Journal of Chromatography A, 1515 (2017) 187–195

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Gas chromatography-mass spectrometry and high-performance liquid chromatography-diode array detection for dating of paper ink

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ARTICLE INFO

Article history:
Received 4 May 2017
Received in revised form 28 July 2017
Accepted 31 July 2017
Available online 1 August 2017

Keywords:
Chromatography
Ink
Dating
Solvent
Dyes
Multiple regression model

ABSTRACT

An extraction and determination method is shown for the analysis of dyes and solvents present in two types of ballpoint pen inks that are deposited onto paper. Ink extracts are analysed using a combination of gas chromatography with mass spectrometry (GC–MS), and high-pressure liquid chromatography with photodiode array detection (HPLC-DAD), within a single sample extraction procedure.

Seventeen solvents and thirteen dyes contained in two Montblanc® inks (black and blue) were monitored for 45 months at monthly intervals, in order to determine variations in the concentrations of the compounds over time. We also studied the relative variations between different compounds and the generation of degradation products such as phenol.

The concentration data obtained from these compounds during their exposure have been analysed and a multiple regression model is developed for each ink type that allows an estimate of the exposure time of the ink on paper with a maximum error of between 4 and 7 months.

1. Introduction

The first ballpoint pens were developed in Europe in the 1930s. The composition of the inks that were used included iron gallotannate or washable dyes with oil based solvents [1]. Since 1954, most inks have been glycol based with copper phthalocyanine pigments [2].

Modern ballpoint pen ink contains three principal components: solvents (around 50%), dyes and pigments (25%), and resins (25%). A fourth component, comprising lubricants, biocides, surfactants and other additives, is present in very small proportions (<5%) but can influence the kinetics of the first three [3,4].

An important question during forensic investigation of potentially fraudulent documents (contracts, testaments, medical records, acknowledgments of debt, tax invoices, holographic wills, etc.) is the ability to establish the point in time when any ink samples present on the document were deposited. For this reason, significant research effort has been directed towards development of ink deposit dating methods; these are generally based on the ageing of dye or solvent compounds [3–6].

Following their manufacture inks may be stored for considerable lengths of time in containers (including pen cartridges and ink bottles). In these cases, the relative proportions and composition of the dyes, solvents and resins that make up the ink remain stable with time [7,8]. Ageing in these containers is therefore insignificant in comparison with the processes that commence once the ink is deposited onto paper [6,9,10].

After deposition onto paper, inks undergo various physical and chemical transformations [1]. These changes are determined by several factors including their initial composition and compound concentrations, storage temperature, light levels, and the chemical and mechanical properties of the paper [7,11].

Upon application onto paper, changes in the aggregation state of an ink begin to take place immediately. Furthermore, the solvents evaporate, the dyes degrade and the resins polymerize [8]. Dating of inks can be based on the equilibrium times of these processes, up until the point at which the ink ceases to be active and undergoes no further changes. This point may vary from a few months to several years after deposition [8].

In the forensic application of ink dating, the main objective is to determine the approximate age of a document (rather than the exact date), in order to establish the authenticity or not of the signed manuscript on the date established in the document [12]. In this sense errors of several months are acceptable for this purpose.

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http://dx.doi.org/10.1016/j.chroma.2017.07.093
0021-9673/

There are two approaches to the dating of inks: relative dating and absolute dating. The first approach, also known as static dating, relies on knowledge of when the components within the ink were first introduced, or when a specific formulation of ink was first commercially introduced to the market. This approach requires an extensive database of inks. The second approach, also referred to as dynamic ageing, uses knowledge of the aging process to estimate the time of ink deposition [13].

With respect to absolute dating methods, some controversy exists about the use of dyes in the study of ink dating [14]. However, the use of solvents to date ink deposition is more extensive and established [15,16]. Volatile solvents typically represent more than 50% of the weight of ballpoint ink, and they disappear very quickly (within a few hours) after application [6]. 2-phenoxyethanol (PE) is of particular interest since it constitutes over 80% of solvents in black and blue ballpoint pens at different concentrations [17–19]. These dating methods can be divided into three groups according to the proposed methodology:

1. Methods that analyse the quantitative decrease of PE in ink samples as a function of time. With this process it is possible to determine drying curves that show changes of the solvent in the ink sample over time [17,20,21].
2. Methods that use artificial ageing to calculate decreases in the aging process of ink solvents [21–23].
3. Methods that analyse decreases of the extractability of solvent and dye content using sequential extractions that are sometimes combined with artificial ageing [24,25].

In general, ageing processes in inks start with a fast and rapidly decreasing rate of drying (solvent evaporation and diffusion into the paper). Following this step, evaporation and diffusion decrease to slower rates of drying. Residual amounts of solvents may even stay trapped in the ink matrix for years (polymerization) [11]. Moreover, dye degradation processes may occur [26], as in the case of increased amounts of phenol produced by the degradation of crystal violet (CV) that has been observed in numerous studies [27].

Sensitive and selective analytical instrumentation is needed to detect the solvents and dyes in ballpoint ink on paper. Gas chromatography (GC) coupled with mass spectrometry (MS) and high pressure liquid chromatography (HPLC) with visible-ultraviolet are the most commonly used techniques for analysis of solvents and dyes, respectively [17,18,23,24,28–31]. In addition, spectroscopic methods such as infrared spectroscopy (IR) and RAMAN can also be used to investigate the timing ink deposits on paper [3,4].

Ink written onto a paper surface is not homogeneously distributed; it varies depending on the intensity of the stroke and/or the amount of pressure exerted by the writer, among other factors. A major concern regarding measurements of ink solvents and dyes is the unknown sample size [17]. Therefore, a method that ensures that measurements are independent of the amount of ink in the sample (mass invariance) is needed. One solution to this problem is to take ratios between different compounds.

This article focuses on the quantitation of 17 solvents and 13 dyes in ink from two types of ballpoint pen after deposition onto paper, with a view to establishing a combined dating method based on multiple regression. Real samples, with a known date of paper deposition, are used to establish a dating methodology for periods of between 0 and 4 years. Initially, we study the concentration of solvents and dyes as a function of time. Chemometric techniques including multiple regression that combine solvents and dyes are used. Finally, the proposed dating method is validated over the temporal range of the study.

2. Experimental

2.1. Chemicals, materials and samples

Methanol (HPLC gradient grade, 99.9%), *n*-hexane (gradient grade, 97%), acetonitrile (HPLC gradient grade, 99.8%) and water for HPLC were obtained from Sigma-Aldrich® (St. Louis. MO, USA).

For the determination of solvents and dyes, a methanolic solution of 3-methylphenol (99.9%, Supelco®) was prepared as an internal standard at 1000 μg mL^{-1}.

Analytical standards used for calibration of all measured solvents were obtained from Sigma-Aldrich® and Dr. Ehrenstorfer Laboratories® (Table 1).

Black Montblanc® (Mystery black, Refills B, ISO 12757 2HB DOC, Nr. 105148 Germany) and blue Montblanc® (Pacific blue, Refills B, ISO 12757 2HB DOC, Nr. 105149 Germany) ballpoint pen entries were drawn onto a piece of white paper from Hewlett-Packard® (80 g m^{-2}, A4 format), spaced as evenly as possible by the same researcher in order to maximise the uniformity of the ink traces used in the study. These ballpoint ink samples were deposited onto the paper four years prior to testing so that they could be analysed at intervals of approximately 1 month.

The samples were stored in the dark in closed filing cabinets at room temperature. Relative humidity during storage stayed within the interval 52–88%; humidity is not a determining factor in storage conditions [15].

A 1.25 mm diameter (Ø) Harris micro-punch and a Harris cutting mat purchased from Sigma-Aldrich (St. Louis, MO, USA) were used for sampling. Small paper disc samples of 1.25 mm diameter were cut using the micro-punch and placed into sealed amber vials with 0.1 mL conical transparent glass inserts for analysis.

2.2. Extraction procedure

For age dating, 8 microdiscs were cut from each sample of black or blue ink on the paper. The paper disc samples with ink deposits were placed into sealed amber vials with 0.1 mL conical glass inserts. These eight discs were extracted with 15 μL of methanol solution containing 0.1 mg L^{-1} of internal standard (IS: 3-methylphenol). The extraction procedure involves agitating the sample in a closed vial with the extraction solution for 30 s in an orbital shaker, and then placing it into an ultrasonic bath for 2 min. In order to determine the respective concentrations of solvents and dyes, the resulting extract was analyzed by gas chromatography coupled to mass spectrometry (GC–MS), and by high-pressure liquid chromatography with a diode array detector (HPLC-DAD).

Blank discs cut from paper without ink were extracted using the same procedure to check for any contamination in the paper that might influence the ink ageing results.

The complete extraction process was carried out every month (from 0 to 45 months) in order to provide sufficient temporal resolution over the study period.

2.3. GC–MS analysis

The solvents were analyzed using GC–MS with an Agilent 6850N/5975C (Agilent Technologies®, Palo alto, CA, USA) equipped with an Agilent 7693A autosampler. DB-5MS 30 m × 0.25 mm i.d × 0.25 μm film thickness and VF-WAXms 30 m × 0.25 mm i.d × 0.25 μm film thickness capillary columns were used (both from Agilent Technologies®). MSD ChemStation software E.02.01 was used for data acquisition. Agilent Technologies® Deconvolutions Reporting A.0400 and NIST 2008 v.2.0. Mass Spectral Library-AMDIS Agilent Technologies® (2010) were used for quantitative analysis.