Ink dating using thermal desorption and gas chromatography / mass spectrometry: Comparison of results obtained in two laboratories

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ABSTRACT

An ink dating method based on solvent analysis was recently developed using thermal desorption (TD) followed by gas chromatography / mass spectrometry (GC/MS) and is currently implemented in several forensic laboratories. The main aims of this work were to implement this method in a new laboratory in order to evaluate if results were comparable at three levels: (1) validation criteria (2) ageing curves and (3) results interpretation. While the results were indeed comparable in terms of validation, the method proved to be very sensitive to maintenances. Moreover, the ageing curves were influenced by ink composition, as well as storage conditions (particularly when the samples were not stored in “normal” room conditions). Finally, as current interpretation models showed limitations, an alternative model based on slope calculation was proposed. However, in the future a probabilistic approach may represent a better solution to deal with ink sample inhomogeneity.

Keywords: Forensic science; questioned documents; ink dating; ageing; solvent; thermal desorption; GC/MS; interpretation

Ink dating is a complex and recurrent problem in the examination of questioned documents (1-4). Many researches have been carried out to develop ink dating methods generally based on the ageing of compounds that constitute ballpoint pen ink such as dyes or solvent. Some practical applications have been proposed to analyze dyes (3, 5-15), but a controversy about their use in practical cases was quickly raised and their use was since then widely contested (16-22).

More recently, developments proposed to date ink entries through analysis of their solvent content (20-21, 23-37). The solvent phenoxyethanol was generally targeted, because it was frequently encountered in ballpoint ink composition (38-40). Such dating methods can be separated in three groups according to the proposed methodology:

(1) methods analyzing the quantitative decrease of phenoxyethanol in ink entries as a function of time (23, 27, 30-32, 40-42),

(2) methods using artificial ageing to calculate the decrease in the ageing process of ink solvents (20-21, 25-26, 37),

(3) methods analyzing the decrease of the extractability of solvent content using sequential extractions sometimes combined with artificial ageing (20-21, 25, 34).

Among the latter, a method was proposed by Bügler et al. (2008) (34, 38) and was based on sequential analyses of the questioned ink entry using thermal desorption (TD) coupled with gas chromatography/mass spectrometry (GC/MS). This method was created and has been used routinely at the Landeskriminalamt in Munich since 2004. Currently it tends to be implemented in several laboratories participating to the InCID group (International Collaboration on Ink Dating), which is a sub-group from the European Document Experts Working Group (EDEWG)(43). This group aims at improving the communication on the use of ink dating methods in Europe and around the world. Until now, the implementation of this method in other laboratories proved to be particularly sensitive and time consuming. The amount of experiments required to implement and validate the procedure adequately must not be underestimated since this stage should be performed every time a method is developed or implemented in a laboratory (44-45). Some criteria are particularly important such as the limit of applicability and the precision of the method. It is also essential that the results are repeatable and comparable to those obtained in other laboratories. Finally, another crucial step lies in the interpretation of the data in a legal perspective (45-46). In literature, threshold values (25-26, 37), and more recently the use of trend tests (e.g. Neumann test (45, 47)) was proposed to determine if the ageing is still occuring at a significant rate.

The task of this study was therefore to evaluate the implementation of the TD-GC/MS method created by Dr. Bügler et al. in Munich (34) (Munich) in another laboratory possessing the same instrument (Wiesbaden). Once the method optimized and validated, the ink ageing behaviors were studied and compared with those obtained in Munich. The ageing curve repeatability of one ink stored under different conditions was also studied. Then the ageing curves of different inks were determined and used to test different interpretation models in order to evaluate their adequacy in a legal perspective.

Material and method

Products and material

Acetone (99.9%) was purchased from Merck (Darmstadt, Germany). Phenoxyethanol 99.5% and n-hexadecane 99.8% (Fluka; Buchs, Switzerland, part of Signa-Aldrich, USA) were used in the preparation of control solutions. BSTFA (N,O-bis(trimethylsilyl)trifluoroacetamide) (99%) (Sigma-Aldrich, St. Louis, USA) was used as derivation agent and desorption tubes were purchased from Gerstel (Muehlheim a. d. Ruhr, Germany).

Ballpoint pen ink samples

Samples from four different inks containing phenoxyethanol were analyzed during this study. These inks were selected from the large collection of ballpoint pens and inks of the Landeskriminalamt of Munich (48). The inks 1688, 1774, and 1892 were provided in the form of ballpoint pen cartridges filled in Munich to all laboratories participating to the InCID group. The cartridges used in this study were obtained by the three laboratories at different date: Wiesbaden (May 2009), Lausanne (May 2010) and Munich (filled in December 2009) (Table 1). These three inks were chosen by the InCID group because they showed different ageing curves. The ink 1696 was additionally provided directly by the Landeskriminalamt of Munich under the form of strokes on paper cut at the dimension of 5x1mm. This ink was chosen because ink entries up to nine years old were available.

Ink entries preparation

Ink entries were prepared by three different laboratories: Lausanne, Wiesbaden and Munich. The entries made in Lausanne and Wiesbaden were analyzed using the TD-GC/MS of Wiesbaden: The entries made in Munich were analyzed partly in Munich, partly in Wiesbaden. Strokes were made with a ruler on a paper A4 sheet (80g/m2, copy paper for ink jet and laser printer) at least 2 (Munich) or 3 cm (Wiesbaden/Lausanne) apart from other ink lines. Sheets were then stored in a folder. Between each sheet with ink strokes, blank sheets of paper were inserted. This allowed to avoid cross contamination, while remaining close to what can be observed in reality. In Lausanne the ink samples were then stored in a climatic chamber at 20°C and 55% humidity. The samples made in Wiesbaden were stored in an air conditioned laboratory at 23°C (humidity not controlled). In Munich, samples were stored in an air conditioned laboratory at 25 °C (humidity not controlled). Ink entries preparation, storage conditions and analysis laboratory are summarized in Table 1.

Insert Table 1

TD-GC/MS method

In both laboratories, 5 to 10 mm strokes (of known age) were cut from the paper with a scalpel (corresponding to a piece of paper up to 10mm length and 1mm width) and were introduced in a desorption tube. The volatile compounds were extracted from the samples with a thermal desorption system TDS3 from Gerstel preceded by an autosampler (TDSA). This unit was connected to a cryofocusing system KAS2 injector (Gerstel) in order to trap the desorbed compounds until analysis. The compounds were derivatised in situ through an external device called the derivatisation box. In this box, the entering carrier flow of helium was divided partly into the TD and partly through the derivatisation solution (BSTFA) before reaching the desorber (Figure 1). It was important to settle properly this parameter in order to obtain reproducible results. It was also complicated because the setting required manual manipulation of the two valves regulating the flow in each path (desorber or derivatizing agent). For this purpose, 1 µl of a liquid solution containing 60ng phenoxyethanol (PE) and 10ng hexadecane in acetone was desorbed at 90°C. When the obtained rate of trimethylsilyl-phenoxyethanol (PE-TMS) was maximal, the derivatisation rate was considered optimal. A derivatisation rate up to 98.7 ± 0.3% could be obtained. This derivatisation rate was thus considered optimal for the instrument, since the gas flow through the derivatisation agent could not be raised and the helium flow could not be reduced.

Insert Figure 1

The analysis units consisted of a gas chromatograph 6890N and a mass spectrometer MSD 5973N from Agilent (Santa Clara, USA) for Wiesbaden and for Munich. Thermal desorption was set at 90°C for 5 min, while a program was necessary to reach 200°C reproducibly (initial temperature of 25°C, then 60°C/min to 200°C and isotherm for 4 min). The flow during desorption was set to 40mL/min and contained BSTFA (derivatisation in situ). The compounds were trapped in a KAS system at -100°C. To inject the compounds in the gas chromatograph, the temperature of the KAS system rose from -100°C to 280°C at a rate of 60°C/s and it remained at 280°C for 3.5 min.

For the GC parameters, the column flow was set to 1.2 mL/min, the oven program was isothermal at 45°C/min for 1 min, then 45°C to 100°C at a rate of 30°C/min, then from 100°C to 190°C at a rate of 12°C/min, from 190°C to 270°C at a rate of 50°C/min and finally isothermal for 3.07 min. The transfer line was maintained at 280°C. The detector was a mass spectrometer in electron impact (EI) mode at 230 °C. Mass-to-charge ratios (m/z) were measured in scan mode by a quadrupole mass analyzer set at 180°C. The m/z values were measured between 5 and 7.5 min in a mass range between m/z 35 u to 450 u, between 7.5 and 8.5 min from m/z 70 u to 220 u in n order to increase the number of scan when the PE-TMS derivate elutes from the column and finally after 8.5 min from m/z 35u to 500 u.

To avoid contaminations, the system was baked out between analyses and a standard solution containing PE and n-hexadecane (nC16) (both at 10ng/μL in acetone) was injected every day in order to ensure the quality of the instrument response. The ratio PE-TMS/n-hexadecane was thus monitored over time. It is highly recommended to analyze the control solution in the same tube or in tubes having the same approximate number of injection. In fact, it was observed during the implementation that the ratio between the PE-TMS (m/z 151 u) and n-hexadecane (m/z 57u) of the control solution was dependent on the tube used for desorption. The ratio could be of 2.77 ± 0.09 (n=3) for some tubes, while it was of 3.21 ± 0.04 (n=3) for other tubes (analyses performed on one day).

Data treatment

For the PE-TMS the peak area of ion m/z 151 u was measured. This ion was chosen since it was specific and represented the base peak of the PE-TMS mass spectrum. For n-C16, the ion m/z 57 u was chosen. The peak areas were measured for both desorbing temperatures (PA_{90} at 90°C and PA_{200} at 200° C) and were used to calculate the ageing parameter V%, which represents the relative quantity of phenoxyethanol evaporated with a low temperature divided by the total amount evaporated (34):

$$V\% = \frac{PA_{90}}{PA_{90} + PA_{200}} \times 100 \qquad \textbf{Eq.(1)}$$

Ageing curves were generated using the V% values plotted as function of the sample age. In order to model the curves, a simple exponential regression was used:

$$V\% = V_0 + A_1 \cdot \exp^{-t/\tau_1} \qquad \textbf{Eq.(2)}$$

Experiments

Calibration

In order to calibrate the instrument, control solutions containing PE and nC16 in concentration of 0.005, 0.01, 0.05, 0.1, 0.5, 1, 5, 10, 20, 40, 60, 100 and 200 ng/µL in acetone were injected. Calibrations were performed twice during the experimental period, each time after maintenance of the instrument.

The limits of detection and quantification (LoD and LoQ) were calculated with the software BEN Version 2.03 (Walldorf, Germany) according to the norm DIN 32645, as well as with the background noise method proposed by Miller & Miller (2005) (49). For the latter, the LoD and LoQ were measured as follows:

$$LoD = \overline{X}_{blanc} + 3 \cdot SD_{Blank} \qquad \textbf{Eq.(3)}$$

$$LoQ = \overline{X}_{blanc} + 10 \cdot SD_{Blank} \qquad \textbf{Eq.(4)}$$

,where $\overline{X}_{blanc}$ is the mean peak area of the background noise at the retention time of interest from a blank analysis and SD is the standard deviation measured from 10 different blank analyses.

Repeatability

The repeatability was calculated from measurements carried out with the same instrument by the same operator during one day (44, 50) (March 2011). Three replicate samples from ink 1688 strokes of different ages (2, 44 and 89 days old) were analyzed as well as three sample of the control solution. The relative standard deviations (RSD) were calculated for the quantities of PE-TMS recovered at 90°C and 200°C, as well as the resulting V% ratio for ink samples and the PE/nC16 ratio for standard solutions.

Reproducibility

In order to evaluate the reproducibility of ink entries measured on the same instrument by the same operator, two ageing curves were built using samples from ink 1688 prepared and stored in Wiesbaden. The first ageing curve (W1) was drawn by measuring strokes of 11 different ages (1, 3, 5, 7, 13, 22, 37, 55, 68, 82 and 89 days), while the second ageing curve (W2) was built 2 months later by measuring samples of 9 different ages between 1 and 90 days. An extensive maintenance was carried out on the instrument between both series of measurements.

The reproducibility of the ageing curves was additionally measured on ink samples measured on two different instruments by different operators (50) (in Wiesbaden and Munich). Samples of ink 1688 were prepared and stored in Munich under similar conditions as in Wiesbaden (laboratory at 23°C). A third ageing curve was thus built in Munich (M1) and compared to the curves previously obtained in Wiesbaden (W1 and W2).

Influence of the ink entries preparation

The influence of different ink entries preparation parameters on the ageing curves was evaluated by analyzing sample from ink 1688 prepared and stored differently. Thus, ink entries were prepared and stored in Lausanne (climatic chamber). The sample ages covered a period from 1 to 180 days and were analyzed within the same period as those prepared and stored in Wiesbaden (see W1, chapter reproducibility). The influence of the cartridge and the paper was also determined. Ink lines were drawn using cartridges from Lausanne and Wiesbaden on Xerox paper and were stored in an air conditioned laboratory (23°C). Samples from both cartridges were measured from 42 to 98 days after deposition. The influence of the paper was tested using the cartridge from Wiesbaden to deposit lines on both considered papers (Xerox Business and Xerox Performer). These were stored in an air conditioned laboratory and samples from 4 to 179 days old were then analyzed.

Interpretation

Samples from three different ink formulations (1688, 1774, and 1892) were measured in Wiesbaden to approximately 1 year after deposition.

In the context of ink dating calculation of half-times was proposed by in order to compare ageing curves which were recorded by different analytical techniques (41-42). Thus, in order to compare the ageing between inks, the half-life time was first calculated from the exponential regression applied on the data (see Eq.2) :

$$T_{1/2} = \tau_1 \times \ln(2) \qquad \textbf{Eq.(5)}$$

, where τ_1 is the exponent coefficient from Eq. (2).

The Neumann Test was also applied in order to determine “level–off” age for each ink. The Neumann test is applied on chronological data (51):

$$PG = \frac{1}{(n-1)\cdot\sigma^2}\sum_{i=1}^{i=n-1}(x - x_{i+1})^2 \qquad \textbf{Eq.(6)}$$

, where n is the number of measurements, σ is the standard deviation measured on the data, and x_1, x_2,…x_n are the chronologically ordered measurements. Several measurements made during a defined period are needed for that purpose. The Neumann test was proposed by Bügler et al. (45, 47) to interpret questioned ink data in dating caseworks, It was recommended to measure the questioned ink entry every two weeks during two to three months (i.e. 5 to 7 measurements were proposed) (45, 47).

The obtained result PG was then confronted to a critical statistical value $X_{n,p}$ depending on the number of data points considered and a given confidence interval (e.g. $X_{n,p}$ value for 99.5% (45, 47)). When the value PG calculated was smaller than the critical $X_{n,p}$ value, the measurements indicated a significant trend, and are thus considered to be still ageing. In this work, the test was applied on 5 and 7 measurement (i.e. range of 60 and 74 days, respectively) of the curves 1688, 1774 and 1892 measured in Wiesbaden. The last age presenting a trend was indicated for each curves and configuration.

In addition, an alternative interpretation model was proposed and was tested on the recorded data. It is based on the same concept as the trend tests and consists to determine the inverse of the slope (-m) of a linear regression applied on measurements acquired as for the Neumann test (five or seven measurements, one each two weeks):

$$-m = -\frac{n\sum_{i=1}^{n}(V_i) - n\sum_{i=1}^{n} t_i \sum_{i=1}^{n}(V_i)}{n\sum_{i=1}^{n} t_i^2 - \left(\sum_{i=1}^{n} t_i\right)^2} \qquad \textbf{Eq.(7)}$$

, Where V is the V% of the measurement and t the time of measurement.

The second step consists to determine if the slope is significant (different from 0) by using a t-test:

$$t - test = \frac{m}{S_m} \qquad \textbf{Eq.(8)}$$

, where *m* is the slope *and* S_m is the standard deviation calculated on the slope. The value obtained is confronted to a critical value t with a degree of confidence of 0.05 corresponding to 2.78 for n=5 and 2.45 for n=7.

Finally, in order to determine if inks continue ageing even after one year, a very slow ageing ink was chosen (ink 1696) and analyzed up to 9 years. From 1 week to 6 months, samples were analyzed every 2 weeks, then the age interval between samples increased (i.e. age of t= 0.6, 0.8, 1, 1.5 , 2.5, 3,5 4, 5, 6, 7, 8, 9 years). The quantities of PE were considered as well as the resulting V% in order to determine the amount that can be found for old samples.

Results and discussion

Calibration

Calibration of the instruments was carried out three times within this work: (1) twice in Wiesbaden with a major instrument maintenance in-between (W1 and W2) and once in Munich (M). Differences in calibration curves were observed in Wiesbaden between the desorption temperatures of 90 and 200°C (Table 2). While the first calibration yielded approximately the same amounts of PE-TMS at both desorption temperatures (i.e., slopes of the curves of 837869 and 854423 counts*µl/ng respectively), the second calibration yielded lower amounts at T=90°C than at 200°C, resulting in two distinct and separated curves (i.e. slopes of the curves of 776109 and 1011619 counts*µl/ng respectively). The reason for that could not be determined. In Munich, the PE-TMS evaporated at 90°C was also in lower amount than at 200°C (Table 2).

The limit of applicability was first determined using the program BEN v2.03® (norm DIN 32645) with a significance of 95%. The obtained values in Wiesbaden and Munich were relatively high for all sets of calibrations (LoD around 1.5 ng and LoQ around 5 ng for both temperatures). (see Table 2). However, these relatively high values may represent a problem when considering older samples (i.e., these limits of reliability will be reached very quickly when analyzing older samples). For example, the LoQ was already reached after 44 days for ink 1688 samples desorbed at 90°C (Table 3). Therefore, a second less conservative approach was selected to estimate the LoD and LoQ using the background noise (49). The obtained LoQ values (1.1 ng/cm for the desorption at a temperature of 90°C and 0.9 ng/cm for 200°C) were thus approximately five times lower than those calculated with the BEN software. For example, the LoQ was then never reached for the sample of ink 1688 desorbed at 90°C considered in this study (Table 3). Considering the very low amounts of PE measured in ink entries after a few days, the LoQ calculated from the background noise were deemed more appropriate for the research purpose of this study.

The instruments response was linear for concentrations between 1 and 50 ng for the first calibration W1, as well as for M. Above 50 ng the response was not linear anymore and the curve started to level off over 100 ng PE-TMS. The linearity range was slightly lower for W2 (i.e. between 1 to 40 ng).

Insert Table 2

Repeatability

Replicate analyses of strokes from ink 1688 at three different ages were carried out the same day by the same operator. Relative standard deviation (RSD) were calculated both for the absolute peak area of PE-TMS and for the resulting V% - ratio. Results showed a higher variability for the amount of PE-TMS recovered than for V% for 2 and 89 days old samples (Table 3). At 90°C, the RSD was slightly above 10 %, while the RSD observed for 200°C were generally lower (<10%). Considering that no internal standards were used, the obtained values were acceptable for the low concentrations measured (2.28 to 16.81 ng of PE-TMS detected) (44). The calculation of the V%-ratio allowed to decrease significantly the variability of the results (i.e., obtained RSD were always lower than 5%).The variation observed for the analysis of control samples were comparable when PE-TMS peak areas were calculated (8.39 and 11.31%). This variation could also be decreased by calculating a ratio between the PE-TMS and n-C16. These results showed a good repeatability over a short period of time, meaning that the implementation and the set up of the method were successful.

Insert Table 3

Reproducibility

Two ageing curves were measured for ink 1688 in Wiesbaden at two different times corresponding to the calibrations of the instrument (see W1 and W2 in Table 2). Both sets of measurements yielded an ageing curve following an exponential decay (see Eq. (2)) (Figure 2A). However, despite calibration of the instrument, V%-ratios calculated for samples of same age were different between both curves, corresponding to a mean gap of 10.69 ± 0.36 along the curve. The applied regressions (see Table 4) showed that the obtained *A1* and τ_1 parameters were comparable between both curves. Only the constant V_0 was significantly different, since it was of 36.65 ± 1.36 and 27.42 ± 0.62 for W1 and W2 respectively (this constant is actually linked to the initial V%-value on the y-axis). The difference observed on the V_0 value ($\Delta V_0 = 9.23 \pm 1.73$) was consistent with the difference calculated on the real V%. The cause of the shift seemed to lay mainly in the step of the 90°C desorption. In fact, by decomposing the V% in its primary components, i.e. the quantity of PE-TMS recovered at each desorption temperature (Figure 2B and C), a clear shift appeared on the ageing curves recorded at a desorption temperature of 90°C (5.48± 1.18), twice larger than the difference observed for the desorption of 200°C (2.49 ± 2.34). Such differences were also observed in the calibration of the instrument (see W1, W2 and M in Table 2).

The ageing curve of the ink 1688 was additionally measured in Munich for comparison (Figure 2A). Similar differences in the curves were observed in Munich yielding a mean shift of 8.91 ± 1.15 compared to W1. While the regression parameters *A1* and τ_1 were also comparable to the W1 regression parameter, the constant V_0 was also significantly different (see Table 4).

These three curves showed the calibration is not as reproducible as known from liquid extraction followed by GC/MS analysis. Thus two curves made on the same instrument a few months apart presented significant difference in the V%-values. However, despite the observed difference, the ageing behavior remained comparable for ink samples measured using two different instruments. Thus, in the case of implementation of this method in a new laboratory, the criteria of comparison for repeatability and reproducibility of the instrument should be the ageing behavior rather than the calculated V%-values.

Insert Figure 2

Insert Table 4

Influence of ink cartridge, paper and storage conditions

Samples from ink 1688 prepared in Wiesbaden and in Lausanne were analyzed on the same instrument and compared (Figure 3A). Both ageing curves started with a V% around 55% after 1 day. However the curve from the Wiesbaden samples started to level off already after 30 days (at a V% value of 35%), while the curve from the Lausanne samples leveled off only after 100 days (at a V% value of 15%). The initial V% decrease in the Lausanne ink samples was faster and reached lower values than the one obtained with the Wiesbaden ink samples. The regressions applied on both curves highlighted different ageing curves since all the parameters significantly differed:

Wiesbaden: $$V\% = (37.0 \pm 0.6) + (20.9 \pm 1.1) \cdot \exp^{-t/(18.0 \pm 2.6)} \qquad \textbf{Eq.(9)}$$

Lausanne: $$V\% = (16.5 \pm 1.0) + (38.4 \pm 1.3) \cdot \exp^{-t/(41.8 \pm 4.5)}$$ **Eq.(10)**

Three influence factors may explain the observed differences (Table1): the ink entries were stored in different storage conditions (climatic chamber vs. air conditioned lab), on different paper (Xerox Performer vs. Xerox Business) and were drawn with two ink cartridges (one was filled in 2010 and the other in 2009). Thus the paper substrate and ink cartridge were tested in order to determine if they may explain some of the observed differences. New ink entries were prepared and stored in Wiesbaden (air conditioned conditions).

For papers, the results showed that it had only a small effect on values since these related on the Xerox Business paper were slightly higher than for Xerox Performer paper for same sample age (Figure 3B). However, as the V%-shift reached approximately 4%, it did not explain the whole observed disparity. The ageing curves and absolute V% values were both comparable to those obtained for the Wiesbaden samples (Figure 3A). No influence of the cartridge was observed as the V% obtained were indistinguishable for both cartridge (Figure 3C). Again, the ageing curves and V% were similar to those obtained for the Wiesbaden samples (Figure 3A).

Therefore, the results seem to indicate a strong effect of the tested storage conditions. While the temperature and humidity were slightly different (20°C/55% in Lausanne and 23°C/not controlled in Wiesbaden), the main difference seems to reside in the air fan causing strong air movement in the climatic chamber. Air flux may strongly accelerate drying processes such as the one involved in ink solvent ageing. Indeed the Lausanne samples showed different ageing curves than the Wiesbaden and Munich samples that were stored in “normal” conditions (air conditioned room). This seems to indicate that a climatic chamber is not representative of conditions usually encountered in casework because of the strong air flux provoked by the air fan. Further studies to better characterize the influence of “normal” conditions should thus be the focus of future research on ink dating.

Insert Figure 3

Interpretation

The inks 1688, 1774 and 1892 measured in Wiesbaden presented three different ageing curves (Figure 4); all of them followed an exponential regression according to eq. 2. The determination of the behavior by the different regression parameters (Table 5) showed that the more negative the term (-

$1/\tau_1$) was, the quicker the ageing curve leveled off. This was also showed by the half life time calculated from the curves (eq.3) that were 7.4 days for ink 1892, 30.2 for ink 1688 and 328.5 days for 1774 for the ink in Wiesbaden. Thus ink 1892 was considered as a rapidly drying ink, followed by ink 1688 and finally ink 1774. For the latter, the obtained V_0 for the regression was negative and very variable (-5.7±42.2) (Table6). This was probably caused by the fact that it is a very slowly ageing ink, (i.e., after one year it is probable that the curve did not level off yet). Moreover, the variability of the points around the curve did surely raise the uncertainty on the calculated parameters.

The quantities of PE found in ink samples were not necessarily correlated with the ageing speed (see Table 5). For example, ink 1688 showed the highest content of PE per cm ink: 85.2 ng/cm at seven days (Sum of the quantities recovered at 90 and 200°C) and 19.3 ng/cm at one year, while ink 1892 had the lowest content of PE: 13.3 ng/cm at seven days and 3.6 ng/cm at one year. The quantities recovered in one year old samples also confirmed that small quantities of phenoxyethanol remained in the paper for a long time after deposition (20, 24, 52). Generally ink samples containing more PE at the beginning contained also more residual solvent after one year on paper, but exceptions were observable, e.g. ink 1892 had a higher total amount of PE after one year than ink 1774 (Table 5).

Insert Figure 4

Insert Table 5

It was already reported that an interpretation based on V%-thresholds was not suitable to interpret the results of solvent analysis (34). This was confirmed by the observed shift in ageing curves calculated from the same ink (see Figure 2A). In order to practically use V%-thresholds for decisions regarding ink age, a new validation should be carried out after each maintenance in each laboratory (for a wide range of inks). This would imply a lot of analyses with a non-negligible risk that maintenance may be needed in-between. This is why the Neumann test was proposed as alternative (34). It allows the detection of a tendency (i.e. a statistical trend) on several measurements made over time. If a tendency is detected, it is concluded that the ink is still ageing (e.g. less than 6 months old). If no trend is detected, then no conclusion can be drawn concerning the age of the ink entry. This model is more suitable because the ageing curves proved to be more reproducible than absolute V%-values. In this situation, a false positive result meant that a tendency was falsely detected while the ageing clearly stopped. A false negative meant that no tendency was detected despite the fact that the ink was still ageing. A false positive has generally worse legal consequence than a false negative following the rule “in dubio pro reo” (translated from the latin to “*when in doubt, for the accused*”). Another important problem, not treated in this work, is the significance of the detected trend on the age of the ink entry (i.e. the legal meaning).

This model was applied on the obtained ageing data of the three inks. Five and seven data points (one every two weeks) were considered in the calculation for the Neumann test (see Table 6). With five data, the critical value (0.804 with a confidence limit of 95%) was quickly reached, since no trend was detected after 14 and 10 days for ink 1688 and 1892 respectively. For ink 1774, the obtained Neumann value was already above the critical limit for fresh samples (i.e. no trend was statistically observed on the whole curve). While one false positive was obtained (i.e. a trend was detected while the ageing curve had clearly leveled off) for ink 1892 (at 216 days), these results nevertheless seemed very conservative. Ideally a statistical test should detect a trend until the curve levels off. However, no conclusion could be reached after 14 days for ink 1688 using this test, while visually on the whole curve the V% of ink 1688 continued to decrease until approximately 110 days (see Figure 4). With seven data in the calculation, trends were observed over a longer period for ink 1688 (61 days) as well as for ink 1774 (16 days). For ink 1892, the maximum age was the same as with five data in the calculation and one false positive was again detected at 105 days. However, this trend corresponded to an ascending trend and would therefore normally not yield to a false conclusion. False positive seemed to result from the high variability in the measured data points; this should carefully be considered in order not to reach a false conclusion. Using more data points generally yielded better results. However, this may be a problem in practice, as it may not be possible to sample the required amount of ink on a questioned signature. This would also yield a significant increase in the analysis time (i.e. one more month).

Therefore an alternative model based on the calculation of slopes based on linear fits of the ageing curves obtained with the five (see Figure 5) or seven datapoints considered was proposed and tested in this work. .While the slopes of ink 1892 and 1688 decreased to reach a value around 0, the slopes for ink 1774 were more variable and remained mainly above 0.1. By applying a significance test, results showed a significant slope until 75 days for ink 1688 (for both 5 and 7 data points) (seeTable 6). For ink 1892, a slope was detected until 10 days and interestingly, no false positive were recorded with 7 datapoints (while 1 was recorded using five data at 273 days). The most difficult ageing curve to interpret remained the one of ink 1774. A slope was observed for a longer time period than the Neumann test. Using 7 datapoints, the slope was continuously significant until 52 days, then again from 129 days to 153 days. In-between the variation was too high and no slopes could be detected. These results may represent false negatives (i.e. no conclusion could be reached, while the ink visually seemed to be still ageing considering the whole ageing curve).

Insert Figure 5

The calculation of slopes followed by the significance test actually gave better results than the Neumann test. While the number of measurements considered was less critical than for the Neumann test, the use of 7 instead of 5 data points allowed to eliminate the false positive result for ink 1892. However, this should further be tested on a higher number of data. Additional advantage lies in the possibility to determine the nature of the trend (ascending, descending) contrary to the Neumann test. While the slope approach takes into account the data variability, this remained an important limitation (i.e. limitation of the cases where a conclusion can be reached). Interestingly, the ink with the smallest amount of PE yielded the three false positive of this study. In practice it is therefore advised to relate the absolute amount of PE to the V% in the interpretation and this may indeed limit the number of false positive conclusions.

Insert Table 6

Finally, measurements were performed on samples of ink 1696 with an age of up-to-9 years The obtained ageing curves demonstrated that the quantities of PE in strokes still decreased until an approximate age of 1.5 years before the curves leveled off (Figure 6A). This ink actually contained a relatively high initial quantity of PE (80.1 ng/cm were recovered from a sample with an age of 7 days (Table 5). After 1 year, the recovered PE still reached 30.4 ng/cm (sum of the quantities of PE recovered at 90 and 200°C). This ink was actually considered to age particularly slowly (i.e. the half life time of 349.16 days was the longest measured during this study).

However, no slope was detected due to the high variability of the V% values (particularly up to 2 years). This problem was also highlighted for ink 1774. This tends to demonstrate that interpretation models based on threshold decision do not cope well with extreme values and high variability. The development of another kind of approach is therefore necessary to improve the reliability and the scope of ink dating methods. A probabilistic model such as the likelihood ratio already proposed earlier for ink dating (45-46) and more recently for the interpretation of dating evidence in other forensic fields (53) would probably represent a good solution. However, more data will be needed in order to investigate and implement such a probabilistic model.

Insert Figure 6

Conclusion

The presented results demonstrated the possibility to implement the TD-GC/MS ink dating method developed in Munich in another laboratory. However, the task was not trivial and validation results showed that, while measurement repeatability was reliable over a small period of time, the method proved to be very sensitive to maintenances. The response obtained over a longer time period in a laboratory and between laboratories varied for the ageing parameter V%. In fact, significant shifts in absolute V%-values were observed when analyzing samples of the same ink stored under the same conditions. In spite of this phenomenon, the ageing kinetics calculated with a single exponential regression proved to be comparable between instruments over the whole time period of this study. Therefore, it is strongly advised to evaluate the method implementation and the dating results using the observed kinetics rather than absolute V%-values.

In addition, it was also demonstrated that if the ageing curves remained comparable for samples of the same ink stored in the same storage conditions, this was not the case when storage conditions were modified (for example using a climatic chamber with an air fan). As storage conditions may not be known in practice, this fact should be considered for further interpretation of the results. Further studies should thus aim at characterizing the influence of small differences in document storage on the dating results.

A very important step in ink dating developments also lies in the interpretation of the data in a legal perspective. Two different models based on ageing behaviors were evaluated: the Neumann trend test and an alternative model based on the calculation of slopes from linear regression fits. Results highlighted that the Neumann test was strongly influenced by the number of data points used in the calculation. The presented alternative, the slope model, proved to be more suitable even if the variability remained an important issue for both statistical tests. On the other hand, the variation in results did not originate only from analytical limitations, and could therefore not simply be reduced. Variability was also partly due to the inhomogeneity of ink entries, a particularity of all forensic samples in practice. Thus, other interpretation models, not based on decision threshold, should be investigated to take this particularity into account. A probabilistic approach may be the solution and will therefore be further studied.

Finally, it is important to stress again the extreme care that must be taken in the manipulation of the instrument and samples, as well as for data interpretation. In order to properly implement and use the method in a laboratory, collaboration with laboratories having already implemented this method is strongly recommended, followed by blind testing on realistic samples,.

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References

1. Cantu AA. A sketch of analytical methods for document dating Part I. The static approach: determining age independent analytical profiles. Int J Forensic Doc Examiners. 1995;1(1):40-51.
2. Cantu AA. A sketch of analytical methods for document dating part II. The dynamic approach: determining age dependent analytical profiles. Int J Forensic Doc Examiners. 1996;2(3):192-208.
3. Weyermann C, Kirsch D, Vera CC, Spengler B. Evaluation of the photodegradation of crystal violet upon light exposure by mass spectrometric and spectroscopic methods. J Forensic Sci. 2009 Mar;54(2):339-45.
4. Ezcurra M, Góngora JMG, Maguregui I, Alonso R. Analytical methods for dating modern writing instrument ink on paper. Forensic Sci Int. 2010;197(1-3):1-20.
5. Brunelle RL, Breedlove CH, Midkiff CR. Determining the relative age of ballpoint inks using a single-solvent extraction technique. J Forensic Sci. 1987;32(6):1511-21.
6. Brunelle RL, Lee H. Determining the relative age of ballpoint ink using a single-solvent extraction, mass-independent approach. J Forensic Sci. 1989 Sep;34(5):1166-82.
7. Aginsky V. Determination of the age of ballpoint pen ink by gas and densitometric thin-layer chromatography. J Chromatogr A. 1994;678:119-25.
8. Brunelle RL. A sequential multiple approach to determining the relative age of writing inks. Int J Forensic Doc Examiners. 1995;1(2):94-8.
9. Brunelle RL, Speckin EJ. Technical report with case studies on the accelerated aging of ball-point inks. Int J Forensic Doc Examiners. 1998;4(3):240-54.
10. Andrasko J. HPLC analysis of ballpoint pen inks stored at different light conditions. J Forensic Sci. 2001 Jan;46(1):21-30.
11. Grim DM, Siegel J, Allison J. Evaluation of laser desorption mass spectrometry and UV accelerated aging of dyes on paper as tools for the evaluation of a questioned document. J Forensic Sci. 2002 Nov;47(6):1265-73.
12. Hofer R. Dating of ballpoint pen ink. J Forensic Sci. 2004 Nov;49(6):1353-7.
13. Weyermann C, Kirsch D, Costa-Vera U, Spengler B. Photofading of ballpoint dyes studied on paper by LDI and MALDI MS. J Am Soc Mass Spectrom. 2006 Mar;17(3):297-306.
14. Weyermann C, Marquis R, Mazzella W, Spengler B. Differentiation of blue ballpoint pen inks by laser desorption ionization mass spectrometry and high-performance thin-layer chromatography. J Forensic Sci. 2007 Jan;52(1):216-20.

15. Wang X-F, Yu J, Xie M-X, Yao Y-T, Han J. Identification and dating of the fountain pen ink entries on documents by ion-pairing high-performance liquid chromatography. Forensic Sci Int. 2008;180(1):43-9.

16. Midkiff CR, Starrs JE. Ink dating - in footsteps of cold fusion. Scientific Sleuthing Review. 1994;18(1):1-6.

17. Hicks Champod T, Khanmy A, Margot P, editors. Ink aging: perspectives on standardization. 13th Meeting of the International Association of Forensic Sciences, Duesseldorf, 1993, Advances in Forensic Sciences 3, Forensic Criminalistics 1; 1995; Duesseldorf. Verlag Dr. Koester, Berlin.

18. Margot P, Hicks Champod T, Khanmy A. Ink Dating Up-Dated and Up-Ended – Correspondance of Prof. Starrs. . Int J Forensic Doc Examiners. 1995;1(1):2-5.

19. Starrs JE. Ink Dating Up-Dated and Up-Ended. Int J Forensic Doc Examiners. [Correspondence]. 1995 Jan / Mar 1995;1(1):3 - 5.

20. Aginsky VN. Accelerated Aging- Its Use in Methods for Dating Ink. Int J Forensic Doc Examiners. 1996;2(3):179-81.

21. Aginsky VN. 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. Int J Forensic Doc Examiners. 1998;4(3):214-30.

22. Andermann T. Solvent extraction techniques-possibilities for dating ball point pen inks. Int J Forensic Doc Examiners. 1998;4(3):231-9.

23. Stewart LF. Ballpoint ink age determination by volatile component comparison - a preliminary study. J Forensic Sci. 1985;30(2):405-11.

24. Aginsky VN. Some new ideas for dating ballpoint inks-a feasibility study J Forensic Sci. 1993;38(5):1134-50.

25. Aginsky V. Dating and characterizing writing, stamp, pad, and jet printer inks by gas chromatography/mass spectrometry. Int J Forensic Doc Examiners. 1996;2(2):103-16.

26. Gaudreau M, Brazeau L. Ink dating, a solvent loss ratio method. 6th Annual Conference of the American Society of Questioned Document Examiners, 2002; San Diego, California. 2002.

27. Andrasko J. A simple method for distinguishing between fresh and old ballpoint pen ink entries. Forensic Sci Int. 2003 Sep;136:80-1.

28. Lociciro S, Dujourdy L, Mazzella W, Margot P, Lock E. Dynamic of the ageing of ballpoint pen inks: quantification of phenoxyethanol by GC-MS. Sci Justice. 2004 Jul-Sep;44(3):165-71.

29. Andrasko J, Kunicki M. Inhomogeneity and aging of ballpoint pen inks inside of pen cartridges. J Forensic Sci. 2005 May;50(3):542-7.

30. Xu Y, Wang J, Yao L. Dating the writing age of black roller and gel inks by gas chromatography and UV-vis spectrophotometer. Forensic Sci Int. 2006;162(1-3):140-3.

31. Wang Y, Yao L, Zhao P, Wang J, Wang Y. Determining the relative age of blue ballpoint ink by gas chromatography. Frontiers of Chemistry in China. 2006;1(2):223-6.

32. Brazeau L, Gaudreau M. Ballpoint pen inks: The quantitative analysis of ink solvents on paper by solid-phase microextraction. J Forensic Sci. 2007 Jan;52(1):209-15.

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

34. Bugler JH, Buchner H, Dallmayer A. Age determination of ballpoint pen ink by thermal desorption and gas chromatography-mass spectrometry. J Forensic Sci. 2008 Jul;53(4):982-8.

35. Ezcurra M, Velasco I, Góngora JMG, Maguregui I, Alonso R. Analysis of bic crystal medium ball point pen inks. J Am Soc Questionned Doc Examiners. 2009;12(2):57-68.

36. Ezcurra M, Góngora JMG, Maguregui I, Alonso R. 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. J Am Soc Questionned Doc Examiners. 2010;13(1):9-14.

37. Gaudreau M, Aginsky V. Essentials of the solvent loss ratio method. 68th Annual Conference of the American Society of Questionned Document Examiners (ASQDE), 2010 August 28th-september 2nd 2010 Victoria, USA. 2010.

38. Bugler JH, Buchner H, Dallmayer A. Characterization of ballpoint pen inks by thermal desorption and gas chromatography-mass spectrometry. J Forensic Sci. 2005 Sep;50(5):1209-14.

39. LaPorte GM, Wilson JD, Cantu AA, Mancke SA, Fortunato SL. The identification of 2-phenoxyethanol in ballpoint inks using gas chromatography/mass spectrometry-relevance to ink dating. J Forensic Sci. 2004 Jan;49(1):155-9.

40. Weyermann C, Kirsch D, Vera CC, Spengler B. A GC/MS study of the drying of ballpoint pen ink on paper. Forensic Sci Int. 2007 May 24;168(2-3):119-27.

41. Kirsch D, Guillou V, Anheier B, Seiler P, Köhler F, editors. Different analytical methods of dating ball point ink entries. in: ENFSI, 6th European Document Examiners Working Group (EDEWG) conference; 2010; Dubrovnik, Croatia.

42. Kirsch D, Seiler P, Anheier B, Koehler F. A new approach for dating of ballpoint ink entries. 69th Annual Conference of the American Society of Questionned Document Examiners (ASQDE), 2011 August 20-25th 2011; Philadelphia, USA. 2011.

43. http://www.enfsi.eu/about-enfsi/structure/working-groups/documents. Last access: 20.08.2013.

44. Horwitz W. Evaluation of analytical methods for regulation of foods and drugs. Anal Chem. 1982;52:67-76.

45. Weyermann C, Almog J, Bügler J, Cantu AA. Minimum requirements for application of ink dating methods based on solvent analysis in casework. Forensic Sci Int. 2011;210(1-3):52-62.

46. Weyermann C, Schiffer B, Margot P. A logical framework to ballpoint ink dating interpretation. Sci Justice. 2008 Sep;48(3):118-25.

47. Bügler JH, editor. Method validation for age determination of ballpoint inks. 5th Annual Conference of the European Document Experts Working Group (EDEWG); 2008; Bunratty, Ireland.

48. Bügler JH, Graydon M, Ostrum B, editors. The parctical use of the Munich ink reference collection in daily casework. 6th European Document Examiners Working Group (EDEWG) Conference; 2010; Dubrovnik, Croatia.

49. Miller JN, Miller JC. Statistics and chemometrics for analytical chemistry fifth edition. Harlow: Pearson Education Limited, 2005.

50. E.M. A. ICH topic Q2 (R1). Validation of analytical procedure: text and methodology. London: EMEA; 2006.

51. Neumann J, Kent R, Bellison B, Hart B. The mean square successive difference. Ann Math Stat. 1941;12:153-62.

52. Weyermann C. Mass spectrometric investigation of aging processes of ballpoint ink for the examination of questioned documents [dissertation]. Giessen: Justus-Liebig-University, 2005.

53. Gallidabino M, Weyermann C, Romolo FS, Taroni F. Estimating the time since discharge of spent cartridges: A logical approach for interpreting the evidence. Sci Justice. 2013;53(1):41-8.

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Table 1 : Summary of ink entries preparation and storage in three laboratories

Ink entry preparation	Lausanne	Wiesbaden	Munich
Paper (80 g/m^2)	Xerox Business	Xerox Performer	"Nonstop" copy paper 80 g/cm^2
Stoke preparation :			
Distance between stroke [cm]	3	3	2
Separation (between sheets)	2 blank sheets	2 blank sheets	1 blank sheet
Container	folder	folder	folder
Storage conditions :			
Location	Climatic cabinet	Laboratory	Laboratory
Temperature (°C)	20.00 ± 0.02	23 ± 1	25 +/- 1
Humidity (%)	55.00 ± 0.10	Not controlled	Not controlled
Aeration	Air recycling (fan: 50%)	Not controlled	Not controlled
Ink samples **(date of cartridge filling)**	1688 (05.2010) 1774 (05.2010) 1892 (05.2010)	1688 (05.2009)	1688 (12.2009) 1696 original samples
TD-GC/MS instrument	Wiesbaden	Wiesbaden	Munich (1688) Wiesbaden (1696)

Table2 : Results for the calibrations and the calculation of the LoD/LoQ obtained in Wiesbaden (W1 and W2) and Munich (M) with BEN software

	W1		**W2**		**M**	
Desorption	**90°C**	**200°C**	**90°C**	**200°C**	**90°C**	**200°C**
Calibration :						
Slope [counts * µl/ng]*	837869	854423	776109	1011619	447880	672980
Intercept [counts]	-138942	108991	-71906	-143106	205480	345450
R^2	0.999	0.998	0.999	0.998	0.997	0.999
Limits (95%)						
LoD [ng/cm]	1.2	1.5	1.4	1.6	1.3	1.7
LoQ [ng/cm]	4.3	5.4	4.9	5.8	4.7	6.5
Working range [ng/cm]	4.3 – 50.0	5.4 - 50.0	4.9 – 40.0	5.8 - 40.0	4.7-50.0	6.5-50.0

Table 3 : Quantities of PE-TMS recovered and relative standard deviation calculated on three replicates of ink 1688 for the desorption of 90 and 200°C as well as for the calculated V% ratio. The results obtained for the control sample were also reported for the quantity of PE obtained for both desorption and the ratio between PE-TMS and nC16

Sample	**Mean ± sd (n=3) (RSD %)**		
	PE-TMS(90°C) [ng/cm]	**PE-TMS (200°C) [ng/cm]**	**V%**
Ink of 2 days	16.71 ±1.74 (10.75%)	16.81±1.15 (6.86%)	48.97±2.42 (4.93%)
Ink of 44 days	2.81±0.12 (4.18%)	6.52±0.24 (3.65%)	31.84±0.45 (1.50%)
Ink of 89 days	2.28±0.29 (12.94%)	6.29±0.53 (8.44%)	26.51±0.85 (3.20%)
Control sample	10.96±0.92 (8.39%)	9.90±0.64 (11.31%)	3.21 ± 0.04[1] (1.24%)

[1]: ratio PE_TMS/nC16

Table 4 : Regression parameters for the aging curves of ink 1688 measured in Wiesbaden and Munich

Aging parameter	Calibration	$V\% = V_0 + A_1 \cdot \exp^{-t/\tau_1}$			R^2
		V_0	A_1	τ_1	
R%	W1	36.7 ± 1.4	20.7 ± 1.4	24.5 ± 6.0.	0.97
	W2	27.4 ± 0.6	24.4 ± 0.8	19.5 ± 2.3	0.99
	M	25.2 ± 1.3	24.0 ± 1.4	24.0 ± 3.6	0.99
PE-TMS at 90°C	W1	10.2 ± 1.3	39.8± 4.4	6.8± 1.5	0.95
	W2	5.4± 0.4	43.7 ± 4.7	4.1± 0.7	0.99
PE-TMS at 200°C	W1	16.0 ± 1.5	24.0± 6.7	4.9 ± 2.3	0.78
	W2	12.5± 0.6	40.6± 8.8	3.1 ± 0.8	0.95

Table 5 : Regression parameters, half life times and total amount of PE recovered (90+200°C) at two different ages for ink 1688, 1774, 1892 and 1696 measured in Wiesbaden.

Ink	$V\% = V_0 + A_1 \cdot \exp^{-t/\tau_1}$			R^2	T ½	Total quantity of PE (90+200°C) [ng/cm]	
	V_0	A_1	τ_1		days	7 days	1 year
1688	16.0 ± 0.5	38.8 ± 1.0	43.5 ± 3.3	0.99	30	85.2	19.3
1774	-5.7 ± 42.2	84.5 ± 41.0	474.0 ± 323.9	0.90	328	34.9	3.2
1892	19.3 ± 0.7	25.8 ± 2.9	10.7 ± 2. 6	0.88	7	13.3	3.6
1696	15.9 ± 0.5	38.8 ± 1.0	43.5 ± 3.3	0.92	349	81.0	30.4

Table 6 : Statistical tests to determine the age until when an ink entry was still aging (n is the number of measurements used to perform the tests). The given limit is the age of the ink the day of the first analysis. In brackets, the age of the false positives is indicated.

Ink	Neumann trends [days] (age of false positives)		F-Test on slopes [days] (age of false positives)	
	n=5	n=7	n=5	n=7
1688	14	61	75	75
1774	0	16	21	52
1892	10 (216)	10 (105)	10 (273)	10

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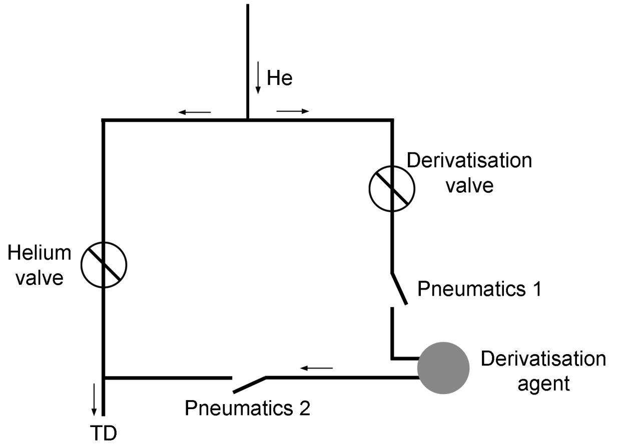

Figure 1 : Schematic representation of the derivatisation box.

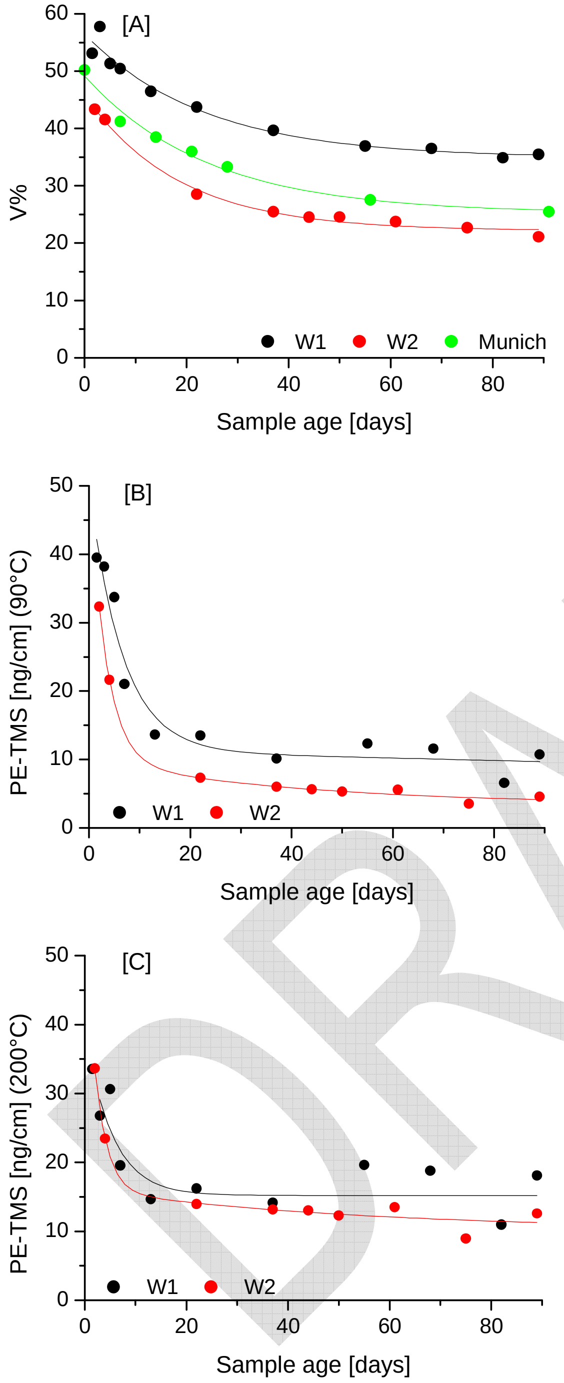

Figure 2: A. Ageing curves built with the V% of ink 1688 measured at two distinct periods in Wiesbaden (W1 and 2) as well as measured in Munich. B. Ageing curves built with the quantities of PE-TMS

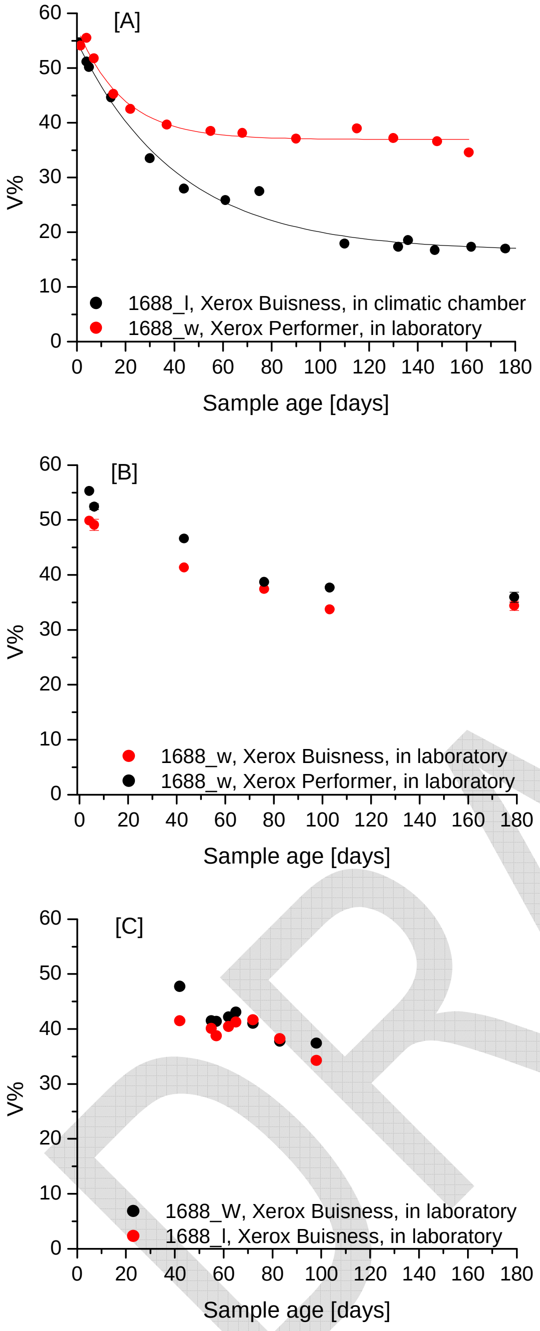

Figure 3 : **A**. Ageing curves according to the ink entry preparation**. B**. Comparison of the ageing curves of sample on Xerox Buisness and Xerox Performer papers. **C**. Comparison of sample made with two different cartridges (1688_w and 1688_l) of the same ink

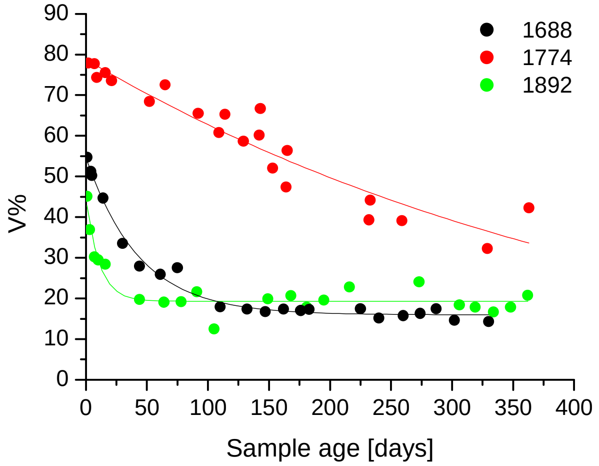

Figure 4 : Ageing kinetic of ink 1688, 1774, 1892 from 1 day to 1 year approximately, obtained in Wiesbaden

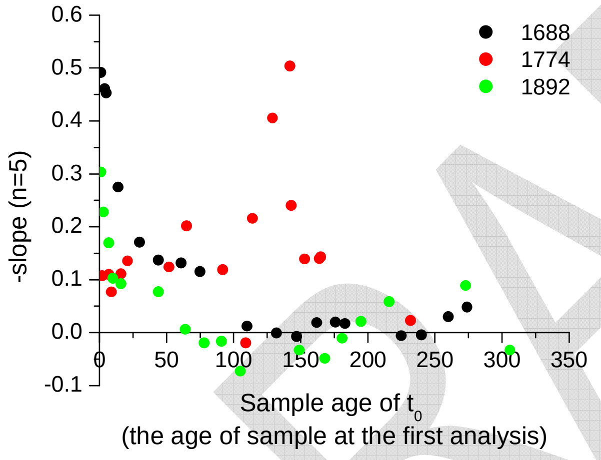

Figure 5 : Minus of the slopes calculated on 60 days (i.e. five datapoints) for inks 1688, 1774 and 1892.

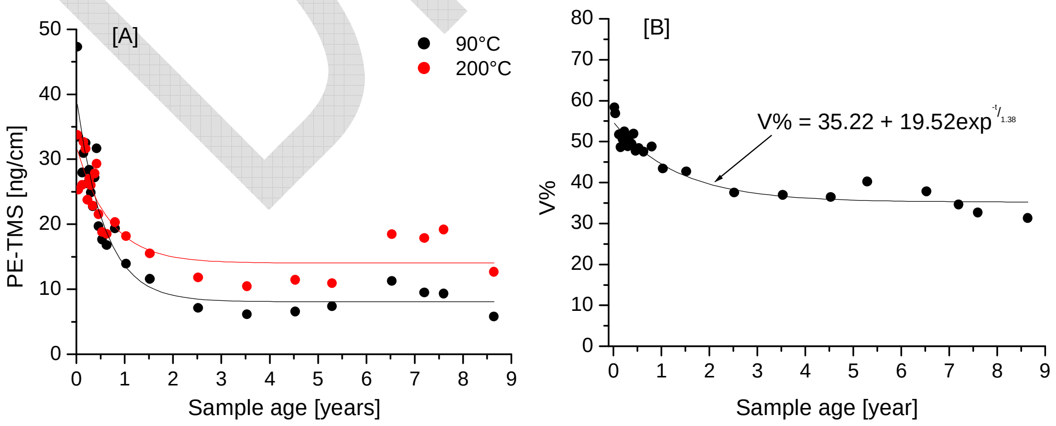

Figure 6 : **A.** Ageing curves built with the quantity of PE-TMS recovered for both desorption temperature for ink 1696**.** **B.** Ageing curve of the resulting V%.