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INK DATING, PART I : STATISTICAL DISTRIBUTION OF SELECTED AGEING PARAMETERS IN A BALLPOINT INKS REFERENCE POPULATION

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Abstract

The development of ink dating methods requires an important amount of work in order to be reliably applicable in practice. Major tasks include the definition of ageing parameters to monitor ink ageing. An adequate parameter should ideally fulfil the following criteria: it should evolve as a function of time in a monotonic way, be measurable in a majority of ink entries, be as accurate and reproducible as possible, and finally it should not be influenced too much by transfer and storage conditions. This work aimed at evaluating the potential of seven ageing parameters for ink dating purposes: the phenoxyethanol quantity, relative peak areas (RPA), three solvent loss ratios (R%, R%*, NR%) and two solvent loss parameters (R_{NORM}, NR_{NORM}). These were calculated over approximately one year for 25 inks selected from a large database to represent different ageing behaviours. Ink entries were analysed using liquid extraction followed by GC/MS analysis. Results showed that natural ageing parameters (NR% and NR_{NORM}) were not suitable ageing parameters for ink entries older than a few weeks. RPA used other compounds present in ink formulations in combination to PE in order to normalise the results. However, it presented particular difficulties as they could not be defined for all inks and were thus applicable only for 64% of the studied inks. Finally, the PE quantity, R% and R_{NORM} allowed to follow the ageing of the selected inks over the whole time frame and were identified as the most promising. These were thus selected to test three different interpretation models in the second part of this article. The possibilities and limitations of ink dating methods will be discussed in a legal perspective.

1   INTRODUCTION

Ink dating remains a particularly challenging forensic task. Despite almost a century of research [1-4], only few methods have been reported as being used in practice [5-11]. This can mainly be explained by the complexity of the ageing processes and the amount of experiments needed to correctly interpret the results in actual caseworks. Several steps were previously described as minimum requirements to reliably estimate the age of an ink entry [12]: method development and validation, aging parameters selection, data collection under different influencing factors and finally, data interpretation in a legal perspective. Indeed, a method must first be developed and validated in order to insure reliable and sensitive analysis of selected ink ageing parameters over time. This step generally represents the easiest task and is well described in the (forensic) literature [13]. More recently proposed approaches focused on the analysis of ink volatile compounds, and mainly phenoxyethanol (PE) and its decrease over time [5-10, 14-32]. While gas chromatography coupled to mass spectrometry (GC/MS) was mainly used to analyse PE and other ink solvents, high performance liquid chromatography (HPLC) was also recently proposed to simultaneously analyse dyes and solvents [10, 11, 23]. Different extraction methods were also proposed such as liquid extraction [6, 8, 9, 12, 21, 22, 25-27, 29, 31, 32], thermodesorption [7, 18, 24, 33] or solid phase microextraction (SPME) ([17, 19].

Once the method is developed and validated, ageing parameters must be selected to monitor ageing according to the following criteria [12, 25, 34]:

- they must   evolve as a function of time in a monotonic way (ascendant or descendent). The ageing must be measurable over a large time scale (ideally months to years for ink dating).
- they must be measurable in most ink formulations using the chosen method.   It is generally known that ink composition has a significant influence on ink ageing [7, 31]. Thus, analysing representative ink reference populations is essential to insure that the selected ageing parameter can be implemented in most cases.
- they should be as reliable as possible yielding precise and accurate measurements, ideally even on different ink specimens of the same age.
- they should be influenced as little as possible by external factors typically encountered in caseworks (such as paper properties, transfer and storage conditions).

In a previous paper using liquid extraction followed by GC/MS [25], four ageing parameters were tested over time under different influence factors: the quantity of PE, different relative

peak areas (RPA) and solvent loss ratios using two samples of the same ink entry, one of them artificially aged. These ratios were calculated from the quantities of PE (R%) or from the RPA values (R%*). While data was collected on a limited ink population (n=3), obtained results were promising. RPA proved to be the most repeatable ageing parameter and the least influenced by the different tested conditions, the solvent loss ratios were the less reproducible parameters.

Finally, an adequate interpretation model must be developed to estimate the age of a questioned ink entry in a legal perspective. Several constraints are attached to this task such as the fact that the "source" ink or pen is generally unknown and thus, a representative ink population has to be considered to adequately interpret the results.

In this article, liquid extraction followed by GC/MS was used to analyse samples from 25 different inks provided by the LKA Münich. These were selected from a large ballpoint pen ink collection as representative of the ageing behaviours measured in previous studies [7, 35]. Ink lines were aged from 4 to 304 days on paper before analysis. Seven ageing parameters, including the PE quantity, the relative peak areas (RPA), three solvent loss ratios (R%, R%*, NR%) and two solvent loss parameters (R_{nom} and NR_{nom}) were calculated. The first part of this paper focused on the evaluation of the collected data. The distribution of each aging parameters over time was used to estimate their potential for ink dating purposes. The second part of this paper focused on testing different interpretation models on selected ageing parameters in order to reliably estimate the age of an ink entry in a legal perspective.

2 MATERIAL AND MÉTHOD

2.1 MATERIAL

Chloroform (99.9%) was purchased from Sigma Aldrich (Darmstadt, Germany). The reference substances phenoxyethanol (PE) 99.5%, benzyl alcohol 98% and heneicosane were purchased from Fluka (Buchs, Switzerland) and the internal standard was deuterated phenoxyethanol (PE-D_2) from EGT Chemie (Tägerig, Switzerland),

For sample preparation, 1.5 ml vials, 300 µl and 50 µl inserts as well as springs were obtained from Swiss Lab (Basel, Switzerland).

2.2 SAMPLES

The analysed samples were drawn with 25 different inks chosen as representative of the different ageing behaviours observed in previous studies [7, 36-38]. The ink were provided

by the LKA Munich from their large collection of inks and ballpoint pens [35] and were of different brands, models and countries (mainly european and american). The chosen inks were divided in the following brands: BIC (2 inks), Papermate (2), Pilot (2), National Ink (2), Dokumental (2), Sanford (1), Formulabs (2), Waterman (2), Staedler (1), Lamy (1), Pelikan (1), Rosinco (1), Pentel (1), Reinol (1) and unknown (4) were analysed in this study. Among them 12 inks were blue and 13 were black.

The samples of each ink consisted in 4 lines drawn on a white copy paper of 80 g/m2 (Xerox Business paper) with a ruler. The strokes were placed 4 cm apart and two white pages were inserted between sheets to avoid cross-contaminations, according to a protocol discussed within the *International Collaboration for Ink Dating* (InCID)[1]. The pages were stored in folders located in an air conditioned laboratory at 23±1°C.

2.3 SAMPLE COLLECTION

Samples were collected at times t = 4, 8, 23, 39, 52, 77, 101, 138, 165, 227, 274, 304 days after the ink lines were written on the paper. The sample were collected in 2 sets of 1 cm; one being artificially aged. Collection from the paper was performed with a microplunger of 1 mm diameter (Sigma-Aldrich, Buchs, Switzerland). 10 dots/punches were taken on different locations of the four lines for each set. For each dot taken for the "natural" set, a second was collected right next to it for the "heated" set in order to limit variations between the two sets [6, 8, 9, 25].

The "natural" sample was introduced into a conical insert of 300 μl and extracted, while the "heated" sample was inserted in a 1.5 ml vial and artificially aged in a dry bath (VWR, Nyon, Switzerland) during 2h at 70°C. Precautions were taken to avoid overlapping inside the vial. After the artificial ageing, the dots were transferred to a 300μl insert through a paper funnel. Once the samples reached room temperature, the extraction was carried out.

The PE of both sets was extracted using 15 μL of chloroform containing PE-D2 as internal standard (1 ng/μl) during 3 min. Every minute the liquid was mixed with a tip. Then, the liquid was collected with a syringe and introduced in a 50 μL insert that was placed on a spring in a 1.5 mL vial. The vial was finally sealed and analysed.

2.4 GC/MS ANALYSIS

The analyses were performed with a gas chromatograph (6890 Agilent technologies) coupled with a mass spectrometer (5790C, Agilent technologies). Separation was carried out on a

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[1] http://enfsi.eu/about-enfsi/structure/working-groups/documents-page/

HP5-MS column (30m x 0.25mm x 0.25μm) with a flow of 1 ml/min of helium. For each analysis, 1 μl of solution were collected and injected in splitless mode in the GC by an autosampler (GC7890; Agilent technologies) with a purge time of 1 min. The injector was settled at 270°C. The program of temperature started at 50°C for 3 min, and then the temperature increased at 25°C/min to 110°C. A new rate was performed from 110°C to 300°C at 45°C/min and finally 300°C was maintained for 3 min. The whole run lasted 12.6 min with a solvent delay of 4.5 min. The transfer line was maintained at 250°C and the electron impact (EI) ion source was maintained at 230°C. The ions were filtered through a quadrupole set at 150°C in scan mode from 30 to 550 m/z.

In order to control the GC/MS performances, a solution containing 1.7 ng/μl of PE (26 ng/cm), 1 ng/μl of PE-D_2, 4 ng/μl of BA and 4 ng/μl of heneicosane was analysed daily.

Calibration was performed by analysing control solutions containing PE at concentrations of 0.01, 0.03, 0.05, 0.1, 0.5, 1, 5, 10, 50, 100, 200 ng/μL in chloroform containing 1 ng/ul of PE-D_2. The concentrations were transformed in ng/cm (= ng/ul x15), yielding quantities from 0.15 to 3000 ng in 1 cm of ink.

The limit of detection (LoD) and limit of quantification (LoQ) were determined using the signal to noise method [39]:

$$LoD = \overline{X}_{Blank} + 3 \cdot SD_{Blank}$$

Equation 1

$$LoQ = \overline{X}_{Blank} + 10 \cdot SD_{Blank}$$

Equation 2

,where $\overline{X}_{Blank}$ is the mean peak area and SD_{Blank} is the standard deviation of the background noise at the retention time of the interest compound calculated on 12 extracting blank solution analyses. It was calculated for all identified compounds.

2.5 DATA TREATMENT

The peak areas (PA) of the ink components were calculated using selected target ions (see Table 2). Those ions were selected because they were abundant and specific to the molecule of interest in the spectra. For each molecule at least two qualifiers were determined to check the peak identification.

The calculated PA for the PE-D_2 (IS) had to be corrected as follows [25]:

$$PA(PE\text{-}D_2) = PA(ion140) - \frac{0.78 \times PA(ion138)}{100}$$

Equation 3

, where PA$_{(ion\ 138)}$ is the peak area of ion 138 m/z and PA$_{(ion\ 140)}$ the peak area of ion 140 m/z obtained at a retention time of 8.48 min.

Relative peak areas (RPA) for the different solvents recorded in the ink samples were calculated in order to monitor their ageing:

$$RPA(X/Y) = \frac{PA(X)}{PA(Y)}$$

Equation 4

, where X is the molecule of interest and Y a stable compound, either the internal standard or another stable ink compound over time.

The ratio R% was calculated using the quantities of PE extracted from both natural (PE_n) and heated (PE_h) samples [6, 9, 40]:

$$R\% = \frac{PE_n - PE_h}{PE_n} \times 100$$

Equation 5

In addition, the parameter R%* was calculated by replacing the quantity of PE in Eq. 6 by the selected RPA_n and RPA_h for a given ink.

Another ageing parameter was calculated from the nominator of Eq. 5 and was called R_{NORM}:

$$R_{NORM} = PE_n - PE_h$$

Equation 6

Finally a new parameter, inspired by the solvent loss ratio (Eq. 5) but using one month natural ageing instead of artificial ageing was also evaluated. It was called NR% for natural solvent loss ratio and was calculated as follows:

$$NR\% = \frac{PE_{t0} - PE_{t0+30}}{PE_{t0}} \times 100$$

Equation 7

; where PE_{t0} is the quantity of PE recovered from the first ink analysis when the document is received and PE_{t0+30} is the quantity of PE recovered from a second sample collected 30 days after the first analysis.

For each ink, the obtained aging parameter, values were plotted as a function of time. When possible a regression was applied according to the model proposed by Cantu [41, 42]:

$$AP = AP_0 + A_1 \times \exp\left(-t/\tau_1\right) + A_2 \times \exp\left(-t/\tau_2\right)$$

Equation 8

, where AP is the ageing parameter and t is the age in days

A trend test was applied in order to statistically determine if an ageing was observed or not over a determined time range. In order to achieve this goal, a slope was calculated [24]:

$$-m = -\frac{n\sum_{i=1}^{n}(AP_i) - n\sum_{i=1}^{n}t_i\sum_{i=1}^{n}(AP_i)}{n\sum_{i=1}^{n}t_i^2 - \left(\sum_{i=1}^{n}t_i\right)^2}$$

Equation 9

, where AP is the ageing parameter of the measurement and t the corresponding time of measurement. Then, a t-test was used to determine if the slope was significant (different from 0):

$$t - test = \frac{m}{S_m}$$

Equation 10

, where m is the slope *and* S_m is the standard deviation calculated on the slope. The value obtained was confronted to a critical value t with a degree of confidence of 0.01 (i.e., more conservative than the generally used value of 0.05). If the value was smaller than the chosen critical value (degree of freedom n-2), then the measured slope was not considered to be significant. This test was applied to select compounds for RPA calculations in order to determine if these compounds were "stable" or still ageing for a given ink (i.e. the data followed a normal distribution). .

Boxplots were additionally constructed using results obtained for all inks with the software Origin Pro 9.0. The box limits represent the 25th and 75th percentile and the whiskers show the 5th and 95th percentile (Figure 1). The median is indicated by a straight line in the box and the mean by a small square. The maximal and minimal values are represented by a cross.
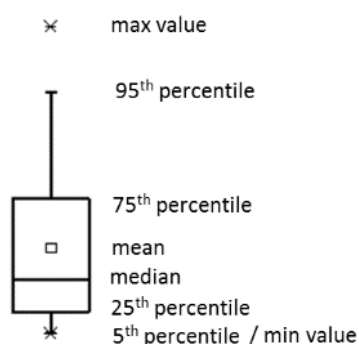

Figure 1 : Scheme of the boxplot signification

Calculation of the mean and variance of the ageing parameters over time were additionally built as a function of time [39].

3 RESULTS AND DISCUSSION

3.1 INK POPULATION COMPOSITION

As expected, different ink formulations were observed for the 25 inks of the reference population using GC/MS (**Table 1**). 19 compounds were identified with the help of the NIST library in 4 days old samples. Among them, well known ballpoint pen ink volatile components were found such as benzyl alcohol (BA), hexylene glycol (HG), 2,2-ethoxyethoxyethanol (EEE), dipropylene glycol derivates (DGP 1, 2 and 3), phenoxyethanol (PE) and phenoxyethoxyethanol (PEE) [9, 25, 26, 31, 43-45]. Other compounds related to colorants were also identified such as leucocrystal violet (LCV), aniline (A), diphenylamine (DPA) or michler ketone (MK) [46]. Phthalic anhydride (PA) was also found in a majority of the ink formulations [26].

All studied inks contained PE, because only such inks were selected for the present study. Indeed, all calculated ageing parameters were based on the presence of PE. Precedent studies reported PE in about 80% of the inks for north America [9, 44] and 92 to 98% for Europe [31, 43], making it an ideal target for ink dating studies. In real casework, it must be kept in mind that up to 20% of the ballpoint pens would produce useless entries for ink dating if we target only PE to calculate ageing parameters. Other compound could then be used, however few were present in a majority of ink and they generally presented an ageing over only a few weeks. In term of initial PE quantity (at t= 4 days), values between 4 and 165 ng/cm of PE were observed. Four ink classes were defined based on their PE quantities (see Figure 2 and Table 1):

1) 0-40ng/cm (8 inks);

2) 40-80 ng/cm (8 inks);

3) 80-130ng/cm (4 inks);

4) 130-180ng/cm (5 inks).

64% of the inks contained less than 80 ng/cm tending to show that highly concentrated PE in inks are less frequent on the ink market than lower concentrations.
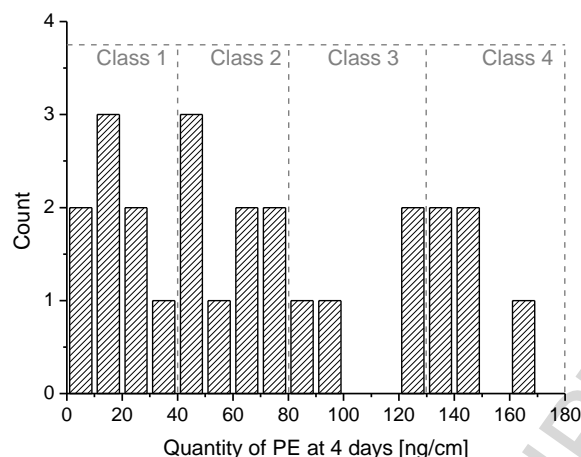
Figure 2 : Histogram of the quantity of PE in 4-days-old samples. The ink population of 25 ballpoint pens was divided in 4 classes according to their initial PE quantity.

Other compounds identified in the composition of the measured inks might also be useful for dating purposes, at least to normalise PE quantities through the calculation of RPA ratios [25]. While BA was present in all samples at time t=4 days, about 24% of the inks contained only traces of BA (i.e. their BA quantity was between the LoD and LoQ). In previous studies, BA appeared in 43% of the analysed ballpoint ink samples from a North American study [9] and in 60% of the samples from a European one [31]. PEE was found in 60% of the studied population similarly to previous European studies [31, 43]. However, North American studies reported PEE in only about 20% of the inks [9, 44]. Thus, while this compound is known to evaporate in a slower rate than PE [31, 45], it is less common in ballpoint pen inks. PA, DPA and MK were also found in 48% of the studied inks, but were rarely reported in previous studies. The remaining compounds including DMCH were present in less than 30% of the inks (see Table 1).

The percentages of compounds found in the current study were more similar to those from European studies (n=31 [31] and n=121 [43]) rather than Americans ones (n=63 [9] and n= 633 [44]). The differences between the studies could be explained by different factors such as the geographical situation (different continent and countries). The time range can also be a factor. While comparable studies were published between 2002 and 2005, the manufacturing date of the studied inks were not specified and could also have influenced the results. Finally the sampling size and selection criteria could have an influence. The reason for these differences should be further studied and ink populations should ideally be updated regularly with new manufactured inks in order to ensure the contemporaneity and reliability of the reference population. Different LoD and LoQ of the methods used to analyse the ink populations may also explain some differences.

Table 1 : List of compounds detected in the 25 different inks (at time t = 4 days after deposition on paper). Their retention time (min) target ions (m/z) and percentage of inks containing them are indicated. For each compound the percentage of ink containing it is indicated (TOT) as well as the percentage present in traces (< LoQ, i.e. limit of quantification) and in measurable quantities (>LoQ).

RT (min)	N° Ink composition	Target Ion (m/z)	# inks <LOQ	# inks >LOQ	TOT # (%)
5.71	Hexylène Glycol (HG)	59	0	3	(3) 16%
6.36	Aniline (A)	93	1	4	(5) 20%
6.60	Ethoxyethoxyethanol (EEE)	45	0	6	(6) 24%
6.78	1,1'-oxybis-2-propanol (DPG1)	45	0	4	(4) 16%
6.92	Benzyl alcohol (BA)	79	3	22	(25) 100%
6.95	2(2-hydroxypropoxy)-1-propanol (DPG 2)	59	0	4	(4) 16%
6.98	2,2'-oxybis-1-propanol (DPG 3)	59	0	4	(4) 16%
7.08	dimethylbenzenemethanamine	58	0	1	(1) 4%
7.19	Dimethylcyclohexadienone (DMCH)	79	1	5	(6) 24%
8.48	**Phenoxyethanol (PE)**	138	0	25	(25) 100%
8.65	Phenoxypropanol (PP)	94	0	3	(2) 12%
9.14	Phthalic anhydride (PA)	104	7	5	(12) 48%
10.12	Phenoxyethoxyethanol (PEE)	94	0	15	(15) 60%
10.64	Diphenylamine (DPA)	169	1	11	(12) 48%
10.93	diethylaminobenzaldehyde	162	4	1	(5) 20%
12.50	leucocrystal violet (LCV)	253	3	3	(6) 24%
13.15	methylenebisbenzeneamine	254	4	3	(7) 28%
15.19	michler ketone (MK)	268	4	8	(12) 48%

3.2 AGEING PARAMETER

3.2.1 PE QUANTITY

The quantity of PE in the 25 measured inks varied greatly as a function of ink composition irrespective of the considered age (Figure 3A and B). Concentrations between 4 and 165 ng/cm were obtained at 4 days ($RSD_{all\ inks}$ = 72%) and between 1 and 84 ng/cm at 304 days ($RSD_{all\ inks}$ = 87%) (Figure 3A). Inks initially containing higher PE concentrations also showed higher decrease over time (e.g. inks A, G and I in Figure 3). As expected from drying theories [31, 41, 42], the mean concentrations dropped from 70 ng/cm (t=4 days) to 22 ng/cm (t=304 days). The strongest decrease happened during the first 23 days (-20 ng/cm). However, very low concentrations of PE (few ng) were also detected at time t=4 days (e.g. inks L, D and F). This demonstrated that finding small quantities of PE in an ink entry is not related to the ink

age, while finding high concentration generally is. Indeed, high concentrations (class 3-4) are only found in young ink entries and may thus significantly contribute to estimate the age of the ink entry. The most concentrated inks were ink A and G.

The decrease of the mean PE quantity was modelled with a double exponential decay (R^2 = 0.97, Figure 3C). The variance of the quantity also decreased as a function of time and could be modelled using exponential decay (R^2 =0.98, Figure 3D): The modelling of the mean and variance as a function of time might be useful to assess the general ageing behaviour of the ink population. It can also be used to extrapolate values for ages that were not measured in this study, theoretically even older ones. According to the model, the mean and variance kept decreasing over the whole measured time frame. It will thus stabilise or present a slower decrease for ages older than 304 days-old samples.
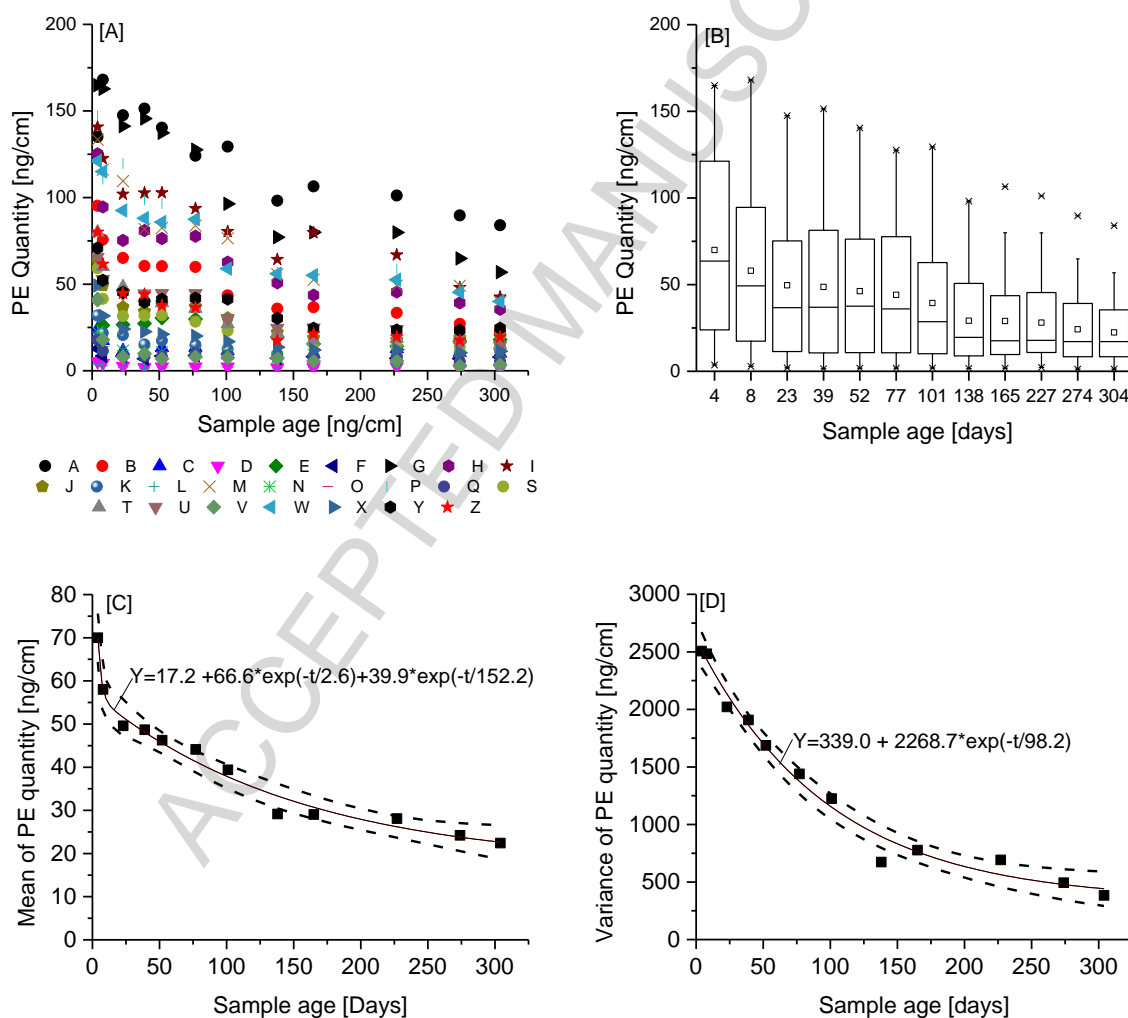

Figure 3 : Quantity of PE as a function of time: A. data for the 25 inks, B. distribution of values given by the boxplots C. Mean value for the PE quantity; D. Variance values for the PE quantity.

It was previously reported that the initial PE quantity could influence the ageing behaviour [12]. Thus, the data were compared between the four ink classes (based on initial quantities

detected at time t = 4 days) (Figure 1). Inks containing little PE (class I) tended to age more quickly and no significant differences between median values could be detected after 8 days (Figure 4A). For the most concentrated inks (class IV), the medians kept decreasing slowly over the whole measured time frame. The decrease started to slow down after 138 days (Figure 4B). The middle classes (II and III) presented a decrease that slowed down after 23 days. After 138 days, no significant decrease was detected in inks from class II, while it was possible to see an ageing over a longer period for ink from class III (see Supporting Information).
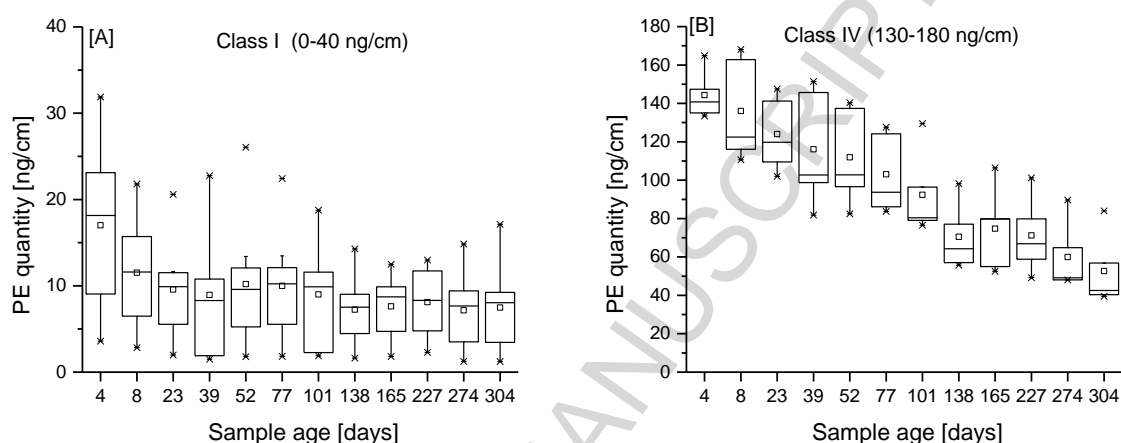

Figure 4 : Quantity of PE per « initial » quantity of PE. A. initial quantity from 0 to 40 ng/cm B. A. initial quantity from 130 to 180 ng/cm

Differences between the black inks (n=13) and blue inks (n=12) were evaluated for each age with a Student test. In fact both populations were normal (this was confirmed using the *Kolmogorov and Smirnov* test) and their variance showed no differences except 274 and 304 days (this was confirmed using a F-test) [39]. The application of a Student-test showed that no significant statistical differences could be seen between black and blue inks (Figure 5), more studies should be carried out using a larger ink population to confirm these results. The same general observation was made for the other studied ageing parameters. Thus, blue and black inks results are presented together.
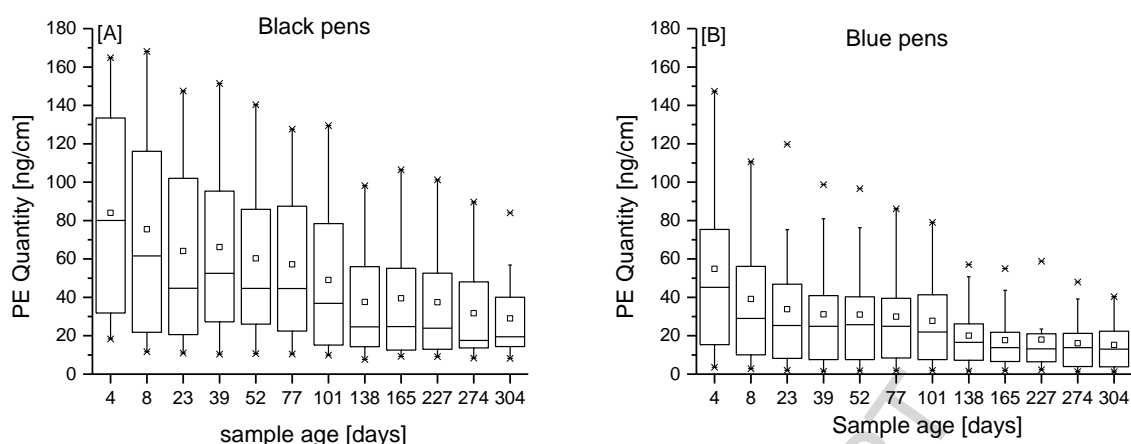
Figure 5 : Quantity of PE according to the ink color, (A) black inks ; (B) blue ink s

The PE quantity tended to significantly decrease as a function of time. Thus, it represents a useful parameter to estimate the age of an ink entry, especially when a high PE quantity is measured. However, only 15% of all samples showed a PE quantity above 84 ng/cm (i.e., the highest quantity was measured at 304 days). This may unfortunately translates into low success rate in practical cases.

3.2.2 SOLVENT LOSS RATIO USING ARTIFICIAL AGEING - R%

The calculated R%-values were also very different between inks. At t=4 days, values fluctuated from 4 to 73%, while at t=304 days, they varied from -52% to 47% (Figure 6A and B). The variability increased strongly between 4 and 304 days samples, as the calculated RSD for all inks raised from 33% to 200%. R%-values decreased rather slowly as a function of time in comparison to PE quantities. Higher values were again indicative of a younger ink, while small values were spread over all ages. After 4 days, negative values were generally observed for ink samples containing less than 20 ng/cm of PE (Figure 7). As the calculation of R% requires two different samples, it was possible to have slight initial differences in the quantity of PE in each (even when being particularly careful during the sampling procedure). These differences can lead to negative values when the ink mass of the heated sample was above the natural sample (the measured difference in PE between samples reached ca. Δ3 ng for R% values around -50%). This means that artificial ageing did not significantly decrease the PE quantity (in such cases, the theoretical value for identical samples should be 0%). Thus, negative values can be explained by a high measurement variability mainly due to ink inhomogeneity and small PE quantities. In addition, one particular ink (ink V) proved to be particularly sensitive to this phenomenon since only about 3/4 of the values were negative (Figure 5A). Negative values coming from other inks were less commonly encountered. Compared to PE quantity, R% values presented more variation, as the median

tended to be more fluctuant, confirming a previous study [25]. In fact, the maximal R% values could be attributed to 5 inks, namely P, L, M, U and W.

The mean R% tended to decrease as a function of time (Figure 6C) and could also be modelled with a double exponential decay (R^2 of 0.87, Figure 6C). The poor correlation value (R^2) can be explained by the incertitude on the A_1 and τ_1 parameters of equation 5, because they were estimated on only two points (fit between t=4 and 8 days).The variance did not show any descending or ascending tendency (Figure 6D) and showed a total mean value of 430 ± 110. Combined with a decreasing mean, the relatively constant variance lead to increasing RSD values over time.
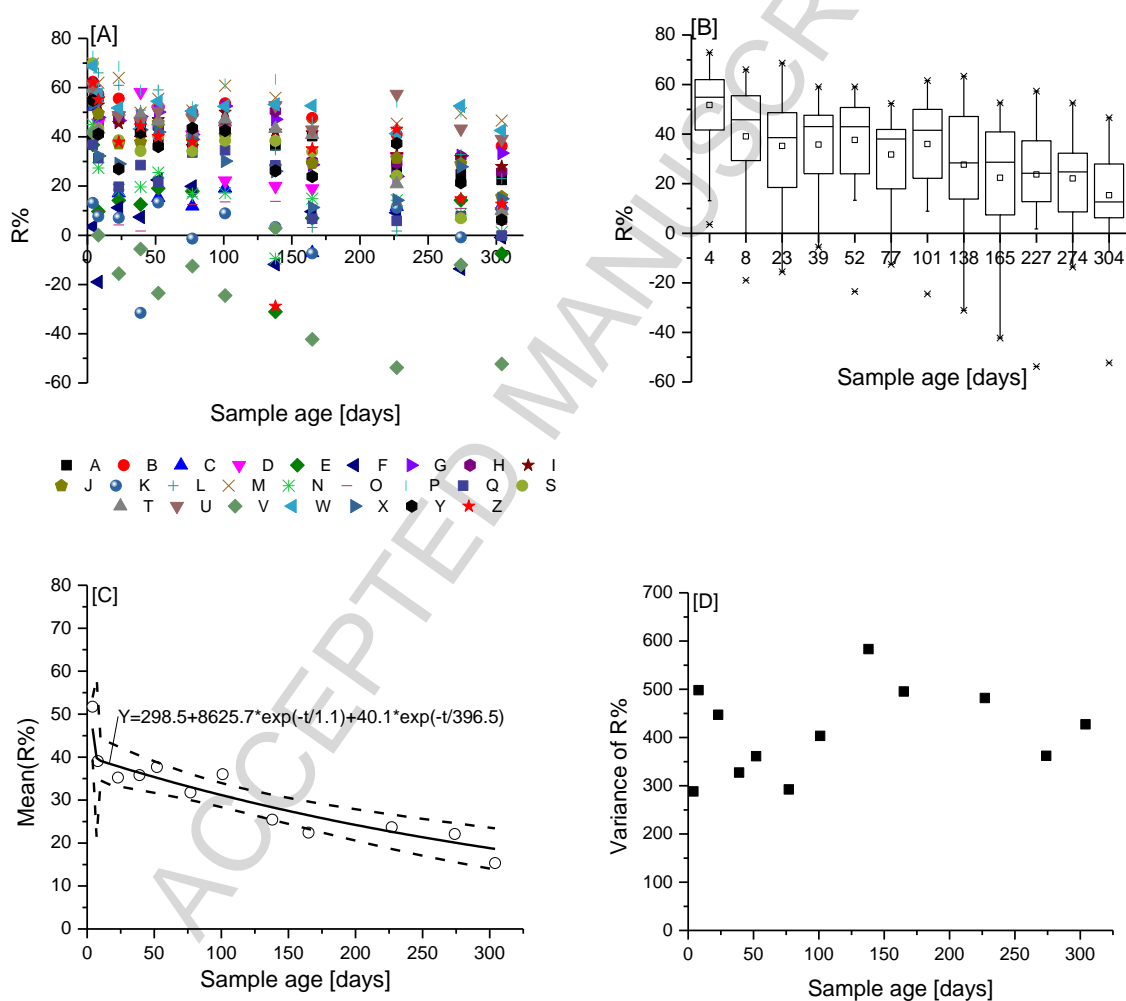

Figure 6 : Solvent loss ratio (R%) values as a function of time in days: A. data of 25 inks, distribution of values given by the boxplots C. Mean R% value; D. R% variance.
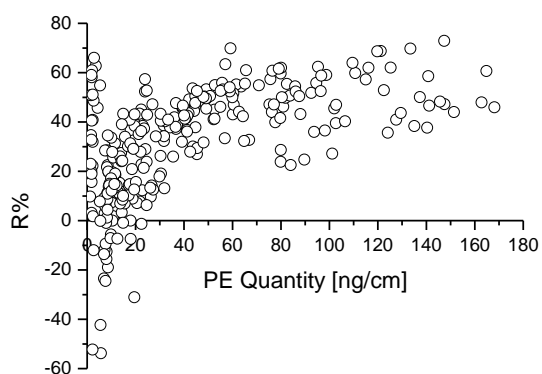
Figure 7 : Relation between the R%-values and the PE quantity measured in the natural sample (PEn)

Table 2 :Pearson Correlation between the ageing parameters

	PE	R%	R_{NORM}	NR%	NR_{NORM}	RPA	R%*
PE	1.00	**0.59**	**0.96**	-0.04	0.00	-0.01	0.01
R%		1.00	**0.68**	-0.02	0.05	0.05	0.00
R_{NORM}			1.00	-0.04	0.01	0.00	0.01
NR%				1.00	**0.64**	0.03	0.11
NR_{NORM}					1.00	0.12	0.26
RPA						1.00	0.26
R%*							1.00

A correlation was observed between obtained R% values and PE quantities (Table 2). It was shown that samples containing higher concentration of PE generally presented higher R% values (Figure 7). However, high values were also reached for samples containing lower PE amounts. For samples initially containing higher PE amounts (i.e. class IV), R% values varied from 39 to 72% at time t=4 days and from 20 to 47% at time t=304 days (Figure 8B). Class I inks (i.e, samples initially containing lower PE amounts) also showed a large range of R% values going from 2% to 64% at time t=4 days and from 0 to 25% at t=304 days (Figure 8A). Class II inks also presented negative values and a lower decrease over the measured time frame, while class III inks gave comparable results to class IV: no negative values and a slower decrease of R% over time (see Supporting Information).Thus, samples concentrated in PE presented higher initial R% values that decreased slowly over time, while samples containing low PE quantities presented a large range of R% values before 52 days (Figure 8). This may be particularly interesting for ink dating, as even an ink containing low PE may

yield a high R% value when young, while no conclusion could be drawn using only the PE quantity.
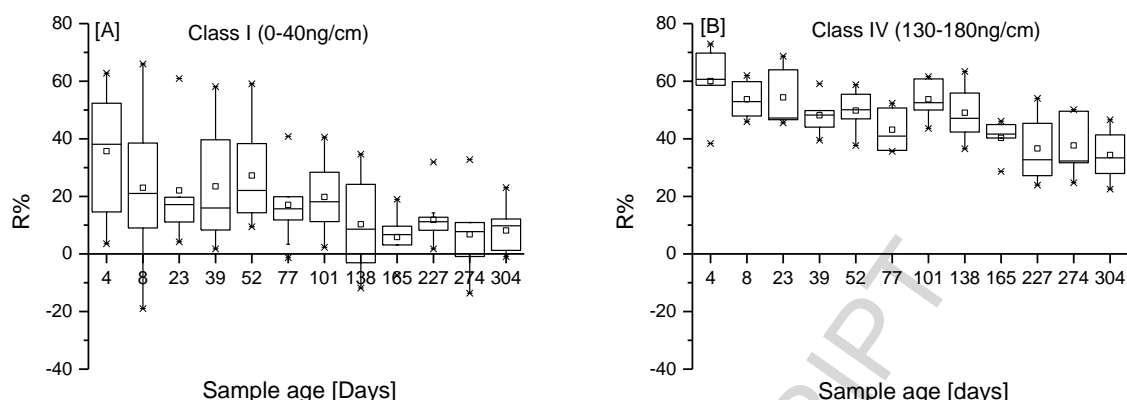

Figure 8 : Boxplot of the R% values as a function of time: A. ink specimen presenting 0-40ng/cm PE at time t= 4days, B. ink specimen presenting class of 120-180ng/cm PE at time t= 4days.

While R% values showed larger RSD than those obtained for PE quantities, their decrease over time was slower, potentially allowing a better chance to differentiate alternative hypotheses about the age of inks entries. Thus, 30% of the R% values for sample younger than 304 days were above 47% (i.e., the maximal R% value obtained at 304 days) indicating globally better feasibility than for PE quantities

3.2.3 PE DIFFERENCE DUE TO ARTIFICIAL AGING R_{NORM}

The PE quantity difference (R_{NORM}) between the natural (PE_n) and heated (PE_h) sample was also considered (Eq. 6). PE_h is supposed to represent the quantity of PE when the ageing stops (i.e., level-off values) [6, 47]. It is obtained by artificially aging the samples through heating. Thus, calculation of R_{NORM} values using PE_h should allow aligning the ageing curve on the same ordinate by eliminating AP_0 of equation 8. The resulting ageing curves should tend to 0 when the ageing stops. This process could be compared to a scaling of the ageing curves. However, the heating step did not exactly yielded the level-off value and was shown to be dependent of the ink formulation and age [25]. Indeed, AP_0 values above zero were encountered.

Observed differences over time were more marked for R_{NORM} than R% values (see Figure 9). Negative values down to - 6 ng were also obtained even for young ink samples (Figure 9A and B). The R_{NORM} values at 4 days were comprised between 1 and 107 ng and decreased to a range from -3 to 19 ng at 304 days, namely a decrease of 88 ng between the highest R_{NORM} values of both ages. In comparison to the R%-parameter (Eq. 4), R_{NORM} showed a

distinct ageing effect on the values. The RSD value ranged between 84% at 4 days and 127% at 304 days.

The mean R_{NORM} values showed a decreasing tendency as a function of time that was modelled using a double exponential ($R^2 = 0.98$, Figure 9C). The curve kept decreasing slightly over the measured time range with no clear level-off after 304 days. The variance also decreased exponentially as a function of time. It could be modelled with a single exponential decay (R^2 of 0.94, Figure 9D). The latter tended to level-off after 200 days (Figure 9D) which indicated that the variance for samples older than 304 days would be close to level-off values.
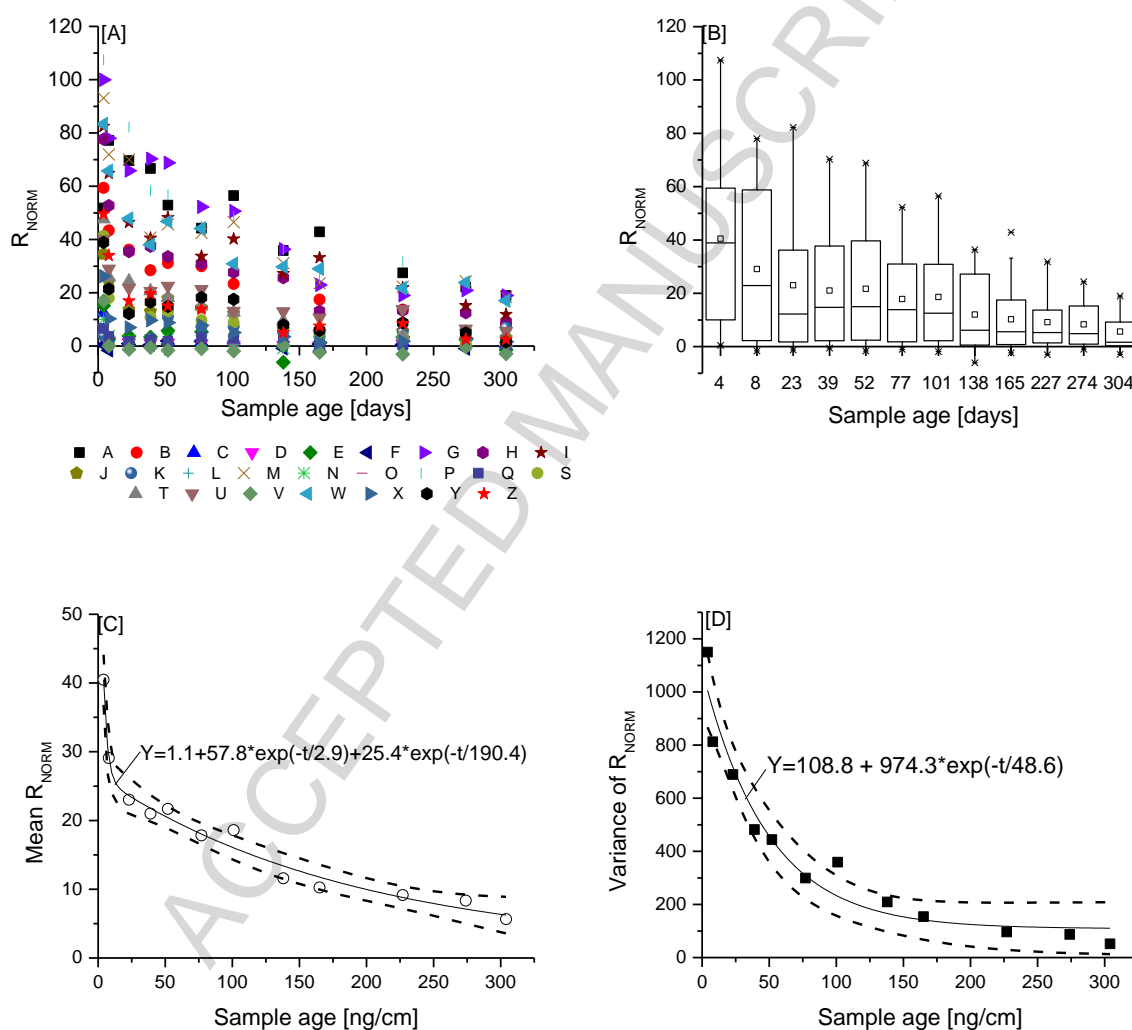

Figure 9 : Difference of quantity of PE in function of time (R_{NORM}); A. data of 25 inks, B. boxplots C. Mean of the R_{NORM} for each age; D. Variance for each age.

The "initial" quantity of PE had an effect on the R_{NORM} values. For sample containing low initial PE quantities (class I), R_{NORM} values never exceeded 12 ng/cm and did not decrease very much after 8 days (Figure 10A). For highly concentrated samples (class IV), a constant

decrease was observed as a function of time until 304 days (Figure 10B). Class II presented a large initial decrease slowing down around 23 days, while class III decreased steadily up to 274 days (see supporting information).

R_{NORM} values were highly correlated with PE quantities (R^2=0.95, Table 2) and less to R% values (R^2=0.67, Table 2).

The R_{NORM} parameter presented a strong decrease over the studied time range providing a good potential for ink dating. Moreover, 38 % of R_{NORM}-values for sample younger than 304 days were above 19 ng (i.e., the maximal R_{NORM}-value obtained at 304 days). This number indicated that potentially R_{NORM} could lead to a higher success rate than PE (15%) and R% (30%) to estimate ink age over a one year interval.
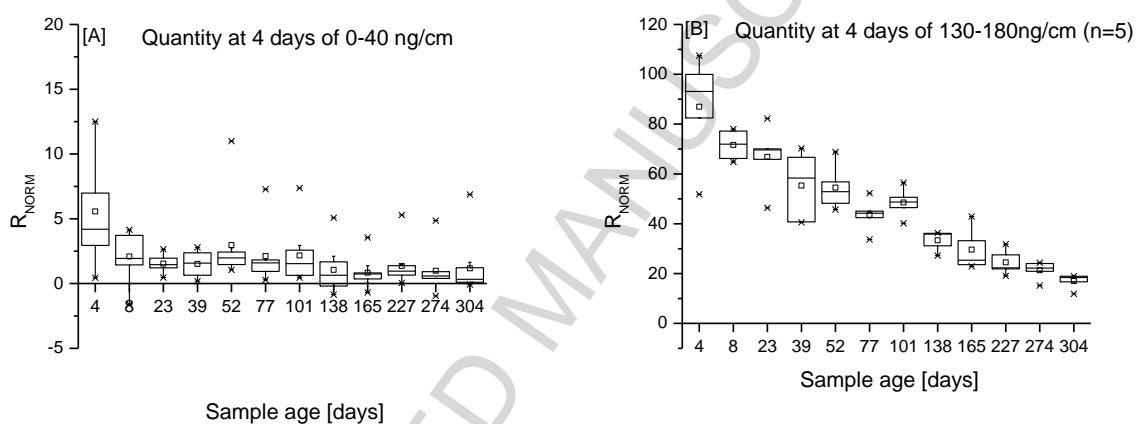

Figure 10 : Boxplot of the R_{NORM} values as a function of time: A. ink specimen presenting 0-40ng/cm PE at time t= 4days, B. ink specimen presenting class of 120-180ng/cm PE at time t= 4days.

3.2.4 SOLVENT LOSS RATIO USING 1 MONTH NATURAL AGEING - NR%

A possible alternative to the use of artificial ageing is natural ageing of the sample over a defined period of time [20, 24]. Thus, solvent loss ratios were also calculated after letting samples age naturally during 1 month (parameter NR% in Eq. 7). The questioned ink entry would then be first sampled and analysed at the time the document is received by the laboratory (PE_{t0}) and again 30 days later (PE_{t30}). The questioned document should be stored in the same storage conditions than the ink reference population to yield comparable ageing conditions (e.g. in a folder in an air conditioned laboratory with no direct sunlight and air flow).

NR% values at t=4-34 days varied between -12 and 76% and decreased rapidly between –18 to 20% after t=274-304 days (Figure 11A and B). However, large variations were encountered and values were lower at t=50-80 days than later (e.g. at t=227-274 days, values up to 52% were measured). The resulting RSD were similar to those obtained for R% and also increased over time: 44% for 4-39 days and up to 292% at 274-304 days. Negative values were more frequently encountered and for almost all measured inks. This can be explained by the very small difference induced by natural ageing over 1 month. The measured loss was significant only for very young samples, i.e. under 2 weeks. Longer natural ageing would probably be necessary to obtain useful results for older samples, thus considerably increasing the time needed to estimate the age of ink entries using this parameter.

The mean NR% was plotted as a function of the age of ink entries. The resulting figure showed a large dispersal of values (Figure 11 C). A single exponential regression was applied and a pearson correlation of 0.66 was obtained. Similarly to R%, the variance showed no tendencies and the mean value was 166 ± 85% (Figure 11 D).
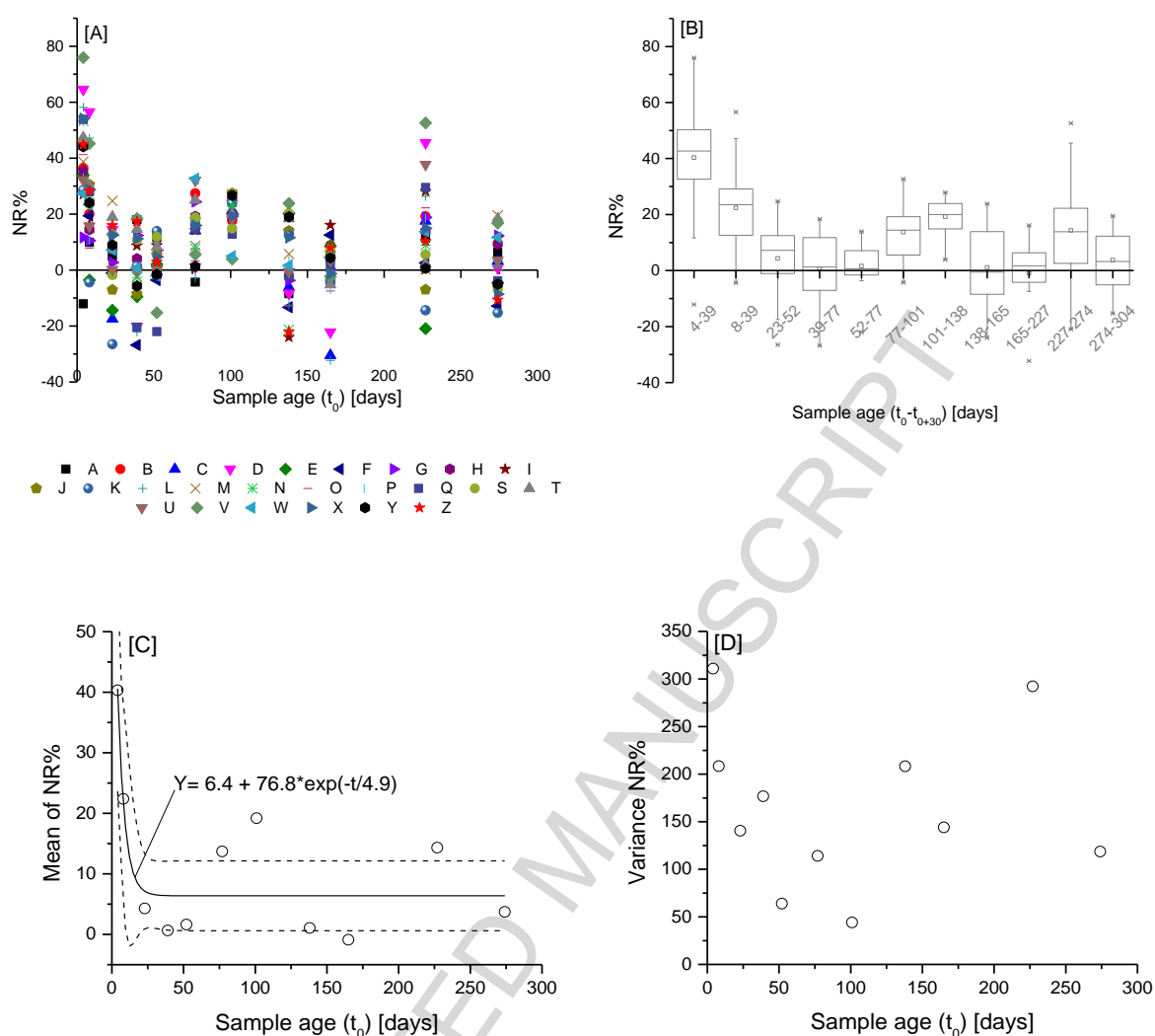
Figure 11 : Percentage of evaporation in one months as a function of time (R); A. data of 25 inks, B. boxplots C. Mean of the NR% for each age; D. Variance for each age.

By evaluating the data as a function of the quantity of PE (class I to IV), it was shown that samples of all classes presented scattered values over the ages and no significant tendencies could be observed as a function of time after one week (Figure 12). Moreover, NR% values were not correlated with the previously studied ageing parameters. Indeed, obtained Pearson's correlation values were close to 0 (Table 2).

NR% allowed seeing an ageing only for a few days old samples, showing a potential only to date very young inks. Moreover, the variability observed for old samples (older than 23 days) make it difficult to reliably discriminate between older samples. In fact, only 3% of the ink samples younger than 227 days possessed a NR%-value above 53% (highest value obtained for 227-274 days interval). This is much less than for PE quantity (15%), R% (30%) and R_{NORM} (38%).
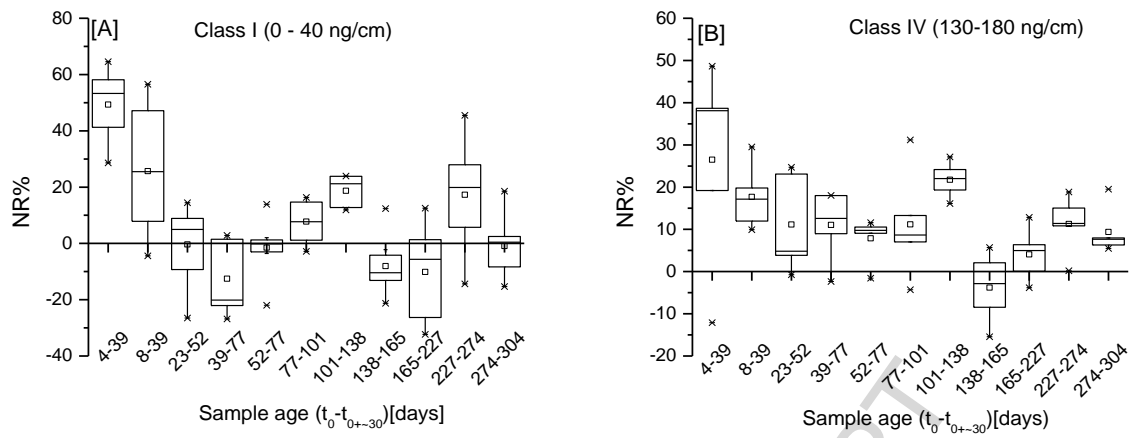
Figure 12 : Boxplot of the NR%-values as a function of time: A. ink specimen presenting 0-40ng/cm PE at time t= 4days, B. ink specimen presenting class of 120-180ng/cm PE at time t= 4days.

3.2.5 PE QUANTITY DIFFERENCE DUE TO NATURAL AGING (NR$_{NORM}$)

Similarly to R$_{NORM}$, the difference between the quantity of PE at t=0 and the quantity in the ink entry 1 month later was calculated (parameter NR$_{NORM}$, Eq 8).

At 4-34 days, NR$_{NORM}$ between -16 and 52 were recovered (RSD = 70%). They decreased between -2 to 10 ng/cm at 274-304 days (RSD 192%) (Figure 13A and B). Comparably to NR%, values were very variable over time. For example, values obtained for ink A went from 16 ng/cm for 52-77 days-old sample, to -5 ng/cm at 77-101days-old samples and again 31 ng/cm for 101-138 days-samples (Figure 13A). Despite this high variability (see more particularly age of 77-101 and 101-138 days in Figure 13B), the NR$_{NORM}$ parameter was globally decreasing over time.
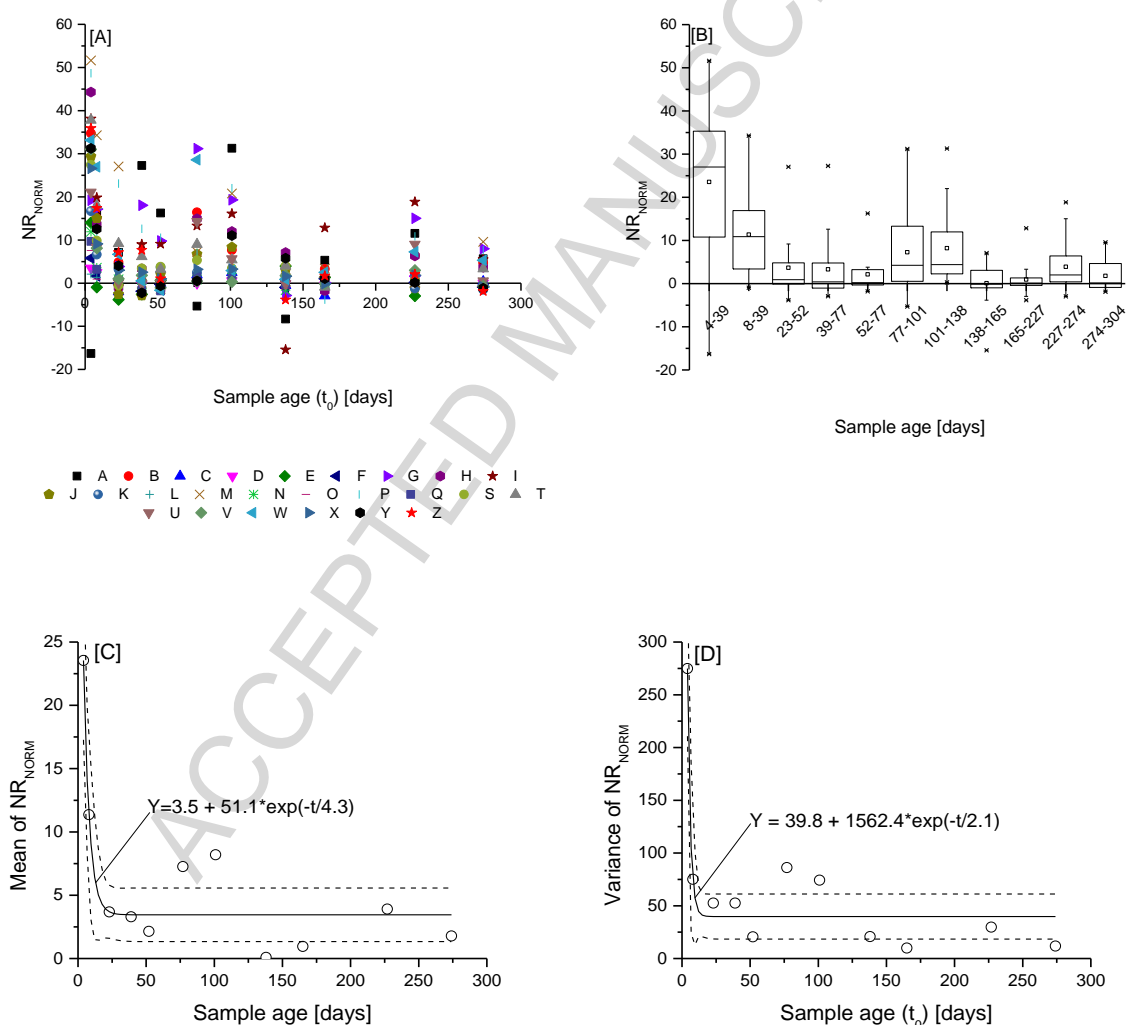

Figure 13 : Difference between the initial quantity of PE and 1 months old sample a function of time (R); A. data of 25 inks, B. boxplots C. Mean of the NR$_{NORM}$ for each age; D. Variance for each age.

The mean NR_{NORM} plot showed similar spreading than the NR% plot (see Figure 13C). A R^2 value of 0.84 was obtained for the model. While better than for NR%, it remains low compared to the R_{NORM} (0.98). The variance also showed a decreasing tendency as a function of time and a single exponential decay regression was applied with a R^2 of 0.86 (Figure 13D). Both the mean and variance levelled off after 23 days and values scattering increased. Similarly to NR%, this indicates that dating inks over 23 days might be problematic using NR_{NORM}.

The effect of the PE quantity at 4 days showed that higher PE quantities (class I) yielded higher NR_{NORM} values, similarly to the R_{NORM} parameter. In opposition to RN% values, low PE quantities were less problematic and yielded less negative values inks from class IV (130-180ng/cm). For all classes, the values obtained for 4-days-old samples were significantly different from the other ages (Figure 14 A and B).

The NR_{NORM} results showed that parameters based on 1 month natural ageing (including NR%) only yield interesting results for very young inks compared to older ones (i.e., 4-8 days vs 23-274 days). After a few days, results scatter too much to allow discrimination between different ages and no conclusions on the age can be inferred anymore. Thus, their potential to age an ink entry in practical cases is significantly lower compared to the previously studied ageing parameters.
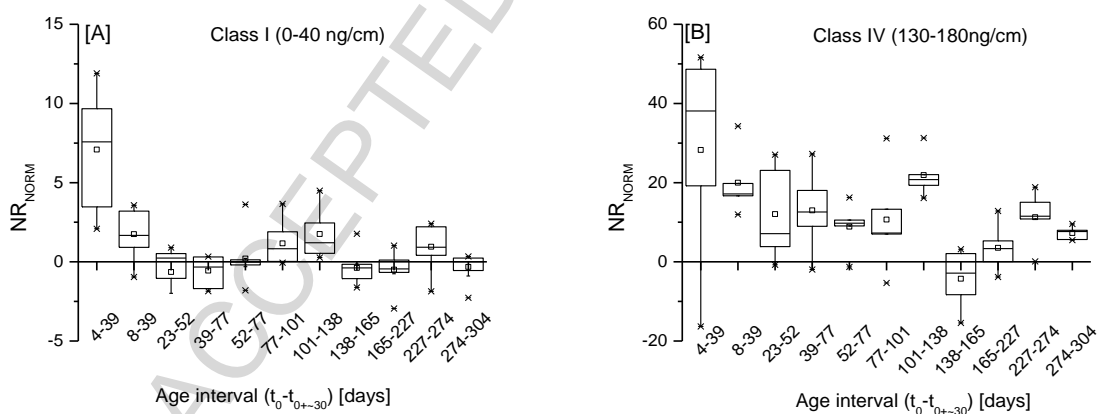

Figure 14 : Boxplot of the NR_{NORM}-values as a function of time: A. ink specimen presenting 0-40ng/cm PE at time t= 4days, B. ink specimen presenting class of 120-180ng/cm PE at time t= 4days.

3.2.6 RELATIVE PEAK AREA (RPA)

Previous studies proposed the use of RPA as an alternative ageing parameter in order to normalise obtained PE quantities and reduce sample variability. The ratio is calculated between PE as nominator and other ink compounds as denominator. While some studies used dyes as "stable" compounds generally by analysing them with another chromatographic

or spectroscopic methods [10, 14, 23, 29, 32, 48], other proposed the use of ink volatile compounds such as PA, BA or DMCH as denominator [6, 14, 25, 27]. Little data was previously published on the potential of RPA values to date inks. Thus, such ratios must be tested in order to evaluate their reliability and actual potential. In fact, the most complicated task is to target compounds that are present in a majority of ink compositions and offer reproducible tendencies over time for unknown inks (i.e., all investigated inks).

Thus, only compounds found in approximately one quarter of the studied ink population were selected as possible candidates to calculate RPA values. In addition, only compounds found in quantities above the LOQ were considered. The most frequent compound was BA found in 88% of the inks (Table 1), followed by PEE found in 60% of the inks. DPA (40%), MK (32%) and EEE (24%) were also selected (Table 1). PA and DMCH, previously proposed for RPA calculation [25, 48], were found in only 20% of the selected ink population. The occurrence of other volatile compounds was also considered too low.

The behaviours of the selected compounds were studied over time. Thus, a slope trend test was applied on the obtained values normalised to the IS between 23 days to 304 days. The 4 and 8 days values were excluded because most volatile compounds present a trend during the first few days [25]. The selected compounds proved to have different behaviours depending on the ink composition. While BA, EEE, DPA and MK were generally stable in a majority of inks, PEE showed decreasing tendencies for a majority of inks. Thus, the stability of these compounds over time was not guaranteed for all inks. While it might be better to select "stable" compounds for normalisation, the use of RPA is also possible using decreasing compounds, however there is a risk to reach a state where the compound is not measurable any more (i.e. amount below the LoQ). The resulting RPA values will combine the ageing behaviours of the different compounds to define new variables.

Among the 22 inks containing BA, 9 yielded a BA quantity under the LoQ after 23 days. Two reached the LoQ after 52 and 77 days (Ink M and Z respectively) preventing from using this RPA on the whole time interval considered. 11 inks presented sufficient amount over the whole time range. For these inks, the RPA presented values between 0.4 and 14.8 at 4 days and between 0.2 to 9.4 at 304 days, showing a slight decrease (Figure 15A). The resulting ageing curves did not all follow an exponential decrease and the data spreading was relatively high, especially for ink I.

The calculation of RPA using PEE was possible for 15 inks, but it did not systematically show descending trends. Values ranged between 0.9 and 3.6 at 4 days and between 1.0 and 7.4 at t= 304 days (Figure 15B). Amongst the 15 inks, 6 presented an ascending trend (Inks E, K, N, O, Q and S) and their slope increased with the samples age. These ink samples

actually contained low PEE amounts. These results were problematic as they show no real universal ageing trend. Only monotonic trends can be considered in ink dating, especially if the values are directly compared (for example with a threshold value).

RPA(PE/DPA) could be applied on 12 inks and the RPA values generally showed descending ageing curves (Figure 15C). However, an ascending trend was detected for ink N, this was principally due to the decrease of the amount of DPA in this ink samples over time (Figure 15C). Moreover, among the 12 inks, 3 were not measurable over the whole time range (inks K, O, S). Values ranged from 1.9 to 23.5 at 4 days and decreased to 2.9 to 5.5 at 304 days. Comparatively to RPA(PE/PEE), this RPA was also problematic.

RPA (PE/EEE) yielded 6 descending ageing curves (Figure 15D). The ageing curves did not all follow exponential regression as inks W and M presented more linear trends. Values between 0.4 and 45.3 were observed at 4 days, while values between 0.2 and 9.4 were obtained at 304 days. Ink H presented very high values because it contained very low amount of EEE and in fact this amount was under the LoQ limit at 304 days preventing from having a value for this age.

Finally, the calculated RPA (PE/MK) was highly variable as a function of time Figure 15E). In fact, no significant trend was observed between 23 and 304 days for the 11 inks containing MK. The values at 4 days ranged between 0.3 and 15.0, and reached from 0.2 to 9.8 at 304 days. MK is a degradation product of a dye frequently contained in ballpoint inks. Thus, its increase in the sample due to the dye degradation cannot be excluded over time [49]. This RPA was judged to be inappropriate as ageing parameter.

The determination of RPAs was ultimately a complicated task. Indeed, for each ink, potential target compounds must be found in sufficient quantity and over the whole time range, however, several RPA were calculable only during a small time range for certain inks. The resulting ageing curve must be monotonic, while some RPA showed ascending as well as descending trends. Finally, the selected RPA were applicable at most to 36% of the population inks if the whole time range was considered (PE/BA) that can hardly be compared to a universal ageing parameter.

As different RPAs had to be calculated for each ink, one possibility to increase feasibility and comparability could be to combine different ink compounds in the denominator of the RPA. This combination would work as a sum of the target component present in the ink. If one is missing then the sum is calculated with the other target compounds present. Thus, several new RPA were calculated considering at first the sum of all 6 target compounds (i.e PE, PEE, BA, EEE, DPA and MK). However, using PEE in the sum yielded again ascending

trends and. the use of MK brought too much variability preventing the observation of any trends. These two compounds were thus removed. The most promising RPA calculation summed BA, DPA and EEE: PE/(BA+DPA+EEE). It could be calculated on 18 inks (72% of the reference population). Among them, 2 inks were not measurable over the whole time range (inks K and O). Moreover, ink K showed an ascending trends before reaching the LoQ (t=77 days).. With this exception, descending ageing trends were observed for 16 inks (64%). Values between 0.1 and 45.2 for 4 days-old samples and between 0.1 and 3.8 for 304 days-old were obtained. Ink H showed very high values and did not present a RPA value at 304 days because the only compound used as denominator reached the LoQ.. Thus, while using several ink compounds in the calculation allowed the calculations of an RPA ageing parameter for 16 inks, problems remained in the comparison of the results between inks (inks H and K would yield problem in the interpretation of the results).

The use of RPA previously found promising in the literature proved to be difficult to implement on a larger ink population. Most compounds detected using GC/MS are volatile and thus, showed changing behaviours as a function of time and ink composition. While interesting in terms of normalisation, it might be difficult to implement as ageing parameters to estimate the age of an ink entry. This ageing parameter was thus not considered for the interpretation in part 2 of this article.
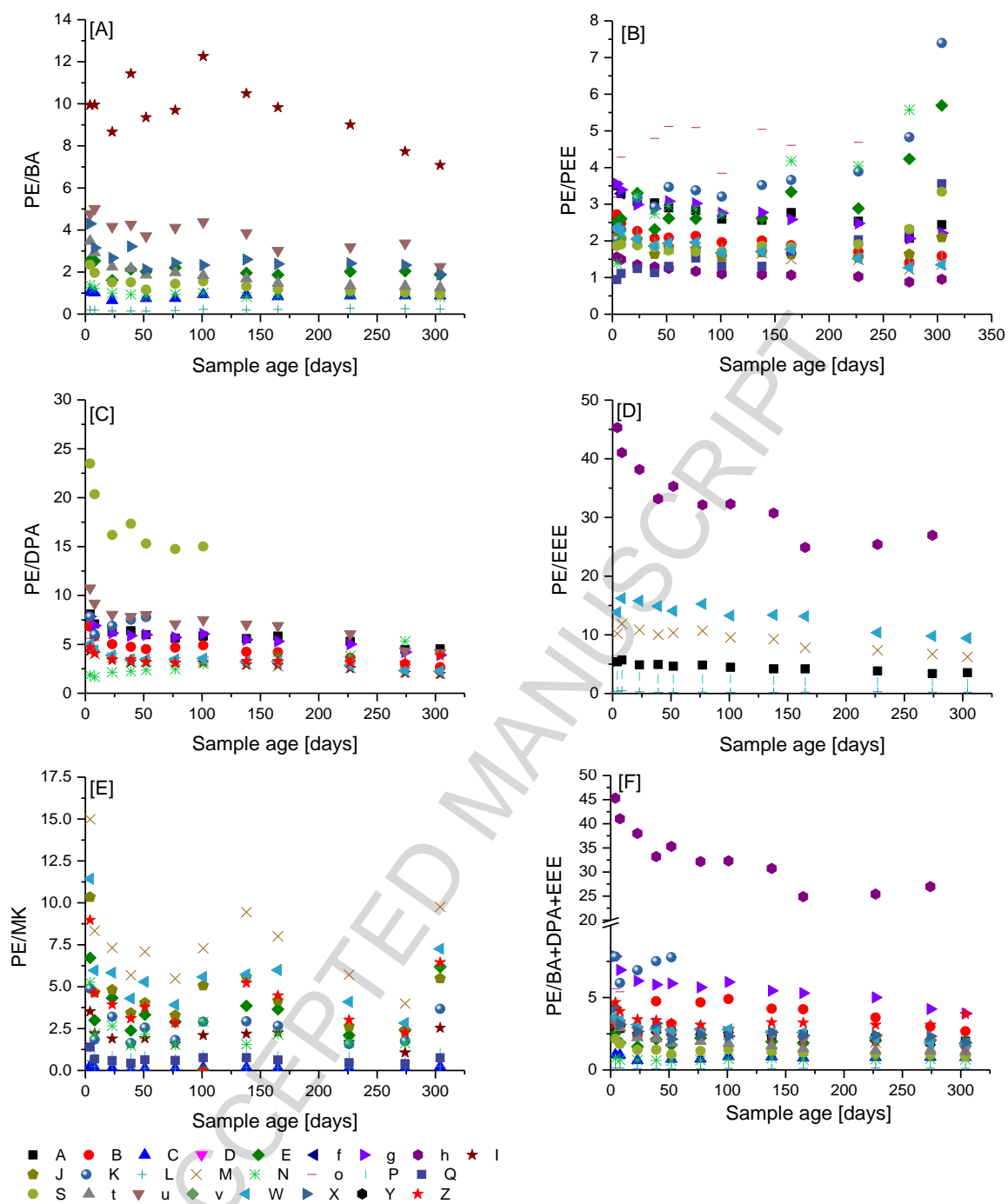
Figure 15 : Ageing curve of the resulting RPA, [A] PE/BA; [B] PE/PEE; [C] PE/DPA; [D] PE/EEE; [E] PE/MK; [F] PE/(BA+DPA+EEE)

3.2.7 SOLVENT LOSS RATIO CALCULATED USING RPA R%*

It was previously proposed to calculate an alternative solvent loss ratio, called R%*, using RPA values [25]. RPA (PE/(BA+DPA+EEE)) seemed interesting compared to other tested RPAs. Thus, it was used to evaluate and calculate an alternative R%* ageing parameter for 16 inks.

Values of R%* ranged between -19% and 67% for 4 days samples (RSD = 42%) and decreased to -70% - 45% at 304 days (RSD= 148%) (Figures 15 A and B). The values were actually comparable to the one obtained for the original R% (see Figure 5). Again negative values were found for ink Z and K. These inks only possessed DPA in their denominator and for both inks, the DPA values presented significant differences between the natural and heated samples. This indicated that similarly to PE, DPA quantities were influenced by artificial ageing.

The mean R%* and variance were also calculated on the whole population (Figure 16 C and D). The mean was best modelled using a single exponential decay regression, but the correlation coefficient was relatively lower that for R% (R^2=0.78 and 0.87 respectively). Again, the variance did not show any clear trend and was modelled with a constant at 451 ± 174, namely slightly above the variance of R% (Figure 16D).

In contrary to previous results [24], R%* results did not show significant improvements in comparison to R% values in terms of reproducibility and showed no correlation with other parameters (Table 2). It is additionnally much more complicated to implement than other solvent loss ratios as it cannot be calculated for all inks.
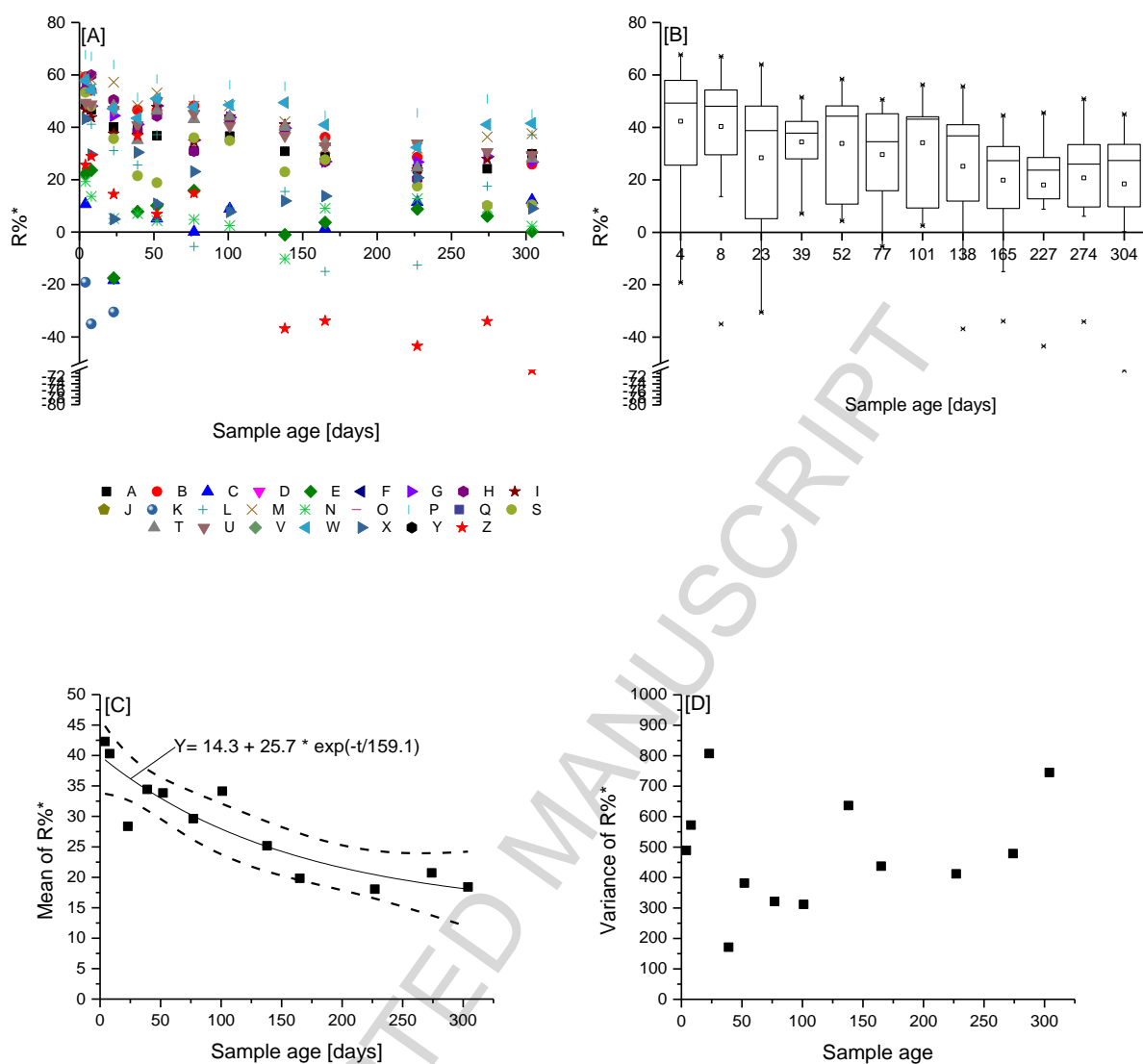
Figure 16 : Solvent loss ratio calculated with the RPA (PE/(BA+DPA+EEE) (R%*) values as a function of time in days: A. data of 25 inks, distribution of values given by the boxplots C. Mean R% value; D. R% variance.

4   CONCLUSION

This paper presented the ageing curves obtained from 25 ballpoint pen entries over one year. Seven ageing parameters were calculated, among these, four were previously proposed in the literature:

1) the phenoxyethanol quantity (PE)
2) the solvent loss ratio based on artificial aging (R%)
3) the solvent loss based on artificial aging (R_{NORM})
4) the solvent loss ratio based on natural aging (NR%)
5) the solvent loss based on natural aging (NR_{NORM})
6) the relative peak areas between compounds (RPA)
7) the solvent loss ratio based on RPA and artificial ageing (R%*)

The results showed that all ageing parameters were significantly influenced by the ink composition and a wide range of values were obtained for each parameter over the studied time range. The ageing parameters using PE and artificial ageing in their calculation (PE quantity, R%, R%* and R_{NORM}) presented a descending trend over the whole time range, demonstrating their potential to date a document created a few weeks to a few months before the analyses. The PE quantity and R_{NORM} ageing curves distributions were highly correlated and influenced by inks containing a high concentration of PE (Class III and IV). Thus, these two parameters would mainly work to date younger inks up to a few weeks. From the two, R_{NORM} showed the strongest differences between young and old samples and is thus more promising to estimate the age of ink entries of unknown origin.

The solvent loss ratio R% was less influenced by inks initially containing few PE, presenting the advantage of being able to discriminate young inks from older ones even for low initial PE concentration (class I and II) in contrary to the PE quantity and R_{NORM}. However, it showed a higher variability particularly for older samples. The R%*, previously proposed as an alternative to the R%, showed no real improvement in this study and will not be considered in the second part.

The use of natural ageing instead of artificial ageing in the calculation of ageing parameters (NR% and NR_{NORM}) tended to give interesting results only for very young inks (i.e., under one week). After that, it presented a very high variability and no more distinctive trends. Such parameters would thus be effective only on very recent documents (i.e. a few days) and will thus rarely be implementable in practice.

Finally, the calculation of RPA, proposed as a promising alternative to the calculation of the PE quantity proved to be quite difficult to implement on a larger collection of inks. Few identified compounds were present in more than a quarter of the population and in sufficient concentrations over the whole time range: Benzyl alcohol (BA), Phenoxyethoxyethanol (PEE), Diphenylamine (DPA), Ethoythoxyethanol (EEE) and Michler Ketone (MK). This yielded very different values between inks and even, to some extent, ascending trends. While such normalisation procedures are current in forensic science, it seemed quite problematic to implement for ink dating, due to the high variability of ink formulations. A multivariate approach based on several compounds from the inks present a nice alternative for interpretation purpose. Further studies should be carried out on a larger number of inks to properly evaluate its potential.

The second part of this article will focus on the development and evaluation of interpretation models allowing the production of evidence from the analytical results in a legal perspective. The most promising ageing parameters, as evaluated in this study, will be considered: the PE quantity, the R_{NORM} and the R%.

5   ACKNOLEDGEMENTS

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Highlights (first part):

- Three new ink dating ageing parameters tested based on natural ageing and/or solvent loss
- Data acquired and shown for 25 ballpoint pen inks
- Statistical treatments performed in order to evaluate the potential of ageing parameters
- Comparative and critical studies of the ageing parameters in a forensic perspective