



A comparative study of ballpoint ink ageing parameters using GC/MS



Agnès Koenig*, Sophie Magnolon, Céline Weyermann

Ecole des Sciences Criminelles, Université de Lausanne, Batochime 1015 Lausanne-Dorigny, Switzerland

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ABSTRACT

For more than a decade scientists tried to develop methods capable of dating ink by monitoring the loss of phenoxyethanol (PE) over time. While many methods were proposed in the literature, few were really used to solve practical cases and they still raise much concern within the scientific community. In fact, due to the complexity of ink drying processes it is particularly difficult to find a reliable ageing parameter to reproducibly follow ink ageing. Moreover, systematic experiments are required in order to evaluate how different factors actually influence the results over time. Therefore, this work aimed at evaluating the capacity of four different ageing parameters to reliably follow ink ageing over time: (1) the quantity of solvent PE in an ink line, (2) the relative peak area (RPA) normalising the PE results using stable volatile compounds present in the ink formulation, (3) the solvent loss ratio ($R\%$) calculated from PE results obtained by the analyses of naturally and artificially aged samples, (4) a modified solvent loss ratio version ($R\%^*$) calculated from RPA results. After the determination of the limits of reliable measurements of the analytical method, the repeatability of the different ageing parameters was evaluated over time, as well as the influence of ink composition, writing pressure and storage conditions on the results. Surprisingly, our results showed that $R\%$ was not the most reliable parameter, as it showed the highest standard deviation. Discussion of the results in an ink dating perspective suggests that other proposed parameters, such as RPA values, may be more adequate to follow ink ageing over time.

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1. Introduction

Ink dating is a major issue in the field of questioned document examination [1–5]. For about a century, scientists have addressed more or less successfully the development of methods to date ink entries [6–32]. Indeed, the task proved to be particularly difficult as many parameters have to be studied in order to develop a validated ink dating method accepted by the scientific community. It is not sufficient to select a parameter to monitor the ageing (i.e., an ageing parameter). The resulting ageing dynamics must be reproducible in realistic conditions such as those encountered in forensic caseworks [33]. For example, ink dating methods targeting dyes were highly controverted in forensic science because identified ageing parameters were too dependent on ink composition and exposure to light [34–39]. While most of the methods reported in the literature considered the influence of ink initial composition, many neglected the influence of the substrate and the storage conditions.

Recent research has focused mainly on developing methods based on ink volatile compounds analysis [6–14,16,21–26, 28,33,34,40–50]. They generally targeted one specific solvent called phenoxyethanol (PE), because it is present in more than 80% of the ballpoint pen ink formulations [28,51,52]. While measuring the decrease of PE was found problematic in terms of reproducibility and/or small time frame of detection [9,22,28,41], alternative ageing parameters were proposed in order to reduce variability and increase the time frame of reliable measurements [6,10,14,16,21,22,41,42,48–50,53]. Among them, methods based on the calculation of a solvent loss ratio ($R\%$) were reported for practical use in North America [14,21,41]. These methods proposed sequential analysis of two samples (which, ideally, contain the same amount of ink) from the questioned ink entry using gas chromatography coupled to mass spectrometry (GC/MS): the first sample is directly extracted, while the second is artificially aged before extraction. The results are used to calculate the ageing parameter referred as $R\%$. In order to date the ink entry, interpretation of the $R\%$ values is made through the definition of decision thresholds representing the maximal possible age of a questioned ink entry. While used to solve practical cases, very few researches were published on methods using artificial ageing to calculate $R\%$ values [14,21,41]. Thus, the added value of this

* Corresponding author. Tel.: +41 216924653.
E-mail address: agnes.koenig@unil.ch (A. Koenig).

particular ageing parameter in comparison to others such as the quantity of PE and the calculation of relative peak areas [22,42,50] was never thoroughly evaluated.

This article aims at comparing objectively four ageing parameters to study the decrease of ballpoint pen solvents in ink entries over time. Ink entries from three representative ballpoint inks, chosen in the frame of the International Collaboration on Ink Dating (InCID) [54], were studied over 1 year using GC/MS, including the analysis of naturally and artificially aged samples (in order to be able to calculate *R%* values). Validation criteria, such as sensitivity and repeatability of the method were first determined. Then, the reproducibility of the different ageing parameters was evaluated for the first time over ca. 1 year for samples from one ink as well as for samples from different inks. Influence factors, such as storage conditions and line pressure, were also evaluated over time. Finally, the results were then discussed in an ink dating perspective.

2. Material and method

2.1. Products and material

Chloroform (99.9%) was purchased from Sigma–Aldrich (Darmstadt, Germany). The reference substance phenoxyethanol (PE) 99.5% was purchased from Fluka (Buchs, Switzerland) and the internal standard was deuterated phenoxyethanol (PE-D₂) from EGT Chemie (Tägerig, Switzerland).

For sample preparation, 1.5 mL vials, 300 μ L and 50 μ L inserts as well as springs were obtained by Swiss Lab (Basel, Switzerland).

2.2. Sample preparation

The analysed samples were drawn with three different inks labelled 1688, 1774 and 1892, supplied in pen cartridges. These were chosen and sent by the Landeskriminalamt (LKA) in Munich in the frame of the International Collaboration on Ink Dating (InCID) of the European Network of Forensic Science Institutes [54]. The LKA Munich has a large collection of inks and ballpoint pens [55] and selected these three inks because they represented different ageing rates (so-called middle, slow and fast respectively).

Lines were drawn on a white copy paper of 80 g/m² (Xerox Business paper) with a ruler by a single operator. The pressure was not controlled in order to remain close to real cases conditions. The strokes were made 3 cm apart and two white pages were inserted between sheets with ink strokes to avoid cross-contaminations. The pages were stored in folders located in an air conditioned laboratory at 23 °C or in a climatic chamber at 20 °C and 55% of humidity with an air fan set at 50%. Additional ink 1688 entries were made at controlled pressure 100 g, 250 g and 350 g with a homemade device [56].

The principle of the solvent loss ratio method is to compare the quantity of PE extracted from two sets of samples collected from the same ink entry, one being artificially aged at 70 °C during 2 h [14,21]. Thus, sample collection represented a particularly critical step since both sets must contain the same amount of ink for the calculation of the *R%*. Because questioned ink entries are considered to be inhomogeneous, sample collection from the paper was carried out according to a previously reported procedure [21]. It was performed with a microplunger of 1 mm diameter (Sigma–Aldrich, Buchs, Switzerland). Two sets of 1 cm of ink were collected (10 dots/punches for each set). For each dot taken for the “natural” set, a second was collected next to it for the “heated” set, in order to reach a homogeneous distribution of dots in both sets (see Fig. 1).

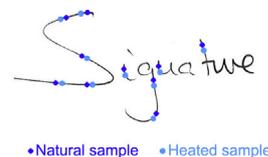


Fig. 1. Sample collection procedure [14,21].

While the “natural” sample was introduced into a conical insert of 300 μ L for extraction, the “heated” sample was introduced in a 1.5 mL vial and aged artificially in a dry bath (VWR, Nyon, Switzerland) for 2 h at 70 °C. The dots inside the vial were positioned to avoid overlapping between them. After artificial ageing, the dots were transferred from the vial to a 300 μ L insert. After 5 min (in order for the heated samples to reach again room temperature), the PE of both sets was extracted using 15 μ L of chloroform containing PE-D₂ as internal standard (4 ng/ μ L) during 3 min. Every minute the liquid was mixed with the tip of a syringe. Before analysis, the liquid was collected with a syringe and introduced in a 50 μ L insert that was then placed on a spring in a 1.5 mL sealed vial in order to avoid the solvent to evaporate too quickly.

2.3. GC/MS analysis

The analytical method was adapted from the method proposed by Brazeau and Gaudreau [14,21]. The analyses were performed with a gas chromatograph (6890 Agilent technologies) coupled with a mass spectrometer (5790 C, Agilent technologies). Separation was carried out on a HP5-MS column (30 m \times 0.25 mm \times 0.25 μ m) with a flow of 1 mL/min of Helium. For each analysis, 1 μ L 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 single ion monitoring [57]. The main solvents of each ink were actually monitored additionally to phenoxyethanol (see details in Table 1). The following ions were analysed as a function of time:

- From 4.5 min to 6.0 min.: ions 59.1, 85.1 and 103.0 (dwell time 100 ms);
- From 6.0 min to 7.0 min.: ions 59.0, 79.1, 89.1, 103.1, 108.1 (dwell time 80 ms);
- From 7.0 min and 8.0 min.: ions 45.1, 138.1, 47.1; 140.1 (dwell time 80 ms);
- From 8.0 min to 23 min.: ions 77.0, 94.0, 182.1 (dwell time 100 ms).

In order to control the GC/MS performances, a solution containing 1.7 ng/ μ L of PE (26 ng/cm) and 4 ng/ μ L of PE-D₂ was analyzed daily.

Calibration was performed by analyzing control solutions containing PE at concentrations of 0.005, 0.01, 0.03, 0.05, 0.1, 0.5, 1, 5, 10, 50, 100, 400, 600 ng/ μ L in chloroform containing 4 ng/ μ L of PE-D₂. The concentrations were extrapolated to ng/cm, yielding quantities from 0.075 ng to 9000 ng in 1 cm of ink.

The limits of detection (LoD) and quantification (LoQ) were estimated by the signal to noise method [58]:

$$\text{LoD} = \bar{X}_{\text{Blank}} + 3\text{SD}_{\text{Blank}} \quad (1)$$

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