

TECHNICAL NOTE

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The Identification of 2-Phenoxyethanol in Ballpoint Inks Using Gas Chromatography/Mass Spectrometry—Relevance to Ink Dating*

ABSTRACT: Developing and implementing a generally accepted procedure for the dating of ink found on documents using dynamic approaches has been a very formidable undertaking by forensic document examiners. 2-Phenoxyethanol (PE), a common volatile organic compound found in ballpoint inks, has been recognized for over a decade as a solvent that evaporates as ink ages. More recently, investigations have focused on the solvent loss ratio of PE prior to and after heating. To determine how often PE occurs in ink formulations, the authors analyzed 633 ballpoint inks utilizing a gas chromatograph/mass spectrometer. 2-Phenoxyethanol was identified in 85% (237/279) and 83% (293/354) of black and blue inks, respectively.

KEYWORDS: forensic science, questioned documents, phenoxyethanol, ballpoint ink, ink dating, ink aging, GC/MS, volatile analysis, SPME

An examination to determine the age of ink on a document can be quite challenging. Cantu (1,2) outlines two approaches to determine the age of ink on a questioned document. The first of these is the static approach, which generally applies to methods based on the comparison of various ink components to a standard reference collection to determine the first date of production. In fact, the United States Secret Service (USSS) and the Internal Revenue Service (IRS) jointly maintain the largest known collection of writing inks from around the world. These inks date back to the 1920s and include over 8000 inks obtained from various manufacturers throughout the world. Annually, contact is made with the pen and ink manufacturers requesting that they send any new formulations of inks, along with appropriate information, so that the submitted standards can be chemically tested and added to the reference collection. Writing pens are also obtained from the open market and compared to the library of standards to verify and identify additional inks. This is a formidable task that obviously requires significant resources and maintenance. Indeed, this is not always a practical solution for every forensic facility to achieve.

Ideally, ink tags would be the most reliable method for the dating of inks. Tags can be added to formulations in the form of fluorescent

compounds or rare earth elements and were evident in some formulations from about 1970 until 1994. Factors have precluded some ink manufacturers from participating in such a program, including, but not limited to, insufficient resources, low priority, and/or disagreement about the type of tag utilized. This is not to say that a widespread tagging agenda is not achievable. On the contrary, efforts do continue to convince ink companies to add tags to their formulations. As recently as November 2002, a dominant ink manufacturer has begun adding tags to their ink in collaboration with the U.S. Secret Service.

With stringent demands from the forensic community to develop and validate scientifically reliable laboratory techniques, implementing other methods for ink dating is an arduous endeavor as well. Such methods include those involving the dynamic approach, which incorporates procedures that measure the physical and/or chemical properties of ink that change with time. The changes that occur over a given period of time can generally be referred to as aging characteristics. Ballpoint inks mainly consist of colorants (dyes and/or pigments) and vehicles (solvents and resins). There is also a wide array of other ingredients, which may include antioxidants, preservatives, and trace elements, but these are typically a small component of the overall ink composition. Nevertheless, the importance of their presence should not be diminished since the combination of all ingredients may play a pivotal role in the aging characteristics of an ink formulation. However, the subject of this paper will focus on the vehicles found in ballpoint inks. More specifically, the authors have chosen to investigate a single volatile compound that has been reported by the industry to be in many formulations of inks.

Volatile analysis of ballpoint inks, using GC/MS, for determining the age of inks on paper has been studied and reviewed in the literature for more than a decade (3–8). These authors have laid the

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Chemical Abstract Services (CAS) Number: 122-9-6

Molecular Weight: 138.17

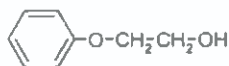


FIG. 1—The chemical structure and formula for 2-phenoxyethanol.

groundwork for what may be a very promising dynamic approach to the future of ballpoint ink age determination. These works have honed in on the analysis of 2-phenoxyethanol (PE), a common volatile organic compound found in some ballpoint writing inks. 2-Phenoxyethanol, also referred to as ethylene glycol monophenyl ether, 1-hydroxy-2-phenoxyethane, beta-hydroxyethylphenyl ether, Dowanol EP, and Phenyl Cellosolve, is a glycol ether and is used as the principal solvent in many ballpoint ink formulations. It is a colorless, slow evaporating, viscous liquid with a faint aromatic odor and is used in most ballpoint ink formulations because it is stable in the presence of acids and alkalis. It is also nonhygroscopic (does not absorb water, making it amenable to hot, humid climates), nonhazardous, economical, and especially good at solubilizing resins and nigrosine (a common solvent soluble black dye used in the writing ink formulations). It is recognized as Chemical Abstracts Service (CAS) number 122-9-6 and has a molecular weight of 138.17 with a boiling point of 245.2°C (9). Figure 1 depicts the chemical formula and structure of PE. Beshanishvily et al. (4) were the first to discuss the identification of PE as it relates to the aging of inks. Since then, Aginsky (5) reported that, "... significant aging [takes] place over a period of about 3 months. After this period until the age of 15 years the extent of the extraction of the volatile component (phenoxyethanol) from the ink entries has been kept at a level about 20%." Aginsky also describes the ink-drying process and surmises that volatile components stop emitting from a dried sample of ink until they are freed by heating or a solvent extraction.

More recently, Gaudreau and Brazeau (10) presented their findings on an extensive research effort that focuses on how PE levels change over time following an ink entry placed on paper. They discuss solvent loss and state that the "... phenoxyethanol in ink evaporates at a high rate during the first six to eight months following its application on paper. The rate of evaporation stabilizes over a period of six to eighteen months. This process is no longer significant after a period of about two years." Given the chemical properties of PE, its loss due to evaporation is most affected by heat. With these caveats, they developed a dynamic approach to ink dating that incorporates comparing the PE ratio of an ink prior to and after heating.

In addition, Brazeau et al. (11) have experimented with solid phase micro-extraction (SPME), which utilizes a specially coated silica fiber that is mounted in a syringe-like device. A small glass vial is placed over the ink entry with the SPME device inserted in the sealed environment. Volatile solvents that emit from the ink adsorb onto the fiber for a set time, i.e., until an equilibrium is achieved within the system. The fiber is then withdrawn and injected into a gas chromatograph (GC), whereby the volatile components are desorbed due to the high temperature (e.g., 250°C) in the injection port. The analytes are then separated in the GC and identified using an appropriate analytical instrument such as a mass spectrometer (MS). SPME has proven to be an efficient and effective method for the extraction of volatile components (12,13) and has been utilized

in the authors' laboratory for the detection of PE in some ballpoint inks.

Chemical analysis of writing inks by means of thin layer chromatography (TLC) is viewed by the scientific community as a valid procedure to compare inks (14–18). Since TLC is an effective and efficient method for separating and identifying various colored components such as dyes, and nearly all ink formulations are proprietary, forensic examinations that employ TLC analysis are invaluable. For instance, two or more questioned inks can be compared to determine if they are the same, or questioned inks can be associated to a known standard to determine the age of an ink, i.e., the static approach. With respect to this latter instance, appropriate information and documentation acquired from a manufacturer regarding their ink will allow a forensic document examiner to make significantly reliable conclusions, assuming there is access to a thorough ink collection. Although obtaining a supplemental volatile profile may increase the degree of discrimination, limitations include solvent loss over time or other external factors such as exposure to high temperatures, light, and/or humidity.

With the benefit of having a large collection of standards, the authors determined that it would be advantageous to begin conducting volatile profiles of writing inks to investigate the percentage of ballpoint inks that actually contain PE since it is an important compound of interest for the determination of ink age. An extensive search of the literature was conducted, but no studies investigated a large population of inks to determine how often PE is present in ballpoint ink formulations. Thus, the focus of this paper will be on the examination for the presence of 2-phenoxyethanol in 633 ballpoint inks.

Materials and Methods

Ink Standards

As stated, ink standards are received by the USSS from all over the world and date back to the 1920s. As new ink formulations are received, samples of the ink are placed onto Whatman™ filter paper No. 2 (also referred to as scribble sheets), allowed to air dry, placed in a protective sheet and binder, and finally stored in dark cabinets to ensure minimal degradation due to environmental factors such as light, temperature, and humidity. Many of the ink standards are received as a liquid in a bottle and permanently retained, and others are received in pens, pen refills, or as samples on paper. For this study, whenever possible, ballpoint ink samples in liquid form were analyzed directly from the bottle or pen. Other ink samples were taken off the scribble sheets; however, volatile profiles of scribble sheet samples were closely examined to determine if they were suitable to include in the study since some were over 30 years old. This topic will be discussed under Results and Discussion. A total of 279 black ballpoint inks from 31 companies and 354 blue ballpoint inks from 26 companies were chosen for analysis using a PerkinElmer TurboMass™ gas chromatograph/mass spectrometer.

Extraction

Liquid inks were sampled utilizing a disposable capillary glass pipette in order to minimize sample handling. The pipette was then placed into a glass vial containing 1 mL of acetonitrile. The ink and solvent were agitated/stirred to ensure a homogenous mixture. Dried ink samples from scribble sheets were sampled using a 5-mm hole punch. The punches were taken from a highly dense area and allowed to extract in a vial with 1 mL of acetonitrile for approximately 1 min. The solvent was decanted and placed into a separate vial.

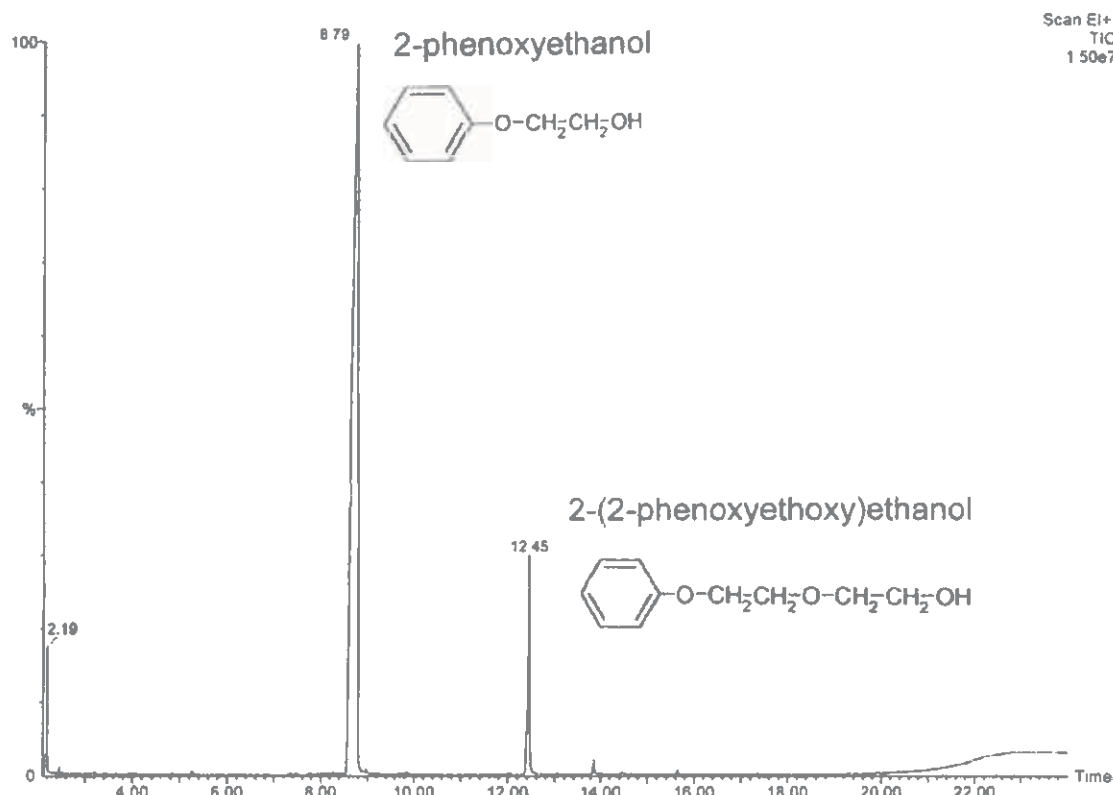


FIG. 2a—The total ion chromatogram for 2-phenoxyethanol standard (J.T. Baker™ product No. T-319-07).

Gas Chromatography/Mass Spectrometry (GC/MS)

All of the extracted ink samples were analyzed using an auto sampler attached to a PerkinElmer Turbomass™ GC/MS. One-microliter samples were injected into the GC. The column used was an HP-5 (30 m × 0.32 mm × 0.25 μL) cross-linked 5% phenylmethylsiloxane. The injector temperature was set to 260°C and the flow rate was 1.2 mL/min split mode at 20 mL/min. The temperature program started at 50°C for 1 min and increased at a rate of 10°C/min to 200°C with a 2-min hold. The second rate was 25°C/min to 300°C with a final 2-min hold. The mass spectrometer detector was set for full scan from 1.8 to 24 min with the 1.8-min delay set to begin following the solvent elution, i.e., solvent delay. The detector was programmed to scan compounds ranging from 28 to 500 atomic mass units (amu).

Results and Discussion

A review of the standards library indicated that at the inception of this project there were 516 black ballpoint inks from 53 companies and 854 blue ballpoint inks from 65 companies. All the liquid ink samples that were obtained from bottles were extracted and exhibited significant volatile profiles with sufficient peak abundance for accurate integration. In contrast, there were numerous scribble sheet samples that did not produce a significant, or very limited, chromatographic profile. The lowest level of detection for sufficient interpretation was estimated to be 0.1 ppb. It was determined that insignificant peak area was the result of the age of the ink on the scribble sheet (e.g., some scribble sheets were 20 to 30 years old). The results for the samples determined to have poor chromatographic profiles were recorded, but not used to calculate the statistics presented in this paper. A total of 279 black ballpoint inks

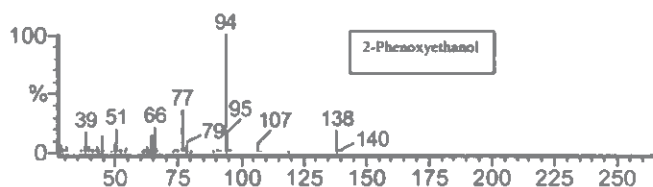


FIG. 2b—The mass spectrum for Peak 1 at retention time (RT) = 8.79 min.

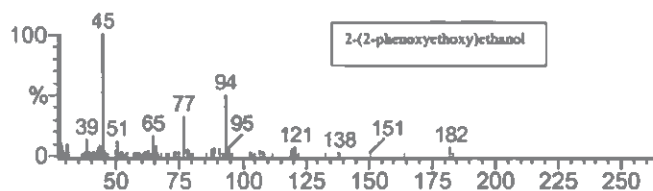


FIG. 2c—The mass spectrum for Peak 2 at RT = 12.45 min.

from 31 companies and 354 blue ballpoint inks from 26 companies were determined to have significant chromatographic profiles necessary for peak integration and, hence, accurate identification of chemical composition. 2-Phenoxyethanol was identified in 85% (237/279) and 83% (293/354) of the black and blue inks, respectively. Furthermore, 20 of the 31 companies that have manufactured black ballpoints used PE in the vehicle in 100% of their ballpoint formulations and 11 of the 26 manufacturers incorporated PE in all of their blue ballpoint inks.

The 2-phenoxyethanol standard (J.T. Baker product No. T319-07, Lot No. N35622) contained two major peaks on the TIC (total ion chromatogram), and the GC/MS results are depicted in Figs. 2a, 2b, and 2c. In addition to the PE at retention time (RT) 8.79 min,

2-(2-phenoxyethoxy)ethanol, also referred to as diethylene glycol phenyl ether (DGPE) or phenyl carbitol, was detected at a RT of 12.45 min. It is identified as CAS number 104-68-7. The Sigma-Aldrich catalogue (2003-2004) indicates that Dowanol EPH, i.e., PE, can contain up to 10% DGPE.

DGPE was detected in 21.5% (60/279) and 12.1% (43/354) of the black and blue ballpoint inks that contained PE, respectively. There was no evidence that the level of DGPE was directly related to the level of PE (e.g., DGPE was occasionally absent in samples with relatively high levels of PE and was present in samples with relatively low levels of PE). However, no further study was conducted to examine if the ratio of PE/DGPE changed with aging. The authors did infer that there may be differences in the composition of 2-phenoxyethanol that may be attributable to a particular chemical manufacturer. Indeed, this information could be utilized to differentiate ink manufacturers depending on their supplier.

GC/MS is an obviously powerful analytical tool, not only for the dating of inks, but for the identification of some components of inks. Brunelle and Crawford (19) recently wrote, "GC-MS shows great promise for strengthening ink identifications, because it can be used to identify both volatile and non-volatile ingredients of inks." Accordingly, the authors were cognizant of this at the outset of the study and maintained data of all the identifiable components in the 633 black and blue ballpoint inks to determine if there are chemical class characteristics specific to a manufacturer. A thorough review of the results and all subsequent conclusions pertaining to the use of GC/MS to profile company ink formulations was considered a secondary objective. The authors determined that this analysis would be better suited in a future work with an extensive and dedicated discussion to the GC/MS analysis of a large population of ballpoint inks.

The analysis of volatile components such as PE to determine the age of an ink is promising, especially when using methods that are based on the relative loss of a solvent between heated and unheated samples. There are different scenarios of a document examination that an examiner may encounter that will significantly affect the degree of qualification of a conclusion. For example, an examiner may be requested to compare two or more inks on the same document to determine if they were produced contemporaneously. If prior examinations indicate that the inks are matching formulations, but they are suspected of being made at two different time periods (e.g., several months apart), then factors such as storage conditions, the type of paper, exposure to a variety of environments, and differences in formulation should not preclude a forensic examiner from making conclusions with limited qualifications. It is important to note that the Merck Index (9) indicates that PE is used as a fixative in perfumes, which would require handlers to be cognizant so as not to possibly contaminate a questioned document. As well, the approaches discussed in this paper are not mass independent when sampling the ink; therefore, care and accuracy need to be administered when removing ink plugs for analysis. One final caveat that requires some consideration is the rate of PE migration on paper once an entry is made. Since PE is a liquid solvent, it is feasible to ascertain that it may dissipate through the paper into a questioned entry if ink is present on the reverse side of a page. Ink may also migrate from nearby adjacent entries, but taking blank samples (e.g., samples of the paper with no ink) in close proximity may aid the examiner in understanding the extent of PE migration.

Another scenario that may be encountered is the analysis of ink entries on a document that are not of the same formulation. Although one may argue that the document is likely to have been stored under the same conditions, the level of PE may exist in different levels in different formulations from the same manufacturer.

Finally, one may be requested to date entries on multiple pages that are part of the same document submission (e.g., multi-page wills or contracts) to determine if they were produced at, or around, the same time. Differences in paper, storage conditions, and how the document is arranged (e.g., the presence of ink solvents on subsequent or overlying pages that transfer to adjacent pages) should be taken into consideration. Indeed, more research and validation into these unknown effects will be fundamental in developing standard allowable variations. Standard error can then be incorporated to account for human error and experimental deviation that are necessary to make qualified conclusions of forensic significance.

Conclusion

The identification of PE in over 80% of black and blue ballpoint ink formulations has shown that studies investigating PE as it relates to the aging of writing inks have been and continue to be significant. As our field undergoes necessitated scrutiny of forensic examinations, GC/MS is an excellent and well-proven analytical tool for the identification and quantification of chemical compounds. Validation of the instrumentation and the procedures utilized to identify PE should therefore be minimal. This will allow future researchers to concentrate their efforts on the development and implementation of a generally accepted procedure for a dynamic approach to ink dating.

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