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Ink Aging Testing—Do Preceding Indentation Examinations Affect Ink Aging Parameters?[1]

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This paper discusses various aspects of two ink aging methods involving the analysis of volatile ink components: the Sequential Extraction Technique (SET) and the Solvent Loss Ratio Method (SLRM). Multiple ballpoint ink writings of various ages were tested by the SET and SLRM both before and after the pages bearing the writings were examined for indented writing impressions using an electrostatic detection apparatus (ESDA). The results obtained show that the indentation examination does not cause any significant changes to the ink aging parameters that are measured by the SET and SLRM.

Introduction

Current ink aging approaches utilize analytical (chemical) methods which measure the aging processes occurring in ink on documents. When one is tasked to determine an approximate age of a handwritten entry or signature on a document, a common approach typically begins with non-destructive physical examinations including visual, microscopic, and other examinations which include, but are not limited to, the examinations of handwritten information and writing ink on the document, and the examinations of the document for indented writing impressions.

The work described herein was conducted with the aim to determine whether a preceding indentation examination can have any detrimental effect on results of subsequent ink aging analyses.

Ink Aging Methods Used

Two ink aging methods were used in this study which both analyze for the volatile ink component 2-phenoxyethanol (PE). These two methods are the Sequential Extraction Technique ("**SET**") and the Solvent Loss Ratio Method ("**SLRM**").

SET

The Sequential Extraction Technique is a version of the Percent (Extent) of Extraction Methodology developed by Dr. Antonio Cantu (Cantu and Prough 1987) and is applicable for measuring ink aging characteristics through the analysis of volatile/semi-volatile ink components. The SET is based on the same scientific theory as Dr. Cantu's method and uses the same stages of the procedure he developed and thoroughly described. What sets the SET apart is that it makes possible the application of Dr. Cantu's methodology to the analysis of volatile ink components as opposed to the components of ink dye.

The SET determines the rate, *D*%,[2] at which the resin, a component of ballpoint ink, is aging (*i.e.* thickening, hardening, setting) at the time

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[2]*D*% is not truly a rate (in the sense of a change per unit time), but rather an ink aging parameter that can be associated with a rate in that a high value implies a high (fast) rate and a low number implies a low (slow) rate. Mathematically, this ink aging parameter can be considered as the derivative of a function (*D*% is a function of the age of ink on paper) at a chosen input value that describes the best linear approximation of the function near that input value. In other words, the derivative at a point of a function (*D*%) of a single variable (age of ink) is the slope of the tangent line to the graph (the SET aging curve "ink aging parameter *D*% - age of ink") of the function at that point.

when the ink is being examined (Aginsky 1994, 1996, 1998, 2002, 2012).[3] This ink aging method is practically **mass independent.**[4] The SET has proven its reliability via multiple "blind" proficiency tests performed in 1995, 2001, and 2011 all using samples of ballpoint ink entries of differing age. The results of the 2011 outside proficiency test are considered in the "Discussion" section that follows.

For each ink aging test conducted for a particular ink on paper, several pairs of ink samples are removed and divided into two equal parts: "Sample 1" and "Sample 2". The samples are taken from ink areas where the amount of ink deposited on the paper appears uniform. Each pair of microplugs of ink on paper (one microplug —for "Sample 1" and the other – for "Sample 2") is taken from two adjacent parts of an ink line which are similar in thickness, appearance and arrangement.

Sample 2 is heated for 1 or 2 hours at 70°C while Sample 1 remains at ambient temperature.

Sample 1 is placed in a vial and extracted with 15 µL of a slowly-extracting "weak" solvent (*e.g.*, carbon tetrachloride – chloroform = 8:2 containing internal standard – deuterated PE, 0.5 ng/µL). Approximately 1 µL of the extract is analyzed by Gas Chromatography-Mass Spectrometry-Selective Ion Monitoring (GC-MS-SIM), specifically for ion fragments (molecular ions) of PE and its deuterated internal standard. The sample is then removed from the vial, dried for approximately 5 minutes at ambient temperature, placed into a second vial, and extracted with 15 µL of a fast-extracting "strong" solvent (chloroform, also containing internal standard). Approximately 1 µL of the second extract is analyzed by GC-MS-SIM using the same instrumental method as the first. The mass of PE in each extract (M_{weak} and M_{strong}) is calculated by means of the internal standard method, and the percent of the mass of PE extracted in the weak solvent (*%E*) is calculated using *Equation 1*:

$$\%E = 100 \times [M_{weak}/(M_{weak} + M_{strong})] \qquad \text{(Eq. 1)}$$

Sample 2 is analyzed using the same procedure as for Sample 1 in order to determine the percent of extraction of PE in the weak solvent after heating ($\%E_T$). The distance (*D%*) between the values *%E* and $\%E_T$ is calculated as follows:

$$D\% = \%E - \%E_T \qquad \text{(Eq. 2)}$$

As ballpoint ink ages on a document, the value of *D%* gradually decreases down to zero during a certain period of time, the length of which mainly depends on the ink's composition and the conditions under which the document is stored. For ballpoint inks under normal environmental conditions, this period of time ranges approximately from as few as 6 months to as long as 2 years.

To establish a time frame within which a questioned entry was written, the value of *D%* obtained for the ink analyzed is compared with the set of quantitative criteria/threshold values, $\mathbf{D_{THD}(\%)}$. Each of these threshold values has been predetermined by analyzing a representative set of ballpoint inks of different formulas stored at normal conditions on different paper:

- **The 8-month threshold, $D_{THD\text{-}8}(\%) = 12\%$,** was determined as a result of the analysis of 50 eight-month old entries written with ballpoint inks of different formulations.
- **The 12-month threshold, $D_{THD\text{-}12}(\%) = 8\%$,** was determined as a result of the analysis of 30 one-year old entries written with ballpoint inks of different formulations.
- **The 24-month threshold, $D_{THD\text{-}24}(\%) = 4\%$,** was determined as a result of the analysis of 30 two-year old entries written with ballpoint inks of different formulations (Aginsky 2002).

[3]In the 2002 paper (Aginsky 2002), the mechanism of thickening/setting/hardening of the resin(s) as the ink ages was described as follows: "*Hardening ('solidifying') of ink resins is a complex physical and chemical age-transforming process that can include crosslinking, polymerization, decreasing of intermolecular distances (this leads to decrease of solubility) due to solvent evaporation, and so forth.*" It should be noted that no matter which of the above physical and/or chemical age-transforming processes dominate for an aging (on paper) ballpoint ink, the result of the aging of the ink will be a measurable decrease of the extractability of volatile ink components (such as PE) from the thicken(ed)ing/harden(ed)ing "**matrix**," the major (with regard to ink aging) component of which is the **resin** of the ink.

[4]As the SET calculates mass invariant ratios for both unheated and heated ink samples (see Equation 1 that follows), this ink aging method is practically independent of the amount of ink sampled, and thus it is not required that both the heated and unheated samples have the same or nearly the same amount of ink.

If the value of *D*% obtained for the ink analyzed *exceeds* one of the above thresholds, it demonstrates that the ink is *younger* than the age corresponding with this threshold, *e.g.*:

a. If the value of D% obtained for the ink analyzed exceeds the 8-month threshold, $D_{THD\text{-}8}$(%) = 12%, then it shows that the writing (written with this ink) has been produced within 8 months preceding the date of the analysis;
b. If the value of D% obtained for the ink analyzed exceeds the 12-month threshold, $D_{THD\text{-}12}$(%) = 8%, then it shows that the writing has been produced within one year preceding the date of the analysis;
c. If the value of D% obtained for the ink analyzed exceeds the 24-month threshold $D_{THD\text{-}24}$(%) = 4%, then it shows that the writing has been produced within two years preceding the date of the analysis.

SLRM

The Solvent Loss Ratio Method of ink aging determines the rate, *R*%,[5] at which the volatile component content of ink is decreasing at the time of analysis. This method was first reported as an ink aging method that measures the "*decrease in the evaporation rate (R%) of ink volatile components due to aging*" (Aginsky 1996) and then as the SLRM (Gaudreau and Brazeau 2002, Gaudreau and Aginsky 2010).

When the SLRM is used to evaluate the age of ink, several pairs of microplugs of ink on paper are removed, as described for the SET above (*i.e.*, two equal and adjacent microplugs are removed from a uniform ink line: one microplug—for "Sample 1" and the other—for "Sample 2"). As opposed to the SET, the SLRM is inherently **mass dependent** (not mass invariant),[6] and it is therefore critical that the sampling procedure should minimize sample size variation. To meet this requirement, care must be taken to assure that each pair of microplugs of ink on paper is removed from adjacent parts of an ink line which are similar in thickness (degree of pressure), appearance and arrangement (distribution) of ink. It is important to stress that the microplugs of ink on paper should not be taken close to or from the points of crossing of ink lines and from the areas of ink lines which are close to other ink lines (written with the same or a different ink).

Sample 2 is heated for 1 or 2 hours at 70°C (a certain portion of PE contained in the "Sample 2" ink will evaporate during this process) and Sample 1 remains "as is". Then, following solvent extraction (using a fast-extracting "strong" solvent), the amounts of PE extracted from Sample 1 (P) and Sample 2 (P_T) are determined using the GC-MS-SIM, and the value of *R*% characterizing the solvent loss ratio is calculated as follows:

$$R\% = 100 \times [(P - P_T) / P] \qquad \text{(Eq. 3)}$$

The following two "broad time thresholds" for evaluating the actual age of ink on paper using the SLRM were reported in 2002: if the value of *R*% is larger than 50%, then the age of the ink is less than 5 months, and if the value of *R*% is larger than 25%, then the age of the ink on paper is less than 10 months (Gaudreau and Brazeau 2002). In 2010, the latter threshold was abandoned (as it had shown false-positive

[5]*R*% is not truly a rate (in the sense of a change per unit time), but rather an ink aging parameter that can be associated with a rate in that a high value implies a high (fast) rate and a low number implies a low (slow) rate. Mathematically, this ink aging parameter can be considered as the derivative of a function (*R*% is a function of the age of ink on paper) at a chosen input value that describes the best linear approximation of the function near that input value. In other words, the derivative at a point of a function (*R*%) of a single variable (age of ink) is the slope of the tangent line to the graph (the SLRM aging curve "ink aging parameter *R*% - age of ink") of the function at that point.

[6]Unlike the (mass independent) SET, the SLRM does not calculate mass invariant ratios for both unheated and heated ink samples. That is, the SLRM does not compare mass independent relative values (ratios), and instead it compares mass dependent absolute values – the contents of PE in the unheated and heated ink samples.

[7]Marc Gaudreau provided this author with pertinent experimental data in 2010 (Gaudreau 2010). The review of those experimental data has shown that if one were to apply the 25% threshold to the data (*R*% values obtained for ballpoint inks tested), then multiple inks not only older than 10 months, but sufficiently older than 2 years exhibited false-positive results (*i.e.*, the inks older than 2 years produced *R*% significantly larger than 25%, which led to the erroneous, false-positive conclusions that the corresponding inks tested were younger than 10 months).

results[7]) and revised to an *R*% value larger than 35% indicating the age of the ink to be less than 18 months (Gaudreau and Aginsky 2010). It should be noted that neither the experimental data (ink aging curves and/or numerical data) nor the statistical evaluation relating it to any of the claimed SLRM thresholds have been published to date in a peer-reviewed article or even a conference paper. Additionally, the SLRM has yet to be subjected to outside proficiency testing to determine its error rate.[8] Finally, the scope of applicability of the SLRM has recently become a matter of considerable controversy, discussed further in the next section reviewing pertinent publications relating to the SLRM.

Pertinent Publications regarding the Solvent Loss Ratio Method

In a number of recent civil cases, some ink chemists have claimed in written reports that the ink aging parameter *R*%, measured by the SLRM, may correlate with the age of ballpoint ink on paper within *up to 2 years* after the ink was placed on paper. Such claims have yet to be substantiated by any published experimental data. Moreover, these claims contradict multiple publications containing pertinent experimental data clearly demonstrating that, at normal storage conditions, the aging processes which the SLRM measures cease within *less than 6 months* after a placement of any ballpoint ink on paper (in total, hundreds different ballpoint inks have been tested).

These publications are listed chronologically in Table 1.

Table 1. Peer-reviewed articles and published (in conference proceedings) papers relating to the Solvent Loss Ratio Method (SLRM) (listed in chronological succession)

Year	Author(s)	Reported scope of applicability	Information directly relating to the SLRM in the publication
1996	Aginsky	Several months	The SLRM was first published. It was described as a method for "*Dating Inks by Evaluating Decrease of the Evaporation Rate [R%] of Ink's Vehicle Solvents Due to Aging*." (Aginsky 1996) For a Senator (Germany) black ballpoint ink tested, the aging curve "*R*% - age of ink" leveled off within **less than 6 months** after the ink was placed on paper. When considering the scope of applicability of the SLRM it was stressed that the method is "*effective to discriminate between fresh (age is **up to several months**) and old inks [about one year old or older]*." (Aginsky 1996)
2002	Aginsky	6 months	This conference paper reviewed the state of the art in the area of ink aging analysis in 2002 and, in particular, reported that, "*The vehicle-to-dye ratio method [and the] **ink dating method that evaluates decrease in the evaporation rate of ink volatile components as a function of the ink age** [i.e., the **SLRM**] allow one to obtain a good correlation between the ink aging parameter measured and the actual age of ink for a period of time comprising **up to six months** after the ink has been placed on paper (document)*." (Aginsky 2002)
2002	Gaudreau and Brazeau	10 months	This conference paper reported the following two "broad time thresholds" for evaluating the actual age of ink on paper using the SLRM: 1. if the value of *R*% is larger than 50%, then the age of the ink is less than 5 months, and 2. if the value of *R*% is larger than 25%, then the age of the ink on paper is less than 10 months (Gaudreau and Brazeau 2002). No aging curves and/or corresponding numerical data were reported in (Gaudreau and Brazeau 2002) (or in any other paper/article published thereafter) that would show that the ink aging parameter *R*% was correlating with the age of a particular ink(s) during a timeframe *as long as 10 months* (*i.e.*, that the decrease of *R*% with the age of ink was statistically valid during up to 10 months after the ink's placement on paper).
2003	Andrasko	4 to 6 months	A modified SLRM (involving a different sample preparation—solidphase microextraction) was reported as being able to "*reveal if an ink is fresh (4–6 months old at most)*" (Andrasko 2003). Andrasko 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 (Weyermann et al. 2011, p. 56).

[8]For these reasons, since its first publication in 1996, this author has never used the SLRM solely in his casework and has been using the SLRM only in combination with (and as a subsidiary method to) the SET.

Table 1. *(continued)*

Year	Author(s)	Reported scope of applicability	Information directly relating to the SLRM in the publication
2006	Wang et al.	3 months	The study of **74** different blue ballpoint ink formulations ("*of domestic and international origins*") (Wang 2005, 2006) was a continuation of the previous similar studies published in (Bezhanishvili et al. 1990) and (Aginsky 1993). Writing samples were produced every 2 weeks for 10 months. This ink aging method uses gas chromatography to measure the amount of phenoxyethanol (PE) and/or benzyl alcohol extracted from a sample of ink on paper (using acetonitrile with 2-cresol as an internal standard) and spectrophotometry to measure the amount of phthalocyanine or triarylmethane dyes extracted from the same ink sample. For each of the 74 inks tested, the PE/dye ratio was decreasing with the age of ink, and **the aging curve leveled off within three (3) months after the ink was placed on paper**. To make sure that results were repeatable, each test was repeated 5 times. Based of the results obtained, Wang et al. concluded that this ink aging method can only be used for determining the approximate age of ballpoint ink on document if the actual age of the writing is ***less than 3 months***.
2008	Bügler et al.	*Improved SLRM:* 6 months	Bügler et al. have developed an improved (*mass independent*) version of the SLRM, in which a two-step thermo desorption of PE (first at a low temperature and then at a high temperature) is used instead of a liquid extraction of PE (Bügler et al. 2008). The improved SLRM uses elevated temperatures to "extract" PE from the *same* (that is why the improved SLRM is mass independent) ink sample—first a moderate temperature, such as 70^0C, and finally a high, "all-extracting," temperature, such as 200^0C, while the parent SLRM uses an extracting solvent to extract PE from two (*different*) ink samples, one of which is then heated at 70^0C to determine a PE loss during the heating process. As two ink samples, *A* and *B*, will typically contain *different* amounts of PE, the parent SLRM is *a priori* mass dependent (*i.e.*, its ink aging results depend not only on the age of the ink but also on an inevitable and unknown to the examiner difference between PE contents in samples *A* and *B*), and thus it is less reliable than the improved, mass independent SLRM. Bügler et al. established that "*fresh ink releases a relative amount of solvent at a certain low temperature in a defined period of time, which decreases as the ink ages. As a consequence, this relative amount of solvent [PE] released at a certain low temperature, and its decrease with time, can be used [as an age-dependent parameter] to estimate ink age. This age-dependent parameter was studied in* ***85 different inks ranging in age from 1 week to 1.5 years****. It was found that some [****slow aging****] inks showed a significant decrease of this parameter* ***up to an age of several months****, and that the aging process can be monitored within this period*" (Bügler et al. 2008). "*[A low] desorption temperature [T = 70^0C] seemed to be best suited to differentiate between fresh and old ink entries. Herein, 'fresh' means less than 3 month, and* ***'old' means more than 6 months***." Bügler et al. conclude the article as follows: "*Practical casework confirmed that the dating procedure described herein can be applied to ink entries with a* ***maximum age of several months***" (Bügler et al. 2008).
2010	Gaudreau and Aginsky	18 months	In 2010, the above 25%-threshold, which was reported in (Gaudreau and Brazeau 2002) and used to determine whether ballpoint ink on paper is less then 10 months old, was abandoned (as it showed multiple false-positive results) and revised to an "*R% value larger than 35% indicating the age of the ink to be less than 18 months*" (Gaudreau and Aginsky 2010). However, no aging curves or numerical data were reported in the 2010 paper that would show that the ink aging parameter *R*% correlated with the age of a ballpoint ink(s) during a timeframe *as long as 18 months* (*i.e.*, that the decrease of *R*% with the age of ink was statistically valid during up to 18 months after the ink's placement on paper). Furthermore, a recent evaluation of unpublished experimental data (provided to this author by Marc Gaudreau in 2010) showed that, even if one were to use this new (revised) 35% threshold, multiple false-positive results were obtained for ink samples known to be older than both 18 months and 2 years.

Table 1. *(continued)*

Year	Author(s)	Reported scope of applicability	Information directly relating to the SLRM in the publication
2011	Weyermann, Bügler, Cantu, Almog	Outside proficiency testing using "blind" ink samples is necessary to test the validity of current ink aging methods	This article reviews the state of the art in the area of ink aging analysis and stresses as follows: – "*there is a serious need for outside proficiency testing of current ink dating methods*," and – "*the time span that can be considered to date inks through solvent analysis using GC/MS is seriously questioned in the forensic community […] Bügler et al. recommended to analyze ink with a* ***maximum age of 3–4 months*** (Bügler et al. 2006). ***The feasibility of such dating techniques on ink older than that must therefore be demonstrated.***" (Weyermann et al. 2011) [Emphases added] It should be noted that, as of present, no experimental data and/or results of outside proficiency testing have yet been published that would show that the ink aging parameter *R%* measured by the SLRM correlates with the age of a ballpoint ink on paper *after* the ink reaches the above age of "*3-4 months*."
2012	Kirsch et al.	3.5 months	The study was a further development of the previous works (Bezhanishvili et al. 1990, Aginsky 1993, and Wang et al. 2005, 2006). This ink aging method was based on using high performance liquid chromatography (HPLC) to measure the amount of PE (fluorescence at 310 nm) and triarylmethane dyes (absorbance at 580 nm). The decrease of the PE/dye ratio with the age of ink was evaluated using Neumann trend tests. For all inks tested, including "Medium Aging" Ink #2 (see Table 2 that follows), the **aging curves leveled off within 3.5 months**. (Kirsch et al. 2012)
2012	Bügler	6 months	The application of the above improved (mass independent) version of the SLRM to **80** different ballpoint inks showed significant variations in slopes of aging curves between different inks. The aging curves obtained for **slow aging inks** leveled off after ***ca.* 4 months**. Bügler states that the "*method is* ***applicable if*** *ink is* ***not older than a few months***" and that the only scientifically sound conclusion in an ink aging case (when using this improved version of the SLRM) is either "***Ink fresher than 6 months***" or "*Case is Inconclusive*." (Bügler 2012)
2012	Koenig and Weyermann	< 2 months	The aging of the three inks, Cat. Numbers 1892 (ink #1), 1688 (ink #2) and 1774 (ink #3), which represent fast, medium and slow aging ballpoint inks, respectively (in Table 2 below, these inks are listed as inks 1, 2 and 3, respectively), was studied using the procedure for the SLRM described in (Gaudreau and Brazeau 2002). Writing samples with known dates of preparation were produced using strong, medium and weak writing pressure (350 grams, 250 grams, and 100 grams, respectively). In addition, different storage conditions were tested by keeping the writing samples 1) at normal laboratory environmental conditions, and 2) in a climatic chamber. It was found that the ink aging parameter *R%* depends not only on the age of ink but also on the writing pressure: **R% significantly increased with increased writing pressure** (*i.e.*, with increased amount of ink deposited by the ballpoint pen on paper) (Koenig and Weyermann 2012). It means that if two entries, *A* and *B*, were written on the same day and with the ink of the same composition, they may nevertheless produce significantly different *R%* values, *e.g.*, in any of the following two cases: – If both entries were written with the same pen, but entry *A* was written with a higher pen pressure than entry *B*, the results of the SLRM may show that entry *A* was significantly "younger" than entry *B*; and – If both entries were written with the ink of the same composition and similar pen pressure, but entry *A* was written with a Medium Point pen (deposited *more* ink within the confines of ink lines on paper) and entry *B* was written with a Fine Point pen (deposited *less* ink within the confines of ink lines on paper), the results of the SLRM may show that entry *A* was significantly "younger" than entry *B*. Besides, Koenig and Weyermann determined, for each of the above three inks tested, a timeframe during which the ink aging parameter *R%* was correlating with the age of the ink (that is, the timeframe during which the decreasing of *R%* with the age of ink was statistically valid). These timeframes were as follows: Ink #1 (**fast** aging ink): practically **zero** (*R%* does not correlate with the ink's age at all) Ink #2 (**medium** aging ink): **19 days** Ink #3 (**slow** aging ink): **48 days** (Koenig and Weyermann 2012).

Methods and Materials

Inks

Ballpoint inks examined in this work are listed in Table 2. These inks had been selected for preparing writing samples (each with a known date of preparation) for this research because practically all of them are ubiquitous and thus frequently examined in forensic document examination cases.

Indentation Examinations

A Foster & Freeman electrostatic detection apparatus ESDA-2 was used in this study. A sheet of paper bearing a particular writing sample,

Table 2. Ballpoint inks examined in this work

Ink #	Description (pertinent information on cartridge, barrel of the pen, etc.)
1	"Fast Aging" black ballpoint ink (Cat. No. 1892)*
2	"Medium Aging" black ballpoint ink (Cat. No. 1688)*
3	"Slow Aging" blue ballpoint ink (Cat. No. 1774)*
4	ZEBRA black ballpoint ink (Z-Grip pen, Med. Pt., made in China)
5	BIC black ballpoint ink (4-color pen, Med. Pt., made in France)
6	BIC black ballpoint ink (refill, Med. Pt., made in Mexico)
7	PILOT black ballpoint ink (refill, Med. Pt., made in Japan)
8	PENTEL black ballpoint ink (refill, Med. Pt., made in Japan)
9	AVERY black ballpoint ink (refill, Med. Pt., made in Korea)
10	UNI-BALL black rollerball ink (refill, bold – 1.0 mm, made in Japan)
11	BIC black ballpoint ink (Bic ATLANTIS, made in France)
12	BIC black ballpoint ink (Bic SOFT Feel, Med. Pt., made in U.S.A.)
13	BIC black ballpoint ink (Bic JOYAS)
14	PARKER black ballpoint ink (refill, Med. Pt., made in U.K.)
15	LAMY black ballpoint ink (refill, broad, made in Germany)

*Three inks marked with the asterisk in Table 2 (inks # 1, 2 and 3) were in ballpoint pen refills (cartridges) sent to this author by the European Document Experts Working Group (EDEWG) chairperson Jürgen H. Bügler, Ph.D. Dr. Bügler and his colleagues, Huns Buchner, Ph.D., and Anton Dallmayer, Ph.D., at the Institute of Forensic Sciences (Bavarian State Bureau of Investigation, Munich, Germany) had researched the aging of a representative set of ballpoint inks of different formulations, and as a result of that research, they have determined that the above three inks represent fast, medium and slow aging ballpoint inks, respectively. Since then, all of the three inks have been subjected to an extensive inter-laboratory EDEWG research project entitled "*Ink Dating*." It should be noted also that these three inks were manufactured by large ink manufacturers in Europe and North America, and therefore each of these three inks can be found in numerous pens bearing different brand names. For example, at the level of TLC analysis, Ink #2 matches[9] black ballpoint ink(s) used in pens of numerous pen companies, such as: Parker (UK); Pentel (USA); Papermate (France); Cartier, Dunhill, Dupont, Faber Castel, Hauser, Lamy, Montblanc, Waterman, Schmidt, Pelikan (all Germany); Montegrappa (Italy); Caran d'Ache (Switzerland); and Penatia (Cross, China).

[9]In the event that two inks contain colorant components that separate and migrate practically identically on a TLC plate(s), the inks are then considered to "match" each other as per the *Standard for Test Methods for Forensic Writing Ink Comparison,* which is published and endorsed by the Scientific Working Group for Forensic Document Examiners (SWGDOC) (http://www.swgdoc.org/index.php/standards/published-standards). It should be noted that "match" does not necessarily imply that the two inks are of the same formula – there are other chemicals in ink that are not detectable by TLC. In this connection, it is important to stress that unless an ink has a unique component or combination of dye components (that may result in a high level "match" of two ink samples), a TLC chromatographic (low level) "match" simply shows the "similarity" of two inks. This shows a weakness and vagueness of the term "match" as such a low level "match," showing merely a similarity between two ink samples, may well be erroneously interpreted by a layperson as an "identification," or as "identical ink," or the "same ink." (A further discussion of this important for forensic ink analysis topic goes beyond the subject of this paper and will be addressed elsewhere.)

which was chosen to be tested, was cut into two parts, A and B. Part A remained untreated, and Part B was humidified for about 30 minutes in a hygrostatically controlled laboratory (small room) at approximately 65% RH[10]—the level of relative humidity in the laboratory maintained during all experiments conducted using ESDA in this work (controlled by an RS digital thermo-hygrometer). Part B was then placed on the document platen with a working vacuum pump and kept there for 1 minute, after which it was covered with a transparent imaging film and "vacuumed" for an additional 7 minutes. After the vacuum was turned off, the Part B document was turned over on the document platen, and the above steps of the procedure repeated.

Writing samples

Some writing samples were prepared over a span of several years. Within the last year preceding the beginning of this study writing samples were prepared every month (some samples—every week) using each of the above 15 pens. The writing samples consisted mainly of horizontal lines each written with approximately the same pen pressure (in order to avoid, as much as possible, variations along each written line in the amount of ink deposited on paper[11]). Writing samples with varying pen pressure were also prepared. They included repetitions of the overlapping numerals "0," ovals, crossed horizontal and diagonal lines, and handwritten notations that related to the make and model of the pen and/or ink cartridge. Each writing sample typically occupied 20 to 30% of a letter-sized sheet of white paper.

Paper

Most writing samples in this study were prepared on OfficeMax laser paper (96 brightness, 24 lb weight, manufactured in USA). Some writing samples were prepared on paper samples of various types.

Sampling Device

The Harris Micro-Punch™ (Electron Microscopy Sciences, Hatfield, PA), a hypodermic needle-like device which removes *ca.* 0.5-mm and 0.75-mm samples (micro plugs) of ink on paper. The bored out ink samples were removed with a plunger. For every ink aging test using the SLRM, 10 pairs of ink samples (circular discs of *ca*. 0.5 millimeter in diameter) were taken from ink strokes in accordance with published recommendations (Aginsky 1996, Gaudreau and Brazeau 2002, Gaudreau and Aginsky 2010). In addition, for some inks, the aging of which was tested using the SET, five pairs of ink samples (circular discs of *ca*. 0.75 millimeter in diameter) were also taken from ink lines.

Extracting Vessels

0.1-mL 986281 Wheaton vials with conical interior and screw caps.

GC Conditions and MS parameters

Ink extracts were obtained (see section "*Ink Aging Methods Used*" above) and analyzed using an Agilent 6850 gas chromatograph equipped with a split/splitless injection system interfaced with an Agilent 5975C mass selective detector.

Other hardware and parameters of the GC-MS analyses were as follows:

Column: DB-5MS UI, 30 m × 0.25 mm ID × 0.25-micrometer film thickness (cross-linked 5%-phenyl-95%-dimethylpolysiloxane)
Ultra inert inlet liner: splitless, single-taper, deactivated glass wool
Carrier: Helium (column flow 1 mL/min)
Oven program: Isothermal for 1.2 min at 35°C, program 15°C/min to 270°C and hold for 10 min
Injection: *ca.* 1 µL, pulsed splitless, T=260°C
Pressure pulse: 120 kPa until 1.2 min
Purge flow to split vent: 30 mL/min at 1.2 min
GC/MS transfer line: 280°C
Tune: autotune
Scan range: 45 - 450 atomic mass units (amu)
SIM mode: detector set to monitor molecular ions of PE (138 amu) and deuterated PE (140 amu)

[10]As recommended in (D'Andrea et al. 1996).
[11]This was done deliberately to create more reproducible data (less dependent on the inevitable variations in the amount of ink and thus in the levels of PE between microplugs taken from ink lines) when the inks on paper were examined using the mass dependent SLRM.

Table 3. Scope of applicability of the SLRM for 15 ballpoint inks (BPI) examined in this work

Ink #	Description of Ink	How long a trend (a statistically valid decrease of R% as ink ages on paper) can be detected
1	"Fast Aging" black BPI	< 1 day
2	"Medium Aging" black BPI	ca. 3 weeks
3	"Slow Aging" blue BPI	< 2 months
4	ZEBRA black BPI (China)	ca. 1.5 months
5	BIC black BPI (France)	< 3 months
6	BIC black BPI (Mexico)	< 3 months
7	PILOT black BPI (Japan)	ca. 1 month
8	PENTEL black BPI (Japan)	< 1 month
9	AVERY black BPI (Korea)	< 1 month
10	UNI-BALL black rollerball ink (Japan)	< 1 month
11	BIC black BPI (France)	< 3 months
12	BIC black BPI (U.S.A.)	< 3 months
13	BIC black BPI ("JOYAS")	< 3 months
14	PARKER black BPI (U.K.)	< 1 month
15	LAMY black BPI (Germany)	< 1 month

Table 4. SLRM results obtained for six slow aging (#3, 5, 6, 11-13) and three other inks before and after indentation examinations using ESDA-2

Ink: "age"	Before ESDA			After ESDA		
	PE content, ng per 1-cm ink line		R%	PE content, ng per 1-cm ink line		R%
	Unheated	Heated		Unheated	Heated	
Ink #3:						
28 days	47.5	32.9	31	38.2	27.1	29
2.5 months	27.6	23.6	14	28.9	22.8	21
Ink #4:						
1.5 months	79.1	49.2	38	84.9	56.1	34
Ink #5:						
7 days	244.8	128.3	48	229.3	129.1	44
1.5 months	231.2	137.1	41	214.6	120.8	44
2.5 months	123.2	89.7	27	134.3	95.5	29
4 months	174.5	136.5	22	151.7	115.3	24
6 years	67.4	51.9	23	60.8	50.0	18
Ink #6:						
7 days	244.7	141.9	42	214.4	138.5	35
1.5 months	193.9	127.0	34	186.5	116.0	38
2.5 months	126.8	96.4	24	116.7	86.3	26
4 months	149.4	116.5	22	161.9	134.0	17
6 years	81.6	69.5	15	73.5	64.3	13
Ink #7:						
28 days	19.2	14.7	24	17.9	14.0	22
Ink #8:						
28 days	11.1	9.3	16	N/A	N/A	N/A
Ink #11:						
4 years	50.6	41.9	17	62.3	48.6	22
7 years*	67.0	41.3	38	79.8	60.0	25
Ink #12:						
4 years	95.7	82.2	14	79.8	64.1	20
7 years*	83.8	59.5	29	N/A	N/A	N/A
Ink #13:						
4 years	111.9	81.8	27	97.0	76.9	21
7 years*	90.5	59.0	35	N/A	N/A	N/A

*For the 7-year old handwritten entries (marked with the asterisk in Table 4), all pairs of ink samples were deliberately taken from curved portions of ink strokes and from the areas of ink lines which were close to the points of crossing of ink lines.

Results

Preliminary Ink Aging Tests

Prior to conducting a study to determine whether preceding indentation examinations do or do not cause any significant changes to the ink aging parameters that are measured by the SET and SLRM, the above 15 inks were initially examined using SLRM (some of the inks were also examined using SET, which is a significantly more time-consuming ink aging method than SLRM). The purposes of the initial ink aging examinations were as follows:

a. To determine, for each ink, a time frame during which the ink will cease aging (so that the indentation examination could be applied mainly to inks on paper that are still aging at a measurable rate); and
b. Based on the ink aging results obtained, to choose best candidates, from the above 15 inks, for a subsequent indentation examination.

The results of the ink aging examinations of the 15 inks using the SLRM are shown in Table 3.

Ink Aging Tests conducted before and after Indentation Examinations

Some of the above slow aging inks were further tested to determine whether preceding indentation examinations could cause any significant changes to the ink aging parameter *R*% that is measured by the SLRM. The results of the tests are listed in Table 4.

The results of the ink aging examinations of Ink #2 ("Medium Aging" black BPI) using both SLRM and SET are shown in Table 5.

Discussion

The data indicated in Tables 4 and 5 show that the ink aging parameters *R*% and *D*% measured by the Sequential Extraction Technique (SET) and Solvent Loss Ratio Method (SLRM), respectively, were not significantly affected by preceding indentation examinations.

Other findings of this study relate to the scopes of applicability of the SLRM and SET for evaluating the age of ink on documents. In particular,

Table 5. SLRM and SET results obtained for known dated entries written with Ink #2 ("Medium Aging" ink) before and after the writing samples were examined using ESDA-2

Age of Ink	Ink Aging Method				
	SLRM		SET		
	R% Before ESDA	Aging	D% Before ESDA	D% After ESDA	Aging
2.5 months	11,* 22, 25*	No	11.8, 12.5	11.6	Yes
4 months	15,* 22,* 23	No	8.5, 9.7	9.5	Yes
7 months	18,* 20, 23*	No	6.7, 7.2	6.4	Yes
9 months	6,* 12,* 14	No	4.7, 5.4	5.1	Yes
11 months	12,* 20,* 21	No	0.9, 2.1	N/A	No

NOTE: For each known dated entry listed in Table 5, first *two* SET tests were conducted *before* the entry was examined using ESDA (see column "*D*% Before ESDA") and then *one* SET test was conducted (except for the 11-month old entry, the ink of which had ceased aging) *after* the entry had been examined using ESDA (see column "*D*% After ESDA"). Finally, for each known dated entry, *one* SLRM test (one-step extraction procedure) was conducted before the entry was examined using ESDA (see the *R*% values without asterisks in the column "*R*% Before ESDA").

*The *R*% values indicated with the asterisks in Table 5 were calculated from the raw numerical data when testing ink samples using the SET[12] (*i.e.*, for each known dated entry, the abovementioned two ink aging tests were conducted using the two-step extraction procedure for the SET and then, based on the raw numerical data obtained, both *D*% [see column "*D*% Before ESDA"] and *R*% [see the *R*% values indicated with the asterisks in the column "*R*% Before ESDA"] ink aging parameters were calculated). As mentioned above, the *R*% values without the asterisks were calculated when testing ink samples using the one-step extraction procedure of the SLRM (see column "*R*% Before ESDA").

[12]Note, *e.g.*, that *P* in Eq. 3 is equal to (M_{weak} + M_{strong}) in Eq. 1 (see above).

Table 3 shows the ink aging results obtained for the 15 inks using the SLRM. These results show that the ink aging parameter *R%*, measured by the SLRM, correlates with the age of the inks within a rather short timeframe which proved to be less than 3 months, even for the slow aging ballpoint inks designated in this research as inks # 3, 5, 6, 11, 12, and 13.

Such a very limited scope of applicability of the SLRM for the 15 inks tested in this work is a somewhat unexpected result, especially when taking into consideration that all these inks are ubiquitous and almost half (40%) of them represent **slow** aging ballpoint inks. At the same time, it should be noted that such a result is in agreement with all pertinent experimental data and conclusions of multiple articles and conference papers considered in Table 1 above, including the conclusions that the ink aging methods that measure the rate of evaporation of PE as a function of the age of ink (and the SLRM is one of such methods) are only applicable to rather "fresh" inks on paper, specifically to inks the age of which do not exceed 6 months.

Based on the results obtained in this research and corresponding results obtained in the above works considered in Table 1, it seems that the maximum scope of applicability of the SLRM to evaluate the age of ink cannot exceed the above 6-month timeframe. In other words, in casework, it could only be meaningful to use the SLRM if there is a possibility that a questioned entry(s) could have been written within 6 months preceding the date of its ink aging examination.

Table 5 shows the SLRM and SET results obtained for Ink #2, which was considered "medium" aging ink in the EDEWG research project "*Ink Dating*" mentioned above. The ink aging results listed in Table 5 are for the writing samples which were from 2.5-months to 11-months old. The *R%* parameter measured by the SLRM showed no indication of aging for any of these entries. The *D%* parameter measured by the SET showed that the ink (on paper) ceased aging prior to reaching the 11-month old age. The SET aging curve "*ink aging parameter D% – age of ink*" built for Ink #2 leveled off when the age of the ink reached approximately *10 months*. The SLRM aging curve "*ink aging parameter R% – age of ink*" built for Ink #2 leveled off when the age of the ink reached approximately *3 weeks* (see Table 3 above).

The data in Tables 3 and 5 illustrate what this author has been observing during the last 18 years when both researching and examining (in casework) the aging of ballpoint ink using the SET and SLRM (as noted in the footnote to Table 5 above, the parameter *R%* was typically calculated using raw numerical data obtained when testing ink samples using the SET), namely, that the SET is significantly superior than the SLRM in determining the age of ink on documents.

One of the main reasons for this (in addition to the one, considered in section "*Ink Aging Methods Used*" above, that the SET is mass independent, while the SLRM is mass dependent) is as follows:

1. The SET uses a two-stage extraction, in which a properly chosen slowly-extracting "weak" solvent (Aginsky 1994, 1996, 1998, 2002, 2012) is a "fine probe" of appropriate sensitivity for such a relatively slow and thus long (up to two years long) age-dependent process in ink on paper as the thickening/hardening of the ink's resin.
2. The SLRM is a one-stage extraction method, which does not use a slowly-extracting "weak" solvent ("fine probe") and which therefore is unable to monitor/measure the age-dependent processes of the thickening/hardening of the resin of ink on paper. By utilizing solely a "coarse-probe" fast-extracting "strong" solvent, the SLRM is capable of monitoring/measuring only a relatively fast and thus short (not longer than six months) age-dependent process in ink on paper – the process of the "evaporation" of phenoxyethanol (or similar high boiling volatile components of ink) from ink strokes.

Another typical example showing significantly different capabilities of the SLRM and SET includes the data and results of an outside proficiency test conducted in 2011 and summarized in Table 6.

As follows from the data listed in Table 6, all of the SET results obtained for five "blind" ink samples[13] were correct. It should be noted that the SET determined that ink No. IV and ink No. V were aging, and it correctly defined the time-

[13]This author did not know the actual ages of the inks on paper until after he submitted his results to the foreign agency that had prepared the samples for the proficiency test.

Table 6. Outside proficiency testing using five "blind" ink samples (tests conducted by Valery N. Aginsky on April 8-11, 2011)

Ink No.*	Ink Aging Parameters, R% and D%				Age of Ink	
	R%	*%E*	*%E_t*	*D%* = %E − %E_t	Reported Age	Actual Age *(Date of writing)*
I	**4**	25.3	24.4	**0.9**	**> 6 months**	**14 months** *(February 19, 2010)*
	2	30.6	28.6	**2.0**		
II	**3**	33.1	32.3	**0.8**	**> 6 months**	**23 months** *(May 12, 2009)*
	3	32.8	30.4	**2.4**		
III	**5**	32.9	29.7	**3.2**	**> 6 months**	**38 months** *(February 15, 2008)*
	4	29.3	26.8	**2.5**		
IV	**4**	64.0	58.6	**5.4**	**< 2 years**	**16 months** *(December 17, 2009)*
	8	66.2	60.5	**5.7**		
V	**7**	39.8	25.0	**14.8**	**< 8 months**	**3.5 months** *(December 29, 2010)*
	3	38.9	26.3	**12.6**		

* For each of the five ink entries listed in Table 6, two ink aging tests were conducted using the two-step extraction procedure for the SET and then, based on the raw numerical data obtained, both *D%* (see column "*D%* = %E − %E_t") and *R%* (see column "*R%*") ink aging parameters were calculated. Based on this author's experience, for each of the five inks, the repeatability of the *D%* and *R%* values obtained was good (*e.g.*, for the *D%* values, the range was from 0.3%, for ink No. IV, to 2.2%, for ink No. V) and rather typical for the SET and SLRM, respectively.

frames during which these inks were placed on paper (less than 2 years, for the 16-month old ink No. IV, and less than 8 months, for the 3.5-month old ink No. V). The SLRM was unable to determine that ink No. IV or ink No. V were aging. This is consistent with the capabilities of the SLRM considered in this paper, namely, that this ink aging method is only applicable to rather "fresh" inks on paper, specifically to inks placed on paper *less than 6 months* prior to analysis.

Finally, in response to recent opinions expressed by multiple ink chemists in various court cases, this author would like to offer the following comments. It has been asserted that if a level of PE (or another high boiling volatile component, such as benzyl alcohol) in a sample of ink is higher than what one might expect to see for a several-years-old ballpoint ink on paper, than this allegedly evidences that the ink is "fresh" (younger than 2 years or even younger than one year) and cannot be several years old as purported.

Such an opinion is completely mistaken.

This author has researched ink aging processes for many years and reported results in peer-reviewed literature, including the findings that,

> *"Ballpoint inks contain high boiling volatile components (vehicle solvents [such as phenoxyethanol, benzyl alcohol, or other similar solvents with high boiling points]) which, as it has been confirmed on numerous examples,[14] never evaporate completely from an aging ink. Even very old inks contain [inside the hardened matrix of ink's resin] the residues of their volatile components the amount of which per about 1-cm sample taken from an ink line is usually quite enough for their GC/MS quantitative determination in the extracts in weak and strong solvents …"* (Aginsky 1998)

These findings have been independently verified by Bügler, Buchner and Dallmayer who,

[14]See, e.g. (Aginsky 1994, 1995, 1996). In numerous GC-MS analyses of inks of various formulations conducted by this author in his career, both phenoxyethanol and benzyl alcohol have been detected and quantified in multiple old (several to decades years old) ballpoint inks on paper.

having analyzed multiple ballpoint inks (230 ballpoint pens from the collection of more than 4500 samples of inks maintained by the Forensic Sciences Institute of the Bavarian State Bureau of Investigation), determined that,

- "*the binder resin seems to be the key component influencing the long-term aging behavior of a ballpoint ink on paper*", and
- "*more than 95% of the initial amount of PE* [phenoxyethanol] *in ballpoint inks is lost during first 3 days after writing. Thereafter, the amount of PE decreases slightly and steadily and stays constant within the accuracy of the analytical method within a few weeks. This remaining amount of the ink solvent PE is trapped in the matrix ink resin/paper and can be detected in significant quantities even in samples as old as 50 years.*" (Bügler et al. 2005)

In their recent work, Bügler, Buchner, and Dallmayer (Bügler et al. 2008) measured the decrease of phenoxyethanol (PE) as inks were aging on paper in order to determine whether this method could be applicable to ballpoint ink up to 22 weeks old (approximately 5 months). They used thermal desorption and GC-MS to assess the variation of 25 ballpoint inks of different formulations with respect to their solvent content. Having determined that variation in pen pressure can result in a difference in the solvent content of up to 800% for ink samples taken from the same writing, they then compared 1-week and 22-week old ink lines on paper that were drawn with approximately the same pen pressure using the same 25 different ballpoint inks. They found that, for these 25 ballpoint inks, the solvent (PE) content ranged from 3 up to 250 nanograms (ng) per 1-cm ink line, for ink samples with an age of 1 week, and from 1 up to 150 ng per 1-cm ink line, for samples with an age of 22 weeks. Due to such a significant variance in the solvent content for different ballpoint ink entries of the same age, they concluded that **monitoring the evaporation of ink solvent from ink on paper is <u>not</u> a suitable method for ink dating**, especially if the examiner is unable to identify the "*formulation of the ink under investigation and to obtain knowledge about its composition and its aging behavior.*" (Bügler et al. 2008, p. 984)

These findings by Bügler, Buchner, and Dallmayer are in agreement with the results shown in Table 4 above. For example, Table 4 shows that ink lines of similar age and line characteristics, which were written with medium point pens and approximately the same pen pressure but with inks of different formulations, differ significantly in PE contents. Thus, the PE content in 2.5-month old Ink #3 is approximately 5 times (500%) less than the PE content in 2.5- and 4-month old Inks #5 and 6. Moreover, the PE content in 4 and 7-year old Inks, #11-13 ("old" entries), as well as in 6-year old Inks, #5 and 6 ("old" entries), is several times larger than the PE content in 2.5-month old "slow aging" Ink #3 ("fresh" entries) and even in 28-day old Inks #7 and 8 (very "fresh" entries).

Based on this author's many years of research relating to GC-MS analyses of ballpoint ink, the reason for such a sufficiently large content of PE in inks #5, 6, and 11-13 is explained as follows: these inks belong to a group of Bic black ballpoint inks, the resin(s) of which retains PE much more strongly than the resins used in most other ballpoint ink formulations. For this reason, even significantly old entries written with Bic black ballpoint ink will typically contain the residues of PE in their lines on paper at much higher levels than similar in age (or even much younger) entries written with most other ballpoint ink formulations.

Summing up the findings relating to the above final remark, it should be stressed that when an ink on paper becomes older than several months (not to mention older inks, *e.g.*, several years old inks or older), a level (absolute amount) of PE in the ink's strokes no longer depends on (and thus does not correlate with) the *age* of the ink, and it mainly depends:

a. on the chemical composition of the ink's *resin*, and
b. (to a lesser extent than a chemical composition of the ink's resin) on such parameters of ink on paper as ink lines' thickness and width (that, in their turn, depend on the size of a ball-pen tip point [*i.e.*, on the size of the rotating ball in the housing of the pen cartridge] and the pen pressure).

Therefore, no meaningful conclusion as to the actual (approximate) age of an ink on paper is possible if one tries to draw such a conclusion based on the level (absolute amount) of PE (or another high boiling ink volatile component) detected in the ink's strokes by GC-MS or any other analytical method.

Conclusion

In this work, two ink aging methods, the Sequential Extraction Technique and the Solvent Loss Ratio Method, were used to examine the aging of fast, medium and slow aging ballpoint inks and to determine whether a preceding indentation examination can have any detrimental effect on results of subsequent ink aging tests. The results of this work clearly show that the indentation examination preceding the ink aging examination does not cause any significant changes to the ink aging parameters, *D%* and *R%*, measured by these respective methods.

Another result of this work relates to the scope of applicability of the Solvent Loss Ratio Method, which appears to be restricted by a rather short period of time of a few months passed after a placement of an ink on paper. This result is in agreement with multiple publications discussed in this paper, namely, that the ink aging methods that measure the rate of evaporation of phenoxyethanol as a function of the age of ink (the Solvent Loss Ratio Method is one of such methods) are only applicable to rather "fresh" inks on paper, specifically to inks the age of which do not exceed 6 months.

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