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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

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Quantification of the loss of phenoxyethanol (PE) once an ink is deposited on the paper is 1 of the methods currently used to determine the relative ages of inks on paper. This work reports an in-depth study on differences in the aging curves, based on the loss of PE, between an ink placed on the 1st page or an ink placed on an internal page of the document. A possible cross-contamination in the values of PE has been also studied, taking into account the amount of PE absorbed and retained by the paper fibres in the pages preceding the page on which the signature is placed. Gas chromatography-mass spectrometry (GC-MS) has been used to evaluate the PE.

Introduction

Ballpoint pen inks are typically composed of a colorant or mixture of colorants and a carrier or vehicle with 1 or several solvents and resins. Colorants are composed of dyes (soluble in the vehicle and used in viscous and fluid inks) and pigments (dispersed in the vehicle and used, in certain cases, in fluid inks in addition to dyes). The vehicle contains a solvent or mixture of them (fast-drying organic solvents, water). One or several resins contribute to the properties of the inks, such as the viscosity or adhesion of the ink to the paper. Other components are also added in smaller proportion in order to modify the rheological properties of inks. These additives are usually proprietary to a manufacturer. Once an ink is deposited on paper, several processes take place as a function of time—the so-called aging process. Such processes include the loss of volatile components (as PE), dye degradation, hardening through resin polymerisation, ink-paper interaction, or a combination (Cantú and Agüí 2006).

The phenoxyethanol (PE) is a volatile organic compound, a glycol ether (b.p. 247 ºC), moderately soluble in water used as a solvent in the majority of the ballpoint pen ink formulas (near 90%) (LaPorte and others 2004). Since Stewart (1985) began the age evaluation of an ink writing based on the loss of volatile components once it is deposited on the paper, many studies have been developed with this purpose (Aginsky 1993, 1994, 1996, 1997, 1998; Brazeau and Gaudreau 2000, 2002, 2007; Weyermann 2005; Bügler and others 2005, 2008).

Lociciro et al. (2004) reported the loss of PE as a process in which a large quantity is evaporated very quickly at the ink-air interface, while the remaining compound is absorbed in the sub-layers of the papers and is diffused. This residual solvent will evaporate gradually with time and penetrate the paper and ink of preceding pages.

Gaudreau and Brazeau (2002) studied the influence of different storage conditions of a document (i.e., in plastic or cardboard folders) on the loss of PE. Weyermann (2005) reported a possible contamination of old strokes through solvent from fresh strokes on adjacent sheets of paper. Thus, contamination of stroke from 1 page to the other must be taken into account when interpreting the concentration of PE remaining on a document.

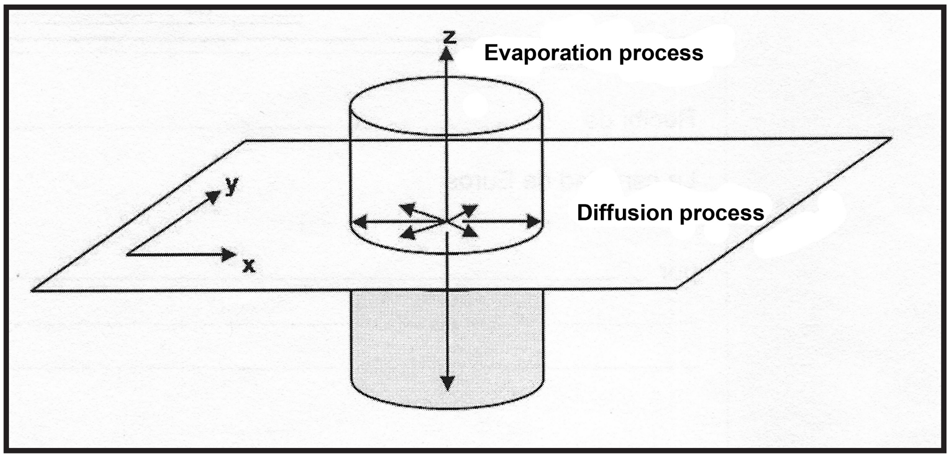

Figure 1 Evaporation and diffusion processes of PE when an ink is deposited on a paper.

If a signature is placed on an internal page of a document, the ink-air interface becomes an ink-paper interface.

Therefore, the PE should evaporate through or be absorbed by the overlaying pages of the document. This raises the question of whether this component is absorbed into the fibres of the overlaying papers and whether this value can interfere with measures of PE that are made in these sheets (Figure 1).

The aim of this work is to evaluate the possible differences in aging curves based in the loss of PE between an ink placed on the top page of a document versus ink on internal pages. Possible cross-contamination will also be studied to determine whether paper fibres absorb enough PE to affect measurements of nearby ink lines.

Liquid-solid extraction followed by a GC-MS analysis allows discriminating volatile ink components. This methodology, reported by Aginsky (1993, 1994), Gaudreau and Brazeau (2002), and Weyermann (2005), is used to determine the volatile components remaining in an ink as well as estimating the quantity absorbed or otherwise lost after the ink is deposited on the paper.

In the present work, a GC-MS method has been developed for the separation, determination, and quantization of the ink volatile components. Full scan mode is used to identify the ink volatile components and selected ion mode (SIM) for the detection of specific analytes. In SIM mode, the MS gathers data for the masses of interest rather than looking for all the masses over a wide range. In this way, the components can be quantitatively evaluated with increased sensitivity compared (by a factor of 10 to 100 times) to full scan mode. GC-MS in scan mode has been used to evaluate the ink volatile components, and the SIM mode was used for quantifying phenoxyethanol.

Method and Materials

Chemical and Reagents

Phenoxyethanol (> 99%) from Fluka (Steinheim, Germany).

Acetonitrile gradient grade was supplied by Teknokroma (Barcelona, Spain).

Ink Samples

USA Bic medium blue ballpoint ink placed on an 80g multipurpose white paper.

Sampling

Harris Uni-core (Shunderson Communications, Inc., Canada) used to punch ten 1.20 mm-sized plugs of each ink-on-paper sample (equivalent to ca. 1.2 cm).

The sampling was carried out on 28 documents divided into 4 groups. Each group contained 7 documents with different ages (1, 9, 22, 36, 43, 50 and 57 days). Group A contained documents with only 1 page; Group B was constituted by 2-page documents; Group C by 3-page documents, and Group D contained 5-page documents. All of the 28 documents were signed only on the last page.

Extracting Vessels

Agilent 1.5 ml vials with 0.1 ml micro inserts, 28×6 mm with spring bottom (polymer) PK100 were purchased from Supelco.

	Group A- 1st sheet	Group B- 2nd sheet	Group C- 3rd sheet	Group D- 5th sheet
1	2,1	1,9	2,1	1,7
9	0,8	0,7	0,7	1,2
22	0,6	0,5	0,4	0,7
36	0,4	0,4	0,3	0,5
43	0,3	0,4	0,4	0,5
50	0,4	0,3	0,5	0,4
57	0,4	0,4	0,3	0,3

Table 1 Amount of PE (mg/L) obtained by GC-MS in SIM mode for the 28 samples.

GC-MS

The inks sampled from paper (10 plugs), as well as paper blanks, were extracted in acetonitrile (30 µl) for 2 mins in a rotary mixer before GC analysis.

The extracts were analyzed using an Agilent 6890N gas chromatograph interfaced with an Agilent 5973 inert mass selective detector and equipped with a split/splitless injection system. The column used was a HP-5MS (30 m × 25 mm i.d. × 0.25 µm film thickness).

GC Conditions and MS Parameters

The injection volume was 1 µL and was achieved in splitless mode. Helium was employed as carrier gas with a column flow rate of 1,3 mL/min. Initial oven temperature was 60 ºC (2 min), then ramped at 15 ºC/min to 250 ºC, remaining at this temperature for 2 mins.

The injector and ion source was set at 250 ºC, transfer temperature was set at 260 ºC, and the detection voltage at 1588. Quantification of peaks was made in time-scheduled selected ion monitoring (SIM mode), choosing the following ions: m/z 94/138/77.

Calibration Method

The calibration of PE solutions was performed by measuring 8 patterns in the linearity range of

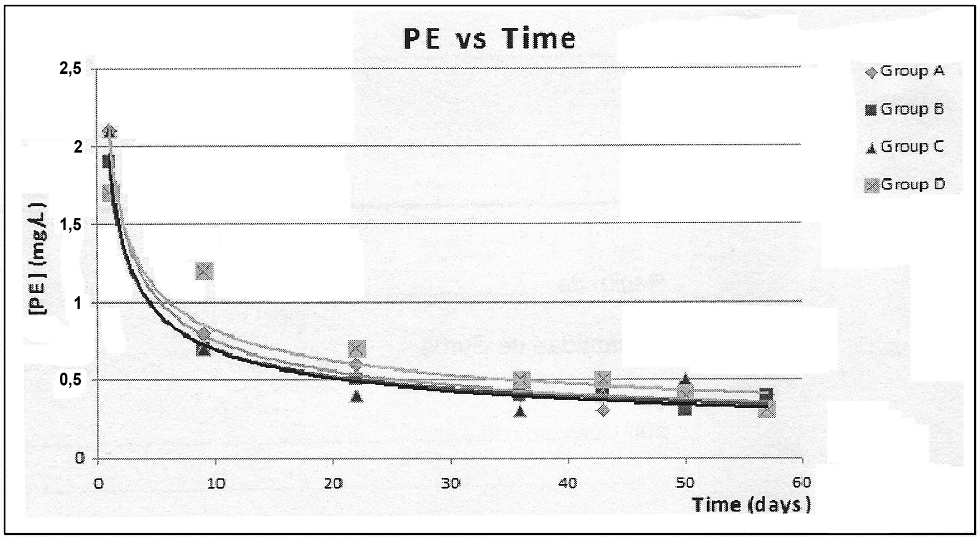

Figure 2 Aging curves corresponding to Group A (1 page), Group B (2 pages), Group C (3 pages), and Group D (5 pages)

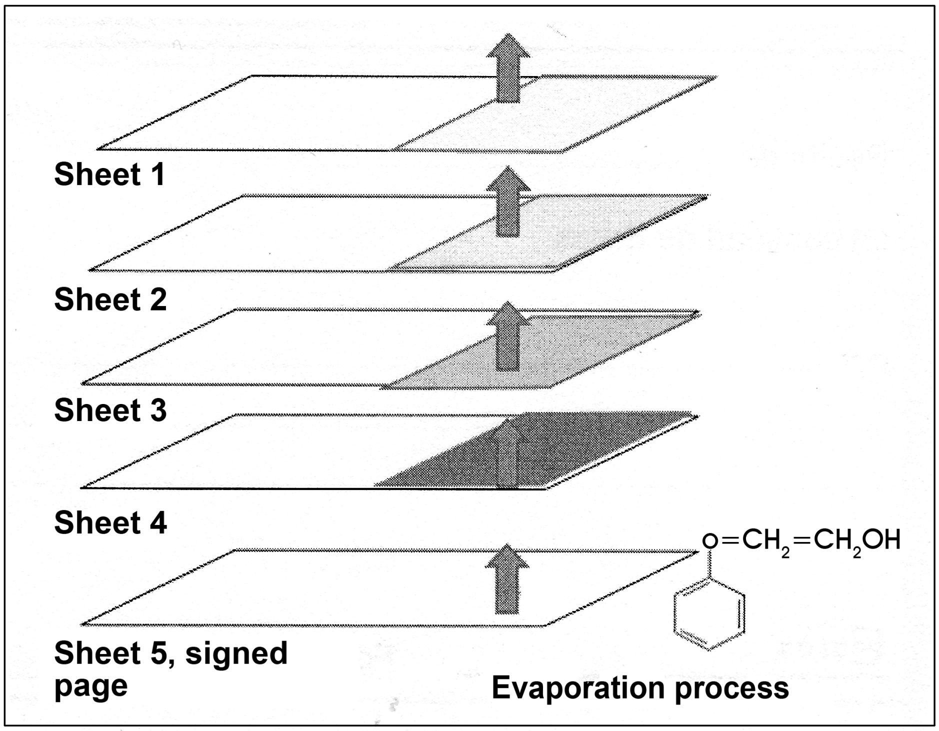

Figure 3 Diagram of the evaporation of PE of the ink of the signature located on the last page of a 5-page document.

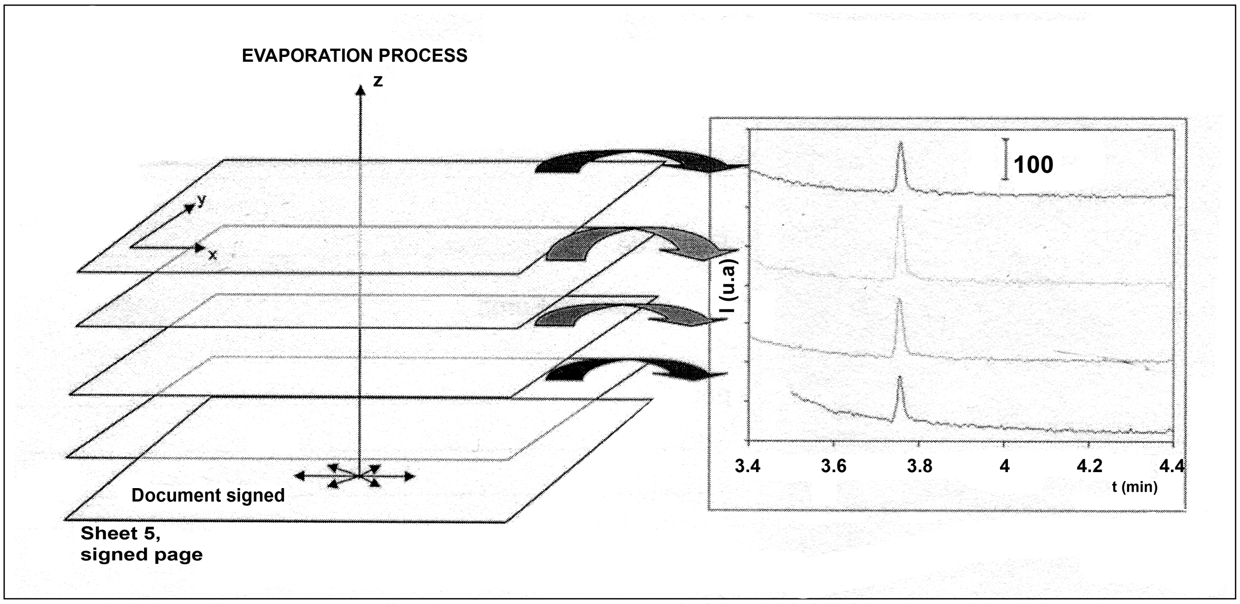

Figure 4 Evaporation of PE of the ink of the last page signature of a 5-page document.

Page 5	[PE] after 1 h (ppm)	[PE] after 5 months (ppm)
Page 4	0.83	0.04 *
Page 3	0.31	0.04 *
Page 2	0.05 ppm*	0.04 *
Page 1	0.05 ppm*	0.04 *

Table 2 Amount of PE (mg/L) analysed in the same area of the pages situated above the page signed. All (*) results are below LOD.

concentration from 0.1 mg/mL to 3 µg/mL. The regression coefficient (R^2) obtained was always above 0.9950.

The limit of quantification (LOQ) 0.08 mg/L and the limit of detection (LOD) 0.06 of the instrument were determined from the calibration curve. (The limits are calculated as, $LOQ=10*s_{blank}$ and $LOD=3*s_{blank}$).

Results and Discussion

First part: The loss of PE versus the number of document pages

Care was taken to minimize variation in the amount of ink removed for each sample. All the samples were immediately measured after 2 mins of solid-liquid extraction.

The results obtained for the documents studied are shown in Table 1.

If these results are plotted on a curve (amount of PE (mg/L) versus time the ink is deposited on paper in days), 4 aging curves for the 4 groups are formed, as shown in Figure 2.

The aging curves of the different groups fitted to exponential curves attending to R^2 values shown in the following equations:

Group A:
[PE] (mg/L) = 2,1167 $t^{-0,4466}$ $R^2 = 0,9540$ Ec. 1
Group B:
[PE] (mg/L) =1,8483 $t^{-0,4207}$ $R^2 = 0,9714$ Ec. 2
Group C:
[PE] (mg/L) = 1,9468 $t^{-0,4474}$ $R^2 = 0,8975$ Ec. 3
Group D:
[PE] (mg/L) = 2,064 $t^{-0,3994}$ $R^2 = 0,8745$ Ec. 4

R^2 values for groups C and D are below 0.9. If the points "9 days" in group D and "50 days" in group C are considered outliers (test Q), all R^2 values are above 0.95.

After comparing the 4 curves, no significant differences were noted in the loss of PE between inks placed on tops sheets of multi-page documents as compared to those placed on inner pages. Similarly, the kinetics of evaporation did not vary with the number of layers of paper that were placed above the sheet containing the signature.

Second part: Study of cross-contamination

If a paper containing ink is in contact with another paper, the fibres can absorb the volatile components of ink placed on adjacent pages. The amount of PE retained by the fibres of the sheets located over the signed page of the document in the area of the signature was measured.

The sample procedure was the same as in the previous part (10 punch 1 mm Ø) from the same area of the signature of pages 1, 2, 3, and 4 of a 5-page document, and after 1 h 5 mins (Figure 3).

The results obtained from the first 5-page document show that 1 h after the document was signed on the 5th page, 0.83 ppm of PE was found in the same area of the signature on the 4th page and 0.31 ppm of PE in the same area of the 3rd page. No significant amount of PE was detected on the 2nd and 1st pages of the document.

Five months after the signature was placed on the 5th page, the measurement process was repeated. No significant amounts of PE were found on pages 1 to 4.

A signature placed on the last page of a document loses PE, which can migrate to overlaying pages and modify the amount of PE detected in the ink of signatures on those pages.

The PE evaporates through the adjacent papers and is absorbed by the fibres which retain a small amount of the volatile component.

There is a small but significant page-to-page cross-contamination of PE that must be taken into account in the aging curve of an ink which is located in an intermediate sheet of a multi-page document that has ink writings on other pages.

Conclusions

The number of pages in a document and the location of the signature on the 1st or the last page had no influence on the kinetics of PE evaporation.

If a document is signed in the same area on 2 or more pages, a possible cross-contamination must be taken into account.

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