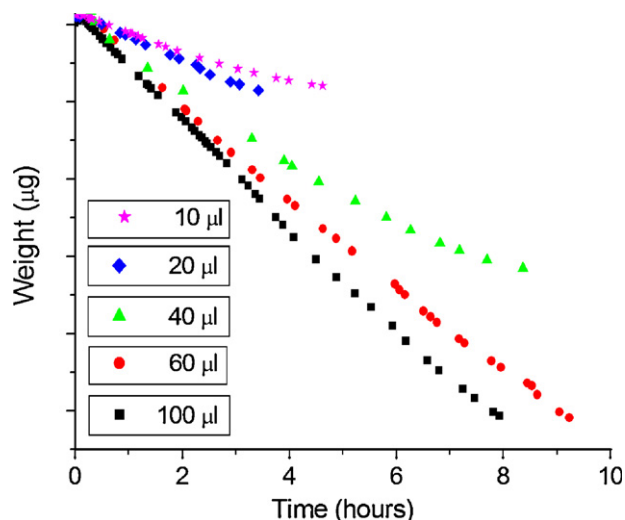
Fig. 3. Superimposed curves for the evaporation of 10, 20, 40, and 100 μl of the solvent ethoxyethanol from paper: the loss of weight in micrograms (steps of 5000 μg) is presented as a function of the time in hours. Lower evaporation rates were observed when smaller volumes of solvents were initially deposited on paper [61].

ink) or and/or also on the size of the ball in the ballpoint pen. Lower evaporation rates were observed for smaller volumes of solvents on paper (Fig. 3), when the solvent ethoxyethanol was placed on the paper surface using a micropipette. With larger quantities of solvent applied to the paper, a larger accessible surface area will be available for evaporation (Fig. 4), and thus a higher evaporation rate will be observed.

This is problematic as the relative content of phenoxyethanol varies considerably among different ballpoint inks [38]. The size of the ball of the ballpoint pen and the pressure applied while writing, both of which determine the thickness and depth of the ink line, respectively, also affect the initial quantity of phenoxyethanol found in 1 plug or 1 cm of ink line. Moreover, in research works, ink entries are generally drawn as straight lines, allowing solvents to diffuse away from the stroke. Questioned documents will most probably carry texts with curved lines from any alphabet. For
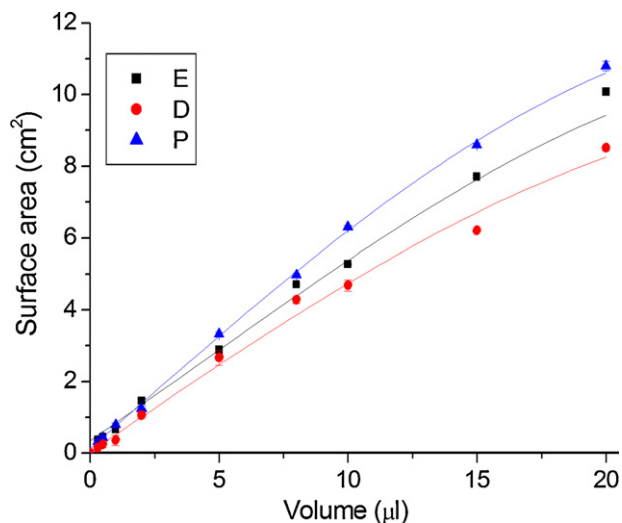

Fig. 4. Visible surface area [cm²] taken up by the solvents ethoxyethoxyethanol (E), dipropylene glycol (D) and phenoxyethanol (P) a short time after deposition on paper with a micropipette, as functions of the volume deposited [μl]. The surface areas increased with the volume, but were also influenced by the viscosity, density, hygroscopicity and volatility of the solvents [61].
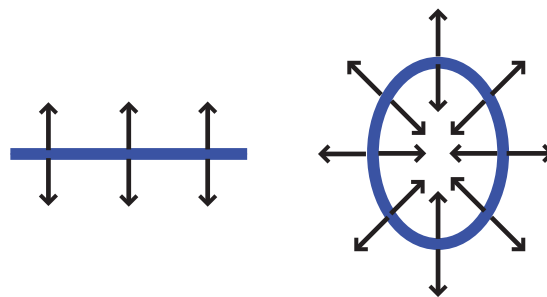

Fig. 5. Solvents diffusion from two ink entries: (left) diffusion away from a straight line and (right) diffusion inside the loop of the letter 'o'. The solvent concentration may be significantly higher in 1 cm of the loop compared to 1 cm of the straight line.

example, in the letter "o", the solvents will diffuse to some extent away from the letter and partly inside the ring. Higher quantities of solvents may be found in letters with dense lines compared to a straight line of the same length (Fig. 5). This represents a major problem. When extracting 1 cm ink lines from different letters, one is not guaranteed to have always the same solvent quantity. Aginsky tried to minimize this effect by calculating a mass invariant ratio between two samples [34,52]. Bügler et al. even tested the mass independence of a given aging parameter by analysing ink entries of different lengths on the same paper [56]. For example, if 2 cm of an ink line containing 0.3 μg of phenoxyethanol per cm was analysed, one would record twice as much phenoxyethanol than in 1 cm (Table 1). However if you calculate a ratio between two compounds found in the ink [50,52] or between two sequential extractions of the same ink entry [52,56], the ratio should be the same regardless of the length of the ink line.

However, only the *length independence* between two samples of the same entry is guaranteed, and not the *mass independence*, as pressure (i.e., thickness) and density (i.e., distribution) vary along a stroke (Fig. 5) [56].

In practice, it is impossible to ensure the homogeneity of the ink applied on paper, thus the influence of such parameters on the solvents aging kinetics must be quantified. Dating would then be possible only if the errors provoked by different solvent quantities resulting from the above situations were smaller than expected changes as a function of the age. This actually requires more research than was published so far.

2.3. Paper type

The influence of substrate structure (paper type) on the drying process should not be underestimated, as their porosity can differ quite widely within a same sheet of paper (pores diameter between 0.05 and 10 μm). Molecular diffusion, Knudsen (through pore) diffusion, surface diffusion, capillary condensation of vapors, physisorption (absorption and adsorption), chemisorption, migration and evaporation will all be influenced by the porous structure, the fibers (e.g., cellulose fibrils) and the paper chemistry (alkaline

Table 1
The parameters M_1 and M_2 are absolute quantities of phenoxyethanol and are dependent of the length of the stroke, while calculating a ratio between these two parameters yield a length independent feature.

Ink line length (cm)	First parameter	Second parameter	Ratio (Table 4; Eq. (3))
	M_1 (ng)	M_2 (ng)	$M_1 \cdot 100\%/(M_1 + M_2)$
1	30	70	30
2	60	140	30

Table 2
Procedure to determine the rate of decrease of volatile components (R) in inks on documents.

Method 1	Sample set 1 (normal)	Sample set 2 (artificially aged)
Sampling	10 microdiscs (1 mm diameter) of the ink on paper	
Treatment	No treatment	Moderate heating (e.g. 70 °C, 1 h [52] or 2 h [49])
Extraction	10 μl [52] or 15 μl [49] of appropriate solvent (e.g. acetonitrile with an internal standard)	
Analysis	1 μl of extract analysed by GC/MS (SIM mode)	
Results	P = mass of solvent	P_T = mass of solvent
Eq. (2)	$R(\%) = [(P - P_T)/P] \cdot 100$ [49,52]	

or acidic, fillers, detergents, additives, etc.). Aginsky stated having studied the influence of paper type ([52], footnote 10) reporting it to be negligible, but no details have been disclosed. Bügler et al. also studied the influence of the paper type on the aging process and reported a strong dependence on paper type for his method [56].

2.4. Storage and environmental conditions

Due to the fact that diffusion and evaporation mechanisms play such an important role in the drying of solvents on porous media, a wealth of external factors must be taken into account. Among these are temperature (of air, substrate, ink), solvents' vapour pressure, humidity, air movement (laboratory, cabinets), the properties of solvents mixtures (vaporization of the solvent mixture, viscosity), and those properties of ink and paper that could affect heat transfer and mass transfer coefficients. On that aspect, Aginsky wrote that his results 'suggest that the Q (questioned) writing is old (...) on condition that the document bearing the Q writing has been stored under normal environmental conditions, for example, under room temperature and constant humidity and light conditions [52]'. Lower temperatures and air flows will slow down the drying process. Moreover, room temperatures may vary considerably between summer and winter (except for air conditioned rooms), whereas humidity is rarely constant even in an air conditioned environment.

Possible contamination of old strokes through solvent migration from fresh strokes on adjacent sheets of paper should also be taken into account [47,51,61,62]. It was observed that solvents from a fresh stroke ($t = 0$) can very efficiently migrate to adjacent sheets of paper in a pile. It was found that the quantities of solvent involved in this migration exceeded those found in a stroke after two weeks [51], so that conversely, contamination of a stroke by migration must be taken into account for the dating of ink entries by solvents quantification. Paper blank analysis will help reduce the risk [46]; however the contamination may be very local [62]. Since solvents diffuse from the ink stroke into the paper, the paper blank should not be sampled too close to the ink entries [51]. One has to be particularly careful regarding the way documents are stored, due to the possibility of contamination (in a notebook or file folder), but also because of the suppression or reduction of drying processes in tightly sealed (e.g., glass vial) [61] or semi-hermetic (e.g. plastic cover) situations respectively. Additional measurements are needed to follow the drying of inks on papers for long storage times under such conditions. Storage conditions were barely studied up to now in spite of their crucial influence on aging kinetics. Most reports contain data collected from documents which have been stored only under laboratory conditions. From a validation point of view it is therefore important in practice to apply a method within its range of applicability and to state exactly under which circumstance the results are valid.

3. Dating methods based on solvents analysis described in the literature

First proposed by Stewart [44], further developments of dating methods based on solvents analysis were inspired by the works of Cantu on sequential extraction [11] and artificial aging [12]. Aginsky proposed two multi-staged 'absolute dynamic dating methods' [34,45,52]. These methods' principles were briefly addressed in two preceding papers [17,18]. Aginsky's methodology [52] is based on the supposition that as ink ages, its resins harden (solidify) and subsequently the ink solvent extractability decreases over time [45]. Solvents (volatile ink vehicles) are analysed and more specifically the rate of decrease of solvents amounts (method 1 described below) and the rate of decrease of solvents extractability (method 2 described below). Gaudreau and Brazeau of the Forensic Document Examination Section of the Canada Border Services Agency reported in a conference presentation the use of a dating method based on the same principles [49] (modification of method 1 described below). More recently, Bügler et al. described a method based on the same principles, but involving a different sample preparation [55,56,63,64] that has been implemented by several laboratories in Germany, Switzerland and Canada (modification of method 2 described below as method 3). The first step of dating measurements generally consists of detection and identification of the volatile components of the ink (described, for example, as procedure 1 in [52]). As explained above, the ink component used for dating is phenoxyethanol, since it is the most commonly found in ballpoint pen inks [51,56,57].

Additionally, some recent developments based on previous tests [17,44,50] proposed to calculate the loss of phenoxyethanol in relation to a stable compound quantification such as a dye as a function of time [65–67]. For the moment no further information were published about this alternative approach and it will therefore not be directly treated in this paper. However the same principles would apply to their potential future application in practical cases.

3.1. Method 1

Described as Rate of decrease of volatile components R% by Aginsky [52] and Solvent loss ratio by Gaudreau and Brazeau [49].

Aginsky's procedure [52] implies the removing of two sets of samples each consisting of 10 microdiscs (about 1 mm in diameter)

Table 3
Summary of R thresholds values defined in the literature and in conference proceedings.

Aging parameter (%)	Threshold value	Ink entry age	Literature
R	≥20	Fresh	Aginsky [52]
R	≥50	Less than 6 months	Gaudreau and Brazeau [49]
R	≥25	Less than 1 year	Gaudreau and Brazeau [49]

Table 4
Procedure to determine the rate of decrease of solvent extractability (D) of inks from documents described by Aginsky [52].

Method 2	Sample 1 (normal)	Sample 2 (artificially aged)
Sampling	10 microdiscs (1-mm diameter) of the ink on paper	
Treatment	No treatment	Moderate heating (e.g. 70 °C, 60 min)
Weak extraction	10 μl of an appropriate weak solvent (e.g., carbon tetrachloride)	
Analysis 1	Extract analysed by GC/MS	
Results 1	M_{weak} = mass of solvent	M_{weak} = mass of solvent
Strong extraction	After drying, in 10 μl of an appropriate strong solvent (e.g. chloroform)	
Analysis 2	Extract analysed by GC/MS	
Results 2	M_{strong} = mass of solvent	M_{strong} = mass of solvent
Eq. (3)	$P = 100 \cdot [M_{weak}/(M_{weak} + M_{strong})]$	$P_T (\%) = 100 \cdot [M_{weak}/(M_{weak} + M_{strong})]$
Eq. (4)	$D (\%) = P - P_T$ [52]	

of the ink on paper using a boring device (also called micro-punch device). Sample set 1 is placed in a vial and extracted with 10 μl of an appropriate solvent with an internal standard. 1 μl of the extract is analysed by GC/MS (SIM mode with detector set to monitor ions which are specific for the identified substances and internal standard). The mass of the ink solvent detected (i.e. the ink aging parameter P) is calculated by means of the internal standard method. Sample set 2 is heated moderately and analysed using the same procedure as for sample set 1 to determine the mass of the ink solvent after heating (i.e. the ink aging parameter P_T). The rate of decrease of volatile components is calculated using Eq. (2) in Table 2. If the value of R is ca. 20% or larger, it shows (on condition that the content of the analysed ink's solvent is not too small, at least, not less than 1 ng per sample) that the natural aging of the ink analysed is still in progress, i.e., the ink writing is fresh (Table 2) [52]. In his paper [52], Aginsky proposed an alternative ink aging parameter P if any volatile solid component of the ink was detected: P = ratio solvent peak areas to non-volatile component peak areas. However this method was not mentioned again in later publications.

Gaudreau and Brazeau reported using a similar method to determine the approximate age of an ink entry in conference proceedings [49]. Two sample sets each containing 10 plugs of ink are removed. One sample set is heated at 70 °C for 2 h and then both are extracted with 15 μl acetonitrile containing internal standard for 5 min. Using Eq. (2) in Table 2, the authors determined the following threshold values for phenoxyethanol: $R \geq 50\%$ and 25% (including error) allowing to state that ink has been applied to paper less than six months (150 days) and less than one year (300 days) prior to the test respectively (Table 3).

As of today, nobody else reported in the literature using this method. However, Andrasko presented a modified solvent loss ratio technique involving a different sample preparation (solid-phase microextraction) [46,47] that was able to reveal if an ink is fresh (4–6 months old at most). He later communicated his strong doubts about the feasibility of such ink dating methods stating that the method he had presented was unreliable and that the results were not reproducible.[2] A solid-phase microextraction method was also studied by Brazeau and Gaudreau [54]. It should be noted that this method requires that both the heated and unheated samples have the same or nearly the same amount of ink. The method is not independent of the amount or length of ink sampled.

3.2. Method 2

Described as rate of decrease of solvents extractability D% by Aginsky [52].

According to Aginsky's report [52], two samples, each of 1 cm slivers of the ink on paper are removed using a sharp scalpel. Sample 1 is placed in a vial and extracted with 10 μl of a 'slowly extracting weak' solvent. 1 μl of the extract is analysed by GC/MS (SIM mode with detector set to monitor ions which are specific for the identified substances and internal standard). The sample is removed, dried, placed in another vial and extracted with 10 μl of a 'fast extracting strong' solvent. 1 μl of the extract is analysed by GC/MS (same analysis settings). The mass of solvent in each extract (M_{weak} and M_{strong}) are calculated by means of the internal standard method and the percent of the solvent mass extracted in the weak solvent (P) is calculated using Eq. (3) in Table 4. Sample 2 is then heated moderately and analysed using the same procedure as for sample 1 in order to determine the percent of extraction after heating (P_T). The distance (D) between the value P and P_T is calculated using Eq. (4) in Table 4. Method 2 is actually an upgrade of method 1, as the total amount of extract M_{weak} + M_{strong} (Table 4) should theoretically have the same value as P (Table 2). Therefore the final $R\%$ can be extrapolated from the raw results obtained by method 2, without additional analyses.

Aginsky summarized: *If the value of D is ca. 15% or larger, it shows that the natural aging of the ink analysed has not levelled off yet, i.e., that the ink writing is fresh* [52]. The following thresholds definitions were proposed in the literature in 1996 [52]:

- $D >$ ca. 15% – It suggests that the questioned writing is fresh, i.e. it is less than eight-month old. If such a result has been obtained for a questioned document dated, e.g. by over a year preceding the analysis, the examiner can state with confidence that this document has been backdated.
- $D <$ ca. 10% – It suggests that the questioned writing is old, that is its age is larger than ca. two months, on condition that the document bearing the questioned writing has been stored under normal environmental conditions, for example, under room temperature and constant humidity and light conditions. It should also be stressed that such results can also mean that the questioned ink's binder is not capable of cross-linking or undergoing other processes of 'solidification' due to aging (though there are very few such inks on the market).
- ca. 10% $< D <$ ca. 15% – This means that additional samples of the questioned entry should be taken (if enough ink is available) to ascertain statistically if the mean of the D values obtained are closer to 10% or 15%; in this case, the conclusion on whether the ink in question is fresh or old is made with a certain degree of confidence.

It was then specified in an appendix to the article [52] that if, in a real case situation, a necessity arises to narrow the interval

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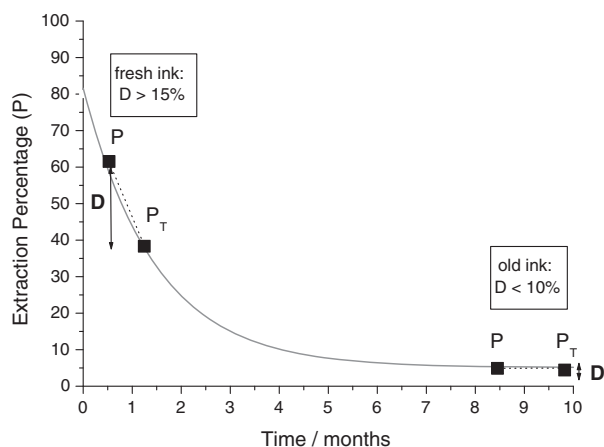[2] Personal communication from J. Andrasko, 2003.

Fig. 6. Graphical presentation of the threshold values proposed by Aginsky [33] to determine a time frame within which a questioned entry has been actually written.

Table 5
Summary of D threshold values defined in the literature and in conference proceedings.

Aging parameter (%)	Threshold value	Ink entry age	Literature
D	ca. >15	Less than 8 months	Aginsky [52]
D	ca. <10	More than 2 months	Aginsky [52] proficiency
D	ca. >10 ca. <15	More analyses	Aginsky [52]
D	≥20	Less than 5 months	Aginsky [52]
D	≤5	More than 6 months	Aginsky [52]
D	≥18	Less than 6 months	Aginsky [45]
D	≥12	Less than 8 months	Aginsky [45]
D	≥8	Less than 12 months	Aginsky [45]
D	≥6	Less than 18 months	Aginsky [45]
D	≥4	Less than 24 months	Aginsky [45]

comprising the real age of the ink in question, there were at least two possibilities for this: (1) the ink formula is known and reference samples may be prepared; (2) further thresholds determination as follows:

• $D \geq 20\%$ corresponds to ballpoint inks younger than 5 months.
• $D \leq 5\%$ corresponds to ballpoint inks older than approximately 6 months.

New upper-threshold values were later presented in a conference proceeding in 2002 (Table 4) [45].

This D parameter is then used to ascertain that the aging of the ink sample has not stopped yet (Fig. 6). The principle follows the idea that, when ink is fresh, P is high and P_T is lower (then the difference D is high and the sample is still drying). When the ink is old, P is low and P_T is also low (then the difference D is low and the sample decreased its rate of drying).

The threshold values were defined using different ballpoint pens. If the type is not always reported in the literature, the number of pens was specified: between 30 and 50 [45]; 64 [49] and up to 85 [56]. Thus the influence of ink formulation was to some extent tested, particularly in the work of Bügler et al. [56] who selected representative inks from the ink library at the Forensic Science Institute of The Bavarian Bureau of Investigation. As a consequence, the influence of the initial quantity of phenoxyethanol was also evaluated. This is why only an upper-threshold indicating the maximum age of an ink may be used [45,49,56]. The presence of a high quantity of phenoxyethanol or the finding of a high aging parameter may indicate a fresh ink, whereas its absence does not allow any conclusion about the age [56] (see detailed explanations below) (Table 5).

No published account from other authors reported using this specific method. However, a method based on the same principles, but involving a different sample preparation, was reported recently in the literature and is described below [56,60,63,64].

3.3. Method 3

Described as *Ink age assessment procedure* by Bügler et al. [56].

Instead of a sequential extraction into weak and strong solvents, the sample is thermally desorbed at two different temperatures (e.g. 90 °C and 200 °C). The peak areas of phenoxyethanol obtained at low desorption temperature M_{low} and high desorption temperature M_{high} are used to calculate a ratio V (corresponding to P in Eq. (3) in Table 4) (see Table 6).

If the experimental procedure considers only sample 1 and V_1 (%) is computed, then the decision criteria were defined by Bügler et al. [56] as follows (Table 7):

• if $V > 10\%$, ink is fresh. For example, if $V > 25\%$, ink is not older than two months.
• if $V < 10\%$, no conclusion can be drawn.

Bügler et al. found out that a large number of the inks aged too fast and therefore no conclusion can be drawn when the ratio V is

Table 6
Procedure to determine the ink age factor ($V\%$) of inks from documents described by Bügler et al. [56].

Method 2	Sample 1 (normal)	Sample n = 2, 3, 4 and 5 (naturally aged)
Sampling		0.5 mm of the ink on paper
Treatment	No treatment	After several weeks
Weak extraction		90 °C thermodesorption
Analysis 1		Extract analysed by GC/MS
Results 1	M_{low} = mass of solvent	M_{low} = mass of solvent
Strong extraction		200 °C thermodesorption
Analysis 2		Extract analysed by GC/MS
Results 2	M_{high} = mass of solvent	M_{high} = mass of solvent
Eq. (3)	V_1 (%) = 100·[$M_{low}/(M_{low}+M_{high})$]	V_n (%) = 100·[$M_{low}/(M_{low}+M_{high})$]
Evaluation test		Statistical Neumann's trend test [69]

Table 7
Summary of V thresholds values defined in the literature and in conference proceedings.

Aging parameter (%)	Threshold value	Ink entry age	Literature
V	>25%	Less than 2 months	Bügler et al. [56]
V	>10%	Less than 3–4 months	Bügler et al. [64]
V	<10%	No conclusion	Bügler et al. [56]

Table 8
Aspects of reliability for analytical methods. These aspects must be further evaluated before the application of proposed dating methods in real cases.

Aspects of reliability	Short definition
Specificity [73]	Ability to detect ink solvents
LoD, LoQ [38,73]	Limit of reliable measurements (detection and quantification)
Systematic error [38,73]	Accuracy
Repeatability [73,75]	Within laboratory precision
Reproducibility [73]	Between laboratory precision
Outside proficiency testing [27,31,33]	Blind testing on realistic samples

below 10%. Moreover the authors stated that while according to their test results, the proposed method for age determination was applicable to ballpoint inks not older than 1.5 years [55,64]. In practice, however, the accuracy of the method and the properties of the inks used in office work limit the measurable time scale to an ink age of up to 3–4 months [64].

In order to minimize the potential occurrence of false positive, the authors later considered performing a series of five analyses every two weeks for a period of two months, while letting the samples naturally age (these are samples 2–5 in Table 6) [64,68]. The authors also proposed derivatization of phenoxyethanol in order to increase sensitivity and decrease variability[64,68]. The results thus obtained are then used for calculating a similar aging parameter as the one proposed by Aginsky (D in Table 4) [33] with the difference that the subsequent samples are aged naturally instead of artificially. In fact, artificial aging is faster, but actually still debated largely in the scientific community and it was not yet demonstrated to reproduce adequately the natural aging of ink [42]. In this way, using the V% values of the five samples, each of which is older than the previously analysed, an aging curve for the questioned ink entry is obtained. It is then assumed, that a significant drop in the slope of the curve reflects an ink which is still aging, and that no significant drop in the curve reflects an ink which is not aging anymore. From mass screening it was deduced, that aging of inks can be followed analytically with this method up to 6 months. As a consequence, an ink which is still aging is regarded as being not older than 6 months. Otherwise no conclusion can be drawn. The assessment of a ''significant drop'' in the slope of the aging curve is performed using the statistical Neumann's trend test. The value Q is calculated as follows [69,70]:

$$Q = \frac{1}{(n-1) \cdot s^2} \sum_{i=1}^{n-1} (x_i - x_{i+1})^2 \qquad (5)$$

where n is the number of measurements (e.g., $n = 5$), x_i, x_{i+1}, . . . are the measurements ordered chronologically and s is the standard deviation. This statistical treatment provides a threshold value for Q to decide if there is a trend in a series of points given a selected probability p. The probability level has to be fixed by the examiner and is generally 95%. For example, a threshold value of 0.8204 is obtained for $n = 5$ and $p = 95\%$. If the Q value is below the threshold value, then the conclusion can be drawn that the investigated ink is still aging given the selected probability level.

4. Validation of ink dating methods

The analytical dating methods require a considerable amount of time and resources. It is therefore important not to underestimate the task of ensuring their scientific validity before implementing them in practice [71,72] (Table 8). In forensic ink dating, it is extremely important not to confound the results of research experiments performed under laboratory conditions on controlled samples, with results obtained in real situations on uncontrolled specimens of limited size, unknown composition and undefined

storage conditions [41]. Published works present interesting ideas and promising orientations, but its reporting stage in publications does not allow yet for a wide application in casework. Stewart and Fortunato [32] warned that 'the need to routinely determine the age of a document appears to have been a driving force in development of new ink analysis techniques. This could be dangerous, in that the field may be driven to advance faster than the stage of development of some of the techniques should allow.'

It is also of particular concern that measurement errors and irregulars are very rarely mentioned in the literature and are generally not represented in the figures. It is essential however, to make certain that predicted differences provoked by aging (under different influencing factors) are in fact higher than measurement errors [73]. Furthermore, the ink available in real cases is generally not sufficient to repeat analysis several time in order to obtain a mean and a standard deviation. When low quantities are analysed, such as solvents in ink entries, the detection and quantification limits (LoD and LoQ, respectively) play an important role in determining a threshold at which the method is not applicable anymore [4]. Due to this small sample size and the flowing time, it is seldom possible to perform ink dating by solvent analysis again after some time has passed. The most demanding aspect is actually the inter-laboratory validation. As stated earlier, in the literature all necessary data are actually required so that any new technique(s) being proposed can be scrutinized by other experts in the field [32]. The transparency in forensic science has been often acknowledged as an essential factor to avoid errors [74,75] and is a must, in order to develop a methodology in several laboratories. Often, only final values or given examples (no raw data) are published in the literature and the reader must accept the conclusions for granted. This lack of transparency about dating methods was criticized early in the questioned documents literature. Stewart and Fortunato wrote in 1996 [32] that 'If a technique can be shown to be scientifically sound then the next logical step would be to conduct independent validation studies at different laboratories. Before this can occur, however, each technique must be carefully researched and described so that others can reproduce the methods and evaluate their effectiveness.' To that Aginsky answered as follows [33]: 'However, this recommendation does not seem irreproachable. Of course, each method proposed for applying in casework must be minutely described in a professional journal and properly scrutinized. But, at the same time, it should be realized that this natural way related, mainly, to the method presentation, practically has nothing to do with the method validations, at least, as for ink dating methods. The matter is that these methods are the complicated many-staged procedures containing a number of limitations, "technological nuances" and pitfalls which all are difficult to exhaustively explain in the article and which may serve as contributing factors to possible inconsistencies between the procedure, as it is used by the author(s), and its improper reproductions made by others who want to evaluate its' effectiveness or conduct independent validation study. (. . .) With the above reasons in mind, it becomes clear why attempts to reproduce similar methods by using their

description, even very detailed, may well lead to confusing results'. If a method may be reproduced incorrectly by other scientists because of its difficulty, then the robustness of the method may be questioned. A robust method would not be significantly affected by small variations (i.e., error) introduced during the procedure; and the procedures may be easily exported in other laboratories. Therefore forensic scientists performing ink dating methods should contribute actively to the exportation of their method to other laboratories, thus avoiding misunderstanding leading to improper reproductions. In fact, to the present date, no two laboratories that do ink dating via solvent analysis use the same method, however several laboratories participating in the International Collaboration on Ink Dating (InCID, a subgroup of the European Document Examiners Working Group) are striving to harmonize their dating methodologies inspired by the work of Bügler et al. [56].

Once the validation of the tested methods is carried out satisfactorily [71,72], blind testing on realistic samples will be imperative, in order to check the reliability of the method under real casework conditions. Brunelle and Cantu [27], Margot et al. [31] and Aginsky [33] agreed on the fact that 'there is a serious need for outside proficiency testing of current ink dating methods'. Aginsky reported having been subjected to outside proficiency testing in the Division of Identification and Forensic Science of the Israel Police for method 2 (decrease in extraction efficiency) [33,52,76]. A document attesting that fact is available on the website of Riley Welch LaPorte and Associate [76]. According to this document, Aginsky examined six different ballpoint inks written on different dates and his results were all correct. The age of the inks at the time of analyses varied between 1 and 12 months. Five were younger than 8 months and one was older than 2 months. No indication about the preparation of samples was detailed (e.g., type and number of different inks, type of paper, storage conditions). The number of samples of this testing was very limited and the conclusion given used only two thresholds (less than 8 months corresponding to $D > 15\%$ and more than 2 months corresponding to $D < 10\%$ [52]). In our opinion, this can by no means serve as a proof that the method will work on realistic samples (i.e., corresponding to uncontrolled conditions encountered in caseworks) and that different threshold values [45] would provide correct answers. For example, recent studies by Bügler et al. [56] showed that about half of the investigated inks were 'fast aging' and yielded low ratio even when still fresh and thus, a lower-threshold value cannot be interpreted as coming from an old ink. Moreover, the time span that can be considered to date inks through solvent analysis using GC/MS is seriously questioned in the forensic community. Brunelle and Crawford stated that the ink dating technology which is based on GC/MS analysis cannot be used to date inks over six months old [15,46] and Bügler et al. recommended to analyze ink with a maximum age of 3–4 months [64]. The feasibility of such dating techniques on ink older than that must therefore be demonstrated.

Aginsky added that 'Both techniques (i.e., named here as methods 1 and 2) described have been used numerously in actual cases involving tax evasion, medical malpractice, altered wills, contractual disputes, rackets, corruption and organized crime, and many times the conclusions stated on the basis of the results of the ink dating examinations (accepted as conclusive by the courts of law in Russia) directly affected a case [52]'. The fact that acceptance by the courts is sometimes considered as proof of validation of methods, while stating that the same methods are probably too delicate to be reproduced correctly by scientific colleagues should be strongly questioned. In fact all dating methods should follow complete validation according the above-mentioned criteria (Table 8) before their application in court. In conclusion of this Section, Brunelle and Cantu underlined earlier the ethical responsibilities of forensic scientists performing ink dating examinations [27] by stating that 'Testimony involving ink dating that does not clearly state the significance of results obtained and the limitations of what can be concluded from the results of examination (...) would be unethical according to AAFS (American Academy of Forensic Sciences) guidelines because it would be misleading.'

5. Ink dating interpretation

Interpretation of ink dating evidence plays an essential role in the dating process and should not be underestimated in the development of dating methods [4]. It is very important to consider all the possible alternative hypotheses for the obtained result to allow for a balanced interpretation of the evidence [27,38,74,75,77]. A logical statistical framework based on a likelihood approach was proposed [38], because it is more correct than the threshold approach generally reported in the literature. It has the advantage of taking into account the occurrence of false positive results which cannot be completely avoided [27], particularly in a field with many influencing factors that may introduce additional errors.

For cases where an ink tests as being fresh Aginsky wrote [52] that 'If such a result has been obtained for a questioned document dated, e.g., by over a year preceding the analysis, the examiner can state with confidence that this document has been backdated.' One has to be particularly careful as such a statement is actually influenced by all the factors mentioned above. In fact, it is not unconceivable that an ink older than 8 months may in some circumstances show a ratio D above 12% (for example, an ink signature on a document placed in a plastic cover with several other documents also carrying ink entries and stored in a cold, humid room). Forensic interpretation must therefore take into account all logical possibilities (i.e., alternative sources for observed results) and the probability should not be expressed on the hypotheses (e.g., it is wrong to state the following: 'it is more probable that the ink is fresh given the obtained D% ratio'). In order to formulate a statement in a balanced way, the probability should actually be formulated on the evidence given two hypotheses (e.g. 'it is more probable to observe the obtained D% ratio if the ink is fresh rather than if the ink is old') [74,75,78]. The likelihood ratio (LR) is thus defined by the probability of observing a given value of D% if the ink is of age $t_1 = A$ months compared to the probability of observing the same D% value if the ink was older than A i.e., $t_2 = (A + n)$ months:

$$LR = \frac{p(D|t_1)}{p(D|t_2)} \tag{6}$$

For example, the evidence can be evaluated given the following two hypotheses:

- the prosecution states that the ink is 8 months old (t_1);
- the defence reports that the ink is 24 months old (t_2).

Aginsky [45] reported that the mean value and the standard deviation for 8 months old blue ink strokes (from 50 different ballpoint pens) was $D = 7.56 \pm 1.13\%$, while the values for 24 months old blue ink strokes (from 30 different ballpoint pens) was $D = 1.25 \pm 0.85\%$. Accepting for simplicity that D values for a given time t_n are normally distributed, the LR can be calculated from the following equation [79,80]:

$$LR = \frac{f(D|\mu_{t_1}, \sigma_{t_1}^2)}{f(D|\mu_{t_2}, \sigma_{t_2}^2)} \tag{7}$$

where μ is the mean and σ^2 is the standard deviation of the D% value. The density of probability for a given value of $D = d$ is
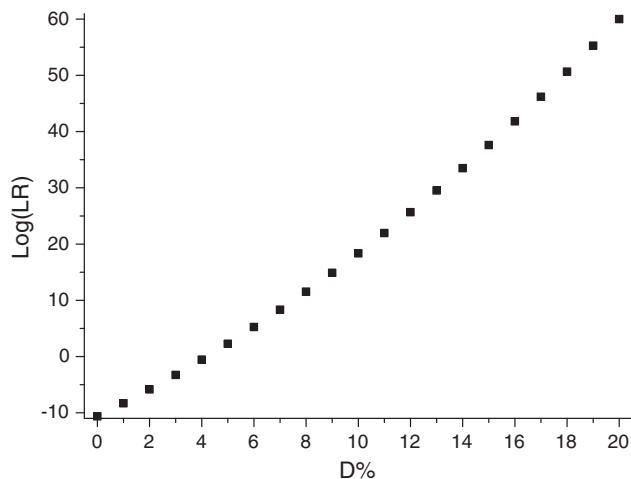
Fig. 7. Distribution of likelihood ratio (LR) calculated as a function of the D% values for the pair of proposition: the ink is 8 months old (t_1) and the ink is 24 months old (t_2). Up to a D% of 4, the evidence support the hypothesis t_2, while for $D \geq 5\%$, the evidence is more probable given t_1.

generally given by the following function [79,80]:

$$f(D|\mu, \sigma^2) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left[-\frac{(d-\mu)^2}{2\sigma^2}\right] \qquad (8)$$

If a D% value of 5% is obtained for the scenario considered here, the LR is then written as follows:

$$\text{LR} = \frac{f(D|7.56, 1.13)}{f(D|1.25, 0.85)} = \frac{0.02065}{0.00011} \approx 188$$

This would mean that it is 188 times more likely to observe D = 5% if the ink is 8 months old (t_1) rather than if it is 24 months old (t_2). This calculation can be repeated for all potential values of D in order to represent a distribution of possible LR for the given pair of propositions t_1 and t_2 as a function of D% (Fig. 7).

However, as can be seen both densities of probability are considerably low and the LR value may change considerably if another set of propositions were to be compared. Unfortunately, the necessary data is not available from the literature to test other scenarios. This logical approach to interpret ink dating evidence has two main advantages, non negligible for the court: (1) it is more correct because it takes into account the hypotheses of the justice and the error rate (false positive occurrence should not be neglected) and (2) it allows to test all possible scenarios and not limit the results to values above a certain threshold. Additionally this approach can be adapted to continuous data and the influence of several factors on the aging can be introduced in the model to evaluate their impact on the strength of evidence [79].

6. Conclusion

The drying of ink on paper can to some extent be compared to the drying of a towel. Thus if the towel was dipped in water or only used to wipe a wet surface, one takes longer to dry than the other (i.e., dependence on the initial quantity of solvent). If the towel is made of cotton or synthetic fabric, again the length of time to dry will differ (i.e., dependence on the type of substrate) and finally the time to dry will not be comparable if the towel was kept in a plastic bag or hung up outside exposed to the sun and wind (i.e., dependence on the storage conditions). Also, the evaporation and diffusion of the ink solvents can be compared to a drop of perfume on a piece of paper. Over time it evaporates and spreads laterally,

Table 9
Summary of minimum requirements necessary to reach a sufficient level of confidence in the development and application of dating methods.

Minimum requirements	Purpose
Study of aging kinetics and influencing factors	Define limit of applicability of the method
Description of methodology	Achieve transparency enabling reproduction by other laboratories
Validation of methodology	Reach intra and inter-laboratory reliability
Use of a logical interpretation model	Evaluate probability of evidence given alternative hypotheses

through the paper, and into any paper above and below that may be in contact with it. This is why, whatever the ink dating method used may be, the influence of factors such as those mentioned above must be quantified and taken into account when interpreting the results. At least some reservations should be expressed on the results if these were not known (Table 9).

Furthermore, ink dating methods should be validated by determining their limit of quantification, systematic error, repeatability (within laboratory precision) and reproducibility (between laboratories precision). For the latter, communication about the method should be open to allow other laboratories to reproduce it. This step of harmonisation between laboratories is not easy, but should not be underestimated. In fact, for a question as recurrent as the one of documents dating, the necessary resources should not be an issue for forensic laboratories around the world. Ideally the technique should then be submitted to blind testing by an outside qualified laboratory on realistic samples such as is done in many other forensic disciplines. This is not a small task because preparing older realistic samples is not straightforward. However the methods seem to work for ink up to 24 months old at most. It is therefore feasible.

This last requirement for ink dating methods is an adequate and logical interpretation model taking into account the methodology's error rates, which cannot be neglected in an ethical approach. Calculations of likelihood ratios should allow for balanced answers to the court considering both the prosecution and the defence hypotheses. This will give the justice the necessary information to consider all information at hand in a global Bayesian framework.

To conclude this article, we wish to quote from Professor Michael J. Saks' recent article: "Forensic identification: From a faith-based "Science" to a scientific science" [81]:

"What can forensic scientists do while waiting for a serious body of research to evolve that illuminates their particular subfield? The short answer is: honesty and humility. Confine reports and testimony within the bounds of the empirically tested findings of the field, intelligently understood (meaning: not relying excessively on any single study of a limited aspect of a phenomenon and not overgeneralizing). If very little is based on empirically tested findings, simply say so, while stating conclusions in a way that recognizes and respects the limits of the available knowledge. What one believes or hopes about a field and what one can know on existing research are not the same. Refrain from exaggerating what actually is known at the present stage of the field's development. Remain within the bounds of actual knowledge. Abandon claims of uniqueness and absoluteness. Recognize that forensic identification is a probabilistic endeavor. Abandon the use of misleading terminology, such as "match" or "identification" or "scientific certainty." Offer descriptions and opinions with clarity and candor. Offer conclusions with modesty, unless and until a body of serious empirically based knowledge allows more. Resist the culture of exaggeration. Strive for science-based, not faith-based, forensic science".

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Exhibit 28

STANDARD OPERATING PROCEDURES

INK ANALYSIS

1. REFERENCES:

Refer to the Questioned Documents Library Reference File under the locations "Inks", "Ink", "Alteration/Obliteration" and "Ink Dating".

2. SCOPE AND BASIC PRINCIPLES:

Ink is analyzed in order to see whether it is similar to or different from other inks. This becomes important when examining a document for the presence of alterations or obliterations or to determine authentication through date.

It is rarely possible to say that ink from written material came from a particular pen. At best, ink analysis shows whether the questioned ink and a suspected source have the same composition.

The "age" of a written entry is often in question. Many approaches exist and have been shown to be reliable for the approximation of age for an ink entry. Examiners are directed to reference material, updated regularly, that can be found in the Division library. Within this material, the latest approaches along with associated procedures may be referenced. Before "new" approaches are authorized for use in USSS casework, appropriate reliability and validity studies must be conducted, with the results reviewed by the Laboratory Director. A listing of the acceptable procedural approaches is referred to in the "Comments" section of this guide.

Ink analysis includes examinations, some of which are destructive. It is always preferable to conduct the non-destructive tests first and then decide whether the additional, destructive tests will be needed. If it is decided that destructive testing should be conducted, it is essential that permission is obtained from the submitting agency and the condition of the document is recorded before the destructive testing takes place.

3. APPARATUS AND REAGENTS:

A) Stereomicroscope

B) Comparison microscope

C) VSC

D) Laser and/or alternate light sources and filters

4. SAFETY CONSIDERATIONS:

(10/08/09) *PRINT DATE*
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Refer to safety considerations outlined in the Standard Operating Procedures for the specific instruments or procedures used.

5. PROCEDURE:

A) Visually study the document using unaided vision and microscopic assistance. Use different lighting sources, including daylight. Note the apparent colors and densities.

Also note the characteristics of the type of inks used (e.g. ballpoint, felt tip, rollerball, porous tip, fountain, etc.).

B) Use the VSC to examine the inks to see if they react similarly or differently in ultraviolet and infrared illumination modes with and without filters.

C) If the examiner determines the need, use the laser or an alternate light source to examine the inks.

D) When the non-destructive examinations are completed and differences are noted in the inks, incorporate this information into a document examination or issue a report.

If at this point the inks still appear similar, make a decision whether additional, destructive testing would be helpful.

E) If a decision is made to conduct destructive examinations, record the condition of the document(s) prior to the start of the testing.

F) Conduct the required XRF, FTIR, HPLC, GC, GC/MS or TLC examination(s).
- TLC examinations provide valuable information concerning visible and invisible components of inks.
  - o For a specific guide to procedures, examiners are directed to the ASTM standards for Writing Ink Comparisons and Identification (E30.02, E1422 and E1789)
  - o Procedures for additional TLC analysis regarding ink "age" determinations can be obtained by referring to the following published articles:

Brunelle, R. L. and Pro, M. J., "A Systematic Approach to Ink Identification," Journal of Official Analytical Chemistry, Vol 55, 1972, pp.823-826.

"Status of U.S.S.S. Ink Dating Program," J.W. Hargett and L.F. Stewart. Presented at the Humboldt University, Berlin, Germany, April 2, 1993. Published in Kriminalistik und Forensische Wissenschaften, No. 82, 1994

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"The Government Response to Ink Age Determination," L.F. Stewart, J.L. Becker. Presented at the American Academy of Forensic Sciences meeting, Seattle, Washington, February 17, 1995. Published in the International Criminal Police Review - INTERPOL, Spring, 1996.

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"Distinguishing Between Relative Ink Age Determination and the Accelerated Aging Technique," L.F. Stewart and S.L. Fortunato. Published in the International Journal of Forensic Document Examiners, January/March, 1996.

"A Sketch of Analytical Methods for Document Dating Part I. The Static Approach: Determining Age Independent Analytical Profiles," A.A. Cantu. International Journal of Forensic Document Examiners 1995; 1(1):40-51.

"A Sketch of Analytical Methods for Document Dating Part II. The Dynamic Approach: Determining Age Dependent Analytical Profiles," A.A. Cantu. International Journal of Forensic Document Examiners 1996; 2(3):192-208.

- Other analytical techniques, such as XRF, FTIR, HPLC, GC and GC/MS may provide valuable information concerning the components found in inks, including solvents, surfactants, humectants and resins, which may be of use in certain situations, but are not generally necessary in performing routine ink comparisons.
- XRF can provide detailed information on the inorganic components of an ink,
    o Depending on the type of ink, decide whether to extract the ink and deposit the solute on an analysis stub or to analyze the ink in situ.
    o Procedures for XRF analysis can be obtained by referring to the following published article:

Brunelle, L. R. and Reed, R. W., Forensic Examination of Ink and Paper, Charles C Thomas, Springfield, IL 1984.

- FTIR can be useful when detailed information is necessary about an ink's organic composition,
    o Depending on the type of ink, decide whether to extract the ink and make a pellet, analyze it as a liquid, or to analyze the ink in situ.
    o Procedures for FTIR analysis can be obtained by referring to the following published articles:

Brunelle, R. L. and Pro, M. J., "A Systematic Approach to Ink Identification," Journal of Official Analytical Chemistry, Vol 55, 1972, pp.823-826.

Humecki, H., "Experiments in Ballpoint Ink Aging Using Infrared Spectroscopy," Proceedings of International Symposium on Handwriting Aspects of Questioned Document Examination, U.S. Government Printing Office, Washington, DC 1985, pp.131-135.

- HPLC has been used to gather information on batch-to-batch variation or when detailed information is necessary about and ink's organic composition,
    o Depending on the type of ink, select an appropriate solvent system.
    o Procedures for HPLC analysis can be obtained by referring to the following published article:

Lyter, A. H., "Examination of Ballpen Ink by High Pressure Liquid Chromatography," Journal of Forensic Sciences, Vol 27, 1982, pp. 154-160.

- GC and GC/MS can provide information on organic components.
    o Depending on the type of ink, determine the appropriate solvent (or solvents) necessary.

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o Procedures for GC and GC/MS analysis can be obtained by referring to the following published article:

Brunelle, R. L. and Pro, M. J., "A Systematic Approach to Ink Identification," Journal of Official Analytical Chemistry, Vol 55, 1972, pp.823-826.

"Ballpoint Ink Age Determination by Volatile Component Comparison — A Preliminary Study," L.F. Stewart. Journal of Forensic Science 1985; 30(2):405-11.

"The Identification of 2-Phenoxyethanol in Ballpoint Inks Using Gas Chromatography/Mass Spectrometry — Relevance to Ink Dating," Gerald M. LaPorte[1], M.S.F.S.; Jeffrey D. Wilson[3], B.S.; Antonio A. Cantu[2], Ph.D.; S. Amanda Mancke[3], B.S.; and Susan L. Fortunato[1], B.A. Journal of Forensic Science, January 2004 49(1).

- For additional information regarding the various instrumental procedures, refer to the specific analytical instrument's log book for instrumentation operation.

G) After all testing is completed, incorporate the results into a document examination or issue a report. Use case note work sheet for this procedure when appropriate.

6. CALCULATIONS:

Make the appropriate calculations when performing TLC for the R_f values. Note the results on the worksheet. If performing XRF, FTIR, HPLC, GC, or GC/MS, conduct the appropriate peak comparison calculations.

7. QUALITY ASSURANCE:

All quality assurance guidelines as explained in the FSD Quality Assurance Manual should be followed. Supervisory personnel as directed in the FSD Quality Assurance Manual (Section 3) should conduct technical and/or administrative reviews.

In addition, known ink samples are run on the VSC before the questioned document. Appropriate standards and calibration procedures should be utilized with the XRF, FTIR, HPLC, GC, GC/MS, and HSCI systems. The results of these tests should be maintained as notes in the case jacket. Appropriate logbook entries should be made. All notes and documentation pertaining to the examination are maintained and reviewed prior to the issuance of a report.

8. COMMENTS:

As new procedures are shown to be reliable and validated, this document will be updated.

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Exhibit 29

The Analysis of Inks Using GC/MS

The examination of writing inks using GC/MS is an analytical approach that has been utilized by a number of researchers in the field of ink chemistry over the past decade. Researchers have shown that the evaporation rate of 2-phenoxyethanol (PE), a volatile component found in some ballpoint inks, can be associated with the age of the ink. The theory that volatile components of inks decrease with time has been validated by two separate researchers (References 8 and 10 found in the LaPorte et al article). Beginning in late 2002, FSD began looking at the frequency of PE in black and blue ballpoint inks. This validation research was submitted to the Journal of Forensic Sciences and reviewed and accepted for publication in August, 2003. The research validated the use of GC/MS as an analytical approach for examining inks. Ongoing studies continue, examining the effects of paper, storage conditions, and different inks and how these interact with each other once an ink begins to age. The Canada Customs Revenue Agency is currently conducting numerous studies with respect to PE, and the USSS continues to track their results very closely. The USSS has regular meeting with CCRA to discuss the methods and further validation studies.

The current procedure for the analysis of PE has been conducted in FSD using the Agilent 6890 GC equipped with the 5973 MSD. The method is a temperature program that begins at 50^0C and ramps to 260^0C and is described in detail in the referenced LaPorte et al article. As well, a copy of the methodology is included in the GC/MS Logbook.

Based on scientific research and validation by other laboratories, the chemical analysis of volatile organic compounds can sometimes indicate that a written entry was created within one year from the time of analysis. Further research and validation is needed, to state with any certainty, that a written entry was created in a certain time interval. These studies are continuing.

Reference: LaPorte et al. The Identification of 2-Phenoxyethanol in Ballpoint Inks Using Gas Chromatography/Mass Spectrometery – Relevance to Ink Dating, Journal of Forensic Sciences, Jan. 2004, Vol. 49, No.1.

Exhibit 30

Training Requirements and Ethical Responsibilities of Forensic Scientists Performing Ink Dating Examinations

Dear Sir:

"A Critical Evaluation of Current Ink Dating Techniques" appears in this issue of the *Journal of Forensic Sciences*, Vol. 32, No. 6, Nov. 1987, pp. 1522–1536. As a necessary adjunct to the performance of these examinations, the authors wish to present certain important considerations, that is, training requirements and ethical responsibilities of forensic scientists performing ink dating examinations.

TRAINING REQUIREMENTS FOR FORENSIC SCIENTISTS PERFORMING INK DATING EXAMINATIONS

Laboratory techniques for dating inks are simple in terms of instrumentation and procedures used. However, as with most forensic science applications, a great deal of knowledge of the material (in this case ink) is required. It is essential to know how inks are made, what they consist of, and how they vary from company to company, formula to formula, and batch to batch. Experience in the manufacturing of inks is necessary to learn how ink formulations differ.

Once knowledge of inks is gained, one must become experienced in the laboratory procedures used for dating inks as well as the constraints of examining dried ink on questioned documents in micro quantities. Then there are problems associated with the effects of paper, storage conditions, and age of the ink to be examined on questioned documents.

Most of the pitfalls described in this paper using the different ink dating methods can be prevented by proper training of the forensic science examiner. This section lists guidelines for the major training requirements for forensic scientists desiring to do ink dating examinations. The purpose here is to provide useful information to the ink examiners and supervisors of ink examiners to ensure adequate training is obtained before attempting this kind of work on actual cases. The list also serves as a checklist for attorneys when they are required to conduct direct or cross examinations of experts in this field.

Minimum Training Requirements

Academic—A bachelors degree in the physical or biological sciences; the chemistry taken should include analytical chemistry, instrumental analysis, organic chemistry, and physical chemistry. This training will provide the background to understand the chemistry of ink and the analytical methodology used to examine inks.

Formal Training—A one semester course on Introduction to Questioned Document Examination. Ink dating examinations are nearly always performed on questioned documents, and they are done in conjunction with handwriting and other types of examinations performed by document analysts. This training is necessary to understand the work done by document analysts so that together the ink examiner and the document analyst can get the most information from the evidence. (An alternative could be to train under a qualified document examiner for approximately one month.)

Informal Training—Visits to each of the various types of writing ink manufacturers. This training is required to gain knowledge of ink manufacturing practices, composition of inks, quality control, frequency of formulation changes, how ink formulations records are maintained, and other information available from the ink manufacturer.

On-the-Job Training—Sufficient time of on-the-job full-time laboratory training, for example, 6 months to a year, devoted strictly to the analysis and dating of inks. This training should include the examination of at least 50 ink dating cases (practice cases, not actual investigations). Also, at least 1000 different ink formulations (including ballpoint inks and nonballpoint inks such as porous tip, rolling ball, and fountain pen inks) should be examined with thin-layer chromatography. This training will provide the knowledge needed regarding the composition of different ink formulations. Working the 50 cases will provide experience in applying the different ink dating techniques under actual case situations.

In addition, practice in the use of the following laboratory instruments should be given so the trainee can become proficient in the use of these techniques when using them on actual ink cases:

- thin-layer chromatography (TLC),
- gas chromatography (GC),
- high performance liquid chromatography (HPLC),
- Fourier transform infrared spectroscopy (FTIR),
- TLC densitometry, and
- fluorescence spectroscopy.

All of the training should be done under the supervision of a qualified forensic ink chemist.

Required Reading—The trainee should conduct a comprehensive literature search of all relevant scientific publications on ink analysis and ink dating. To gain a perspective on development in this field, articles should be studied dating from about 1900 to the present. The

trainee should become totally familiar with the articles listed as references in this letter, because these articles discuss the methods now in use. All written legal opinions involving ink analysis should be studied to gain an understanding of the court admissibility of ink dating techniques. For a complete listing of relevant references, the trainee should refer to the references cited by Brunelle and Reed [*1*].

Proficiency Testing—Forensic scientists should not attempt to examine actual criminal or civil cases until they have been tested.

Proficiency testing demonstrates the competency of the examiner's work. The testing should evaluate the accuracy of the ink identifications/ink dating examinations and the scientific soundness of conclusions reached on the basis of laboratory examinations. The trainee should be given at least ten different ink formulations written on documents to identify and date.

All of the above considerations pertain to the performance of ink dating examinations. Less requirements are needed if a forensic chemist is just performing ink comparisons for the purpose of determining differences or similarities. This still requires considerable experience in analyzing a large number of different ink formulations using at least thin-layer chromatography. Knowledge of ink making and experience with identifying inks by matching with standards is valuable for determining what is meant when two inks being compared cannot be distinguished.

ETHICAL RESPONSIBILITIES OF FORENSIC SCIENTISTS PERFORMING INK DATING EXAMINATIONS

Most professional organizations have codes of ethics that govern the professional and personal conduct of its members. Sections 1 and 2 of the Code of Ethics of the American Academy of Forensic Sciences [*2*] describe the guiding principles for its members.

A problem that exists in any discussion of ethics in the forensic sciences involves whether a forensic scientist knowingly violates acceptable conduct. In many situations it is possible that what appears to be unethical may well be lack of knowledge or incompetency of the forensic scientist.

One solution to this problem lies with the establishment of standard training requirements for forensic scientists, like those previously described. If a person has completed the standard training requirements and still gives misleading conclusions or misrepresents data, then one should probably interpret this as unethical behavior.

On the other hand, in the absence of adequate training, this same behavior could be interpreted as incompetency. This clearly suggests that there is little difference between unethical behavior and incompetency for the forensic scientist. To quote a cliche, "ignorance of the law is no excuse." Neither unethical behavior nor incompetency is acceptable in the justice system.

Using the Code of Ethics of the AAFS and their guiding principles as a reference, this section lists specific guidelines for behavior which is considered unethical with respect to ink dating examinations and conclusions.

AAFS Code of Ethics and Guiding Principles [2]

1. Every member of the AAFS shall refrain from any material misrepresentation of education, training, experience, or area of expertise.
2. Every member of AAFS shall refrain from any material misrepresentation of data upon which an expert opinion or conclusion is based.
   a. The forensic scientist should maintain his professional competency through existing programs of continuing education.
   b. The forensic scientist should render technically correct statements in all written or

oral reports, testimony, public addresses, or publications and should avoid any mis-
leading or inaccurate claims.

c. The forensic scientist should act in an impartial manner and do nothing which
would imply partisanship or any interest in a case except the proof of the facts and
their correct interpretation.

Unethical Behavior with Respect to Ink Dating Examination and Conclusions

1. Ink dating examinations, reports, and testimony on the basis of ink examinations by
forensic scientists that have not successfully completed training requirements such as those
described in this paper. Without adequate training, these actions would be unethical and in
violation of AAFS ethical guidelines. This is because without training, there is no basis for
rendering an expert opinion or conclusion. Any opinion offered would be material misrepre-
sentation of data.

2. Conclusions as to the age of ink by any technique where the accuracy, reproducibility,
and experimental error have not been scientifically established. Here, the basis for determin-
ing unethical behavior according to AAFS guidelines pertains to the requirement to render
technically correct statements in all written or oral reports or testimony and the requirement
to avoid misleading claims. If accuracy, reproducibility, and experimental error are not
known, conclusions will be misleading.

3. Conclusions on the basis of data that are within or even close to the range of experimen-
tal error of the procedure used. These conclusions would be based on misrepresentation of
data and would be technically incorrect. Conclusions of this type also suggest partisanship or
special interest in a case. All of the above violate ethical guidelines.

4. Identification of inks without one or more confirmatory tests. Since this action is con-
trary to acceptable scientific practice, it falls into the category of being technically incorrect.
It also misrepresents the significance of the results of only one test.

5. Conclusions that state or infer absolute identification of an ink formulation. Identifica-
tion of a specific ink formulation with 100% certainty is usually impossible. If an examiner
reports absolute identification without sufficient proof this is material misrepresentation of
results and a technically incorrect statement. It also implies partisanship or special interest
in a case.

6. Conclusions that state or infer the absolute age of an ink without sufficient proof. The
reasons for unethical behavior here are the same as above.

7. Testimony involving ink dating that does not clearly state the significance of results
obtained and the limitations of what can be concluded from the results of examination. The
testimony would be unethical according to AAFS guidelines because it would be misleading.

8. Conclusions made on the age of inks on different documents unless the effects of differ-
ent paper have been proven to have no effect on the age determination.

The authors are not singling out ink dating as the primary field where unethical behavior
could be or is a problem. We do believe it is important to address this as a potential problem
because the advantages and limitations of ink dating techniques are not widely known.

The guidelines for unethical behavior listed should be obvious to any professional scien-
tist. For this reason we do not suggest the guidelines are original. If nothing else, maybe
these guidelines will be memory refreshers and force ink dating chemists and other forensic
scientists to be conscious of their ethical responsibilities as professionals in this field.

References

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

[2] "Code of Ethics, Bylaws," in *Membership Directory*, American Academy of Forensic Sciences, Colorado Springs, CO, 1985, pp. 118-119.

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Exhibit 31

U. S. Department of Justice
Federal Bureau of Investigation
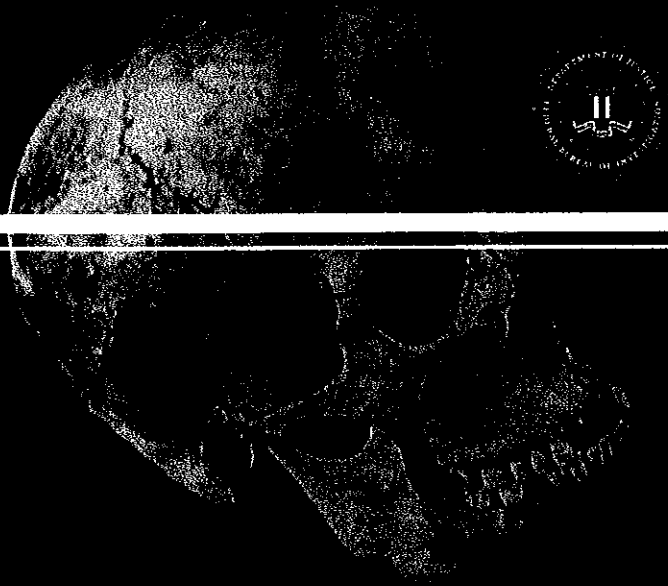*Laboratory Division*

HANDBOOK OF FORENSIC SERVICES

Handbook of Forensic Services
(revised 2007)

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- Address the outer container as follows:

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Ink Examinations

Examining inked writing in conjunction with other techniques (e.g., handwriting analysis, watermark identification) can provide details regarding document preparation. The composition of writing inks varies with the type of writing instrument (e.g., ballpoint pen, fountain pen, porous-tip pen) and the date of the ink manufacture. In general, inks are composed of dyes in solvents and other materials that impart selected characteristics. Ink analysis usually is limited to comparisons of the organic dye components. When ink formulations are the same, it is not possible to determine whether the ink originated from the same source to the exclusion of others. Examinations cannot determine how long ink has been on a document.

Questions concerning ink evidence should be directed to 703-632-8441. Follow the evidence

Exhibit 32

STRENGTHENING

FORENSIC SCIENCE

IN THE UNITED STATES

A PATH FORWARD

Committee on Identifying the Needs of the Forensic Science Community

Committee on Science, Technology, and Law
Policy and Global Affairs

Committee on Applied and Theoretical Statistics
Division on Engineering and Physical Sciences

NATIONAL RESEARCH COUNCIL
OF THE NATIONAL ACADEMIES

FUNDAMENTAL PRINCIPLES OF THE SCIENTIFIC METHOD

The scientific method presumes that events occur in consistent patterns that can be understood through careful comparison and systematic study. Knowledge is produced through a series of steps during which data are accumulated methodically, strengths and weaknesses of information are assessed, and knowledge about causal relationships is inferred. In the process, scientists also develop an understanding of the limits of that knowledge (such as the precision of the observations), the inferred nature of relationships, and key assumptions behind the inferences. Hypotheses are developed, are measured against the data, and are either supported or refuted.

Scientists continually observe, test, and modify the body of knowledge. Rather than claiming absolute truth, science approaches truth either through breakthrough discoveries or incrementally, by testing theories repeatedly. Evidence is obtained through observations and measurements conducted in the natural setting or in the laboratory. In the laboratory, scientists can control and vary the conditions in order to isolate exclusive effects and thus better understand the factors that influence certain outcomes. Typically, experiments or observations must be conducted over a broad range of conditions before the roles of specific factors, patterns, or variables can be understood. Methods to reduce errors are part of the study design, so that, for example, the size of the study is chosen to provide sufficient statistical power to draw conclusions with a high level of confidence or to understand factors that might confound results. Throughout scientific investigations, the investigator must be as free from bias as possible, and practices are put in place to detect biases (such as those from measurements, human interpretation) and to minimize their effects on conclusions.

Ultimately, the goal is to construct explanations ("theories") of phenomena that are consistent with broad scientific principles, such as the laws of thermodynamics or of natural selection. These theories, and investigations of them through experiments and observed data, are shared through conferences, publications, and collegial interactions, which push the scientist to explain his or her work clearly and which raise questions that might not have been considered. The process of sharing data and results requires careful recordkeeping, reviewed by others. In addition, the need for credibility among peers drives investigators to avoid conflicts of interest. Acceptance of the work comes as results and theories continue to hold, even under the scrutiny of peers, in an environment that encourages healthy skepticism. That scrutiny might extend to independent reproduction of the results or experiments designed to test the theory under different conditions. As credibility accrues to data and theories, they become accepted as established fact and become the "scaffolding" upon which other investigations are constructed.

This description of how science creates new theories illustrates key elements of good scientific practice: precision when defining terms, processes, context, results, and limitations; openness to new ideas, including criticism and refutation; and protections against bias and overstatement (going beyond the facts). Although these elements have been discussed here in the context of creating new methods and knowledge, the same principles hold when applying known processes or knowledge. In day-to-day forensic science work, the process of formulating and testing hypotheses is replaced with the careful preparation and analysis of samples and the interpretation of results. But that applied work, if done well, still exhibits the same hallmarks of basic science: the use of validated methods and care in following their protocols; the development of careful and adequate documentation; the avoidance of biases; and interpretation conducted within the constraints of what the science will allow.

Validation of New Methods

One particular task of science is the validation of new methods to determine their reliability under different conditions and their limitations. Such studies begin with a clear hypothesis (e.g., "new method X can reliably associate biological evidence with its source"). An unbiased experiment is designed to provide useful data about the hypothesis. Those data—measurements collected through methodical prescribed observations under well-specified and controlled conditions—are then analyzed to support or refute the hypothesis. The thresholds for supporting or refuting the hypothesis are clearly articulated before the experiment is run. The most important outcomes from such a validation study are (1) information about whether or not the method can discriminate the hypothesis from an alternative, and (2) assessments of the sources of errors and their consequences on the decisions returned by the method. These two outcomes combine to provide precision and clarity about what is meant by "reliably associate."

For a method that has not been subjected to previous extensive study, a researcher might design a broad experiment to assist in gaining knowledge about its performance under a range of conditions. Those data are then analyzed for any underlying patterns that may be useful in planning or interpreting tests that use the new method. In other situations, a process already has been formulated from existing experimental data, knowledge, and theory (e.g., "biological markers A, B, and C can be used in DNA forensic investigations to pair evidence with suspect").

To confirm the validity of a method or process for a particular purpose (e.g., for a forensic investigation), validation studies must be performed.

The International Organization for Standardization (ISO) and the International Electrotechnical Commission (IEC) developed a joint document,

(d) parameters or quantities and ranges to be determined;
(e) apparatus and equipment, including technical performance requirements;
(f) reference standards and reference materials required;
(g) environmental conditions required and any stabilization period needed;
(h) description of the procedure, including
  - affixing of identification marks, handling, transporting, storing and preparation of items;
  - checks to be made before the work is started;
  - checks that the equipment is working properly and, where required, calibration and adjustment of the equipment before each use;
  - the method of recording the observations and results;
  - any safety measures to be observed;
(i) criteria and/or requirements for approval/rejection;
(j) data to be recorded and method of analysis and presentation;
(k) the uncertainty or the procedure for estimating uncertainty.[4]

Uncertainty and Error

Scientific data and processes are subject to a variety of sources of error. For example, laboratory results and data from questionnaires are subject to measurement error, and interpretations of evidence by human observers are subject to potential biases. A key task for the scientific investigator designing and conducting a scientific study, as well as for the analyst applying a scientific method to conduct a particular analysis, is to identify as many sources of error as possible, to control or to eliminate as many as possible, and to estimate the magnitude of remaining errors so that the conclusions drawn from the study are valid. Numerical data reported in a scientific paper include not just a single value (point estimate) but also a range of plausible values (e.g., a confidence interval, or interval of uncertainty).

Measurement Error

As with all other scientific investigations, laboratory analyses conducted by forensic scientists are subject to measurement error. Such error reflects the intrinsic strengths and limitations of the particular scientific technique. For example, methods for measuring the level of blood alcohol in an individual or methods for measuring the heroin content of a sample

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[4] Quoted from Section 5.4.4 of ISO/IEC 17025, "General requirements for the competence of testing and calibration laboratories" (2nd ed., May 15, 2005).

Exhibit 33

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The potential of artificial aging for modelling of natural aging processes of ballpoint ink

Céline Weyermann, Bernhard Spengler ✉

Abstract | Full Text | PDF | Images | References

Abstract

Artificial aging has been used to reproduce natural aging processes in an accelerated pace. Questioned documents were exposed to light or high temperature in a well-defined manner in order to simulate an increased age. This may be used to study the aging processes or to date documents by reproducing their aging curve. Ink was studied especially because it is deposited on the paper when a document, such as a contract, is produced. Once on the paper, aging processes start through degradation of dyes, solvents drying and resins polymerisation. Modelling of dye's and solvent's aging was attempted. These processes, however, follow complex pathways, influenced by many factors which can be classified as three major groups: ink composition, paper type and storage conditions. The influence of these factors is such that different aging states can be obtained for an identical point in time. Storage conditions in particular are difficult to simulate, as they are dependent on environmental conditions (e.g. intensity and dose of light, temperature, air flow, humidity) and cannot be controlled in the natural aging of questioned documents. The problem therefore lies more in the variety of different conditions a questioned document might be exposed to during its natural aging, rather than in the simulation of such conditions in the laboratory.

Nevertheless, a precise modelling of natural aging curves based on artificial aging curves is obtained when performed on the same paper and ink. A standard model for aging processes of ink on paper is therefore presented that is based on a fit of aging curves to a power law of solvent concentrations as a function of time. A mathematical transformation of artificial aging curves into modelled natural aging curves results in excellent overlap with data from real natural aging processes.

Keywords: Artificial aging, Heat, Light, Ballpoint, Dyes, Solvents

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
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