

C. Weyermann, J. Almog, J. Bügler, A.A. Cantu, Minimum requirements for application of ink dating methods based on solvents analysis in casework. *Forensic Science International* 210 (1-3) (2011) 52-62.

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

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.

Keywords: forensic sciences, questioned documents, ink dating, solvent drying, aging, method validation, interpretation,

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) [12,11,13-20]. It was based on the changes in the extractability of the ink supposedly caused by the hardening of the resins [21,10,22-24]. 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 [43,35,34,36,28], while other scientists debated about the necessity for inter-laboratory validation before their use in casework [33,27,31,32,4,38,41].

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 [44,17,18,34,45-58], 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: (A) ink drying principles, (B) ink dating methods, (C) methods validation and (D) ink dating interpretation.

A. 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):

$$RPA = p_1 + p_2 \cdot e^{-\left(\frac{t}{p_3}\right)^{0.5}} + p_4 \cdot e^{-\left(\frac{t}{p_5}\right)^{0.5}} \quad \text{Eq.(1)}$$

, 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 rate of drying (slower evaporation and diffusion processes) [50,51]. Low amounts of solvents may even stay trapped in the ink matrix for years [17,52,45]. 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 (Figure 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 [60,57,61] and therefore most dating methods finally focused exclusively on the analysis of this specific substance (Figure 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 [61,42]. These parameters must therefore be extensively studied before a conclusion can be drawn on the absolute age of an ink entry:

- **Ink formulation**

The influence of the initial ink composition on the aging rates of inks is very important [45,56,23]. Two aspects must be considered: the compounds (dyes, resins, solvents, 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.

- **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 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 (Figure 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 (Figure 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 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 (Figure 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 [52,34]. 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 [52,50] 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 (Figure 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.

- **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 – 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 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].

- **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 [47,62,61,51]. 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.

B. 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*’ [52,34,45]. These methods' principles were briefly addressed in two preceding papers [18,17]. 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 [63,55,64,56] 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 [56,57,51].

Additionally, some recent developments based on previous tests [17,50,44] 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.

• 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 millimetre in diameter) 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 microliters of an

appropriate solvent with an internal standard. 1 microliter 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 Equation 2 in Table 2. If the value of R is ca. 20 % or larger, it shows (on condition that the content of the analyzed ink's solvent is not too small, at least, not less than 1 nanogram per sample) that the natural aging of the ink analyzed 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: $P = \text{ratio solvent peak areas to non-volatile component peak areas}$. 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 hours and then both are extracted with 15 microliters acetonitrile containing internal standard for 5 minutes. Using Equation 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) [47,46] 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 reproducible¹. 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.

• **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 microliters of a 'slowly extracting weak' solvent. 1 microliter of the extract is analysed by GC/MS (SIM mode with

¹ Personal communication from J. Andrasko, 2003.

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 microliters of a 'fast extracting strong' solvent. 1 microliter 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 Equation 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 Equation 4 in Table 4. Method 2 is actually an upgrade of method 1, as the total amount of extract $M_{\text{weak}}+M_{\text{strong}}$ (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 analyzed 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]:

- *$D > \text{ca. } 15\%$ - 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.*
- *$D < \text{ca. } 10\%$ - 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).*
- *$\text{ca. } 10\% < D < \text{ca. } 15\%$ - 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 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 (Figure 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 [45,56,49]. 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).

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 [63,60,56,64].

• **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 Equation 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 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, 3, 4, 5 in Table 6) [68,64]. The authors also proposed derivatization of phenoxyethanol in order to increase sensitivity and decrease variability[68,64]. 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 trend test. The value Q is calculated as follows [69,70]:

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

, where n is the number of measurements (e.g., $n=5$), x_i, x_{i+1}, \dots 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.

C. 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 & 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 month* [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 method 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.’*

D. 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 [38,75,77,74,27]. 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’) [78,75,74]. 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:

$$LR = \frac{p(D | t_1)}{p(D | t_2)} \quad \text{Eq.(6)}$$

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]:

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

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

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

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

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

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 $D\%$ (Figure 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].

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, 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".

Acknowledgments

The author wishes to inform readers of FSI that the work presented in this paper was kindly supported by the Swiss National Foundation (Fund No. PP00P1_123358/1).

References

- [1] R.L. Brunelle, Ink Dating - The State of the Art. *Journal of Forensic Sciences* 37 (1) (1992) 113-124.
- [2] A.A. Cantu, A Sketch of Analytical Methods For Document Dating. Part I. The Static Approach: Determining Age Independent Analytical Profiles. *International Journal of Forensic Document Examiners* 1 (1) (1995) 40-51.
- [3] A.A. Cantu, A Sketch of Analytical Methods For Document Dating. Part II. The Dynamic Approach: Determining Age Dependent Analytical Profiles. *International Journal of Forensic Document Examiners* 2 (3) (1996) 192-208.
- [4] C. Weyermann, Dating a document, in: M.A.e. Jamieson A. (Ed.), *Encyclopedia of Forensic Sciences*, Vol. III, J. Wiley & Sons, Chichester, 2009, pp. 684-692.
- [5] M. Ezcurra, Analytical Methods for Dating Modern Writing Instrument Inks on Paper. *Forensic Science International* 197 (2010) 1-20.
- [6] J.H. Bügler, M. Graydon, B. Ostrum, The practical use of the Munich ink reference collection in daily casework, 6th European Document Examiners Working Group (EDEWG) Conference, Dubrovnik, Croatia, 2010.
- [7] J. Stephens, R. Ramotowski, The Digital Ink Library: a step forward, 6th European Document Examiners Working Group (EDEWG) Conference, Dubrovnik, Croatia, 2010.
- [8] J. Andrasko, M. Kunicki, Inhomogeneity and Aging of Ballpoint Pen Inks Inside of Pen Cartridges. *Journal of Forensic Sciences* 50 (?) (2005) 542-547.
- [9] D.M. Grim, J.A. Siegel, J. Allison, Does Ink Age Inside of a Pen Cartridge? *Journal of Forensic Sciences* 47 (6) (2002) 1294-1297.
- [10] Y. Kikuchi, Estimation of the Age of the Writing in Blue Black Ink (I). *Japanese Police Science Laboratory Report* 12 (3) (1959) 379-386.
- [11] A.A. Cantu, R.S. Prough, On the Relative Aging of Ink - The Solvent Extraction Technique. *Journal of Forensic Sciences* 32 (5) (1987) 1151-1174.
- [12] A.A. Cantu, Comments on the Accelerated Aging of Ink. *Journal of Forensic Sciences* 33 (3) (1988) 744-750.
- [13] R.L. Brunelle, A Sequential Multiple Approach to Determining the Relative Age of Writing Inks. *International Journal of Forensic Document Examiners* 1 (2) (1995) 94-98.
- [14] R.L. Brunelle, C.H. Breedlove, C.R. Midkiff, Determining the Relative Age of Ballpoint Inks Using a Single-Solvent Extraction Technique. *Journal of Forensic Sciences* 32 (6) (1987) 1511-1521.
- [15] R.L. Brunelle, K.R. Crawford, *Advances in the Forensic Analysis and Dating of Writing Ink*. Charles C. Thomas Publisher, Ltd. Springfield, (2003).
- [16] R.L. Brunelle, H. Lee, Determining the Relative Age of Ballpoint Ink Using a Single-Solvent Extraction, Mass-Independent Approach. *Journal of Forensic Sciences* 34 (5) (1989) 1166-1182.
- [17] V.N. Aginsky, Some New Ideas for Dating Ballpoint Inks - A Feasibility Study. *Journal of Forensic Sciences* 38 (5) (1993) 1134-1150.
- [18] V.N. Aginsky, Determination of the age of ballpoint pen ink by gas and densitometric thin-layer chromatography. *Journal of Chromatography A* 678 (1994) 119-125.
- [19] V.N. Aginsky, A Microspectrophotometric Method for Dating Ballpoint Inks - A Feasibility Study. *Journal of Forensic Sciences* 40 (3) (1995) 475-478.
- [20] L.F. Stewart, S.L. Guertin, Current status of ink age determination, in: *Interpol (Ed.), 9th International Forensic Science Symposium*, Vol. 429 (1991), *International Criminal Police Review*, 1989.

- [21] A.C. Mitchell, Estimation of the age of ink in writing. *The Analyst* XLV (435) (1920) 246-258 (Reprinted in the *Journal of Forensic Document Examiners* (1995), Vol. 1991 (1991): 1956-1962).
- [22] Y. Kikuchi, Studies on the Age of Iron-Gallotannate Ink Writing (II) the Chromatic Study of Ink Stain. *Journal of Criminology* 26 (2) (1960) 39-59.
- [23] Y. Kikuchi, Estimation of Age of Blue Black Ink Writing (III). *Japanese Police Science Report* 16 (1) (1963) 83-86.
- [24] N.K. Sen, P.C. Gosh, Dating Iron-Based Ink Writings on Documents. *Journal of Forensic Sciences* 16 (4) (1971) 511-520.
- [25] R.L. Brunelle, E.J. Speckin, Technical Report With Case Studies on the Accelerated Aging of Ballpoint Inks - Several cases on accelerated aging of ballpoint pen ink where the findings were admitted into court. *International Journal of Forensic Document Examiners* 4 (3) (1998) 240-254.
- [26] R.L. Brunelle, A.A. Cantu, A Critical Evaluation of Current Ink Dating Techniques. *Journal of Forensic Sciences* 32 (6) (1987) 1522-1536.
- [27] R.L. Brunelle, A.A. Cantu, Training Requirements and Ethical Responsibilities of Forensic Scientist Performing Ink Dating Examinations. *Journal of Forensic Sciences* 32 (6) (1987) 1502-1508.
- [28] A.H. Lyter, Relative Aging of Ball Pen Ink: Natural Aging vs. Artificial Aging, American Academy of Forensic Sciences Meeting, San Antonio, Texas, 1994.
- [29] T. Hicks Champod, A. Khanmy, P. Margot, Ink aging: perspectives on standardization, in: W.B. B. Jacob, W. Huckenbeck & P. Pieper (eds) (Ed.), 13th Meeting of the International Association of Forensic Sciences, Duesseldorf, 1993, *Advances in Forensic Sciences* 3, *Forensic Criminalistics* 1, Verlag Dr. Koester, Berlin, 1995, pp. 304-309.
- [30] J.E. Starrs, Ink Dating Up-Dated and Up-Ended. *International Journal of Forensic Document Examiners* 1 (1) (1995) 3 - 5.
- [31] P. Margot, T. Hicks Champod, A. Khanmy, Ink Dating Up-Dated and Up-Ended – Correspondance of Prof. Starrs. . *International Journal of Forensic Document Examiners* 1 (1) (1995) 2-5.
- [32] L.F. Stewart, S.L. Fortunato, Distinguishing Between Relative Ink Age Determinations and the Accelerated Aging Technique. *International Journal of Forensic Document Examiners* 2 (1) (1996) 10-15.
- [33] V.N. Aginsky, Accelerated Aging - Its Use in Methods for Dating Ink. *International Journal of Forensic Document Examiners* 2 (3) (1996) 179-181.
- [34] V.N. Aginsky, Measuring Ink Extractability as a Function of Age - Why the Relative Aging Approach is Unreliable and Why it is More Correct to Measure Ink Volatile Components than Dyes. *International Journal of Forensic Document Examiners* 4 (3) (1998) 214-230.
- [35] T. Andermann, R. Neri, Solvent Extraction Techniques - Possibilities for Dating Ball Point Pen Inks *International Journal of Forensic Document Examiners* 4 (3) (1998) 231-239.
- [36] K. Jahns, Altersbestimmung von Schreibmitteln durch Chemische Analyseverfahren. *Mannheimer Hefte Für Schriftvergleichung* (Peter Baier) 3 (04) (2004) 120-129.
- [37] C. Weyermann, Revue des méthodes de datation de l'encre: Est-il possible de déterminer l'âge d'un document en analysant l'encre? *Revue Internationale de Criminologie et de Police Technique et Scientifique* 3 (LXI) (2008) 359-376.
- [38] C. Weyermann, B. Schiffer, P. Margot, A logical framework to ballpoint ink dating interpretation. *Science & Justice* 48 (3) (2008) 118-125.

- [39] C. Weyermann, D. Kirsch, C. Costa-Vera, B. Spengler, Photofading of Ballpoint Dyes Studied on Paper by LDI and MALDI MS. *Journal of the American Society for Mass Spectrometry* 17 (3) (2006) 297-306.
- [40] C. Weyermann, D. Kirsch, C. Costa-Vera, B. Spengler, Evaluation of the Photodegradation of Crysstal Violet upon Light Exposure by Mass Spectrometric and Spectroscopic Methods. *Journal of Forensic Sciences* 54 (2) (2009) 339-345.
- [41] C. Weyermann, W. Mazzella, P. Margot, 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. *Journal of Forensic Sciences* 54 (4) (2009) 967.
- [42] C. Weyermann, B. Spengler, The potential of artificial aging for modelling of natural aging processes of ballpoint ink. *Forensic Science International* 108 (2008) 23-31.
- [43] T. Hicks Champod, Détermination de l'âge des encres - possibilités de standardisation. 4th year research, Institut de Police Scientifique, Lausanne. Presented at a 13th Meeting of the International Association of Forensic Sciences, Düsseldorf. (1993).
- [44] L.F. Stewart, Ballpoint Ink Age Determination by Volatile Component Comparison - A Preliminary Study. *Journal of Forensic Sciences* 30 (2) (1985) 405-411.
- [45] V.N. Aginsky, Current Methods for Dating Ink on Documents, 60th Annual Conference of the American Society of Questioned Document Examiners, <http://www.rileywelch.com/ink.html>, San Diego, California, 2002.
- [46] V.N. Aginsky, Current Methods for Dating Ink on Documents, 65th Annual Conference of the American Society of Questioned Document Examiners, Boulder, Colorado, 2007.
- [47] J. Andrasko, Ink Dating Using SPME and Methanol Extraction, 3rd meeting of the European Network of Forensic Science Institutes, Istanbul, 2003.
- [48] M. Ezcurra, I. Velasco, J.M.G. Góngora, M.I. Maguregui, R.M. Alonso, Analysis of Bic Cristal Medium Ballpoint Pen Inks. *Journal of the American Society of Questioned Document Examiners* 12 (2) (2009) 57-68.
- [49] M. Gaudreau, L. Brazeau, Ink Dating Using A Solvent Loss Ratio Method, 60th Annual Conference of the American Society of Questioned Document Examiners, San Diego, California, 2002.
- [50] S. Locicero, W. Mazzella, L. Dujourdy, E. Lock, P. Margot, Dynamic of the ageing of ballpoint pen inks: quantification of phenoxyethanol by GC/MS. *Science & Justice* 44 (3) (2005) 165-171.
- [51] C. Weyermann, D. Kirsch, C. Costa-Vera, B. Spengler, A GC/MS study of the drying of ballpoint pen ink on paper. *Forensic Science International* 168 (2-3) (2007) 119-127.
- [52] V.N. Aginsky, Dating and Characterizing Writing, Stamp, Pad and Jet Printer Inks by Gas Chromatography / Mass Spectrometry. *International Journal of Forensic Document Examiners* 2 (2) (1996) 103-116.
- [53] J. Andrasko, Some Examples of Applications of a Microthermal Desorption Device in the Forensic Laboratory. *Journal of Forensic Sciences* 54 (5) (2009) 1055-1058.
- [54] L. Brazeau, M. Gaudreau, Ballpoint Pen Inks: The Quantitative Analysis of Ink Solvents on Paper by Solid-Phase Microextraction. *Journal of Forensic Sciences* 52 (1) (2007) 209-215.
- [55] J.H. Bügler, H. Buchner, A. Dallmayer, Age Determination of Ballpoint Ink by Thermal Desorption and Gas Chromatography-Mass Spectrometry, in: ASQDE

- (Ed.), 63 rd Annual Conference of the American Society for Questioned Document Examination (ASQDE), Montréal, Canada, 2005.
- [56] J.H. Bügler, H. Buchner, A. Dallmayer, Age Determination of Ballpoint Pen Ink by Thermal Desorption and Gas Chromatography-Mass Spectrometry. *Journal of Forensic Sciences* 53 (4) (2008) 982-988.
- [57] G.M. LaPorte, J.D. Wilson, C.A. A., S.A. Mancke, S.L. Fortunato, The Identification of 2-Phenoxyethanol in Ballpoint Inks Using Gas Chromatography / Mass Spectrometry - Relevance to Ink Dating. *Journal of Forensic Sciences* 49 (1) (2004) 155-159.
- [58] C. Berger-Karin, U. Hendriks, J. Geyer-Lippmann, Comparison of Natural and Artificial Aging of Ballpoint Inks. *Journal of Forensic Sciences* 53 (4) (2008) 989-992.
- [59] J. Almog, Unsolved Problems in Forensic Science. *Plilim, Israeli Journal of Criminal Justice II* (1991) 67-87.
- [60] J.H. Bügler, H. Buchner, A. Dallmayer, Characterization of Ballpoint Pen Inks by Thermal Desorption and Gas Chromatography-Mass Spectrometry. *Journal of Forensic Sciences* 50 (5) (2005) 1-6.
- [61] C. Weyermann, Mass Spectrometric Investigation of the Aging Processes of Ballpoint Ink for the Examination of Questioned Documents, Faculty of Biology and Chemistry, Justus-Liebig University, 2005. Available on-line: <http://geb.uni-giessen.de/geb/volltexte/2006/3044/>
- [62] M.G. Ezcurra, J.M.G. Góngora, I. Maguregui, R. Alonso, Evaluation of Loss of Phenoxyethanol from a Ballpoint Pen Ink over Time by GC-MS Depending on the Location of the Signature on the Document. *Journal of the American Society for Questioned Document Examiners* 13 (1) (2010) 9-14.
- [63] J.H. Bügler, Analytische Untersuchung von Lösungs- und Bindemitteln in Schreibmitteln, in: B.u. Landeskriminalämter (Ed.), *Urkunden-Konferenz*, Vol. Berlin, Germany, 2004.
- [64] J.H. Bügler, H. Buchner, A. Dallmayer, Age Determination of Ballpoint Pen Inks, in: I. ENFSI (Ed.), 4th Conference of the European Document Examiners Working Group (EDEWG), The Hague, Netherlands, 2006.
- [65] D. Kirsch, V. Guillou, B. Anheier, P. Seiler, F. Köhler, Different analytical methods of dating ball point ink entries, in: ENFSI, 6th European Document Examiners Working Group (EDEWG) conference, Dubrovnik, Croatia, 2010.
- [66] Y. Wang, L. Yao, P. Zhao, J. Wang, Y. Wang, Determination of the Writing Age of Blue Ballpoint Ink by Gas Chromatography. *Chinese Journal of Chromatography* 23 (2) (2005) 202-204.
- [67] Y. Wang, L. Yao, P. Zhao, J. Wang, Y. Wang, Determining the relative age of blue ballpoint ink by gas chromatography. *Frontiers of Chemistry in China* 2 (223-226) (2006).
- [68] J.H. Bügler, Method Validation for Age Determination of Ballpoint Inks, in: i. ENFSI (Ed.), 5th Annual Conference of the European Document Experts Working Group (EDEWG), Bunratty, Ireland, 2008.
- [69] S. Kromidas, *Handbuch Validierung in der Analytik*, Wiley-VCH, Weinheim, 2000.
- [70] J. Neumann, R. Kent, H. Bellison, B. Hart, The mean square successive difference. *Annals of Mathematical Statistics* 12 (2) (1941) 153-162.
- [71] W. Horwitz, Evaluation of Analytical Methods Used for Regulation of Foods and Drugs. *Analytical Chemistry* 54 (1) (1982) 67 -76 A.
- [72] M. Thompson, S. Ellison, R. Wood, Harmonized Guidelines for Single-Laboratory Validation of Methods of Analysis. *Pure Applied Chemistry* 74 (2002) 835-855.

- [73] P. Margot, A question of time. *Science & Justice* 40 (2) (2000) 64-71.
- [74] G. Jackson, The scientist and the Scales of Justice. *Science & Justice* 40 (2) (2000) 81-85.
- [75] I.W. Evett, 'It's not rocket science.' Wouldn't it be wonderful if judges understood the principles of evidence interpretation?, 7th International Conference on Forensic Inference and Statistics, Lausanne, 2008.
- [76] A. Zeichner, Letter to Aginsky V. N. dated 16 May 1997, <http://www.rileywelch.com/ProfTest1.jpg> (last access August 2010).
- [77] I.W. Evett, Bayesian inference and forensic science: problems and perspectives. *The Statistician* 36 (1987) 99-105.
- [78] C.G.G. Aitken, F. Taroni, *Statistics and the Evaluation of Evidence for Forensic Scientists*. Wiley ed., 2nd, Statistics in Practice, West Sussex, England, 2004.
- [79] M. Gallidabino, A pragmatic approach for evidential assessment in cases involving the estimation of time since discharge, Institut de Police Scientifique, University of Lausanne, 2010, pp. 1-47.
- [80] A. Biedermann, F. Taroni, A probabilistic approach to the joint evaluation of firearm evidence and gunshot residues. *Forensic Science International* 163 (2006) 18-33.
- [81] M.J. Saks, Forensic identification: From a faith-based "Science" to a scientific science. *Forensic Science International* 201 (1-3) (2010) 14-17.

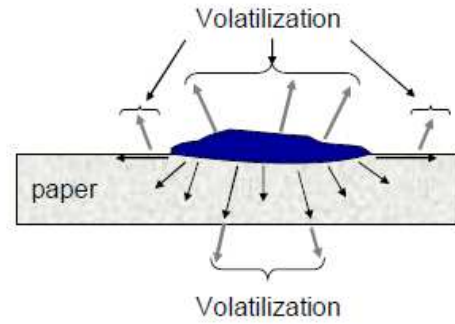
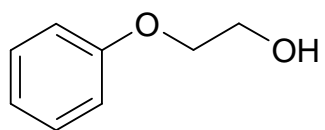


Figure 1 – Simultaneous ink drying processes on paper: the ballpoint pen solvent molecules volatilize (evaporate), diffuse (migrate and penetrate via absorption) and are adsorbed by the paper substrate. While grey arrows represent volatilization, black arrows represents diffusion, migration, penetration,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



m.w.	138.2 g/mol
b.p.	247°C
viscosity at 25°C	21.5 cP

Figure 2 – Structure formula, molecular weight, boiling point and viscosity of the solvent phenoxyethanol.

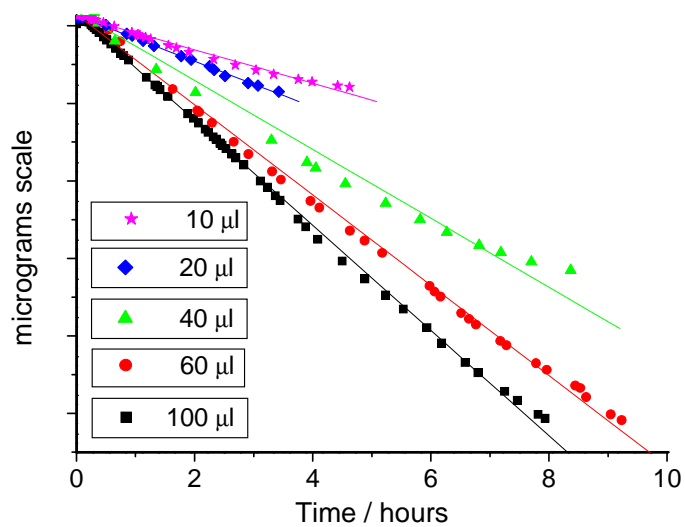


Figure 3 - Superimposed curves for the evaporation of 10, 20, 40, 60, and 100 μl of the solvent ethoxyethanol from paper: the loss of weight in micrograms (steps of 5000 μg) is presented as a function of the time in hours. Lower evaporation rates were observed when smaller volumes of solvents were initially deposited on paper [61].

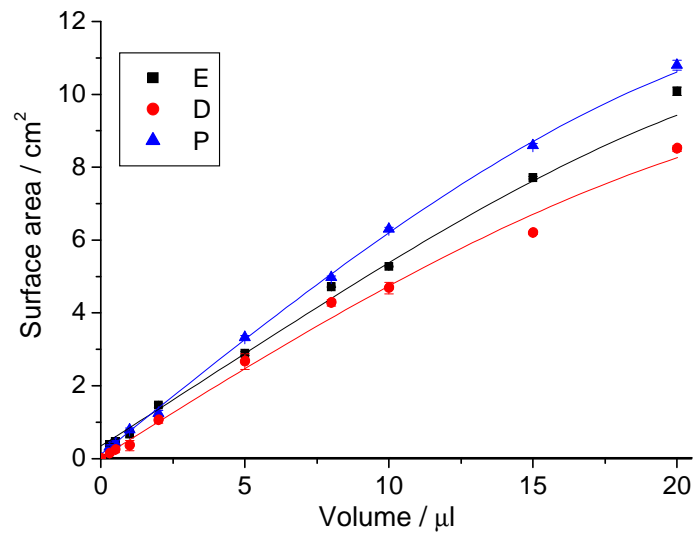


Figure 4 - Visible surface area [cm^2] taken up by the solvents ethoxyethoxyethanol (E), dipropylene glycol (D) and phenoxyethanol (P) a short time after deposition on paper with a micropipette, as functions of the volume deposited [μl]. The surface areas increased with the volume, but were also influenced by the viscosity, density, hygroscopicity and volatility of the solvents [61].

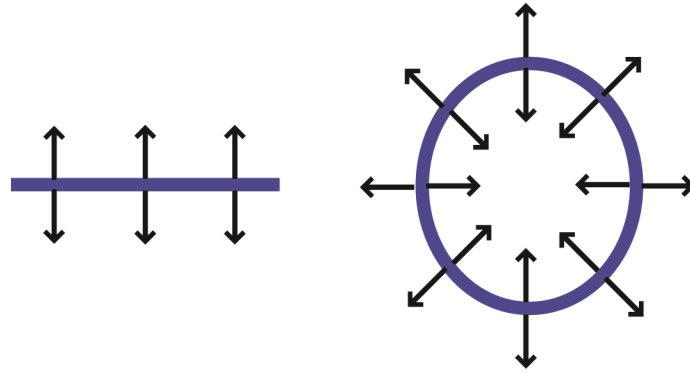


Figure 5 - Solvents diffusion from two ink entries: (left) diffusion away from a straight line, (right) diffusion inside the loop of the letter 'o'. The solvent concentration may be significantly higher in 1 cm of the loop compared to 1 cm of the straight line.

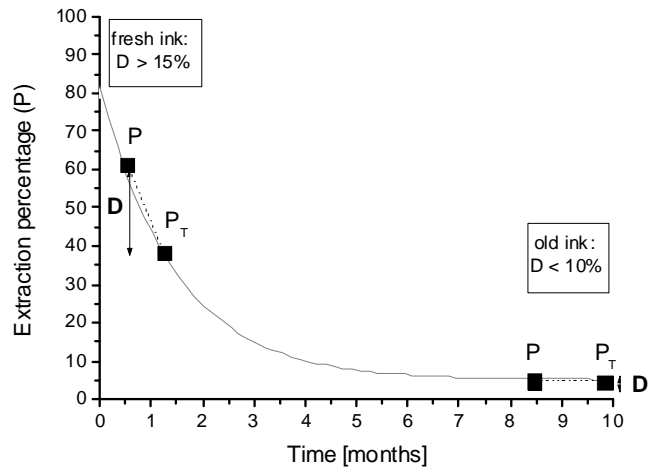


Figure 6 Graphical presentation of the threshold values proposed by Aginsky in 1996 [33] to determine a time frame within which a questioned entry has been actually written.

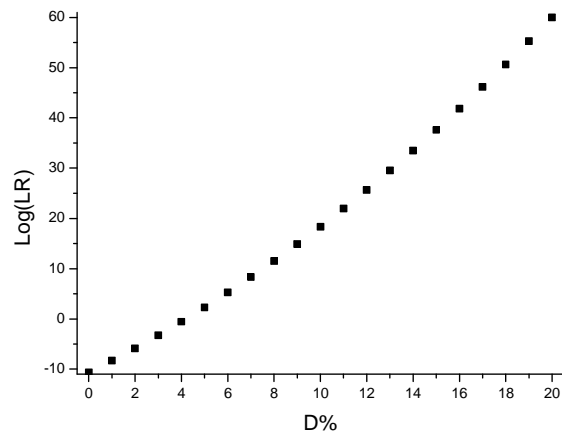


Figure 7 – Distribution of likelihood ratio (LR) calculated as a function of the D% values for the pair of proposition: the ink is 8 months old (t_1) and the ink is 24 months old (t_2). Up to a D% of 4, the evidence support the hypothesis t_2 , while for $D \geq 5\%$, the evidence is more probable given t_1 .

	First parameter	Second parameter	Ratio (Table 4; Eq.(3))
Ink line length (cm)	M₁ (ng)	M₂ (ng)	M₁·100% / (M₁+ M₂)
1	30	70	30
2	60	140	30

Table 1 – The parameters M₁ and M₂ 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.

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, 1h[52] or 2h[49])
Extraction	10 µl [52] or 15 µl [49] of appropriate solvent (e.g. acetonitrile with an internal standard)	
Analysis	1µl of extract analyzed by GC/MS (SIM mode)	
Results	P = mass of solvent	P _T = mass of solvent
Eq.(2)	R(%) = [(P - P_T)/P]·100 [52,49]	

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

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

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 analyzed 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 analyzed by GC/MS	
Results 2	M_{strong} = mass of solvent	M_{strong} = mass of solvent
Eq. (3)	$P = 100 \cdot$ $[M_{\text{weak}} / (M_{\text{weak}} + M_{\text{strong}})]$	$P_T (\%) = 100 \cdot$ $[M_{\text{weak}} / (M_{\text{weak}} + M_{\text{strong}})]$
Eq. (4)	$D (\%) = P - P_T$ [52]	

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

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]

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

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 analyzed by GC/MS	
Results 1	M_{low} = mass of solvent	M_{low} = mass of solvent
Strong extraction	200°C thermodesorption	
Analysis 2	extract analyzed by GC/MS	
Results 2	M_{high} = mass of solvent	M_{high} = mass of solvent
Eq. (3)	$V_1 (\%) = 100 \cdot [M_{low} / (M_{low} + M_{high})]$	$V_n (\%) = 100 \cdot [M_{low} / (M_{low} + M_{high})]$
Evaluation Test	Statistical Neumann trend test [70]	

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

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

Aspects of reliability	Short definition
Specificity [71]	Ability to detect ink solvents
LoD, LoQ [71,38]	Limit of reliable measurements (detection and quantification)
Systematic error [71,38]	Accuracy
Repeatability [71,73]	Within laboratory precision
Reproducibility [71]	Between laboratory precision
Outside proficiency testing [33,31,27]	Blind testing on realistic samples

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

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 <u>and</u> inter-laboratory reliability
Use of a logical interpretation model	Evaluate probability of evidence given alternative hypotheses

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