Exhibit 10

Declaration of Larry F. Stewart

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

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Received 21 June 2003; and in revised form 4 Sept. 2003; accepted for publication 4 Sept. 2003; published 17 Dec. 2003.

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

C₆H₅OCH₂CH₂OH

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 nonhygrosopic (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 WhatmanTM 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 TurboMassTM 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.



Gas Chromatography/Mass Spectrometry (GC/MS)

All of the extracted ink samples were analyzed using an auto sampler attached to a PerkinElmer TurbomassTM GC/MS. Onemicroliter samples were injected into the GC. The column used was an HP-5 ($30 \text{ m} \times 0.32 \text{ mm} \times 0.25 \mu \text{L}$) 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







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,

4 JOURNAL OF FORENSIC SCIENCES

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.

Acknowledgments

The authors wish to extend their gratitude to Dr. Ben Fabian from Sensient Imaging Technologies for the information he provided regarding the use of 2-phenoxyethanol in the writing ink industry. As well, we wish to thank Mr. Marc Gaudreau and Mr. Luc Brazeau of the Canada Customs Revenue Agency for their efforts to accommodate our many questions regarding the analysis of volatile solvents in ballpoint writing inks.

References

- 1. Cantu AA. A sketch of analytical methods for document dating. Part I: The static approach: determining age independent analytical profiles. Int J Forensic Doc Examiners 1995;1(1):40–51.
- Cantu AA. A sketch of analytical methods for document dating. Part II: The dynamic approach: determining age dependent analytical profiles. Int J Forensic Doc Examiners 1996;2(3):192–208.
- Stewart LF. Ballpoint ink age determination by volatile component comparison—a preliminary study. J Forensic Sci 1985;30(2):405–11.
- Beshanishvily GS, Trosman EA, Dallakian PB, Voskerchian GP. Ballpoint ink age—a new approach. Proceedings of the 12th International Forensic Scientists Symposium; 1990 Oct 15–19; Adelaide, Australia.
- Aginsky VN. Some new ideas for dating ballpoint inks—a feasibility study. J Forensic Sci 1993;38(5):134–50.
- Aginsky VN. Determination of the age of ballpoint ink by gas and densitometric thin-layer chromatography. J Chromatogr A 1994;678:117–25.
- Aginsky VN. Dating and characterizing writing, stamp pad and jet printer inks by gas chromatography/mass spectrometery. Int J Forensic Doc Examiners 1996;2(2):103–15.
- Aginsky VN. Measuring ink extractability as a function of age—why the relative aging approach is unreliable and why it is more correct to measure ink volatile components than dyes. Int J Forensic Doc Examiners 1998;4(3):214–30.
- Budavari S, editor. The merck index: an encyclopedia of chemicals, drugs, and biologicals. 12th ed. Whitehouse Station (NJ): Merck Research Laboratories Division of Merck & Co., Inc., 1996:7410.
- Gaudreau M, Brazeau L. Ink dating using a solvent loss ratio method. Proceedings of the 60th Annual Conference of the American Society of Questioned Document Examiners; 2002 Aug 14–18; San Diego (CA).

- Brazeau L, Chauhan M, Gaudreau M. The use of micro-extraction in the development of a method to determine the aging characteristics of inks. Proceedings of the 58th Annual Conference of the American Society of Questioned Document Examiners; 2000 Aug 24–29; Ottawa, Ontario.
- Vu DTT. SPME/GC-MS characterization of volatiles associated with methamphetamine: toward the development of a pseudomethamphetamine training manual. J Forensic Sci 2001;46(5):1014–24.
- Vu DTT. Characterization and aging study of currency ink and currency canine training aids using headspace SPME/GC-MS. J Forensic Sci 2003;48(4).
- Aginsky VN. Forensic examination of "slightly soluble" ink pigments using thin-layer chromatography. J Forensic Sci 1993;38: 1131–3.
- Brunelle RL, Pro MJ. A systematic approach to ink identification. J AOAC Int 1972;55:823–26.

- Kelly JD, Cantu AA. Proposed standard methods for ink identification. J AOAC Int 1975;58:122–25.
- The American Society for Testing and Materials (ASTM) E 1422-98: Standard Guide for Test Methods for Forensic Writing Ink Comparison, 1998;530–7.
- The American Society for Testing and Materials (ASTM) E 1789-96: Standard Guide for Writing Ink Identification, 1996:722–6.
- 19. Brunelle RL, Crawford KR. Advances in the forensic analysis and dating of writing ink. Springfield (IL): Charles C. Thomas, 2003;164.

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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.



Gas Chromatography/Mass Spectrometry (GC/MS)

All of the extracted ink samples were analyzed using an auto sampler attached to a PerkinElmer TurbomassTM GC/MS. Onemicroliter samples were injected into the GC. The column used was an HP-5 ($30 \text{ m} \times 0.32 \text{ mm} \times 0.25 \text{ }\mu\text{L}$) 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







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,

4 JOURNAL OF FORENSIC SCIENCES

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.

Acknowledgments

The authors wish to extend their gratitude to Dr. Ben Fabian from Sensient Imaging Technologies for the information he provided regarding the use of 2-phenoxyethanol in the writing ink industry. As well, we wish to thank Mr. Marc Gaudreau and Mr. Luc Brazeau of the Canada Customs Revenue Agency for their efforts to accommodate our many questions regarding the analysis of volatile solvents in ballpoint writing inks.

References

- 1. Cantu AA. A sketch of analytical methods for document dating. Part I: The static approach: determining age independent analytical profiles. Int J Forensic Doc Examiners 1995;1(1):40–51.
- Cantu AA. A sketch of analytical methods for document dating. Part II: The dynamic approach: determining age dependent analytical profiles. Int J Forensic Doc Examiners 1996;2(3):192–208.
- Stewart LF. Ballpoint ink age determination by volatile component comparison—a preliminary study. J Forensic Sci 1985;30(2):405–11.
- Beshanishvily GS, Trosman EA, Dallakian PB, Voskerchian GP. Ballpoint ink age—a new approach. Proceedings of the 12th International Forensic Scientists Symposium; 1990 Oct 15–19; Adelaide, Australia.
- Aginsky VN. Some new ideas for dating ballpoint inks—a feasibility study. J Forensic Sci 1993;38(5):134–50.
- Aginsky VN. Determination of the age of ballpoint ink by gas and densitometric thin-layer chromatography. J Chromatogr A 1994;678:117–25.
- Aginsky VN. Dating and characterizing writing, stamp pad and jet printer inks by gas chromatography/mass spectrometery. Int J Forensic Doc Examiners 1996;2(2):103–15.
- Aginsky VN. Measuring ink extractability as a function of age—why the relative aging approach is unreliable and why it is more correct to measure ink volatile components than dyes. Int J Forensic Doc Examiners 1998;4(3):214–30.
- Budavari S, editor. The merck index: an encyclopedia of chemicals, drugs, and biologicals. 12th ed. Whitehouse Station (NJ): Merck Research Laboratories Division of Merck & Co., Inc., 1996:7410.
- Gaudreau M, Brazeau L. Ink dating using a solvent loss ratio method. Proceedings of the 60th Annual Conference of the American Society of Questioned Document Examiners; 2002 Aug 14–18; San Diego (CA).

- Brazeau L, Chauhan M, Gaudreau M. The use of micro-extraction in the development of a method to determine the aging characteristics of inks. Proceedings of the 58th Annual Conference of the American Society of Questioned Document Examiners; 2000 Aug 24–29; Ottawa, Ontario.
- Vu DTT. SPME/GC-MS characterization of volatiles associated with methamphetamine: toward the development of a pseudomethamphetamine training manual. J Forensic Sci 2001;46(5):1014–24.
- Vu DTT. Characterization and aging study of currency ink and currency canine training aids using headspace SPME/GC-MS. J Forensic Sci 2003;48(4).
- Aginsky VN. Forensic examination of "slightly soluble" ink pigments using thin-layer chromatography. J Forensic Sci 1993;38: 1131–3.
- Brunelle RL, Pro MJ. A systematic approach to ink identification. J AOAC Int 1972;55:823–26.

- Kelly JD, Cantu AA. Proposed standard methods for ink identification. J AOAC Int 1975;58:122–25.
- The American Society for Testing and Materials (ASTM) E 1422-98: Standard Guide for Test Methods for Forensic Writing Ink Comparison, 1998;530–7.
- The American Society for Testing and Materials (ASTM) E 1789-96: Standard Guide for Writing Ink Identification, 1996:722–6.
- 19. Brunelle RL, Crawford KR. Advances in the forensic analysis and dating of writing ink. Springfield (IL): Charles C. Thomas, 2003;164.

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Available online at www.sciencedirect.com



Forensic Science <u>International</u>

Forensic Science International 168 (2007) 119-127

www.elsevier.com/locate/forsciint

A GC/MS study of the drying of ballpoint pen ink on paper

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Received 31 October 2005; received in revised form 21 June 2006; accepted 26 June 2006

Available online 9 August 2006

Abstract

The determination of the age of an ink entry from a questioned document is often an essential problem and a controversial issue in forensic sciences. Therefore, it is important to understand the aging process of the different components found in ink. The aim of this work was to study the drying process of ballpoint ink, characterised by the disappearance of volatile solvents from the ink entry. Phenoxyethanol is of particularly high interest as it is found in more than 80% of the blue ballpoint pens at different concentrations.

Liquid extraction followed by splitless gas chromatography/mass spectrometry in the selected ion mode was used to measure the quantitative decrease of solvents from ink entries made with a blue Parker[®] ballpoint pen. Quantities of ethoxyethoxyethanol, dipropylene glycol, phenoxyethanol and phenoxyethoxyethanol were studied in ink entries up to 1.5 years old, thus allowing to calculate aging curves for this particular pen. The low quantities of solvents (in the microgram range for a 1 cm ballpoint entry) were found to decrease quickly after deposition of the ink on paper through the competitive processes of evaporation and diffusion. Losses of up to 75% of solvents were observed after a few seconds. The amount of ethoxyethanol stopped decreasing after about 10 days (quantities reached the nanogram range for a 1 cm ballpoint entry), while the aging curves of dipropylene glycol, phenoxyethanol and phenoxyethoxyethanol level off considerably after 2 weeks. It was observed that ethoxyethanol, dipropylene glycol and phenoxyethanol can also migrate from one sheet of paper to another if placed close enough (e.g. in a book or a stack of papers), therefore contamination from fresh ink strokes from other paper sheets has to be taken into account for those solvents.

In this paper we demonstrate that differentiation between fresh ink (<2 weeks) and older inks is possible under laboratory storage conditions. For real cases samples, more parameters have to be studied and other possible pathways have to be considered. © 2006 Elsevier Ireland Ltd. All rights reserved.

Keywords: Forensic sciences; Gas chromatography; Laser mass spectrometry; Solvents; Dyes; Aging and ballpoint ink

1. Introduction

In the forensic field of questioned documents, the following query arises very often: when was a ballpoint pen entry made on a document? For this reason the accurate dating of ink entries has always been of high interest for the document examiner and a large number of methods have been developed throughout the years [1–7] focusing on the aging processes of the substances contained in the ink such as resins, dyes and solvents. Since the aging processes are strongly influenced by the environmental conditions to which the ink entries are exposed (temperature, humidity, light), these methods cannot deliver unambiguous answers except for a relative dating of ink entries (comparison

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of entries of the same ink formula, on the same paper and aged under the same conditions). In addition, these methods are often considered to deliver higher measurement errors than predictable variations, and are therefore not used in many forensic laboratories. Lately interest has arisen again for a method first proposed by Stewart in 1985 [8], in which evaporation of the volatile components of the ink is measured using GC/MS. Interestingly, however, two different studies indicate that the dating of ink by this method is not possible after a few days [9,10], whereas in another study very positive results for analysis over longer periods of time were reported [11–13]. Although these contradictory observations could be explained by the different sample preparation methods used and the different evaluation of the results, more studies are necessary to investigate this situation.

Ink solvent sample preparation for GC analysis can take different forms: extraction with different solvents (acetonitrile

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^{0379-0738/\$ –} see front matter C 2006 Elsevier Ireland Ltd. All rights reserved. doi:10.1016/j.forsciint.2006.06.076

[12], dichloromethane [9] or methanol [14]), derivatisation [10], solid phase microextraction (SPME) [14] and thermodesorption with cryo focusing [15].

In general, solvents represent more than 50% of the weight of ballpoint ink [15,23,24] and disappear from the stroke over time. The basic idea of the analysis of the solvent disappearance kinetics is to extract all the solvents from the stroke and analyse them quantitatively at different times after placement of the ink on paper. With this, it is usually possible to determine aging curves showing the decrease of the solvent in the ink entry with time. In the chromatogram the ratio of the peak area of the solvent to that of any internal standard would decrease with time. It is expected that this dependence of the relative peak area (RPA) on time will be affected by a number of other factors other than volatility. In particular, it may depend on the total solvent mass deposited on the stroke, and thus the extracted mass would scale with the width and thickness of the ink entry. To solve this problem, Aginsky proposed to use the ratio of the peak area of the solvent which evaporates to that of a nonvolatile or solid volatile stable component of the stroke [12]:

$$RPA = \frac{\text{area of peak of volatile solvent}}{\text{area of stable peak}}$$

In this way, this ratio is independent of the extracted quantity and should, in principle, decrease exponentially with time. The difficulty with this procedure, however, is to find a stable nonvolatile substance in the chromatogram. Aginsky proposed dye as a non-volatile component [5,12] or phthalic anhydride as a solid volatile component [12], but Fortini [9] observed that phthalic anhydride does disappear from the stroke with time. Lociciro et al. [10] managed to identify a stable compound in the ink by derivatising the extraction with MSTFA (N-methyl-N-trifluoroacetamide), but this approach probably reduces sensitivity through this additional step. Also SPME was found to be a quick extraction method, but not quantitatively reproducible [14]. Presently, however, cryo-focus thermodesorption seems to be the method of choice, because it avoids potentially modifying preparative steps. Additionally, this method effectively extracts monomers, readily identifiable in the chromatogram and eventually usable as stable peaks [15].

Drying is a very complex phenomenon which is characterised by simultaneous evaporation of the solvents in the ambient air and their adsorption/diffusion in the paper. Among other things, these processes are influenced by temperature, humidity and the adsorption/diffusion properties of the papersolvent system. In a previous forensic study dealing with absolute dating [12], the simplifying assumption has been made that the following elements:

- common storage conditions (temperature, humidity, adjacent material)
- paper properties (pore size, coating, pH)
- composition of ink (solvents, dyes, resins and additives mixture)

have no decisive influence on the aging curves (drying rate), and that threshold values of ink aging parameters can still be used to determine if an ink entry is fresh or old without knowledge of these factors. Later it was stated by the same author [13] that these factors have indeed an influence, but no details about the extent of this influence were described. By taking into account the basic principles of the theory of drying, one can easily see that these factors cannot be neglected and that doing so will lead to mistaken interpretation of the results. The importance of assessing many additional variables when evaluating the drying process has also been mentioned by White [16].

In principle, drying processes proceed as simultaneous mass and heat transfer and the thermal energy needed to evaporate a liquid from a porous solid is provided from the ambient air [17]. For the purpose of analysis, the drying process can be separated in three phases [17–20]:

- (1) *Increasing rate of drying*: In this phase, evaporation rate increases as the wet external surface area grows through lateral diffusion along the paper fibres. This process can be neglected for very small quantities.
- (2) *Constant rate of drying*: This phase is achieved when the evaporation rate and the surface area reach a stationary phase and equilibrium-like conditions at the free surface occur.
- (3) *Falling rate of drying*: In this phase, the migration of solvents towards the surface from the bulk becomes slower than the evaporation rate at the surface (unsaturated). Two mechanisms operate here: The evaporation surface recedes into pores (1st falling), and later, capillary migration stops by increased physisorption (physical absorption) in cellulose fibres and evaporation occurs in paper (2nd falling).

Due to the fact that diffusion and adsorption (physisorption) mechanisms play such an important role in the drying of solvents on porous media, a wealth of external factors must be taken into account. Among these are temperature (of air, solid, ink), vapor pressure (air, solvents), air movement (laboratory, cupboard), solvents mixture properties (vaporization of solvents mixture, viscosity), paper properties affecting heat transfer and mass transfer coefficients. In particular, the drying time would reflect this situation and also is dependent on these parameters. Theoretical drying rate equations have been proposed, but since most of the factors involved are difficult to determine theoretically, these equations are of limited applicability and additional empirical measurements are needed to follow the drying of ink on paper.

Lociciro et al. [10] reported a loss of 89–98% of phenoxyethanol from the ink entries in a few minutes and attributed this loss to evaporation. In other work, Selim et al. [21] reported a rate of penetration of the solvents in the paper at least 20 times higher than the rate of evaporation for waterbased inks. This is consistent with the objectives of ballpoint pen manufacturers of producing a fluid ink which is easily applied on paper (yielding low friction of the ballpoint with the paper), while at the same time is drying very quickly at ambient temperature (to avoid smearing of the ink after deposition). Due to these requirements, as opposite to those of the dyes, solvents are not meant to remain in the ink entries for years, but only to help the application of the ink on paper. In fact, the deposited solvent quantities are typically in the microgram range [22,23] and decrease very quickly.

The aim of this work was to characterise the drying of ballpoint ink on paper by measuring the quantitative decrease of the solvents from the stroke after deposition on paper. For this purpose, both evaporation and diffusion have been taken into account. The results should enable forensic scientists to better understand the aging processes of the solvents on paper and to assess the feasibility and limitations of dating ink by quantitative analysis of solvents. Liquid extraction and subsequent GC/MS analysis were chosen as experimental methods. Preliminary studies over a period of 2 years for the solvents ethoxyethoxyethanol and dipropylene glycol [23] gave encouraging results. The present study focuses on a ballpoint pen containing phenoxyethanol as major component among other solvents. This substance is found in over 80% of the blue and black ballpoint pens [25] and its disappearance from ink entries was studied in previous work [10,12,14,22]. The support of the ink entry clearly has an additional effect on ink drying, but a study of its parameters (paper pH, surface finish, fibre finish, coating, etc.) constitute in itself a whole new survey and was not specifically addressed in this work.

2. Experimental

2.1. Materials

Substances used for reference were pure ethoxyethoxyethanol (E; b.p. 202 °C, viscosity 4 cP) and dipropylene glycol (D; isomers mixture; b.p. 230 °C, viscosity 75 cP) purchased from Sigma-Aldrich (Steinheim, Germany) and phenoxyethanol (P; b.p. 247 °C, viscosity 22 cP) purchased from Riedelde-Haën (Seelze, Germany). Phenoxyethoxyethanol (PE) was not available as a reference standard and has not been purchased for our experiments. Blue Parker[®] ballpoint pen entries (Medium, ISO 12757-2, UK) were applied on multifunction bright-white, wood and chlorine free paper from Igepa Plus (80 g/ m², DINA4, nr. 806 A 80, Reinbeck, Germany). Eleven additional blue ballpoint pens were purchased in Germany for comparison purposes. Extraction of solvents from the ballpoint pen entries for GC/MS measurements was made with DCM (dichloromethane, Merck, Darmstadt, Germany) containing the internal standard (IS) 1,3-benzodioxole-5-methanol. Extraction was made in 50 µl micro glass insert, held in 1.5 ml short amber threaded glass vials (VWR, Darmstadt, Germany). The flasks were locked with screw silicone caps coated with PTFE. A standard 10 µl Hamilton syringe (Bonduz, Switzerland) was used for the injection into the GC.

2.2. Instrumentation and analysis

For the weighting experiments, a micro-balance AX26 Comparator (Mettler Toledo, Greifensee, Switzerland) was used in the microgram range.

Analysis of the solvents relative peak area was made on a Gas Chromatograph/Mass Spectrometer MAT 4500 from Finnigan MAT GmbH, Bremen (now Thermo Electron GmbH, Bremen). The instrument was equipped with the data acquisition software MASPEC Data System (MSS—Mass Spectrometry Services Ltd., Manchester, UK). Separation was carried out on a CP-Sil 8 CB low bleed/MS capillary column from Varian (Chrompack, Middleburg, Netherlands). The column was 60 m long and had an internal diameter of 0.25 mm and film thickness of 0.25 μ m. The chromatographic elution was temperature programmed as follows: isothermal at 50 °C for 6 min, then from 50 to 300 °C at a rate of 10 °C/min, and finally isothermal at 300 °C for 5 min. The carrier gas was helium (Messer Griesheim GmbH, Frankfurt, Germany)

with a constant flow of \sim 3 ml/min (at 30 psi). For the chromatographic separation, a solvent delay of 300 s was chosen. To improve sensitivity, the sample was injected in the splitless mode and the injector temperature was maintained at 200 °C, which was sufficient to volatise all the substances of interest. The interface temperature was set at 250 °C to avoid recondensation. The MS part of the GC/MS was a highly sensitive quadrupole instrument with a mass range up to 1000 u. Ions were formed by electron impact (EI), with a fixed electron energy of 80 eV. The temperature of the ionisation block was kept at 120 °C. For qualitative analysis, the instrument was used in the SCAN or Total Ion Current monitoring (TIC) mode. Masses were scanned in the quadrupole from m/z 33 to 400 u at a sweep time of 0.95 s. The obtained mass spectra were further evaluated employing the NIST database (MS Search Program Version 1.0, NIST, MSS Ltd., Manchester, England), which allowed the identification of the eluting substances. The results were also confirmed by GC/MS analysis of standard substances, which allowed the comparison of the relative retention times and mass spectra of the samples and standards.

To ensure better quantitative accuracy, the Selected Ion Monitoring (SIM) mode was employed, due to its higher sensitivity. This allowed lower quantities of solvents to be detected and quantified than in the TIC mode. For the purpose of the intended analysis, 15 particular ions were selected and monitored, corresponding to the masses: 45, 59, 65, 72, 75, 77, 89, 93, 94, 103, 104, 135, 138, 152 and 182 u. These ions signals correspond to the four solvents found in the chosen ballpoint pen and the internal standard.

2.3. Sample preparation

2.3.1. Calibration curves for quantification

To determine calibration curves, pure solvents were dissolved in dichloromethane at concentrations of 0.0005, 0.001, 0.0025, 0.005, 0.0075, 0.01, 0.05 and 0.1 mg/ml with 0.0227 mg/ml internal standard concentration.

2.3.2. Ballpoint pen entries

Ballpoint pen entries were drawn on paper with the help of a ruler and stored in a cupboard at room temperature. Entries were about 0.5 mm wide and 50 mm long. For logistic reasons, fresh ballpoint pen entries were held in the laboratory (at constant temperature), while older strokes (older than a month) were kept in a separated office (no air conditioning).

2.3.3. Standard extraction procedure

Ballpoint pen entries of about 1 cm were cut in 10 mm \times 2 mm rectangles from the paper sheet and placed in a small vial. The solvents were extracted during 10 min in a ultra-sonic bath in 10 µl DCM with an IS concentration of 0.0227 mg/ml. The extraction procedure takes about 22 ± 1 s. A 2 µl aliquot from the extraction mixture was then injected splitless on the GC column. To perform paper blank and diffusion measurements, pieces of paper of identical dimensions were cut and extraction was carried out following the same procedure. For lateral diffusion experiments, the pieces were cut parallel and at the side of the stroke, at different distances from its centre.

2.4. Experiments

2.4.1. Weighting of the strokes

For the determination of the initial concentration of the solvents in the ballpoint pen, the cartridge of a ballpoint pen Parker[®] was opened and the solvents were quantified by GC/MS with the mentioned procedure. The experiment was repeated three times and the mean percentage weight of solvent in the ink was obtained. The mean weight of 1 cm ballpoint pen ink entries was determined by measuring the following parameters six times and taking the average:

- The weight difference of the pen before and after writing 20 entries of 5 cm length.
- The weight difference of a piece of paper before and after 20 entries of 5 cm length were written on it.

2.4.2. Aging

Changes in the quantity of solvent as a function of the time were measured for entries over 1.5 years old. For each point in time, three entries were extracted

and analysed by GC/MS with the mentioned procedure. To check the reproducibility of the results for the time t = 0 measurements (i.e. just after the strokes were made), the procedure was repeated on different days.

2.4.3. Diffusion and migration

Once the ink is applied on the paper, the solvents diffuse and migrate away from the stroke through the paper until equilibrium-like conditions are reached. To quantify this phenomenon, solvent extraction was performed from rectangular pieces of paper cut at distances of 2, 4, 6 and 8 mm next and parallel to the stroke, as mentioned above. In this way, most of the paper area in which lateral diffusion takes place was covered by the analysis.

During the research, the importance of an additional process relevant to solvent losses from strokes was discovered. This mechanism corresponds to migration of the solvents from one sheet of paper to another one through solvent mass transport perpendicular to the surface of paper and was first addressed by Andrasko [14] To quantify this solvent migration, blank sheets of paper were deposited on top of or under a sheet of paper having fresh ink stroke applied on it. The following arrangements were tested in order to understand the extent and importance of such processes. Contacts without additional pressure lasted 15 min:

- A blank paper was laid *on top* of the paper with the fresh ink entry directly *after* the application of the stroke.
- A blank paper was laid *under* the paper with the fresh ink entry *during* the application of the stroke.
- A blank paper was deposited on top of the paper with the ink entry 30 min *after* the application of the stroke.

3. Results and discussions

In the following presentation of the results, the error bars shown in the figures correspond to the mean standard deviation of the measurements.

3.1. Qualitative analysis

Entries from 31 blue ballpoint pens were extracted from paper and analysed by GC/MS to determine the usual solvent mixtures compositions. From these, 94% of the ballpoint pens were found to contain phenoxyethanol and 61% were found to contain phenoxyethoxyethanol. Benzyl alcohol (61%) and propylene glycol (54%) were also found in several ballpoint pen inks. These substances are more volatile than the ones previously mentioned. Therefore, they disappear faster from the stroke and would not perform as adequately in the possible dating of ink. The following solvents were also detected in some ballpoint pens: hexylene glycol (23%), ethoxyethoxyethanol and dipropylene glycol (10%), butylene glycol (6%),



Fig. 2. SIM chromatograms of the extraction of 1 cm Parker[®] ballpoint pen stroke at time (a) t = 0 and (b) t = 10 days after application of the ink on paper. The *x*-axis represents the relative retention time (RRT) of the solvents to the internal standard (IS). The TIC signals of the 15 selected ions are ethoxyethoxy10.1016/j.forsciint.2006.06.076thanol (E), dipropylene glycol (D), phenoxyethanol (P), the IS at a concentration of 0.0227 mg/ml and phenoxyethoxyethanol (PE).

butoxyethanol (6%) and in one pen phthalic anhydride was detected. Typically, a specific ballpoint pen contained one to five of these solvents.

For further analysis, a Parker[®] blue ballpoint pen was chosen from the pool. Its ink contained four solvents: phenoxyethanol, phenoxyethoxyethanol, ethoxyethoxyethanol and dipropylene glycol (see Figs. 1 and 2). The chromatogram of the solvent blank was taken for reference to allow for



Fig. 1. Structure formula, boiling points and molecular weight of the four solvents found in the ballpoint pen Parker entries on paper by GC/MS analysis.

subtracting the chemical background. Additionally, chromatograms of the paper blank were taken and did not show any peaks.

3.2. Quantitative analysis

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Since no non-volatile compound belonging to the ink composition was found in the chromatograms (i.e. no peak stable in intensity over aging time), it was necessary to introduce an internal standard to perform quantification. The relative peak area for any given substance S_i was calculated as follows to minimize the error:

$$RPA = \frac{\text{peak area of } S_i}{\text{peak area of IS}}$$
(1)

The RPA is a measure of the quantity of solvent in the stroke relative to that of the internal standard. Using this definition, a set of linear calibration curves were determined using reference substances of E, D and P by measuring six different points in the concentration range from 0.005 to 0.1 µg/cm. The following expressions characterize these curves:

 $R^2 = 0.9401$ $\text{RPA}_{\text{E}} = c_{\text{E}} \times 6.9609$ (2a)

$$RPA_{\rm D} = c_{\rm D} \times 5.6275 \qquad R^2 = 0.9643 \tag{2b}$$

$$RPA_{\rm P} = c_{\rm P} \times 10.644 \qquad R^2 = 0.9933 \tag{2c}$$

where c_i is the concentration [µg/cm] of the target substance *i* and R^2 is the regression coefficient of the fitting.

Twelve ballpoint pens containing at least E, D or P were selected for comparative quantitative analysis in their ink entries at time t = 0. The results (see Table 1) show that initial quantities of solvents in different ballpoint pens can significantly diverge. In fact, ballpoint 11 has about 5% of the P content of ballpoint 1. An important conclusion resulting from this observation is that the initial quantitative composition of the ink should be known to interpret correctly the age of an ink by measuring the loss of the solvent from ballpoint pen entries.

Table 1

Initial concentrations of the solvents ethoxyethoxyethanol (E), dipropylene glycol (G), phenoxyethanol (P) in strokes of 12 different ballpoint inks

Pen number	Initial substance content (µg/cm)			
	E	D	Р	
1	0	0	0.66	
2	0	0	0.57	
3	0	0	0.53	
4	0	0	0.42	
5	0	0	0.41	
6	0	0	0.38	
7 (Parker)	0.21	0.33	0.30	
8	0	0	0.22	
9	0	0	0.21	
10	0.18	0.25	0.20	
11	0	0	0.032	
12	0.29	0.83	0	

3.3. Weight of a stroke

Quantitative analysis of the ink in the ballpoint cartridge gave a total weight percentage of solvents of approximately 53% (without including PE as it was not purchased as a standard for quantification) distributed as follows: $24 \pm 8\%$ for E, $11 \pm 1\%$ for D and $18 \pm 2\%$ for P.

As explained before, the mass of 1 cm ballpoint pen entry was calculated by weighing the loss of ink in the ballpoint pen (c_1) and by weighing the gain in ink on a piece of paper after writing (c_2) . Six replicate measurements gave $c_1 = 6.63 \pm 0.49 \,\mu\text{g/cm}$ and $c_2 = 4.63 \pm 0.71 \,\mu$ g/cm, respectively. The higher error with c_2 can possibly be explained because firstly, paper is a porous material and secondly, solvent evaporation occurs quickly during the measurements. Comparatively, the ballpoint pen cartridge is a closed environment and relative evaporation is minimised. It is to be expected then, that c_1 gives a more precise estimation of this parameter. Another source of error is an uneven application of the strokes, particularly when ink accumulates on the ballpoint and is deposited as a thick mass at the beginning or end of a stroke. From the preceding results, the following initial concentration (c_i) of E, D and P in 1 cm stroke can be extrapolated from the cartridge weight loss $(c_1): c_i(E) = 1.59 \ \mu g/cm, c_i(D) = 0.74 \ \mu g/cm and c_i$ $(P) = 1.20 \ \mu g/cm.$

3.3.1. Aging

The aging curves were obtained for each solvent by displaying the RPA values as a function of the square root of time in hours (see Fig. 3a). The RPA values decreased very quickly in the first 3 h. After 2 weeks, the rate of drying slowed considerably. The curves were best fitted with an expression proposed by Lociciro et al. [10]:

$$RPA = p_1 + p_2 \cdot e^{(-t/p_3)0.5} + p_4 \cdot e^{(-t/p_5)0.5}$$
(3)

A double logarithmic scale allows for a better representation of the decrease of the solvents in the ink entries with time (see Fig. 3b). A double logarithmic fit resulted in regression factor R^2 between 0.9346 and 0.9965. RPA values for E decreased very quickly at the beginning and stayed constant after about 10 days. On the other hand, solvent disappearance for D and P could still be measured after 562 days. The RPA values for PE were lower than for the other solvents and were decreasing more slowly. From these results, it can be concluded that the above mentioned constant drying phase is over quickly and cannot be measured for such small quantities. The first derivative of these curves represents the decreasing drying rate. This interpretation can be aided if we consider the first exponential in Eq. (3) to represent the 1st falling rate (diffusion to the surface), and the second exponential to describe the 2nd falling rate (physisorption has occurred).

The concentrations of solvent in the stroke at time t can be directly calculated from the RPA values (see Fig. 4). These quantities decreased very quickly. After 10 days the values reached levels below 0.1 μ g and after a year were in the ng/cm range. For time t = 0, the following quantities were measured:



Fig. 3. Aging curves for the solvents ethoxyethoxyethanol (E), dipropylene glycol (D), phenoxyethanol (P) and phenoxyethoxyethanol from Parker[®] ballpoint pen entries: (a) RPA (relative peak area of solvent to the IS) as a function of the square root of the time in hours (usual display for drying curves) and (b) RPA as a function of time on a double logarithmic scale. These curves can be interpreted by assuming that the solvents disappear from the stroke through the combined processes of evaporation and diffusion.

c (E) = $0.21 \pm 0.01 \ \mu$ g/cm, c (D) = $0.33 \pm 0.02 \ \mu$ g/cm, c (P) = $0.30 \pm 0.03 \ \mu$ g/cm. If compared to the extrapolated values for the solvents losses from the cartridge (c_i) reported above, the loss of solvents right after application on paper, it is possible to conclude that 87% E, 56% D and 75% P disappeared from the stroke in the few seconds after drawing a ballpoint line. This corresponds to a loss of solvent of 75% (if we do not consider PE, which has not been quantitated). The competitive processes of evaporation and diffusion can explain why a solvent with a higher boiling point (P) disappeared faster from the stroke than another one with a lower boiling point (D). The friction of the ballpoint pen eventually heats the ink slightly during the application, thus giving an initial energy and quickening the initial evaporation.

The mean relative standard deviations (RSD) of three measurements were typically between 5 and 30% (only in one case for ethoxyethoxyethanol did the RSD reach almost 68%). The estimated RSD increased with decreasing quantities. Measurements from fresh ink entries (t = 0) carried out on a short period of time (a few weeks) had a mean RSD below 10%. At a few months interval, the RSD increased slightly up to 30%.



Fig. 4. Mass per stroke length of solvents ethoxyethoxyethanol (E), dipropylene glycol (D), phenoxyethanol (P) and phenoxyethoxyethanol from a Parker^(R) ballpoint pen in the cartridge and for different times after application on paper.

4. Diffusion and migration

To quantify solvent diffusion, the concentrations of solvents were measured at distances of 2, 4, 6 and 8 mm from the ink stroke, for times ranging from t = 0 to t = 12 days (Fig. 5). E and P diffused quickly in paper (low viscosity), while D diffused slower (high viscosity). No diffusion of PE was detected next to the stroke.

The points in Fig. 5 were joined with a Gaussian fit to represent the diffusion curves (area under the curves represents the quantities of solvent per length of stroke). The obtained curves can be integrated to estimate the mass of solvents disappearing from the paper through evaporation and eventual migration out of the paper (see below). The diminishing area with time represents approximately the loss of solvents from the paper (diffusion over 8 mm away from ink entry is neglected as it has not been measured, but it is presumably very small as seen from the plotted tendencies). Table 2 shows the percentage of solvents loss from the paper (evaporation) and from the stroke (evaporation and diffusion). The values were extrapolated respectively from the data obtained by integration of the diffusion plots (approximation of the evaporation) and the quantitative GC/MS analysis (rest of solvent in the ink entry).

In Fig. 6, the concentrations of E, D and P as measured 2 mm next to the stroke are displayed as a function of time. The character of these curves can be explained taking into account the complementary processes of evaporation and diffusion: the solvents migrate into the paper and evaporate at the same time.

The fact that diffusion plays such an important role in the disappearance of some solvents from the stroke opens some consideration about the sampling of the stroke. Other researchers in their analyses [10], have tried to cut as little paper as possible together with the ink stroke, to avoid interference of paper with the analysis. Our results about diffusion, however indicate that as much paper as possible should be cut out with the stroke for extraction to collect a meaningful amount of solvents (unfortunately, cutting larger pieces than 10 mm \times 2 mm proved to be inadequate to extract in 10 µl solvent as some parts were not immerged in the



Fig. 5. Diffusion [μ g/cm] of the solvents ethoxyethoxyethanol (E), dipropylene glycol (D), phenoxyethanol (P) away from the ink stroke (0 mm) at different times *t* after application of the stroke on the paper (RPA = relative peak area). For the continuous line curves, Gaussian fits were carried out to characterise the diffusion. The error range (not shown in the graphics) lies between 20 and 50% for such small quantities.

solvent). A small extraction experiment allowed us to demonstrate that fact. A 1 cm stroke was extracted with as little paper as possible, and the results showed that only 29% of E, 74% of D and 66% of the mean values for the normal extraction (10 mm \times 2 mm paper and stroke) were obtained. This fact alone would account for a significant loss in quantification sensitivity.

Possible contamination of old strokes through solvents migration by fresh stroke from adjacent paper sheets has also been tested (Fig. 7). It was observed that solvents from a fresh

Table 2

Loss of the solvents ethoxyethoxyethanol (E), dipropylene glycol (D), phenoxyethanol (P) from 1 cm stroke a few seconds after application of the stroke on paper (percentage amount in 1 cm ink entry)

	% in 1 cm ink entry		
	Е	D	Р
Cartridge	100	100	100
Loss from paper $(t = 22 \text{ s})$	56	11	44
Loss from stroke $(t = 22 \text{ s})$	87	56	75

The loss of solvents from the paper is taken to be mainly due to evaporation, while the loss from the stroke is due to competitive evaporation and diffusion. As E and P diffuse well in paper, the evaporation surface is higher and they disappear quickly (few seconds after application). D diffuses slowly and therefore evaporation is also lower.



Fig. 6. Quantitative evaporation and diffusion $[\mu g]$ of the solvents ethoxyethoxyethanol (E), dipropylene glycol (D), phenoxyethanol (P) as measured 2 mm next to the ink entry as a function of the time elapsed since apposition of the ink on paper.

stroke (t = 0), can migrate very efficiently to the adjacent sheets of paper in a pile. Our measurements show that about 0.025 to 0.075 µg/cm of the solvents E, D and P did migrate into the next sheet of paper during the 15 min contact. Even if the contact is made as late as half an hour after apposition of the



Fig. 7. Measurements of the migration of the amounts of the solvents ethoxyethoxyethanol (E), dipropylene glycol (D), phenoxyethanol (P) transferred from an ink entry to an adjacent sheet of paper during a 15 min contact (values correspond to single measurements): quantities in the stroke at t = 0 (B), quantities in a sheet of paper placed over B (A), quantities in a sheet of paper placed over B (A) 0.5 h after apposition of the ink entry on B.

stroke, more than $0.025 \ \mu g/cm$ of P still migrated into the adjacent paper. In general, the migrating quantities exceeded the quantities found in a stroke after 2 weeks under the studied circumstances, therefore contamination is an eventuality that has to be taken into account, if one wants to date ink entries by solvent quantification.

In general, the quantities diffusing and migrating into the paper are very low. Since additionally the paper structure is not even, the diffusion patterns are not very reproducible and the error in the measurements is rather high (up to 50% relative mean standard deviation). These fluctuations in the diffusion and migration patterns also affect the error in the measurements of the amount of solvents in the ink entries.

5. Conclusion

Liquid extraction followed by splitless gas chromatography/mass spectrometry in the selected ion mode was found to be an adequate method for the quantitative analysis of solvents from ballpoint ink entries down to the ng/cm range. The amount of solvents in the cartridge corresponding to 1 cm ballpoint pen entry are typically in the µg range and vary between different ballpoint pens. Phenoxyethanol is found as an ink solvent in more than 90% of the studied ballpoint pens. More particularly, ink in a Parker[®] ballpoint pen cartridge contained at least 53% of solvents per weight. Even if these solvents have relatively high boiling point, a large fraction has disappeared a few seconds after deposition of the ink on paper (up to 75% of total solvent mass for the ballpoint pen Parker^{\mathbb{R}}). Our results demonstrate that ink aging by solvent disappearance is due to the competitive processes of evaporation and diffusion. Solvents with a low viscosity diffuse quickly in paper, thus increasing the evaporation surface and rate. As a general conclusion resulting from this study, it was found that for quantitative analysis not only the ink stroke itself, but also several mm of the adjacent paper should be used for extraction of the solvents. Quantities of ethoxyethoxyethanol in Parker[®] ballpoint pen entries stopped decreasing about 10 days after deposition on paper. Apparently about 1 ng stays trapped in 1 cm stroke through a physisorption process, and this amount seemed to stay constant afterwards. On the other hand, the amounts of dipropylene glycol, phenoxyethanol and phenoxyethoxyethanol were still noticeably decreasing after 1.5 years. From the analytical point of view, however, the low quantities remaining after a few weeks (ng/cm range) produce higher measurement errors. The determined aging curve levels off considerably after 2 weeks, so it would be theoretically possible to differentiate entries made within less than 2 weeks from older ones. Unfortunately, the time from the moment a potentially backdated document emerges to the moment an analysis is carried out, is of the order of 1-2 months due to bureaucracy.

Giving legal conclusions about the age of an ink entry from the solvent measurements procedures presented in this work would still be a dubious procedure, as our results apply only to laboratory conditions. Many factors which play an important role in the disappearance of solvents are dependent on the

storage conditions, which are in general not known in a real case. For example the influence of different papers and solvent compositions, and of temperature and humidity fluctuations on the aging curves have not yet been studied. Moreover, the initial quantities of solvents in the ink should also be known (first value (t = 0) in the aging curves) to attempt absolute age determination. Unfortunately the ink industry changes compositions frequently with consideration on the prices, quality and availability of the different compounds. Thus, the composition of a particular pen brand and model is not constant in time and it would be difficult to maintain an updated database. In the case of a book or a diary, in which entries are made with one pen, it would be possible to compare the ink entries to determine if some entries are older than others, or if they were all written at the same time. Another problem faced by the analyst and which may influence the measurements is the possibility of contamination from fresh ink strokes through migration of the solvents from one sheet of paper to another provided they are still aging.

The influence of a number of different parameters still has to be determined and blind tests should be carried out to render possible the dating of ink entries through this method. Even then the conditions found in practical cases (in general unknown initial composition and storage conditions) render the dating of ink entries through the presented method very hazardous. Identical conclusions were reached by other scientists recently for GC/MS methods [9,10,14], as the authors did not obtained reproducible results within a sensible error range.

Precise dating would not be possible, but age boundary limits could eventually be determined for all possible situations: any kind of paper, ink type and storage conditions. This could help determine if an ink stroke is fresh, old or very old.

Acknowledgements

The authors would like to thank Stéphanie Lociciro and Williams Mazzella from the Institut de Police Scientifique in Lausanne for giving practical hints to develop this method.

References

- R.L. Brunelle, A.A. Cantu, A critical evaluation of current ink dating techniques, J. Forensic Sci. 32 (6) (1987) 1522–1536.
- [2] L.F. Stewart, S. Guertin, Current status of ink age determination, Int. Crim. Police Rev. (March–April) (1991) 9–13.
- [3] R.L. Brunelle, H. Lee, Ink dating—the state of the art, J. Forensic Sci. 37 (1992) 113–124.
- [4] T. Hicks Champod, A. Khanmy, P. Margot, Ink aging: perspectives on standardization, in: B. Jacob, W. Bonte, W. Huckenbeck, P. Pieper (Eds.), Advances in Forensic Sciences 3, Forensic Criminalistics 1, Proceedings of the 13th Meeting of the International Association of Forensic Sciences, Düsseldorf, 1993, Verlag Dr. Köster, Berlin, 1995, pp. 304– 309.
- [5] V.N. Aginsky, Some new ideas for dating ballpoint inks—a feasibility study, J. Forensic Sci. 38 (5) (1993) 1134–1150.
- [6] A.A. Cantu, A sketch of analytical methods for document dating. Part II. The dynamic approach: determining age dependent analytical profiles, Int. J. Forensic Doc. Examiners 2 (3) (1996) 192–208.

- [7] P. Dormann, Les différentes techniques et la controverse sur la datation des encres, Séminaire de l'Institut de Police Scientifique (IPS), Lausanne University, Lausanne, Switzerland, May 2000.
- [8] L.F. Stewart, Ballpoint ink age determination by volatile component comparison—a preliminary study, J. Forensic Sci. 30 (2) (1985) 405–411.
- [9] A. Fortini, Datation des encres, Séminaire de l'Institut de Police Scientifique (IPS), Lausanne University, Lausanne, Switzerland, May 2000.
- [10] S. Lociciro, W. Mazzella, L. Dujourdy, E. Lock, P. Margot, Dynamic of the ageing of ballpoint pen inks: quantification of phenoxyethanol by GC/MS, Sci. Justice 44 (3) (2004) 165–171.
- [11] V.N. Aginsky, Determination of the age of ballpoint pen ink by gas and densitometric thin-layer chromatography, J. Chromatogr. A 678 (1994) 119–125.
- [12] V.N. Aginsky, Dating and characterizing writing, stamp pad and jet printer inks by gas chromatography/mass spectrometry, Int. J. Forensic Doc. Examiners 2 (2) (1996) 103–116.
- [13] V.N. Aginsky, Measuring ink extractability as a function of age—why the relative aging approach is unreliable and why it is more correct to measure ink volatile components than dyes, Int. J. Forensic Doc. Examiners 4 (3) (1998) 214–230.
- [14] J. Andrasko, A simple method for distinguishing between fresh and old ballpoint pen ink entries, Forensic Sci. Int. (Abstr.) 136 (1) (2003) 80–81.
- [15] J. Bügler, Analytische Untersuchung von Lösungs- und Bindemitteln in Schreibmitteln, Symposium Kriminaltechnick/Urkunden, Materialanalytik und Verfahrenstechnik, Berlin, Germany, May 2004.
- [16] P. White, The age of an ink: an age old problem, in: Oral Presentation at the 17th International Symposium on Forensic Science, ANZFSS, Wellington, New Zealand, March–April 2004.

- [17] A. Avcı, M. Can, A.B. Etemoğlu, A theoretical approach to the drying process of thin film layers, Appl. Thermal Eng. 21 (2001) 465–479.
- [18] R.B. Bird, W.E. Stewart, E.N. Lightfoot, Transport Phenomena, Department of Chemical Engineering, University of Wisconsin, John Wiley & Sons, Inc., New York-London, 1960.
- [19] D. Ondrastschek, M. Schneider, H. Vogelsang, Forcierung des Wasserlackeinsatzes durch neue Trocknungsverfahren, Institut f
 ür Industrielle Fertigung und Fabrikbetrieb (IFF), Universit
 ät Stuttgart, Forschungsbericht, September 2001.
- [20] Strobel Reto, Trocknung eines Kapillarporösen Stoffes, ETH, Zürich, März 2004.
- [21] M.S. Selim, V.F. Yesavage, R. Chebbi, S.H. Sung, J. Borch, J.M. Olson, Drying of water-based inks on plain paper, J. Imaging Sci. Technol. 41 (2) (1997) 152–158.
- [22] C. Weyermann, D. Kirsch, C. Costa-Vera, B. Spengler, Methodenentwicklung zur Alterbestimmung von Kugelschreibereinträge: Massenspektrometrische Untersuchung von Lösungsmittelzusammensetzung in Kugelschreiberpaste mit GC-MS, Poster, Abstract, 36th DGMS Meeting, Westfälische Wilhems Münster University, March 2003.
- [23] C. Weyermann, D. Kirsch, C. Costa-Vera, B. Spengler, Dating of ink entries by MALDI/LDI-MS and GC/MS analysis: reality or utopia? Forensic Sci. Int. (Abstr.) 136 (1) (2003) 71–72.
- [24] C. Weyermann, D. Kirsch, C. Costa-Vera, B. Spengler, Photofading of ballpoint dyes on paper by LDI and MALDI MS, J. Am. Soc. Mass Spectrom. 17 (3) (2006) 297–306.
- [25] G.M. LaPorte, J.D. Wilson, A.A. Cantu, S.A. Mancke, S.L. Fortunato, The identification of 2-phenoxyethanol in ballpoint inks using gas chromatography/mss spectrometry—relevance to ink dating, J. Forensic Sci. 49 (1) (2004) 155–159.

Ballpoint Ink Age Determination by Volatile Component Comparison—A Preliminary Study

REFERENCE: Stewart, L. F., "Ballpoint Ink Age Determination by Volatile Component Comparison—A Preliminary Study," Journal of Forensic Sciences, JFSCA, Vol. 30, No. 2, April 1985, pp. 405-411.

ABSTRACT: Ballpoint pen inks consist primarily of a mixture of dyes. resins, and vehicle components. The vehicles are used to solubilize or suspend dyes, resins, and other components as well as to provide smooth ball movement and flow of ink onto writing surfaces. These vehicles are relatively volatile and make up approximately 50% of the ink by weight. Extraction and formulation identification of the questioned ink is performed. Once identified, the volatile components of the ink are measured quantitatively by gas chromatography. Preliminary studies show that the relative proportions of these volatile ingredients decrease as the ink ages. How long an ink has been on paper is determined by comparison of the relative concentrations of the volatile components of the questioned ink with those of known inks (age) of the same formulation. The relationship between age of ink, storage conditions, and paper will also be discussed.

KEYWORDS: questioned documents, inks, gas chromatography, pens, age determination

The amount of time an ink has been on a document has been a question that has plagued many forensic science examiners since writing inks were first introduced. The conventional approach to dating an ink entry has been the identification of certain ink components which may indicate gross formulation changes. Ballpoint pen inks, first developed in the 1930s [1], used oils for the vehicles. It was not until the 1950s that glycol-based inks were widely used [2]. Additions to formulas such as the introduction of copper phthalocyanine dye (1954) in ballpoint pen inks, fluorescent dyes (1955 to 1957) in fountain pen inks, and the introduction of entirely new markets, for example, felt and fiber tip pen inks (1961) have aided the forensic science investigator in determining the "age" of an entry.² Other methods for dating an ink entry included determining the presence or absence of a dye, for example, the blue dye in blue-black writing inks of the early 1900s [3], and differentiating between the amounts of a component extracted from two entries through the use of chemical reagents (for example, oxalic acid) in the 1920s [4].

During the mid-1960s, in an attempt to improve upon the conventional method by increasing the knowledge of known changes in formulations, Werner Hoffman, Zurich Cantonal Police, Zurich, Switzerland, began collecting samples of European ballpoint pen inks. He began comparing questioned inks with his collection for purposes of showing similarities or differences between formulas [5]. In the mid-1960s, Richard Brunelle, Bureau of Alcohol, To-

Note: the experimental work for this paper was conducted at the Bureau of Alcohol, Tobacco and Firearms Forensic Science Branch, National Laboratory Center, Rockville, MD.

Presented at the 34th Annual Meeting of the American Academy of Forensic Sciences, Orlando, FL, 8-11 Feb. 1982 and the Spring 1982 Joint Meeting of the Mid-Atlantic Association of Forensic Scientists/ Northeast Association of Forensic Scientists, Harrisburg, PA, April 1982. Received for publication 21 May 1984; revised manuscript received 28 June 1984; accepted for publication 29 June 1984.

¹Document analyst, United States Secret Service, Washington, DC.

²A. A. Cantu, private communication, 1980.

406 JOURNAL OF FORENSIC SCIENCES

bacco & Firearms, National Laboratory Center, Washington, DC, began collecting a library of standard inks from U.S. manufacturers. This library has been maintained and expanded to its present-day status of being the largest single collection of inks in the world consisting of over 4000 domestic and foreign inks.³

The Bureau of Alcohol, Tobacco and Firearms (ATF) also initiated a national ink tagging program (1971 to 1974) in an effort to determine more closely the age of an entry produced by an ink whose formulation is not often changed by the manufacturer [6]. Even with these technical advances it is often necessary to determine more closely (less than a few years span) the actual age of an entry. This work will address only ballpoint pen inks because of their amenability to drying determinations.

Composition of Ballpoint Inks

Ballpoint ink is a high viscosity (nonfluid) writing medium. It consists primarily of three components [7]:

- (1) vehicles,
- (2) dyes or pigments or both, and
- (3) resins or polymers.

Vehicles

Vehicles are added to an ink for purposes of solubilizing (or carrying) the dyes/pigments and for ease of flow over the cartridge ball.

Vehicles in ballpoint inks have had only one dramatic formulation change since their inception in the 1930s. Before 1950, inks contained oil as the primary vehicle; after the early 1950s, glycol-based inks were developed and quickly became the favorite among the population.

These inks usually contain one or more of the following vehicle solvents:⁴

1.3 propylene glycol	Hexylene glycol
Diethyl glycol phenyl ether	Octylene glycol
Benzyl alcohol	1.3 butylene glycol
2 ethyl hexoic acid	Di and triethylene glycol
Ethylene glycol	Dipropylene glycol
2,3-butylene glycol	Glycerine
Monophenylether	Phenoxyethanol
1,2-propylene glycol	Phenoxyethylene glycol
Ethylene and diethylene glycol monomethyl ether	

The volatile components of the ink make up approximately 50% of its composition.

Dyes and Pigments

Dyes and pigments are the color giving components of an ink. Some of the more common ones used in ink formulations include:⁴

Methyl violet Victoria blue Crystal violet Copper phthalocyanine Nigrosine Solvent fast blue Luxol fast orange

Dyes and pigments make up approximately 25% of the ink's composition.

³A. A. Cantu, private communication, 1982. ⁴Private communications with ink manufacturers, 1982.

Resins and Polymers

Resins and polymers are added to ballpoint inks for purposes of "extending" the ink (used as a filler) and for thickening the ink. Some resinous components found in writing inks include:⁴

Vinsol® Nevillac Hard® Pyrrolidone (PVP) Krumbhaar K-1717® Phthalopal SEB® Synthetic Resin SK

The resinous additives usually make up approximately 25% of the total ink volume.

The vehicle components are of primary interest in this work. The ink cartridge is considered a "closed" system; essentially no drying takes place in the cartridge. The ink on the paper surface is an "open" system; the ink drying process begins as soon as the ink is placed on the paper.

The vehicles evaporate with time leaving the dyes/pigments and resins/polymers adhering to the writing surface.

This work is based on the fact that volatile components evaporate with time. Ballpoint pen inks contain volatile components that begin evaporating when placed on a document. This indicates that the age of a ballpoint pen ink entry stored under some "constant" conditions could be determined if the amount of volatile components per weight/volume of ink was measured (see Fig. 1). If the temperature and humidity do not remain constant, then only the "relative" age of an entry as compared to another entry (stored on the same paper) may be determined.

Materials and Equipment

The materials and equipment used were:

- Temperature programmable gas chromatograph equipped with a flame ionization detector
- Stainless steel column 1.8 m (6 ft) packed with 3% Tenax GC on 60-80 mesh Supelcoport
- Ten-microlitre syringe
- Micro vials (0.5 dr tapered)
- · High purity methanol
- Micro pipets, $10 \ \mu L$
- Ice bath
- High purity vehicle standards
- $\times 20$ gauge hypodermic needle
- Plunger
- Timer



FIG. 1-Theory of work.

Method

The first step in determining the age or "relative" age of a ballpoint pen ink entry is the identification of the ink formulation. Identification is necessary so the examiner can determine the quality control from the manufacturer and the "uniqueness" of a formula. The method used involves thin-layer chromatographic comparisons of questioned to known ink samples [5]. The known ink samples used in this work are stored and maintained in the standard ink library at the Bureau of Alcohol, Tobacco & Firearms, National Laboratory Center, Rockville, MD.

Once the questioned ink formulation has been identified, the volatile components and percentages present in known "fresh" ink of the same formula are obtained by gas chromatographic analysis.

Fresh ink samples of the same formulation were placed on a single sheet of paper on various dates. This sheet was stored under "standard" conditions (that is, room temperature and humidity) in a file drawer.

Samples of ink were removed from the paper by a micro-pellet technique. This technique utilizes a blunted 20-gauge hypodermic needle fitted with a shortened "syringe type" plunger. The micro-plugs of ink and paper (= 15 plugs) are placed in tapered microvials. Approximately 10 to $15 \,\mu$ L of methanol is slowly added (being careful not to disturb the pellets) by syringe through the capped/stoppered lid of the vial. The vial is placed in an ice bath to minimize "travel" of the methanol up the sides of the tapered vial. The vials remain in the ice bath undisturbed for 5 min. At the end of the extraction process a 5- to $10-\mu$ L aliquot is removed for injection into the gas chromatograph.

A gas chromatograph equipped with a flame ionization detector was chosen as the analysis instrument because of the need for reproducible detection and quantitation of micro-amounts of volatile components.

Fresh ink samples containing different combinations of volatile components were chromatographed using various extraction methods, gas chromatograph columns, and temperature programs. A suitable method for analysis was obtained. The gas chromatographic conditions chosen are as follows:

Temperature programmable gas chromatograph (Perkin-Elmer Sigma 3B) Flame ionization detector 3% Tenax GC on 60-80 mesh Supelcoport (stainless steel, 1.8 m [6 ft]) N₂ gas flow at 25 cm³/min Initial hold, 0-min 12°C/min ramp 50 to 280°C Final hold, 10 min Chart speed, 12.7 mm/min (0.5 in./min) Injections of 5 to 10 μ L using methanol as the extracting solvent Attenuation: ×2 K till methanol peak, then ×100

Once a suitable chromatogram was obtained the vehicle peaks were identified by using known standards and formulation information obtained from the ink's manufacturer.

An "aging" curve for each ink was obtained (Fig. 2). This was done by finding two sufficiently resolved vehicle peaks, quantitatively determining the peak areas, and then ratioing one peak to the other. The ratio of Peak A/Peak B is plotted versus actual age (days). This gives the aging curve for that particular ink formulation (Fig. 3).

The questioned entry is analyzed in the same way. The peak areas are taken, a ratio is obtained, and, using the previously calculated "aging curve," the age of the Q entry is determined (Fig. 4).

This calculated "age" of the Q entry is absolute only if the storage conditions of both the Q and K entries are identical. The storage conditions of the inks used to obtain the aging curve should be equal or better (that is, slower aging process) than those of Q.



FIG. 3—Aging curve calculated from the ratio of Peak A/Peak B versus actual age.



Conclusions

Ideally at least two inks of the same formula should be compared. They should be on the same paper and stored under the same conditions.

If two inks of the same formulation on the same document have different ratios of the volatile components, then one ink can be determined to be fresher than the other, that is,

$$\frac{(A = \text{first eluting comparison peak})}{(B = \text{second eluting comparison peak})} \approx \frac{(A)}{(B)}$$
 old

If two inks of the same formulation are found on different paper, then the paper type is probably not a factor but storage conditions are. The "willingness" of the paper to allow these components to be extracted in the *same* ratio should not be affected by a paper's porosity, thickness, type, or age. However, this must be further tested.

Certain ballpoint pen ink formulations were shown to have reproducible aging curves up to one-and-one-half years after placement on paper. Differences in peak ratios for known inks stored under standard conditions were detected over as small a time frame as a few days. Some ink formulations tested have evaporation rates or vehicle components not amenable to this technique.

Ratioing the chromatograph peaks eliminates the necessity of removing equal masses of "questioned and known age" ink when performing an age comparison.

Further work that should be performed includes testing the paper independence theory and developing a laboratory technique for "controlled" artificial aging of ink standards to obtain "immediate" aging curves for known standard inks.

Acknowledgments

This work was greatly assisted by the knowledge and cooperation of the following: Dr. Antonio A. Cantu, the ink industry, Dr. Phillip M. Daugherty, Richard L. Brunelle, and Connie Lee.

References

- [1] "The Battle of the Ball-Point Pen," Reader's Digest, Dec. 1946, pp. 59-63.
- [2] Daugherty, P. M.: "Composition of Ball Pen Inks," presented at the First Georgetown University Conference on Surface Analysis. Washington, DC. Oct. 1969.
- [3] Waters, C. E., "Blue Dye as Evidence of the Age of Writing," Industrial and Engineering Chemistry, Vol. 25, No. 9, Sept. 1933, pp. 1034-1035.
- [4] Mitchell, C. A. and Hepworth, T. C., "Inks: Their Composition and Manufacture," 3rd ed., Griffin & Co., London, 1924, p. 181.
- [5] Crown, D. A., Brunelle, R. L., and Cantu. A. A., "The Parameters of Ballpen Ink Examinations." Journal of Forensic Sciences, Vol. 21, No. 4, Oct. 1976. pp. 917-922.
- [6] Brunelle, R. L., Cantu, A. A., and Lyter, A. H., "Current Status of Ink Analysis," presented at the 1975 Annual Interpol Meeting, St. Cloud. France.
- [7] Witte, A. H., "The Examination and Identification of Inks." in *Methods of Forensic Science*, Vol. 2, Interscience Publishers, London, 1963, p. 35.

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Forensic Science International

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

Minimum requirements for application of ink dating methods based on solvent analysis in casework

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ARTICLE INFO

Article history: Received 11 November 2010 Received in revised form 21 January 2011 Accepted 25 January 2011 Available online 4 March 2011

Keywords: Forensic sciences Questioned documents Ink dating Solvent drying Aging Method validation Interpretation

1. Introduction

Determining when an ink entry was produced on a document has always been a major issue in the examination of questioned documents. For this reason many scientists aimed at developing dating methods along the years [1-5]. There are three main approaches for ink dating on documents. The first approach is based on the analysis of ink stable components that are specific to a certain period in time. Production methods and compositions change and evolve with time following new industrial developments and processes. This approach is generally named in the literature 'static approach' because the measured parameters are almost invariable in time [2]. It allows the determination of the first possible date of existence for a given composition of ink and may thus highlight anachronisms. Knowledge of some major historical changes in ink manufacturing is available (e.g., introduction dates of the major classes of compounds and dates of major changes in formulation). However, most knowledge of changes is proprietary industrial information and not readily available. This is probably the reason why only the US Secret

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ABSTRACT

Several ink dating methods based on solvents analysis using gas chromatography/mass spectrometry (GC/MS) were proposed in the last decades. These methods follow the drying of solvents from ballpoint pen inks on paper and seem very promising. However, several questions arose over the last few years among questioned documents examiners regarding the transparency and reproducibility of the proposed techniques. These questions should be carefully studied for accurate and ethical application of this methodology in casework. Inspired by a real investigation involving ink dating, the present paper discusses this particular issue throughout four main topics: aging processes, dating methods, validation procedures and data interpretation. This work presents a wide picture of the ink dating field, warns about potential shortcomings and also proposes some solutions to avoid reporting errors in court.

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Service (Washington, USA) and the LKA Bayern (Munich, Germany) reported having extensive ink samples and databases [6,7]. Additionally a program started in the mid 1970s in the USA, in collaboration with the ink manufacturers, for introducing annually modified tags to inks [2], but it covered only a fraction of the whole ink market. The second approach, addressed as the 'absolute dynamic approach' [3] is based on aging processes of ink on documents. It is assumed that ink does not age in the cartridge [8,9], but only after it is placed on paper where dyes fade, solvents diffuse and evaporate, and resins polymerise. Aging processes of ink follow complex pathways that are considerably influenced by several factors other than time, which may accelerate or slow down the aging. The influencing factors can be ordered in three main classes [4,10]: (i) initial composition of the ink (in the cartridge), (ii) physical and chemical properties of the substrate (paper composition, porosity and coatings) and (iii) storage conditions (temperature, light, air flux, humidity, neighbouring material, etc.). In practice, no information on these factors is generally available. This is why the determination of the absolute age of an ink entry remains truly difficult. Measured changes are reported as a function of time in order to establish an aging curve or a portion of it and the objective is therefore more the determination of a time range than a precise date. The time scale considered can significantly vary depending on the measured parameters. For example, while solvents disappear from the ink





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^{0379-0738/\$ –} see front matter 0 2011 Elsevier Ireland Ltd. All rights reserved. doi:10.1016/j.forsciint.2011.01.034

very quickly, dyes degradation occurs more slowly. The third approach aims at determining the relative age of a document in comparison to others (i.e., to order them in chronological sequence) and is referred to as the '*relative dynamic approach*' [3]. The comparison of the extent of ink aging may help reconstructing the sequence of apposition of ink entries on documents. This can only be applied for inks of the same formula stored under the same conditions on the same type of paper (e.g. diaries) [11]. That is, it applies to inks that only differ in the time they were placed on paper. The general evolution of the aging curve must be known [4]; for example if a decrease of the aging parameter is expected as a function of time, it is imperative to insure it will never increase whatever the conditions.

The most promising methods in the 1980s involved the analysis of sequential extraction of dyes using thin layer chromatography (TLC) [11–20]. It was based on the changes in the extractability of the ink supposedly caused by the hardening of the resins [10,21–24]. The use of this technique in caseworks was reported in the literature [18,25], but it was followed by a vigorous controversy among the scientific community about the limitations of this approach [5,26–42]. Several researchers tried reproducing the results obtained in previous studies and reported the methods to be unreliable [28,34–36], while other scientists debated about the necessity for inter-laboratory validation before their use in casework [4,27,31–33,38,41].

During the last decades interest has shifted to methods based on sequential extraction and analysis of ink volatile components by gas chromatography (GC) coupled with mass spectrometry (MS) or other detectors [17,18,34,44–58], which seemed more promising in terms of reproducibility. Although some forensic laboratories do already apply such ink dating methods in practice, several issues remain open including the inter-laboratory validation. Triggered by a recent ink dating case in Israel, this article aimed at clarifying the ink dating field for justice purposes and guiding scientists through validation of their methodologies, while highlighting practical limitations. It was earlier acknowledged that a central unsolved problem in the field of questioned documents examination is the unequivocal determination of their age [59]. Despite the significant progress in analytical techniques and several published propositions for ink dating, the field of document examiners is still divided about this issue, for reasons that will be clarified and discussed throughout this article. The purpose of this work is to give the status of the various ink dating methods that are based on the analysis of an ink's solvent components, show their limitations, and suggest methods to improve them. It is subdivided in four main sections as follows: Section 2: ink drying principles; Section 3: ink dating methods; Section 4: methods validation; Section 5: ink dating interpretation.

2. Ink drying principles

The dating methods considered in this article all focus on the analysis of solvents from ink strokes on paper. It was observed early that the amounts of solvents in the ink strokes decreased as a function of time [44], according to the following equation [50,51] for the relative peak area (RPA):

$$RPA = p_1 + p_2 \cdot e^{-(t/p_3)^{0.5}} + p_4 \cdot e^{-(t/p_5)^{0.5}}$$
(1)

where p_1 is an additive constant, p_2 and p_4 provides the contribution of the first and second exponential, and p_3 and p_5 are time constants associated with the exponential. The ink drying processes were earlier described in the literature as two separated falling rate phases [51]. The first exponential represents the fast falling rate of drying (rapid solvent evaporation and diffusion into the paper) and the second exponential represents the slow falling



Fig. 1. Simultaneous ink drying processes on paper: the ballpoint pen solvent molecules volatilize (evaporate), diffuse (migrate and penetrate via absorption) and are adsorbed by the paper substrate. While grey arrows represent volatilization, black arrows represents diffusion, migration, penetration, absorption and adsorption.

rate of drying (slower evaporation and diffusion processes) [50,51]. Low amounts of solvents may even stay trapped in the ink matrix for years [17,45,52]. Based on previous researches, the following theoretical aging model can be formulated: several processes occur simultaneously when ink is placed on paper, such as evaporation of solvents in the ambient air, diffusion/absorption in the paper and adsorption by the paper substrate (Fig. 1). Volatilization occurs actually in the ink surface, in the paper surface near the ink and in the paper surface the opposite from the ink. Moreover the solvent molecules may diffuse into adjacent surfaces (for example in a stack of paper sheets) [51].

The compound phenoxyethanol is the most widespread solvent in ballpoint pen inks [57,60,61] and therefore most dating methods finally focused exclusively on the analysis of this specific substance (Fig. 2).

As explained above, ink aging pathways and rates are significantly influenced by a number of factors that may slow down or accelerate the phenomenon [42,61]. These parameters must therefore be extensively studied before a conclusion can be drawn on the absolute age of an ink entry.

2.1. Ink formulation

The influence of the initial ink composition on the aging rates of inks is very important [23,45,56]. Two aspects must be considered: the compounds (dyes, resins, solvents, and additives) and their relative amounts (initial solvent quantity in the ink formulation). Bügler et al. actually suggested that the type of resins influenced the aging rates as they observed the presence of acetophenone–formaldehyde–resin in 'slowly aging inks' [56]. It is therefore very important to have a precise knowledge of the ink market (for example through an ink database) in order to develop a method on selected representative inks.

2.2. Initial ink quantity

The initial quantity of solvents in an ink stroke also influences significantly the aging process (i.e., the drying of the ink). For example, it is dependent on the writing pressure (i.e., thickness of



Fig. 2. Structure formula, molecular weight, boiling point and viscosity of the solvent phenoxyethanol.



Fig. 3. Superimposed curves for the evaporation of 10, 20, 40, 60, and 100 μ l of the solvent ethoxyethanol from paper: the loss of weight in micrograms (steps of 5000 μ g) is presented as a function of the time in hours. Lower evaporation rates were observed when smaller volumes of solvents were initially deposited on paper [61].

ink) or and/or also on the size of the ball in the ballpoint pen. Lower evaporation rates were observed for smaller volumes of solvents on paper (Fig. 3), when the solvent ethoxyethanol was placed on the paper surface using a micropipette. With larger quantities of solvent applied to the paper, a larger accessible surface area will be available for evaporation (Fig. 4), and thus a higher evaporation rate will be observed.

This is problematic as the relative content of phenoxyethanol varies considerably among different ballpoint inks [38]. The size of the ball of the ballpoint pen and the pressure applied while writing, both of which determine the thickness and depth of the ink line, respectively, also affect the initial quantity of phenoxyethanol found in 1 plug or 1 cm of ink line. Moreover, in research works, ink entries are generally drawn as straight lines, allowing solvents to diffuse away from the stroke. Questioned documents will most probably carry texts with curved lines from any alphabet. For



Fig. 4. Visible surface area $[cm^2]$ taken up by the solvents ethoxyethoxyethanol (E), dipropylene glycol (D) and phenoxyethanol (P) a short time after deposition on paper with a micropipette, as functions of the volume deposited $[\mu l]$. The surface areas increased with the volume, but were also influenced by the viscosity, density, hygroscopicity and volatility of the solvents [61].



Fig. 5. Solvents diffusion from two ink entries: (left) diffusion away from a straight line and (right) diffusion inside the loop of the letter 'o'. The solvent concentration may be significantly higher in 1 cm of the loop compared to 1 cm of the straight line.

example, in the letter "o", the solvents will diffuse to some extent away from the letter and partly inside the ring. Higher quantities of solvents may be found in letters with dense lines compared to a straight line of the same length (Fig. 5). This represents a major problem. When extracting 1 cm ink lines from different letters, one is not guaranteed to have always the same solvent quantity. Aginsky tried to minimize this effect by calculating a mass invariant ratio between two samples [34,52]. Bügler et al. even tested the mass independence of a given aging parameter by analysing ink entries of different lengths on the same paper [56]. For example, if 2 cm of an ink line containing 0.3 µg of phenoxyethanol per cm was analysed, one would record twice as much phenoxyethanol than in 1 cm (Table 1). However if you calculate a ratio between two compounds found in the ink [50.52] or between two sequential extractions of the same ink entry [52,56], the ratio should be the same regardless of the length of the ink line.

However, only the *length independence* between two samples of the same entry is guaranteed, and not the *mass independence*, as pressure (i.e., thickness) and density (i.e., distribution) vary along a stroke (Fig. 5) [56].

In practice, it is impossible to ensure the homogeneity of the ink applied on paper, thus the influence of such parameters on the solvents aging kinetics must be quantified. Dating would then be possible only if the errors provoked by different solvent quantities resulting from the above situations were smaller than expected changes as a function of the age. This actually requires more research than was published so far.

2.3. Paper type

The influence of substrate structure (paper type) on the drying process should not be underestimated, as their porosity can differ quite widely within a same sheet of paper (pores diameter between 0.05 and 10 μ m). Molecular diffusion, Knudsen (through pore) diffusion, surface diffusion, capillary condensation of vapors, physisorption (absorption and adsorption), chemisorption, migration and evaporation will all be influenced by the porous structure, the fibers (e.g., cellulose fibrils) and the paper chemistry (alkaline

Table 1

The parameters M_1 and M_2 are absolute quantities of phenoxyethanol and are dependent of the length of the stroke, while calculating a ratio between these two parameters yield a length independent feature.

Ink line length (cm)	First parameter M1 (ng)	Second parameter M ₂ (ng)	Ratio (Table 4; Eq. (3)) $M_1 \cdot 100\% / (M_1 + M_2)$
1	30	70	30
2	60	140	30

Table 2

Procedure to determine the rate of decrease of volatile components (R) in inks on documents.

Method 1	Sample set 1 (normal)	Sample set 2 (artificially aged)	
Sampling	10 mic	10 microdiscs (1 mm diameter) of the ink on paper	
Treatment	No treatment Moderate heating (e.g. 70°C, 1 h [52] or 2		
Extraction	10 μl [52] or 15 μl [49] of	$10\mu l$ [52] or $15\mu l$ [49] of appropriate solvent (e.g. acetonitrile with an internal standard)	
Analysis	$1 \mu l$ of extract analysed by GC/MS (SIM mode)		
Results	P=mass of solvent	$P_{\rm T}$ = mass of solvent	
Eq. (2)	$R(\%) = [(P - P_{\rm T})/P] \cdot 100$ [49,52]		

or acidic, fillers, detergents, additives, etc.). Aginsky stated having studied the influence of paper type ([52], footnote 10) reporting it to be negligible, but no details have been disclosed. Bügler et al. also studied the influence of the paper type on the aging process and reported a strong dependence on paper type for his method [56].

2.4. Storage and environmental conditions

Due to the fact that diffusion and evaporation mechanisms play such an important role in the drying of solvents on porous media, a wealth of external factors must be taken into account. Among these are temperature (of air, substrate, ink), solvents' vapour pressure, humidity, air movement (laboratory, cabinets), the properties of solvents mixtures (vaporization of the solvent mixture, viscosity), and those properties of ink and paper that could affect heat transfer and mass transfer coefficients. On that aspect, Aginsky wrote that his results 'suggest that the Q (questioned) writing is old (...) on condition that the document bearing the Q writing has been stored under normal environmental conditions, for example, under room temperature and constant humidity and light conditions [52]'. Lower temperatures and air flows will slow down the drying process. Moreover, room temperatures may vary considerably between summer and winter (except for air conditioned rooms), whereas humidity is rarely constant even in an air conditioned environment.

Possible contamination of old strokes through solvent migration from fresh strokes on adjacent sheets of paper should also be taken into account [47,51,61,62]. It was observed that solvents from a fresh stroke (t = 0) can very efficiently migrate to adjacent sheets of paper in a pile. It was found that the quantities of solvent involved in this migration exceeded those found in a stroke after two weeks [51], so that conversely, contamination of a stroke by migration must be taken into account for the dating of ink entries by solvents quantification. Paper blank analysis will help reduce the risk [46]; however the contamination may be very local [62]. Since solvents diffuse from the ink stroke into the paper, the paper blank should not be sampled too close to the ink entries [51]. One has to be particularly careful regarding the way documents are stored, due to the possibility of contamination (in a notebook or file folder), but also because of the suppression or reduction of drying processes in tightly sealed (e.g., glass vial) [61] or semihermetic (e.g. plastic cover) situations respectively. Additional measurements are needed to follow the drying of inks on papers for long storage times under such conditions. Storage conditions were barely studied up to now in spite of their crucial influence on aging kinetics. Most reports contain data collected from documents which have been stored only under laboratory conditions. From a validation point of view it is therefore important in practice to apply a method within its range of applicability and to state exactly under which circumstance the results are valid.

3. Dating methods based on solvents analysis described in the literature

First proposed by Stewart [44], further developments of dating methods based on solvents analysis were inspired by the works of Cantu on sequential extraction [11] and artificial aging [12]. Aginsky proposed two multi-staged 'absolute dynamic dating methods' [34,45,52]. These methods' principles were briefly addressed in two preceding papers [17,18]. Aginsky's methodology [52] is based on the supposition that as ink ages, its resins harden (solidify) and subsequently the ink solvent extractability decreases over time [45]. Solvents (volatile ink vehicles) are analysed and more specifically the rate of decrease of solvents amounts (method 1 described below) and the rate of decrease of solvents extractability (method 2 described below). Gaudreau and Brazeau of the Forensic Document Examination Section of the Canada Border Services Agency reported in a conference presentation the use of a dating method based on the same principles [49] (modification of method 1 described below). More recently, Bügler et al. described a method based on the same principles, but involving a different sample preparation [55,56,63,64] that has been implemented by several laboratories in Germany, Switzerland and Canada (modification of method 2 described below as method 3). The first step of dating measurements generally consists of detection and identification of the volatile components of the ink (described, for example, as procedure 1 in [52]). As explained above, the ink component used for dating is phenoxyethanol, since it is the most commonly found in ballpoint pen inks [51,56,57].

Additionally, some recent developments based on previous tests [17,44,50] proposed to calculate the loss of phenoxyethanol in relation to a stable compound quantification such as a dye as a function of time [65–67]. For the moment no further information were published about this alternative approach and it will therefore not be directly treated in this paper. However the same principles would apply to their potential future application in practical cases.

3.1. Method 1

Described as *Rate of decrease of volatile components R%* by Aginsky [52] and *Solvent loss ratio* by Gaudreau and Brazeau [49].

Aginsky's procedure [52] implies the removing of two sets of samples each consisting of 10 microdiscs (about 1 mm in diameter)

Table 3

Summary of R thresholds values defined in the literature and in conference proceedings.

Aging parameter (%)	Threshold value	Ink entry age	Literature
R	≥20	Fresh	Aginsky [52]
R	\geq 50	Less than 6 months	Gaudreau and
			Brazeau [49]
R	≥ 25	Less than 1 year	Gaudreau and
			Brazeau [49]

Table 4

rocedure to determine the rate	of decrease o	f solvent extractability	(D) of inks from	documents de	escribed by	Aginsky	[52]
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Method 2	Sample 1 (normal)	Sample 2 (artificially aged)	
Sampling	10 microdiscs (1-mm diameter) of the ink on paper	
Treatment	No treatment	Moderate heating (e.g. 70 °C, 60 min)	
Weak extraction	$10\mu l$ of an appropria	te weak solvent (e.g., carbon tetrachloride)	
Analysis 1	Extract analysed by GC/MS		
Results 1	$M_{\rm weak}$ = mass of solvent	M _{weak} =mass of solvent	
Strong extraction	After drying, in 10 μ l of an appropriate strong solvent (e.g. chloroform)		
Analysis 2	Extract analysed by GC/MS		
Results 2	$M_{\rm strong}$ = mass of solvent	M _{strong} = mass of solvent	
Eq. (3)	$P = 100 \cdot [M_{\text{weak}} / (M_{\text{weak}} + M_{\text{strong}})]$	$P_{\rm T}$ (%) = 100·[$M_{\rm weak}/(M_{\rm weak}+M_{\rm strong})$]	
Eq. (4)		$D(\%) = P - P_T [52]$	

of the ink on paper using a boring device (also called micro-punch device). Sample set 1 is placed in a vial and extracted with 10 µl of an appropriate solvent with an internal standard. 1 µl of the extract is analysed by GC/MS (SIM mode with detector set to monitor ions which are specific for the identified substances and internal standard). The mass of the ink solvent detected (i.e. the ink aging parameter P) is calculated by means of the internal standard method. Sample set 2 is heated moderately and analysed using the same procedure as for sample set 1 to determine the mass of the ink solvent after heating (i.e. the ink aging parameter $P_{\rm T}$). The rate of decrease of volatile components is calculated using Eq. (2) in Table 2. If the value of R is ca. 20% or larger, it shows (on condition that the content of the analysed ink's solvent is not too small, at least, not less than 1 ng per sample) that the natural aging of the ink analysed is still in progress, i.e., the ink writing is fresh (Table 2) [52]. In his paper [52], Aginsky proposed an alternative ink aging parameter *P* if any volatile solid component of the ink was detected: P = ratio solvent peak areas to non-volatile component peak areas. However this method was not mentioned again in later publications.

Gaudreau and Brazeau reported using a similar method to determine the approximate age of an ink entry in conference proceedings [49]. Two sample sets each containing 10 plugs of ink are removed. One sample set is heated at 70 °C for 2 h and then both are extracted with 15 μ l acetonitrile containing internal standard for 5 min. Using Eq. (2) in Table 2, the authors determined the following threshold values for phenoxyethanol: $R \ge 50\%$ and 25% (including error) allowing to state that ink has been applied to paper less than six months (150 days) and less than one year (300 days) prior to the test respectively (Table 3).

As of today, nobody else reported in the literature using this method. However, Andrasko presented a modified solvent loss ratio technique involving a different sample preparation (solid-phase microextraction) [46,47] that was able to reveal if an ink is fresh (4–6 months old at most). He later communicated his strong doubts about the feasibility of such ink dating methods stating that the method he had presented was unreliable and that the results were not reproducible.² A solid-phase microextraction method was also studied by Brazeau and Gaudreau [54]. It should be noted that this method requires that both the heated and unheated samples have the same or nearly the same amount of ink. The method is not independent of the amount or length of ink sampled.

3.2. Method 2

Described as rate of decrease of solvents extractability D% by Aginsky [52].

According to Aginsky's report [52], two samples, each of 1 cm slivers of the ink on paper are removed using a sharp scalpel. Sample 1 is placed in a vial and extracted with 10 μ l of a 'slowly extracting weak' solvent. 1 µl of the extract is analysed by GC/MS (SIM mode with detector set to monitor ions which are specific for the identified substances and internal standard). The sample is removed, dried, placed in another vial and extracted with 10 μ l of a 'fast extracting strong' solvent. 1 µl of the extract is analysed by GC/MS (same analysis settings). The mass of solvent in each extract $(M_{\text{weak}} \text{ and } M_{\text{strong}})$ are calculated by means of the internal standard method and the percent of the solvent mass extracted in the weak solvent (P) is calculated using Eq. (3) in Table 4. Sample 2 is then heated moderately and analysed using the same procedure as for sample 1 in order to determine the percent of extraction after heating $(P_{\rm T})$. The distance (D) between the value P and $P_{\rm T}$ is calculated using Eq. (4) in Table 4. Method 2 is actually an upgrade of method 1, as the total amount of extract $M_{\text{weak}} + M_{\text{strong}}$ (Table 4) should theoretically have the same value as *P* (Table 2). Therefore the final R% can be extrapolated from the raw results obtained by method 2, without additional analyses.

Aginsky summarized: If the value of D is ca. 15% or larger, it shows that the natural aging of the ink analysed has not levelled off yet, i.e., that the ink writing is fresh [52]. The following thresholds definitions were proposed in the literature in 1996 [52]:

- D > ca. 15% It suggests that the questioned writing is fresh, i.e. it is less than eight-month old. If such a result has been obtained for a questioned document dated, e.g. by over a year preceding the analysis, the examiner can state with confidence that this document has been backdated.
- D < ca. 10% It suggests that the questioned writing is old, that is its age is larger than ca. two months, on condition that the document bearing the questioned writing has been stored under normal environmental conditions, for example, under room temperature and constant humidity and light conditions. It should also be stressed that such results can also mean that the questioned ink's binder is not capable of cross-linking or undergoing other processes of 'solidification' due to aging (though there are very few such inks on the market).
- ca. 10% < D < ca. 15% This means that additional samples of the questioned entry should be taken (if enough ink is available) to ascertain statistically if the mean of the *D* values obtained are closer to 10% or 15%; in this case, the conclusion on whether the ink in question is fresh or old is made with a certain degree of confidence.

It was then specified in an appendix to the article [52] that if, in a real case situation, a necessity arises to narrow the interval

² Personal communication from J. Andrasko, 2003.



Fig. 6. Graphical presentation of the threshold values proposed by Aginsky [33] to determine a time frame within which a questioned entry has been actually written.

Table 5

Summary of D threshold values defined in the literature and in conference proceedings.

Aging parameter (%)	Threshold value	Ink entry age	Literature
D D	ca. >15 ca. <10	Less than 8 months More than 2 months	Aginsky [52] Aginsky [52]
			proficiency
D	ca. >10 ca. <15	More analyses	Aginsky [52]
D	≥20	Less than 5 months	Aginsky [52]
D	\leq 5	More than 6 months	Aginsky [52]
D	≥18	Less than 6 months	Aginsky [45]
D	≥12	Less than 8 months	Aginsky [45]
D	≥ 8	Less than 12 months	Aginsky [45]
D	≥ 6	Less than 18 months	Aginsky [45]
D	≥ 4	Less than 24 months	Aginsky [45]

comprising the real age of the ink in question, there were at least two possibilities for this: (1) the ink formula is known and reference samples may be prepared; (2) further thresholds determination as follows:

- $D \ge 20\%$ corresponds to ballpoint inks younger than 5 months.
- $D \le 5\%$ corresponds to ballpoint inks older than approximately 6 months.

New upper-threshold values were later presented in a conference proceeding in 2002 (Table 4) [45].

This *D* parameter is then used to ascertain that the aging of the ink sample has not stopped yet (Fig. 6). The principle follows the idea that, when ink is fresh, *P* is high and P_T is lower (then the difference *D* is high and the sample is still drying). When the ink is old, *P* is low and P_T is also low (then the difference *D* is low and the sample decreased its rate of drying).

The threshold values were defined using different ballpoint pens. If the type is not always reported in the literature, the number of pens was specified: between 30 and 50 [45]; 64 [49] and up to 85 [56]. Thus the influence of ink formulation was to some extent tested, particularly in the work of Bügler et al. [56] who selected representative inks from the ink library at the Forensic Science Institute of The Bavarian Bureau of Investigation. As a consequence, the influence of the initial quantity of phenoxyethanol was also evaluated. This is why only an upper-threshold indicating the maximum age of an ink may be used [45,49,56]. The presence of a high quantity of phenoxyethanol or the finding of a high aging parameter may indicate a fresh ink, whereas its absence does not allow any conclusion about the age [56] (see detailed explanations below) (Table 5).

No published account from other authors reported using this specific method. However, a method based on the same principles, but involving a different sample preparation, was reported recently in the literature and is described below [56,60,63,64].

3.3. Method 3

Described as *Ink age assessment procedure* by Bügler et al. [56]. Instead of a sequential extraction into weak and strong solvents, the sample is thermally desorbed at two different temperatures (e.g. 90 °C and 200 °C). The peak areas of phenoxyethanol obtained at low desorption temperature M_{low} and high desorption temperature M_{high} are used to calculate a ratio *V* (corresponding to *P* in Eq. (3) in Table 4) (see Table 6).

If the experimental procedure considers only sample 1 and V_1 (%) is computed, then the decision criteria were defined by Bügler et al. [56] as follows (Table 7):

- if *V* > 10%, ink is fresh. For example, if *V* > 25%, ink is not older than two months.
- if *V* < 10%, no conclusion can be drawn.

Bügler et al. found out that a large number of the inks aged too fast and therefore no conclusion can be drawn when the ratio *V* is

Та	ble	6

Procedure to determine the ink age factor (V%) of inks from documents described by Bügler et al. [56].

n paper
After several weeks
ption
GC/MS
$M_{\rm low}$ = mass of solvent
rption
GC/MS
$M_{\rm high}$ = mass of solvent
V_n (%) = 100·[$M_{\rm low}/(M_{\rm low} + M_{\rm high})$]
end test [69]

58

 Table 7

 Summary of V thresholds values defined in the literature and in conference proceedings.

Aging parameter (%)	Threshold value	Ink entry age	Literature
V	>25%	Less than 2 months	Bügler et al. [56]
V	>10%	Less than 3-4 months	Bügler et al. [64]
V	<10%	No conclusion	Bügler et al. [56]

below 10%. Moreover the authors stated that while according to their test results, the proposed method for age determination was applicable to ballpoint inks not older than 1.5 years [55,64]. In practice, however, the accuracy of the method and the properties of the inks used in office work limit the measurable time scale to an ink age of up to 3–4 months [64].

In order to minimize the potential occurrence of false positive, the authors later considered performing a series of five analyses every two weeks for a period of two months, while letting the samples naturally age (these are samples 2-5 in Table 6) [64,68]. The authors also proposed derivatization of phenoxyethanol in order to increase sensitivity and decrease variability[64,68]. The results thus obtained are then used for calculating a similar aging parameter as the one proposed by Aginsky (D in Table 4) [33] with the difference that the subsequent samples are aged naturally instead of artificially. In fact, artificial aging is faster, but actually still debated largely in the scientific community and it was not yet demonstrated to reproduce adequately the natural aging of ink [42]. In this way, using the V% values of the five samples, each of which is older than the previously analysed, an aging curve for the questioned ink entry is obtained. It is then assumed, that a significant drop in the slope of the curve reflects an ink which is still aging, and that no significant drop in the curve reflects an ink which is not aging anymore. From mass screening it was deduced, that aging of inks can be followed analytically with this method up to 6 months. As a consequence, an ink which is still aging is regarded as being not older than 6 months. Otherwise no conclusion can be drawn. The assessment of a "significant drop" in the slope of the aging curve is performed using the statistical Neumann's trend test. The value Q is calculated as follows [69,70]:

$$Q = \frac{1}{(n-1) \cdot s^2} \sum_{i=1}^{n-1} (x_i - x_{i+1})^2$$
(5)

where *n* is the number of measurements (e.g., n = 5), $x_i, x_{i+1}, ...$ are the measurements ordered chronologically and *s* is the standard deviation. This statistical treatment provides a threshold value for *Q* to decide if there is a trend in a series of points given a selected probability *p*. The probability level has to be fixed by the examiner and is generally 95%. For example, a threshold value of 0.8204 is obtained for n = 5 and p = 95%. If the *Q* value is below the threshold value, then the conclusion can be drawn that the investigated ink is still aging given the selected probability level.

4. Validation of ink dating methods

The analytical dating methods require a considerable amount of time and resources. It is therefore important not to underestimate the task of ensuring their scientific validity before implementing them in practice [71,72] (Table 8). In forensic ink dating, it is extremely important not to confound the results of research experiments performed under laboratory conditions on controlled samples, with results obtained in real situations on uncontrolled specimens of limited size, unknown composition and undefined

Table 8

Aspects of reliability for analytical methods. These aspects must be further evaluated before the application of proposed dating methods in real cases.

Aspects of reliability	Short definition
Specificity [73]	Ability to detect ink solvents
LoD, LoQ [38,73]	Limit of reliable measurements
	(detection and quantification)
Systematic error [38,73]	Accuracy
Repeatability [73,75]	Within laboratory precision
Reproducibility [73]	Between laboratory precision
Outside proficiency	Blind testing on realistic samples
testing [27,31,33]	

storage conditions [41]. Published works present interesting ideas and promising orientations, but its reporting stage in publications does not allow yet for a wide application in casework. Stewart and Fortunato [32] warned that 'the need to routinely determine the age of a document appears to have been a driving force in development of new ink analysis techniques. This could be dangerous, in that the field may be driven to advance faster than the stage of development of some of the techniques should allow.'

It is also of particular concern that measurement errors and irregulars are very rarely mentioned in the literature and are generally not represented in the figures. It is essential however, to make certain that predicted differences provoked by aging (under different influencing factors) are in fact higher than measurement errors [73]. Furthermore, the ink available in real cases is generally not sufficient to repeat analysis several time in order to obtain a mean and a standard deviation. When low quantities are analysed. such as solvents in ink entries, the detection and quantification limits (LoD and LoQ, respectively) play an important role in determining a threshold at which the method is not applicable anymore [4]. Due to this small sample size and the flowing time, it is seldom possible to perform ink dating by solvent analysis again after some time has passed. The most demanding aspect is actually the inter-laboratory validation. As stated earlier, in the literature all necessary data are actually required so that any new technique(s) being proposed can be scrutinized by other experts *in the field* [32]. The transparency in forensic science has been often acknowledged as an essential factor to avoid errors [74,75] and is a must, in order to develop a methodology in several laboratories. Often, only final values or given examples (no raw data) are published in the literature and the reader must accept the conclusions for granted. This lack of transparency about dating methods was criticized early in the questioned documents literature. Stewart and Fortunato wrote in 1996 [32] that 'If a technique can be shown to be scientifically sound then the next logical step would be to conduct independent validation studies at different laboratories. Before this can occur, however, each technique must be carefully researched and described so that others can reproduce the methods and evaluate their effectiveness.' To that Aginsky answered as follows [33]: 'However, this recommendation does not seem irreproachable. Of course, each method proposed for applying in casework must be minutely described in a professional journal and properly scrutinized. But, at the same time, it should be realized that this natural way related, mainly, to the method presentation, practically has nothing to do with the method validations, at least, as for ink dating methods. The matter is that these methods are the complicated many-staged procedures containing a number of limitations, "technological nuances" and pitfalls which all are difficult to exhaustively explain in the article and which may serve as contributing factors to possible inconsistencies between the procedure, as it is used by the author(s), and its improper reproductions made by others who want to evaluate its' effectiveness or conduct independent validation study. (...) With the above reasons in mind, it becomes clear why attempts to reproduce similar methods by using their description, even very detailed, may well lead to confusing results'. If a method may be reproduced incorrectly by other scientists because of its difficulty, then the robustness of the method may be questioned. A robust method would not be significantly affected by small variations (i.e., error) introduced during the procedure; and the procedures may be easily exported in other laboratories. Therefore forensic scientists performing ink dating methods should contribute actively to the exportation of their method to other laboratories, thus avoiding misunderstanding leading to improper reproductions. In fact, to the present date, no two laboratories that do ink dating via solvent analysis use the same method, however several laboratories participating in the International Collaboration on Ink Dating (InCID, a subgroup of the European Document Examiners Working Group) are striving to harmonize their dating methodologies inspired by the work of Bügler et al. [56].

Once the validation of the tested methods is carried out satisfactorily [71,72], blind testing on realistic samples will be imperative, in order to check the reliability of the method under real casework conditions. Brunelle and Cantu [27], Margot et al. [31] and Aginsky [33] agreed on the fact that 'there is a serious need for outside proficiency testing of current ink dating methods'. Aginsky reported having been subjected to outside proficiency testing in the Division of Identification and Forensic Science of the Israel Police for method 2 (decrease in extraction efficiency) [33,52,76]. A document attesting that fact is available on the website of Riley Welch LaPorte and Associate [76]. According to this document, Aginsky examined six different ballpoint inks written on different dates and his results were all correct. The age of the inks at the time of analyses varied between 1 and 12 months. Five were younger than 8 months and one was older than 2 months. No indication about the preparation of samples was detailed (e.g., type and number of different inks, type of paper, storage conditions). The number of samples of this testing was very limited and the conclusion given used only two thresholds (less than 8 months corresponding to D > 15% and more than 2 months corresponding to D < 10% [52]). In our opinion, this can by no means serve as a proof that the method will work on realistic samples (i.e., corresponding to uncontrolled conditions encountered in caseworks) and that different threshold values [45] would provide correct answers. For example, recent studies by Bügler et al. [56] showed that about half of the investigated inks were 'fast aging' and yielded low ratio even when still fresh and thus, a lowerthreshold value cannot be interpreted as coming from an old ink. Moreover, the time span that can be considered to date inks through solvent analysis using GC/MS is seriously questioned in the forensic community. Brunelle and Crawford stated that the ink dating technology which is based on GC/MS analysis cannot be used to date inks over six months old [15,46] and Bügler et al. recommended to analyze ink with a maximum age of 3-4 months [64]. The feasibility of such dating techniques on ink older than that must therefore be demonstrated.

Aginsky added that 'Both techniques (i.e., named here as methods 1 and 2) described have been used numerously in actual cases involving tax evasion, medical malpractice, altered wills, contractual disputes, rackets, corruption and organized crime, and many times the conclusions stated on the basis of the results of the ink dating examinations (accepted as conclusive by the courts of law in Russia) directly affected a case [52]'. The fact that acceptance by the courts is sometimes considered as proof of validation of methods, while stating that the same methods are probably too delicate to be reproduced correctly by scientific colleagues should be strongly questioned. In fact all dating methods should follow complete validation according the above-mentioned criteria (Table 8) before their application in court. In conclusion of this Section, Brunelle and Cantu underlined earlier the ethical responsibilities of forensic scientists performing ink dating examinations [27] by stating that 'Testimony involving ink dating that does not clearly state the significance of results obtained and the limitations of what can be concluded from the results of examination (...) would be unethical according to AAFS (American Academy of Forensic Sciences) guidelines because it would be misleading.'

5. Ink dating interpretation

Interpretation of ink dating evidence plays an essential role in the dating process and should not be underestimated in the development of dating methods [4]. It is very important to consider all the possible alternative hypotheses for the obtained result to allow for a balanced interpretation of the evidence [27,38,74,75,77]. A logical statistical framework based on a likelihood approach was proposed [38], because it is more correct than the threshold approach generally reported in the literature. It has the advantage of taking into account the occurrence of false positive results which cannot be completely avoided [27], particularly in a field with many influencing factors that may introduce additional errors.

For cases where an ink tests as being fresh Aginsky wrote [52] that 'If such a result has been obtained for a questioned document dated, e.g., by over a year preceding the analysis, the examiner can state with confidence that this document has been backdated.' One has to be particularly careful as such a statement is actually influenced by all the factors mentioned above. In fact, it is not unconceivable that an ink older than 8 months may in some circumstances show a ratio D above 12% (for example, an ink signature on a document placed in a plastic cover with several other documents also carrying ink entries and stored in a cold, humid room). Forensic interpretation must therefore take into account all logical possibilities (i.e., alternative sources for observed results) and the probability should not be expressed on the hypotheses (e.g., it is wrong to state the following: 'it is more probable that the ink is fresh given the obtained D% ratio'). In order to formulate a statement in a balanced way, the probability should actually be formulated on the evidence given two hypotheses (e.g. 'it is more probable to observe the obtained D% ratio if the ink is fresh rather than if the ink is old') [74,75,78]. The likelihood ratio (LR) is thus defined by the probability of observing a given value of D% if the ink is of age $t_1 = A$ months compared to the probability of observing the same D% value if the ink was older than A i.e., $t_2 = (A + n)$ months:

$$LR = \frac{p(D|t_1)}{p(D|t_2)} \tag{6}$$

For example, the evidence can be evaluated given the following two hypotheses:

- the prosecution states that the ink is 8 months old (t_1) ;
- the defence reports that the ink is 24 months old (t_2) .

Aginsky [45] reported that the mean value and the standard deviation for 8 months old blue ink strokes (from 50 different ballpoint pens) was $D = 7.56 \pm 1.13\%$, while the values for 24 months old blue ink strokes (from 30 different ballpoint pens) was $D = 1.25 \pm 0.85\%$. Accepting for simplicity that D values for a given time t_n are normally distributed, the LR can be calculated from the following equation [79,80]:

$$LR = \frac{f(D|\mu_{t_1}, \sigma_{t_1}^2)}{f(D|\mu_{t_2}, \sigma_{t_2}^2)}$$
(7)

where μ is the mean and σ^2 is the standard deviation of the *D*% value. The density of probability for a given value of *D* = *d* is


Fig. 7. Distribution of likelihood ratio (LR) calculated as a function of the D% values for the pair of proposition: the ink is 8 months old (t_1) and the ink is 24 months old (t_2). Up to a D% of 4, the evidence support the hypothesis t_2 , while for $D \ge 5$ %, the evidence is more probable given t_1 .

generally given by the following function [79,80]:

$$f(D|\mu,\sigma^2) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left[-\frac{(d-\mu)^2}{2\sigma^2}\right]$$
(8)

If a D% value of 5% is obtained for the scenario considered here, the LR is then written as follows:

$$LR = \frac{f(D|7.56, 1.13)}{f(D|1.25, 0.85)} = \frac{0.02065}{0.00011} \approx 188$$

This would mean that it is 188 times more likely to observe D = 5% if the ink is 8 months old (t_1) rather than if it is 24 months old (t_2) . This calculation can be repeated for all potential values of D in order to represent a distribution of possible LR for the given pair of propositions t_1 and t_2 as a function of D% (Fig. 7).

However, as can be seen both densities of probability are considerably low and the LR value may change considerably if another set of propositions were to be compared. Unfortunately, the necessary data is not available from the literature to test other scenarios. This logical approach to interpret ink dating evidence has two main advantages, non negligible for the court: (1) it is more correct because it takes into account the hypotheses of the justice and the error rate (false positive occurrence should not be neglected) and (2) it allows to test all possible scenarios and not limit the results to values above a certain threshold. Additionally this approach can be adapted to continuous data and the influence of several factors on the aging can be introduced in the model to evaluate their impact on the strength of evidence [79].

6. Conclusion

The drying of ink on paper can to some extent be compared to the drying of a towel. Thus if the towel was dipped in water or only used to wipe a wet surface, one takes longer to dry than the other (i.e., dependence on the initial quantity of solvent). If the towel is made of cotton or synthetic fabric, again the length of time to dry will differ (i.e., dependence on the type of substrate) and finally the time to dry will not be comparable if the towel was kept in a plastic bag or hung up outside exposed to the sun and wind (i.e., dependence on the storage conditions). Also, the evaporation and diffusion of the ink solvents can be compared to a drop of perfume on a piece of paper. Over time it evaporates and spreads laterally,

Table 9

Summary of minimum requirements necessary to reach a sufficient level of confidence in the development and application of dating methods.

Minimum requirements	Purpose
Study of aging kinetics and influencing factors	Define limit of applicability of the method
Description of methodology	Achieve transparency enabling reproduction by other laboratories
Validation of methodology	Reach intra and inter-laboratory reliability
Use of a logical interpretation model	Evaluate probability of evidence given alternative hypotheses

through the paper, and into any paper above and below that may be in contact with it. This is why, whatever the ink dating method used may be, the influence of factors such as those mentioned above must be quantified and taken into account when interpreting the results. At least some reservations should be expressed on the results if these were not known (Table 9).

Furthermore, ink dating methods should be validated by determining their limit of quantification, systematic error, repeatability (within laboratory precision) and reproducibility (between laboratories precision). For the latter, communication about the method should be open to allow other laboratories to reproduce it. This step of harmonisation between laboratories is not easy, but should not be underestimated. In fact, for a question as recurrent as the one of documents dating, the necessary resources should not be an issue for forensic laboratories around the world. Ideally the technique should then be submitted to blind testing by an outside qualified laboratory on realistic samples such as is done in many other forensic disciplines. This is not a small task because preparing older realistic samples is not straightforward. However the methods seem to work for ink up to 24 months old at most. It is therefore feasible.

This last requirement for ink dating methods is an adequate and logical interpretation model taking into account the methodology's error rates, which cannot be neglected in an ethical approach. Calculations of likelihood ratios should allow for balanced answers to the court considering both the prosecution and the defence hypotheses. This will give the justice the necessary information to consider all information at hand in a global Bayesian framework.

To conclude this article, we wish to quote from Professor Michael J. Saks' recent article: "Forensic identification: From a faith-based "Science" to a scientific science" [81]:

"What can forensic scientists do while waiting for a serious body of research to evolve that illuminates their particular subfield? The short answer is: honesty and humility. Confine reports and testimony within the bounds of the empirically tested findings of the field, intelligently understood (meaning: not relying excessively on any single study of a limited aspect of a phenomenon and not overgeneralizing). If very little is based on empirically tested findings, simply say so, while stating conclusions in a way that recognizes and respects the limits of the available knowledge. What one believes or hopes about a field and what one can know on existing research are not the same. Refrain from exaggerating what actually is known at the present stage of the field's development. Remain within the bounds of actual knowledge. Abandon claims of uniqueness and absoluteness. Recognize that forensic identification is a probabilistic endeavor. Abandon the use of misleading terminology, such as "match" or "identification" or "scientific certainty." Offer descriptions and opinions with clarity and candor. Offer conclusions with modesty, unless and until a body of serious empirically based knowledge allows more. Resist the culture of exaggeration. Strive for science-based, not faith-based, forensic science".

References

- R.L. Brunelle, Ink dating—the state of the art, Journal of Forensic Sciences 37 (1) (1992) 113–124.
- [2] A.A. Cantu, A sketch of analytical methods for document dating. Part I. The static approach: determining age independent analytical profiles, International Journal of Forensic Document Examiners 1 (1) (1995) 40–51.
- [3] A.A. Cantu, A Sketch of analytical methods for document dating. Part II. The dynamic approach: determining age dependent analytical profiles, International Journal of Forensic Document Examiners 2 (3) (1996) 192–208.
- [4] C. Weyermann, Dating a document, in: M.A.E. Jamieson (Ed.), Encyclopedia of Forensic Sciences, vol. III, John Wiley & Sons, Chichester, 2009, pp. 684–692.
- [5] M. Ezcurra, Analytical methods for dating modern writing instrument inks on paper, Forensic Science International 197 (2010) 1–20.
- [6] J.H. Bügler, M. Graydon, B. Ostrum, The practical use of the Munich ink reference collection in daily casework, in: 6th European Document Examiners Working Group (EDEWG) Conference, Dubrovnik, Croatia, 2010.
- [7] J. Stephens, R. Ramotowski, The digital ink library: a step forward, in: 6th European Document Examiners Working Group (EDEWG) Conference, Dubrovnik, Croatia, 2010.
- [8] J. Andrasko, M. Kunicki, Inhomogeneity and aging of ballpoint pen inks inside pf pen cartridges, Journal of Forensic Sciences 50 (2005) 542–547.
- [9] D.M. Grim, J.A. Siegel, J. Allison, Does ink age inside of a pen cartridge? Journal of Forensic Sciences 47 (6) (2002) 1294–1297.
- [10] Y. Kikuchi, Estimation of the age of the writing in blue black ink (I), Japanese Police Science Laboratory Report 12 (3) (1959) 379–386.
- [11] A.A. Cantu, R.S. Prough, On the relative aging of ink-the solvent extraction technique, Journal of Forensic Sciences 32 (5) (1987) 1151-1174.
- [12] A.A. Cantu, Comments on the accelerated aging of ink, Journal of Forensic Sciences 33 (3) (1988) 744–750.
- [13] R.L. Brunelle, A sequential multiple approach to determining the relative age of writing inks, International Journal of Forensic Document Examiners 1 (2) (1995) 94–98.
- [14] R.L. Brunelle, C.H. Breedlove, C.R. Midkiff, Determining the relative age of ballpoint inks using a single-solvent extraction technique, Journal of Forensic Sciences 32 (6) (1987) 1511–1521.
- [15] R.L. Brunelle, K.R. Crawford, Advances in the Forensic Analysis and Dating of Writing Ink, Charles C. Thomas Publisher, Ltd., Springfield, 2003.
- [16] R.L. Brunelle, H. Lee, Determining the relative age of ballpoint ink using a singlesolvent extraction, mass-independent approach, Journal of Forensic Sciences 34 (5) (1989) 1166–1182.
- [17] V.N. Aginsky, Some new ideas for dating ballpoint inks-a feasibility study, Journal of Forensic Sciences 38 (5) (1993) 1134–1150.
- [18] V.N. Aginsky, Determination of the age of ballpoint pen ink by gas and densitometric thin-layer chromatography, Journal of Chromatography A 678 (1994) 119–125.
- [19] V.N. Aginsky, A microspectrophotometric method for dating ballpoint inks–a feasibility study, Journal of Forensic Sciences 40 (3) (1995) 475–478.
- [20] L.F. Stewart, S.L. Guertin, Current status of ink age determination, in: Interpol (Ed.), 9th International Forensic Science Symposium, Vol. 429 (1991), International Criminal Police Review, 1989.
- [21] A.C. Mitchell, Estimation of the age of ink in writing, The Analyst XLV 435 (1920) 246–258 (reprinted in the Journal of Forensic Document Examiners 1991 (1991) (1995) 1956–1962).
- [22] Y. Kikuchi, Studies on the age of iron-gallotannate ink writing (II) the chromatic study of ink stain, Journal of Criminology 26 (2) (1960) 39–59.
- [23] Y. Kikuchi, Estimation of age of blue black ink writing (III), Japanese Police Science Report 16 (1) (1963) 83–86.
- [24] N.K. Sen, P.C. Gosh, Dating iron-based ink writings on documents, Journal of Forensic Sciences 16 (4) (1971) 511–520.
- [25] R.L. Brunelle, E.J. Speckin, Technical report with case studies on the accelerated aging of ballpoint inks-several cases on accelerated aging of ballpoint pen ink where the findings were admitted into court, International Journal of Forensic Document Examiners 4 (3) (1998) 240–254.
- [26] R.L. Brunelle, A.A. Cantu, A critical evaluation of current ink dating techniques, Journal of Forensic Sciences 32 (6) (1987) 1522–1536.
- [27] R.L. Brunelle, A.A. Cantu, Training requirements and ethical responsibilities of forensic scientist performing ink dating examinations, Journal of Forensic Sciences 32 (6) (1987) 1502–1508.
- [28] A.H. Lyter, Relative aging of ball pen ink: natural aging vs. artificial aging, in: American Academy of Forensic Sciences Meeting, San Antonio, TX, 1994.
- [29] T. Hicks Champod, A. Khanmy, P. Margot, Ink aging: perspectives on standardization, in: W.B.B. Jacob, W. Huckenbeck, P. Pieper (Eds.), 13th Meeting of the International Association of Forensic Sciences, Duesseldorf, 1993, Advances in Forensic Sciences 3, Forensic Criminalistics 1, Verlag Dr. Koester, Berlin, (1995), pp. 304–309.
- [30] J.E. Starrs, Ink dating up-dated and up-ended, International Journal of Forensic Document Examiners 1 (1) (1995) 3–5.
- [31] P. Margot, T. Hicks Champod, A. Khanmy, Ink dating up-dated and up-ended correspondence of Prof. Starrs, International Journal of Forensic Document Examiners 1 (1) (1995) 2–5.
- [32] L.F. Stewart, S.L. Fortunato, Distinguishing between relative ink age determinations and the accelerated aging technique, International Journal of Forensic Document Examiners 2 (1) (1996) 10–15.
- [33] V.N. Aginsky, Accelerated aging-its use in methods for dating ink, International Journal of Forensic Document Examiners 2 (3) (1996) 179–181.

- [34] V.N. Aginsky, Measuring ink extractability as a function of age—why the relative aging approach is unreliable and why it is more correct to measure ink volatile components than dyes, International Journal of Forensic Document Examiners 4 (3) (1998) 214–230.
- [35] T. Andermann, R. Neri, Solvent extraction techniques—possibilities for dating ball point pen inks, International Journal of Forensic Document Examiners 4 (3) (1998) 231–239.
- [36] K. Jahns, Altersbestimmung von Schreibmitteln durch Chemische Analyseverfahren, Mannheimer Hefte Für Schriftvergleichung (Peter Baier) 3 (04) (2004) 120– 129.
- [37] C. Weyermann, Revue des méthodes de datation de l'encre: Est-il possible de déterminer l'âge d'un document en analysant l'encre? Revue Internationale de Criminologie et de Police Technique et Scientifique 3 (LXI) (2008) 359–376.
- [38] C. Weyermann, B. Schiffer, P. Margot, A logical framework to ballpoint ink dating interpretation, Science & Justice 48 (3) (2008) 118–125.
- [39] C. Weyermann, D. Kirsch, C. Costa-Vera, B. Spengler, Photofading of ballpoint dyes studied on paper by LDI and MALDI MS, Journal of the American Society for Mass Spectrometry 17 (3) (2006) 297–306.
- [40] C. Weyermann, D. Kirsch, C. Costa-Vera, B. Spengler, Evaluation of the photodegradation of crytsal violet upon light exposure by mass spectrometric and spectroscopic methods, Journal of Forensic Sciences 54 (2) (2009) 339– 345.
- [41] C. Weyermann, W. Mazzella, P. Margot, Commentary on: Berger-Karin C, Hendricks U, Geyer-Lippmann J. Comparison of natural and artificial aging of ballpoint inks. J Forensic Sci 2008;53(4):989–92, Journal of Forensic Sciences 54 (4) (2009) 967.
- [42] C. Weyermann, B. Spengler, The potential of artificial aging for modelling of natural aging processes of ballpoint ink, Forensic Science International 108 (2008) 23–31.
- [44] L.F. Stewart, Ballpoint ink age determination by volatile component comparisona preliminary study, Journal of Forensic Sciences 30 (2) (1985) 405–411.
- [45] V.N. Aginsky, Current Methods for Dating Ink on Documents, 60th Annual Conference of the American Society of Questioned Document Examiners, San Diego, California, 2002 http://www.rileywelch.com/ink.htlm.
- [46] V.N. Aginsky, Current Methods for Dating Ink on Documents, 65th Annual Conference of the American Society of Questioned Document Examiners, Boulder, CO, 2007.
- [47] J. Andrasko, Ink Dating Using SPME and Methanol Extraction, 3rd Meeting of the European Network of Forensic Science Institutes, Istanbul, 2003.
- [48] M. Ezcurra, I. Velasco, J.M.G. Góngora, M.I. Maguregui, R.M. Alonso, Analysis of bic crystal medium ballpoint pen inks, Journal of the American Society of Questioned Document Examiners 12 (2) (2009) 57–68.
- [49] M. Gaudreau, L. Brazeau, Ink Dating Using A Solvent Loss Ratio Method, 60th Annual Conference of the American Society of Questioned Document Examiners, San Diego, CA, 2002.
- [50] S. Lociciro, W. Mazzella, L. Dujourdy, E. Lock, P. Margot, Dynamic of the ageing of ballpoint pen inks: quantification of phenoxyethanol by GC/MS, Science & Justice 44 (3) (2005) 165–171.
- [51] C. Weyermann, D. Kirsch, C. Costa-Vera, B. Spengler, A GC/MS study of the drying of ballpoint pen ink on paper, Forensic Science International 168 (2–3) (2007) 119–127.
- [52] V.N. Aginsky, Dating and characterizing writing, stamp, pad and jet printer inks by gas chromatography/mass spectrometry, International Journal of Forensic Document Examiners 2 (2) (1996) 103–116.
- [53] J. Andrasko, Some examples of applications of a microthermal desorption device in the forensic laboratory, Journal of Forensic Sciences 54 (5) (2009) 1055–1058.
- [54] L. Brazeau, M. Gaudreau, Ballpoint pen inks: the quantitative analysis of ink solvents on paper by solid-phase microextraction, Journal of Forensic Sciences 52 (1) (2007) 209–215.
- [55] J.H. Bügler, H. Buchner, A. Dallmayer, Age determination of ballpoint ink by thermal desorption and gas chromatography-mass spectrometry, in: ASQDE (Ed.), 63 rd Annual Conference of the American Society for Questioned Document Examination (ASQDE), Montréal, Canada, 2005.
- [56] J.H. Bügler, H. Buchner, A. Dallmayer, Age determination of ballpoint pen ink by thermal desorption and gas chromatography-mass spectrometry, Journal of Forensic Sciences 53 (4) (2008) 982–988.
- [57] G.M. LaPorte, J.D. Wilson, C.A.A., S.A. Mancke, S.L. Fortunato, The identification of 2-phenoxyethanol in ballpoint inks using gas chromatography/mass spectrometry-relevance to ink dating, Journal of Forensic Sciences 49 (1) (2004) 155–159.
- [58] C. Berger-Karin, U. Hendriks, J. Geyer-Lippmann, Comparison of natural and artificial aging of ballpoint inks, Journal of Forensic Sciences 53 (4) (2008) 989–992.
- [59] J. Almog, Unsolved problems in forensic science, Plilim, Israeli Journal of Criminal Justice II (1991) 67–87.
- [60] J.H. Bügler, H. Buchner, A. Dallmayer, Characterization of ballpoint pen inks by thermal desorption and gas chromatography-mass spectrometry, Journal of Forensic Sciences 50 (5) (2005) 1–6.
- [61] C. Weyermann, Mass Spectrometric Investigation of the Aging Processes of Ballpoint Ink for the Examination of Questioned Documents, Faculty of Biology and Chemistry, Justus-Liebig University, 2005 available on-line: http://geb.unigiessen.de/geb/volltexte/2006/3044/.
- [62] M.G. Ezcurra, J.M.G. Góngora, I. Maguregui, R. Alonso, 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, Journal of the American Society for Questioned Document Examiners 13 (1) (2010) 9–14.

- [63] J.H. Bügler, in: B.U. Landeskriminalämte (Ed.), Analytische Untersuchung von Lösungs- und Bindemitteln in Schreibmitteln, Urkunden-Konferenz, Berlin, Germany, 2004.
- [64] J.H. Bügler, H. Buchner, A. Dallmayer, Age determination of ballpoint pen inks, in: ENFSI (Ed.), 4th Conference of the European Document Examiners Working Group (EDEWG), The Hague, Netherlands, 2006.
- [65] D. Kirsch, V. Guillou, B. Anheier, P. Seiler, F. Köhler, Different analytical methods of dating ball point ink entries, in: ENFSI (Ed.), 6th European Document Examiners Working Group (EDEWG) Conference, Dubrovnik, Croatia, 2010.
- [66] Y. Wang, L. Yao, P. Zhao, J. Wang, Y. Wang, Determination of the writing age of blue ballpoint ink by gas chromatography, Chinese Journal of Chromatography 23 (2) (2005) 202–204.
- [67] Y. Wang, L. Yao, P. Zhao, J. Wang, Y. Wang, Determining the relative age of blue ballpoint ink by gas chromatography, Frontiers of Chemistry in China 2 (223–226) (2006).
- [68] J.H. Bügler, Method validation for age determination of ballpoint inks, in: ENFSI (Ed.), 5th Annual Conference of the European Document Experts Working Group (EDEWG), Bunratty, Ireland, 2008.
- [69] S. Kromidas, Handbuch Validierung in der Analytik, Wiley-VCH, Weinheim, 2000.[70] J. Neumann, R. Kent, H. Bellison, B. Hart, The mean square successive difference,
- Annals of Mathematical Statistics 12 (2) (1941) 153-162. [71] W. Horwitz, Evaluation of analytical methods used for regulation of foods and
- drugs, Analytical Chemistry 54 (1) (1982) 67A–76A.

- [72] M. Thompson, S. Ellison, R. Wood, Harmonized guidelines for single-laboratory validation of methods of analysis, Pure Applied Chemistry 74 (2002) 835–855.
- [73] P. Margot, A question of time, Science & Justice 40 (2) (2000) 64-71.
- [74] G. Jackson, The scientist and the scales of justice, Science & Justice 40 (2) (2000) 81-85.
- [75] I.W. Evett, 'It's not rocket science.' Wouldn't it be wonderful if judges understood the principles of evidence interpretation? in: 7th International Conference on Forensic Inference and Statistics, Lausanne, 2008.
- [76] A. Zeichner, Letter to Aginsky V.N. dated 16 May 1997, 2010 http://www.rileywelch.com/Proftest1.jpg (last accessed August 2010).
- [77] I.W. Evett, Bayesian inference and forensic science: problems and perspectives, The Statistician 36 (1987) 99–105.
- [78] C.G.G. Aitken, F. Taroni, Statistics and the evaluation of evidence for forensic scientists, in: Statistics in Practice, 2nd ed., Wiley, West Sussex, England, 2004.
- [79] M. Gallidabino, A Pragmatic Approach for Evidential Assessment in Cases Involving the Estimation of Time Since Discharge, Institut de Police Scientifique, University of Lausanne, 2010, pp. 1–47.
- [80] A. Biedermann, F. Taroni, A probabilistic approach to the joint evaluation of firearm evidence and gunshot residues, Forensic Science International 163 (2006) 18–33.
- [81] M.J. Saks, Forensic identification: from a faith-based "Science" to a scientific science, Forensic Science International 201 (1–3) (2010) 14–17.

Exhibit 12

Declaration of Larry F. Stewart





Standard Guide for Test Methods for Forensic Writing Ink Comparison¹

This standard is issued under the fixed designation E 1422; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

INTRODUCTION

This guide is intended to be a general guide for forensic ink examinations, both for the experienced document examiner (**E 444**) and for forensic ink comparison specialists. The aim is to include those techniques that will provide the most information about an ink with the least damage to the document. Therefore, this guide refers to well-reported and thoroughly tested techniques currently in use by document examiners in general practice and dedicated forensic ink comparison facilities.

By following the procedures outlined here, an examiner can accurately discriminate ink formulas and reduce the possibility of false matches of ink samples from different sources or incorrect differentiation of ink samples with a common origin.

1. Scope

1.1 This Guide is intended to assist forensic examiners comparing writing or marking inks. Included in this analysis scheme are the necessary tools and techniques available to reach conclusions as to the common or different origin of two samples of ink.

1.2 Identifying ink formulas as to their manufacturer or time of manufacture as well as performing ink dating examinations are beyond the scope of this guide.

1.3 This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2. Referenced Documents

2.1 ASTM Standards: ²

D 1535 Practice for Specifying Color by the Munsell System

E 131 Terminology Relating to Molecular Spectroscopy

E 284 Terminology of Appearance

E 444 Descriptions of Scope of Work Relating to Forensic Document Examiners

2.2 NIST Standards:

NBS Standard Sample No. 2106 ISCC-NBS Centroid Color Charts³

NBS Special Pub. 440 Color: Universal Language and Dictionary of Names³

3. Terminology

3.1 Definitions:

3.1.1 *batch to batch variation—within an ink formulation,* difference in the concentration of a component of an ink formula due to deviations during production that are within the manufacturer's tolerance limit.

3.1.2 *chromatography*—a method of separating substances that is widely used in analytical and preparative chemistry. It involves the flow of a liquid or gas mobile phase over a solid or liquid stationary phase. As the mobile phase flows past the stationary phase, a solute will undergo repeated adsorption and desorption and move along at a rate depending, among other factors, on its ratio of distribution between two phases. If their distribution ratios are sufficiently different, components of a mixture will migrate at different rates and produce a characteristic pattern (chromatogram).

3.1.3 *fluorescence*—a process by which radiant flux of certain wavelengths is absorbed and reradiated nonthermally at other, usually longer, wavelengths. (E 284)

3.1.4 *infrared (IR)*—referring to radiant flux having wavelengths longer than the wavelengths of light, usually wavelengths from about 760 nm to about 3 mm. (E 284)

3.1.5 *light*—electromagnetic radiant energy that is visually detectable by the normal human observer, radiant energy having wavelengths from about 380 nm to about 780 nm.

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¹ This guide is under the jurisdiction of ASTM Committee E30 on Forensic Sciences and is the direct responsibility of Subcommittee E30.02 on Questioned Documents.

Current edition approved Dec. 1, 2005 Published January 2006. Originally approved in 1991. Last previous edition approved in 2001 as E 1422 – 01.

² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

³ Available from U.S. Department of Commerce, National Bureau of Standard Reference Materials, R. B311, Chemistry Building, Gaithersburg, MD 20899.

(E 284)

3.1.6 *luminescence*—the emission of radiant energy during a transition from an excited electronic state of an atom, molecule or ion to a lower electronic state. (E 131)

3.1.7 *metamers*—specimens differing in spectral reflectance but having colors that match in light of one spectral composition, when viewed by one observer, but may not match in light of other spectral compositions, or when viewed by another observer. (E 284)

3.1.8 *spectroscopy*—in the most general sense spectroscopy is the study of the absorption or emission of electromagnetic energy by a chemical species as a function of the energy incident upon that species.

3.1.9 *source*—an object that produces light or other radiant flux. (E 284)

3.1.10 *ultraviolet (UV)*—referring to radiant flux having wavelengths shorter than the wavelengths of light, usually wavelengths from about 10 nm to 380 nm.

3.1.10.1 *Discussion—Long-wave UV* usually refers to the spectral range of UV-A, with wavelengths from about 315 nm to 380 nm. *Short wave UV* usually refers to the spectral range of UV-C, with wavelengths from about 100 nm to 280 nm.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *ballpoint pen ink*—writing or marking media intended for use in a ball point pen. Typically, a thick, high viscosity ink with an oil, glycol or rubber base.

3.2.2 *dichroic filter*—a filter with two transmission bands. These bands are usually widely separated, and can be of significantly different size.

3.2.3 gel pen ink—writing or marking media intended for use in a "gel-type" roller pen. Gel pen inks constitute a unique class of non-ballpoint pen inks. Typically, gel pen ink is an aqueous ink of high viscosity, capable of maintaining a stable dispersed or dissolved state of the coloring material even after a prolonged period and exhibiting high fluidity under a shearing force. The ink contains a coloring material (pigment or dyes), acid-modified heteropolysaccharide and aqueous medium (water and water-soluble organic solvent), in which water constitutes at least 50 % by weight. Due to the incorporation of pigments into these formulations, the procedures outlined in this guide for TLC evaluations will be of limited value.

3.2.4 *infrared luminescence (IRL)*—the emission of radiant energy during a transition from an excited electronic state of an atom, molecule or ion to a lower electronic state (fluorescence or phosphorescence, or both), where the spectrum of the excitation source is in the ultraviolet (UV) or visible region of the electromagnetic spectrum, or both, and the spectrum of the emitted energy is in the far red or infrared (IR) region of the electromagnetic spectrum.

3.2.5 *ink formula*—a precise recipe or set of ingredients and their quantities that the manufacturer specifies for the final ink product. These ingredients are colorants (dyes and pigments) and vehicle components (volatile solvents, resins, etc.).

3.2.6 *match between ink samples*—the inability to distinguish between ink samples at a given level of analysis.

3.2.7 *non-ballpoint pen ink*—writing or marking media intended for use in a writing or marking instrument other than

a ballpoint pen, including a dip or fountain pen, porous point pen, roller pen, marking instrument, etc. Typically, a thin, low viscosity ink with a water or solvent base.

4. Significance and Use

4.1 Ink comparisons are usually performed to answer four basic categories of question: (1) whether an ink is the same (in formula) as that on other parts of the same document or on other documents; (2) whether two writings with similar ink have a common origin, that is, the same writing instrument or ink well; (3) whether the ink of entries dated over a period of time is consistent with that dating or indicates preparation at one time; (4) whether ink is as old as it purports to be (1).⁴

4.2 The procedures set forth in this guide are directly applicable to giving a full answer to only the first of these four questions.

4.3 With regard to the second question, differentiation of formula (question one) would indicate a negative answer to this question, as would differentiation with any of the additional methods listed in Section 3. When dealing with contemporary inks, however, a match of ink samples involving agreement in all observable aspects of all the techniques considered in this guide, while consistent with common origin, would not be sufficient to support a definite opinion of common origin (2). Contemporary ink rarely has sufficient individuality to support a determination of common origin at less than the manufacturing batch level.

NOTE 1—Contemporary mass-produced inks are usually distributed as a component in a complete writing instrument or in a cartridge. With such packaging the ink is not subject to the mixing of inks and exposure to environmental contamination that could individualize ink from a given ink well at a specific point in time (1, 3). This sort of analysis, potentially useful in the examination of older documents or those prepared under certain circumstances, is beyond the scope of this guide, as is examination of the ink line to individualize the writing instrument that produced it based on its performance characteristics.

4.4 As to the third and fourth questions involving the age of ink, dating techniques for determining either the relative age of ink samples (from the same or different documents) or the absolute amount of time since the writing of an ink line are also beyond the scope of this guide.

4.5 However, regarding question three, it may be of great importance in a forensic situation involving writing dated over a period of time to determine that one or more than one ink formula is present, that the use of various ink formulas fits a pattern, that a particular ink formula matches samples of a known date, etc.

4.6 As to the last question, a limit as to the possible age of an ink entry can be inferred by establishing the date of first production of the ink formula. Although beyond the scope of this guide, identifying ink formulas as to their manufacturer or time of manufacture utilizes many of the analytical procedures described here. Specialized knowledge and experience on the part of the examiner, as well as access to a collection or *library* of ink reference samples is also required.

⁴ The boldface numbers in parenthesis refer to the list of references at the end of this guide.

4.6.1 Such an ink library consists of samples of ink formulas from known sources, usually manufacturers of ink, or writing or marking instruments, or a combination thereof. The ink reference samples are usually cataloged, analyzed, and stored according to the methods described in Refs (2, 4, 5 and 6). Even with access to a comprehensive collection, association of an unknown ink sample with a single known formula is not always possible. This is because some ink formulas are not distinguishable, however, in most cases the analytical procedures outlined here are sufficiently discriminating that formulas are distinguishable.

4.7 Comparison of ink samples by analysts without an ink library can still provide valuable information. However, added significance can be given to the meaning of a match if the relative rarity or commonness of the ink formula is known. Familiarity with or access to a comprehensive reference collection of inks is useful for this purpose.

4.8 In expressing conclusions it should be remembered that a match indicates that the ink samples are of the same formula or of two similar formulas with the same nonvolatile components. The possibility that other analytical techniques might be able to differentiate them should always be considered (2).

4.8.1 Therefore, conclusions in this situation should never indicate that two ink samples are "identical" or "the same ink," but must be limited to statements indicating "inability to distinguish the ink samples at this level of analysis" or "exhaustive chemical and physical testing failed to detect any differences between the ink samples" (2).

5. Interferences

5.1 Most interferences with ink examinations come from variables that interact with the ink. These can be part of the writing process, such as blotting wet ink (1, 2), or variations in the paper (7), or various forms of contamination on the document (7, 8), or a combination thereof. Simple precautions can usually avoid problems.

5.2 Note and record any differences in the substrate, such as the use of different paper for different documents or pages of a multipage document. Also note and record variations in the document, such as a signature written over a photograph on an identity document, multicolored paper with different dyes or colors of underprinting, intersections with printed or typed material, etc. (7, 8).

5.3 The results of prior handling or testing should also be noted and recorded. These effects can include discoloration or fading from ageing, exposure to light or heat, as well as stains from food or drink, dirt or grease, cellophane or other tape, adhesives, perspiration or finger smudges, water, or chemicals, including ninhydrin or other reagents for visualizing latent friction ridge impressions, etc. (7, 8, 9).

5.4 In optical examinations care should be taken to consider the potential effects of these variables (7, 8). In chemical analyses paper blanks should be run as controls for these variables (4, 5).

6. Reagents and Equipment

NOTE 2-It is important that all reagents are uncontaminated.

6.1 Purity of Reagents-Reagent Grade.

6.2 Purity of Water-Distilled or equivalent.

6.3 Reagents for Spot Testing, Solubility Testing, and TLC Extraction Solvents:

6.3.1 Pyridine.

6.3.2 Ethanol.

6.3.3 Water.

6.3.4 Other reagents as required by Refs (1, 3, and 23).

6.4 Reagents for Thin Layer Chromatography (TLC) Developing Solvents:

6.4.1 Solvent System I—Ethyl acetate, ethanol, water (70 + 35 + 30).

6.4.2 Solvent System II—N-butanol, ethanol, water (50 + 10 + 15).

6.5 Other ink extracting solvents and developing solvents in accordance with Refs (5, 6, and 10).

6.6 Equipment for Optical Examinations:

6.6.1 *Stereomicroscope*:

NOTE 3—Five to one hundred power total magnification is a range that has been found useful.

6.6.2 *UV Lamps or View Box*, with both long-wave UV and short-wave UV lamps.

6.6.3 *Colored Filters*, (gelatin, colored glass, interference filters) as needed for visual and photographic differentiation of inks.

6.6.4 Dichroic Filters, See Ref (11).

6.6.5 Photographic or other imaging equipment with appropriate film or other sensor, lighting, and filters for differentiation of ink samples.

6.6.6 Photographic or other imaging equipment with appropriate film or other sensor, lighting, and filters for recording reflected infrared (RIR) and infrared luminescence (IRL).

6.6.7 IR image conversion device or system with appropriate light sources and filters for use in RIR and IRL modes as well as appropriate photographic or other imaging equipment, computer hardware and software for image acquisition or processing, or both.

6.6.8 *Barrier Filters for RIR and IRL*—Long pass filters, preferably sharp cut, that block visible flux. Suitable gelatin, colored glass, and interference filters are commercially available (12, 13, 14).

NOTE 4—Since ink reactions can vary, it is advisable to use a series of filters with cut on wavelengths from the red through the IR range of the film or detector.

6.6.9 *Excitation Source for IRL*—Sources include: a continuous spectrum lamp with a filter to eliminate flux in the IR and far red region of the spectrum, for example, a 10 % to 15 % solution of copper sulfate in a cell with a 1 cm to 3 cm light path, or appropriate colored glass or interference filters; or lasers or other monochromatic sources.

NOTE 5—A variety of sources with different spectral distributions or a variety of filters on a continuous spectrum source may be helpful in discriminating ink samples.

When using a filtered source it is advisable to use a heat absorbing filter between the source and the filter. This both protects the filter (15) and eliminates a significant portion of the undesirable IR flux.

6.6.10 Photographic or other imaging equipment for recording observations as required. 6.7 Equipment for Spot Testing, Solubility Testing, and TLC—It is important that all equipment is uncontaminated.

6.7.1 Stereomicroscope (See Note 2).

6.7.2 *Hypodermic Needle*, with an approximately 20 gage hollow boring point or blunted point, scalpel or similar sampling device.

6.7.3 *Disposable Vial or Transparent Sample Container*—1 dram or smaller suggested.

6.7.4 Disposable Micropipettes—10 μ L or smaller suggested.

6.7.5 *Precoated Plastic or Glass Sheets/Plates of Silica Gel*, without fluorescent indicator (60 Å pore size⁵).

Note 6—It is recommended that the TLC sheets/plates be kept in a desiccator.

6.7.6 *Glass Developing Tank with Air Tight Cover*—This tank should be the appropriate size for the sheet/plate being developed.

6.7.7 UV Lamps or View Box, with both long-wave UV and short-wave UV lamps.

6.8 Appropriate equipment for the additional methods listed in Section 8.

6.9 All equipment and apparatus shall be properly maintained and calibrated.

7. Procedure

NONDESTRUCTIVE OPTICAL EXAMINATIONS

7.1 Light Examination:

7.1.1 Determine the Class of Ink—Under ambient lighting conditions (natural or artificial), with or without the aid of magnification as required, determine whether the class of the ink is ballpoint pen or non-ballpoint pen (6). Observe the overall appearance of the writing. Note and record anything that might provide information about the kind of writing or marking instrument used. For example, if there is an indentation down a central *track*, then the writing instrument may be a ballpoint pen or rolling ball marker. Double indentations may indicate a bifurcated nib dip pen or fountain pen. This step may be performed with the use of reference standards prepared with various classes of writing instruments on different substrata.

7.1.2 Determine the Condition of the Ink and the Overall Appearance of the Writing—Note and record the presence of anything that might have induced a change in the ink as described in Section 2; for example, stains, burns, aging, blotting, fading, attempts at mechanical erasure or chemical eradication, discolorations, etc.

7.1.3 Determine the Color of the Ink—Inks that are metamers can sometimes be differentiated by the use of illuminants with varying color temperatures or spectral characteristics, as well as by narrow band or laser illumination. Various filters can also be used for direct viewing, photography, or electronic viewing, including wide and narrow band, short and long pass, and dichroic filters (1, 6, 11, 16).

NOTE 7-The use of standard color notation may be helpful in

recording these observations. (NBS Standard Sample No. 2106, NBS Special Pub. 440)

7.1.4 Microspectrophotometry (17) can be useful in differentiating inks by measuring their wavelengths of maximum transmission or reflectance spectra, or both.

7.2 Ultraviolet (UV) Examination:

7.2.1 Observe the ink sample under both long-wave UV and short-wave UV sources. Note and record the fluorescence characteristics of the ink as well as the emission of any fluorescence (18). (See Note 7.)

NOTE 8—Except for some red formulas, few inks fluoresce in their dried state on paper. A fluorescent halo is occasionally observed around an ink line; capillary migration of a vehicle component into the substrate is a known cause.

7.2.2 Note and record any effect of the substrate. Strong fluorescence of the paper may affect the observer's perception of the ink.

7.2.3 UV examination may reveal indications that the document has been stained by chemicals or other material that may affect the ink comparison as discussed in Section 5 (7, 8, 9). These can include the detection of the use of chemical ink eradicators, liquid or dry opaquing material, cellophane or other tape, adhesives, etc., that may have significance beyond the ink comparison. These should be noted and recorded.

7.3 Infrared (IR) Examination:

7.3.1 Determine the Reflected Infrared (RIR) and Infrared Luminescence (IRL) characteristics of the ink: As these effects are beyond the range of human vision, some technological extension of the eye is required.

7.3.1.1 These characteristics may be photographed with IR sensitive film or observed directly with an IR image conversion device (7, 8, 11, 15, 16, 19, 20, 21). With either system, a suitable barrier filter is required in front of the lens to block visible flux (see 6.6.8 and Note 4). For IRL a suitable excitation source will also be required (see 6.6.9 and Note 5).

NOTE 9—Both photographic and electronic systems work well; each has its advantages and drawbacks.

Photography provides a permanent, high resolution record of results and long exposures can capture faint luminescence. However, exposures can be long (up to 20 min. for faint luminescence), and considerable experience is required before dispensing with time consuming bracketing in a series of exposures using different filters (19, 20). The amount of time required for processing and printing may also be a problem.

Electronic systems, including units with image conversion tubes and closed circuit television systems, have the advantage of real time results, facilitating optimization of filter combinations, focus, exposure, etc. (21). These systems are well suited to screening batches of documents (such as passports) for alterations. However, resolution is limited, some faint luminescence may not be easy to detect, and separate photographic or electronic imaging equipment is required to record results. Modern integrating infrared video cameras are able to detect faint IR information that cannot be seen otherwise.

7.3.2 Reflected Infrared (RIR):

7.3.2.1 Record the characteristics as opaque or transparent, indicating the degree of opacity. The more opaque the ink (the more it absorbs), the darker it will appear; the less opaque, the lighter it will appear, until it seems to be transparent or to drop out. An arbitrary four point scale of -3 to 0 (opaque to transparent) may assist in recording these observations. 7.3.3 Infrared Luminescence (IRL):

 $^{^5\,\}rm Merck$ Silica Gel, Whatman PE SIL G, and Merck HPTLC Silica Gel 60 have been found satisfactory.

7.3.3.1 Record the IRL characteristics of the ink relative to the substrate as darker, similar, or lighter, indicating degree as appropriate. Ink that luminesces more brightly than the substrate will appear lighter than the substrate; strongly luminescent ink may appear to glow brightly. If ink does not luminesce or does not luminesce as brightly as the substrate, the ink will appear darker than the substrate (this is sometimes referred to as *black luminescence* or *negative luminescence*). Ink that luminesces at an intensity similar to that of the substrate appears invisible, and is said to *drop out*. An arbitrary seven point scale of -3 to 0 to +3 (black to indistinguishable to very bright) may assist in recording these observations.

NOTE 10—Depending on the characteristics of the substrate and the combination of source or filters, or both, the appearance of ink samples with the same formula can vary from nonluminescing to strongly luminescent. The appearance of ink luminescence can be affected by the amount of ink and the substrate.

7.3.3.2 A luminescent halo is occasionally observed around an ink line; capillary migration of a vehicle component into the substrate is a known cause.

7.3.3.3 Inks that luminesce with similar but not identical intensity can sometimes be differentiated by placing a nonluminescing or brightly luminescing object behind the substrate (22).

7.4 When recording UV fluorescence, IR absorption, and IRL characteristics of an ink sample, it is important to note and record any influence imparted by the substrate. It is also important to be aware of factors (such as those discussed in Section 2) that may affect the results of this portion of the examination (7, 8, 9).

7.5 The reaction of an ink sample can vary at different wavelengths. Therefore, in differentiation of ink samples it is useful to use a range of different light sources, filters, filter combinations, etc. (16) (See Note 4 and Note 5). In noting and recording the reaction of the ink sample, also record the source, filters, etc.

CHEMICAL EXAMINATIONS

7.6 Spot Testing and Solubility Testing:

7.6.1 Spot testing of an ink sample can be done directly on the substrate. Minimal damage to the document is possible if the solvents are applied in small amounts to the ink line and the resulting changes are observed under magnification. Spot testing of an ink sample can be done on a removed sample, if performing the test in situ is not indicated. These tests can be used to differentiate ballpoint and non-ballpoint ink based on the solvent that solubilizes the vehicle, to determine the proper extraction solvent for subsequent analysis, or to provide presumptive information on the colorants used in the ink formula.

NOTE 11—These tests may consume a great deal of material relative to the amount of information provided.

7.6.2 Spot tests to determine the solubility or color reaction of an ink sample to various reagents were once widely used to differentiate ink formulas and to presumptively identify the constituents of an ink formula. Information on older ink formula can be found in Osborn (1) and Mitchell (3). A study

of more modern blue ballpoint inks has been conducted, and an analytical scheme published (23).

7.6.3 At present spot tests are most often used to differentiate ballpoint and non-ballpoint ink based on the solvent that solubilizes the vehicle. Ballpoint inks are either oil based or glycol based. Oil based ballpoint inks were used in the earliest ballpoint pens. Generally, glycol based ballpoint inks (widely used since around 1950) are very soluble in pyridine. Inks formulated for fountain pens, porous point pens, and roller pens are generally water or alcohol based and compositions that are readily soluble in ethanol and water (1 + 1) (2). Indelible markers are solvent based and would generally be soluble in pyridine. Note and record the results. If TLC is planned, these results can be used for selecting the appropriate extracting solvent.

7.6.4 These tests, performed in situ or on a removed sample with various solvents, can be sufficient to determine that two or more ink samples are not of the same ink formula. In many situations, once such a determination is made, further testing may be unnecessary.

7.7 Chromatography—Thin Layer Chromatography (TLC)—Many forms of chromatography have been used successfully to differentiate writing inks, including paper chromatography, high pressure liquid chromatography (HPLC), gas chromatography (GC), and thin layer chromatography (TLC). Except for substrate specific items, the procedure for paper chromatography is similar to TLC (**2**, **5**).

7.7.1 *TLC Sheet/Plate Activation*—Activate a TLC sheet/ plate in a pre-heated oven (approximately 100°C for 10 to 15 minutes) immediately prior to spotting. Allow sheet/plate to cool.

NOTE 12—Heating the sheet/plate merely drives off plate moisture. If the sheet/plate were stored under ideal desiccate conditions, activation would theoretically be unnecessary; however, it would still be advisable to heat the sheet/plate as a precaution.

7.7.2 Sampling for TLC:

7.7.2.1 Using a blunted or hollow boring hypodermic needle, or similar device, remove a sufficient number of plugs (usually 7 to 10 plugs of ink from a line are sufficient). If a scalpel is used, remove about 1 cm of the line. The number of plugs (or length of line) required depends on the concentration and solubility of the ink.

7.7.2.2 Avoid sampling areas on a document that may be contaminated by writing on the reverse, or by stains or other contaminants on either side. (See Section 2)

7.7.2.3 Place the plugs of ink in a vial.

7.7.2.4 Place the same number of plugs of paper (or the same size piece of paper) from a control area of the substrate in another vial.

7.7.2.5 If the writing is limited, microsampling techniques using a single plug may be necessary (24).

7.7.3 Extracting the Ink:

7.7.3.1 Add approximately 3 to 5 μ L of solvent (pyridine for ballpoint inks or ethanol and water (1 + 1) for non-ballpoint inks) to the vials. (Other solvents may be used based on the ease of extraction. The comparison standard inks must have been extracted using the same solvent.) The amount may vary depending on the absorptivity of the substrate and the type and

age of the ink line. Adjust the amount of extracting solvent as needed. If both ballpoint and non-ballpoint ink from the same sheet of paper (or other substrate) are being analyzed, two paper control samples will be necessary since the ink extractions will require two solvents and each solvent may extract different components from the substrate.

7.7.3.2 Gently agitate the plugs and solvent for approximately 1 min or until sufficient extraction has occurred. Note and record the color of extract in the vial. The use of standard color notation may be helpful in recording these observations. (Test Method D 1535, NBS Standard Sample No. 2106, NBS Special Pub. 440)

7.7.4 Spotting the Ink:

7.7.4.1 Spot the extract on the activated TLC sheet/plate approximately 15 mm from the designated bottom of the plate. It is important to maintain uniformity in the intensity and size of the spot (a spot size of approximately 2 to 3 mm works well). Spots should be placed no closer than 1 cm from either the left or right side of the plate and should be adequately separated so they will not interfere with each other during the migration of the components of the sample. The boundaries (left and right) of each area to be spotted may be scribed with a stylus or pencil. Do not place these boundary marks closer than 1 to 2 mm from the area of the plate to be spotted. This is so there will be no interference for the solvent system traveling up the plate. If a pencil is used, do not spot the extract directly on the pencil mark or in the same lane since many inks contain carbon or graphite, as do pencils.

7.7.4.2 Numerous ink samples can be analyzed simultaneously by spotting each ink sample and paper blank on the same chromatographic sheet/plate with sufficient separation to avoid interference or cross contamination, or both. These spots should be equal in intensity and size. This is attainable through manipulation of the number of ink plugs (or length of ink line) and the amount of extracting solvent. If the maximum number of samples are to be compared on a sheet/plate, do not spot the extract closer than 1 cm from either side of the plate. Extraction spots placed closer to the edge of a plate can cause a skewed separation that may affect the comparative value of the chromatogram.

7.7.4.3 Allow the sheet/plate to air dry to remove any residual solvent. The amount of time will vary depending on the laboratory conditions and the solvent(s) utilized. Do not expose the sheet/plate to extreme heat or light during the spotting procedure. This has been shown to induce changes in the resultant chromatograms of some ink formulas (5, 9).

7.7.4.4 If the intensity of the spot is weak, it may be necessary to respot. This is done by carefully applying additional extract directly over the original spot and air drying again.

NOTE 13—This technique requires experience. It is important to keep the spot size consistent when respotting (for example, do not spot a 1 mm spot over an existing 2 mm spot). Otherwise you may create rings that can skew the appearance of the resulting separation. Respotting can be accomplished through the careful adjustment of the amount of extract to be spotted.

7.7.4.5 Use of a suitable calibration standard is recommended. It should be spotted onto the plate in the same manner.

7.7.5 Developing the TLC Sheet/Plate:

7.7.5.1 Place the sheet/plate in a developing tank previously equilibrated for approximately 15 min with Solvent System I. The level of solvent in the tank should be between 5 and 10 mm and should not touch the ink extraction spots when initially submerged. Let the chromatogram develop until the components exhibit sufficient separation to allow comparison or for approximately 15 min.

7.7.6 *Evaluating*:

7.7.6.1 Remove the chromatogram from the developing tank and immediately evaluate the fluorescent characteristics using long-wave UV and short-wave UV sources. Note and record the color, the fluorescent characteristics, the retardation factor (R value), and the relative concentration of all fluorescent bands present for each ink sample.

7.7.6.2 Follow the same procedure for the corresponding paper (or other substrate) control (blank), to determine if there is any contribution from the substrate, for example, from tinting materials or optical brighteners (5).

7.7.6.3 Allow the sheet/plate to air dry and promptly evaluate it again following the same procedures. Note and record any change.

NOTE 14—The appearance of certain fluorescent components can change in the time between these two observations.

7.7.6.4 Under ambient light note and record the color, the Rf value, and the relative concentration of all bands present for each ink sample and control.

7.7.6.5 The completed plate should be stored away from light, heat, and air, since, in their separated form, ink dyes are very susceptible to fading or change of color. Results may be preserved by color photography.

7.7.7 *Interpretation*:

7.7.7.1 Samples of ink with qualitatively different colorant compositions can be easily distinguished by comparison of the characteristics observed in 7.7.6.

8. Additional Methods

8.1 If more information is needed to distinguish similar inks, some of the following techniques may be tried.

8.1.1 Additional Thin Layer Chromatography (TLC) Techniques:

8.1.2 Solvent System II allows development in a solvent system of a different polarity that may affect a different separation of the components (2, 4).

8.1.3 It may be advisable to use a different TLC sheet/plate along with the additional solvent systems. This may give a different separation and allow another means of comparison (2, 4, 10).

8.1.4 The chromatograms can be evaluated with the aid of laser or other monochromatic illumination, RIR and IRL, or other techniques described in 7.1.3.

8.1.5 The chromatograms can be imaged and the densities evaluated using appropriate instrumentation. This can give an accurate quantitative comparison of the relative concentrations of components (5).

8.2 Other Analytical Techniques:

8.2.1 These techniques may provide valuable information concerning components found in inks, including solvents,

surfactants, humectants, and resins. They may be of use in certain situations, but are not generally necessary in performing routine ink comparisons.

8.2.1.1 Batch-to batch variation within an ink formula may be detectable utilizing analytical methods, such as chromatography, electrophoresis, spectrometry, spectrophotometry, or a combination.

8.2.2 *Fourier Transform Infrared Spectroscopy (FTIR)* can be useful when detailed information is necessary about an ink's organic composition (4, 25).

8.2.3 Gas Chromatography (GC), Gas Chromatography/ Mass Spectrometry (GC/MS) can provide information on organic components (4). GC/MS operating in the selected ion monitoring mode permits reliable detection and identification of the ink's primary vehicle solvents (28).

8.2.4 *High Pressure Liquid Chromatography (HPLC)* has been used to gather information on batch-to-batch variation or when detailed information is necessary about an ink's organic composition (26).

8.2.5 *Microspectrophotometry* can be used to obtain the ink's spectral transmittance curve or reflectance curve, or both (17).

8.2.6 *Spectrofluorometry* has been used when an emission spectra is desired (27).

8.2.7 *X-Ray Fluorescence Spectroscopy (XRF)* can provide detailed information on the inorganic components of an ink (5).

8.2.8 *Capillary Electrophoresis* has been used to provide detailed organic comparisons of two or more inks (29).

9. Reporting Conclusions

9.1 Conclusions resulting from the comparison of two ink samples may be reached once sufficient examinations have been conducted. In reporting conclusions, the tests performed shall be listed. The number of necessary tests is dependent on the inks involved.

9.2 Differentiation:

9.2.1 If significant, reproducible, inexplicable differences between ink samples are found at any level of the optical or chemical analyses, it may be concluded that the inks do not have a common origin.

9.2.2 However, when inks give differing test results, the possibility of batch-to-batch variation within an ink formula must be considered: this kind of variation may be detectable utilizing analytical methods, such as chromatography, electrophoresis, spectrometry, spectrophotometry, or a combination. The potential influences of interfering factors that can alter the composition of an ink sample must also be considered (see Section 5).

9.3 Matches:

9.3.1 When the comparison of two or more ink samples by optical or chemical analyses, or both reveals no significant, reproducible, inexplicable differences and there is significant agreement in all observable aspects of the results, it may be concluded that the ink samples match at that level of analysis and that the results of the examination indicate that the ink samples are of the same formula or of two similar formulas with the same nonvolatile components (2). The possibility that other analytical techniques might be able to differentiate the samples should be considered.

9.3.2 This conclusion does not eliminate the possibility that the ink samples being compared are from different manufacturing batches or from different writing or marking instruments (2).

9.3.3 Reports of conclusions should never state that two ink samples are *identical* or *the same ink*. Statements must be within the limits of 9.3.1.

10. Keywords

10.1 forensic sciences; ink comparison; questioned documents

REFERENCES

- (1) Osborn, A. S. *Questioned Documents*, 2d ed., Boyd Printing Co., Albany, NY, 1929.
- (2) Crown, D. A., Brunelle, R. L. and Cantu, A. A. "Parameters of Ballpoint Ink Examination," *Journal of Forensic Sciences*, Vol 21, 1976, pp. 917–922.
- (3) Mitchell, C. A. Inks: Their Composition and Manufacture, Including Methods of Examination and a Full List of British Patents, 4th ed., Charles Griffin & Co., Ltd., London, 1937.
- (4) Brunelle, R. L. and Pro, M. J. "A Systematic Approach to Ink Identification," *Journal of Official Analytical Chemistry*, Vol 55, 1972, pp. 823–826.
- (5) Brunelle, L. R. and Reed, R. W. *Forensic Examination of Ink and Paper,* Charles C Thomas, Springfield, IL, 1984.
- (6) Kelly, J. D. and Cantu, A. A. "Proposed Standard Methods for Ink Identifications," *Journal of Official Analytical Chemistry*, Vol 58, 1975, pp. 122–125.
- (7) Ordidge, M. and Totty, R. N. "The Examination of Ink Writing on Photographic Paper," *Journal of the Forensic Science Society*, Vol 24, 1984, pp. 43–47.
- (8) Sensi, C. A. and Cantu, A. A. "Infrared Luminescence: Is It a Valid Method to Differentiate Among Inks?" *Journal of Forensic Sciences*, Vol 27, 1982, pp. 196–199.

- (9) Stewart, L. F. "Artificial Aging of Documents," *Journal of Forensic Sciences*, Vol 27, 1982, pp. 450–453.
- (10) Hamilton, R. J. and Hamilton, S. *Thin Layer Chromatography*, John Wiley & Sons, Inc., Chichester, UK, 1987.
- (11) Godown, L. "New Nondestructive Document Testing Methods," *Journal of Criminal Law, Criminology, and Police Science*, Vol 55, 1964, pp. 280–286.
- (12) Eastman Kodak, *Kodak Filters for Scientific and Technical Uses*. Eastman Kodak Co., Rochester, NY.
- (13) Kopp, Color Filter Glasses, Kopp Glass, Pittsburgh, PA, 1986.
- (14) Schott, Optical Glass Filters, Schott Glass Technologies, Durea, PA.
- (15) Hoover, H. L. and MacDonell, H. L. "Infrared Luminescence Using Glass Filters," *Journal of Forensic Sciences*, Vol 9, 1964, pp. 89–99.
- (16) Veillon, P., Rothenbuehler, O. and Mathyer, J. "Some Remarks on the Optical Examination of Inks," *International Criminal Police Review*, Vol 27, No. 11, November 1972. No. 262, pp. 238–255.
- (17) Zeichner, A., et al. "Transmission and Reflectance Microspectrophotometry of Inks," *Journal of Forensic Sciences*, Vol 33, 1988, pp. 1171–1184.
- (18) Eastman Kodak, *Ultraviolet and Fluorescence Photography*. Eastman Kodak Co., Rochester, NY.

- (19) Costain, J. E. and Lewis, G. W. "A Practical Guide to Infrared Luminescence Applied to Questioned Document Problems," *Journal* of Police Science and Administration, Vol 1, 1973, pp. 209–218.
- (20) Eastman Kodak, *Applied Infrared Photography*, Eastman Kodak Co., Rochester, NY.
- (21) Richards, G. B. "The Application of Electronic Video Techniques to Infrared and Ultraviolet Examinations," *Journal of Forensic Sciences*, Vol 23, 1977, pp. 53–60.
- (22) Radley, R. W. "Examination of Infrared Luminescence Responses of Ballpoint Inks Using Luminescent Backgrounds," *International Journal of Forensic Document Examiners*, Vol 2, No. 2, April/June 1996, pp. 151–152.
- (23) Crown, D. A., Conway, J. A. and Kirk, P. L. "Differentiation of Blue Ballpoint Pen Inks," *Journal of Criminal Law, Criminology, and Police Science*, Vol 52, 1961, pp. 338–343.
- (24) Kuranz, R. L. "Technique for Transferring Ink from a Written Line to a Thin-Layer Chromatographic Sheet," *Journal of Forensic Sciences*, Vol 31, 1986, pp. 655–657.

- (25) Humecki, H. "Experiments in Ballpoint Ink Aging Using Infrared Spectroscopy," *Proceedings of International Symposium on Non-Handwriting Aspects of Questioned Document Examination*, U.S. Government Printing Office, Washington, DC, 1985, pp. 131–135.
- (26) Lyter, A. H. "Examination of Ballpen Ink by High Pressure Liquid Chromatography," *Journal of Forensic Sciences*, Vol 27, 1982, pp. 154–160.
- (27) Kelly, J. H. "Spectrofluorometric Analyses of Ball Point Ink," *Journal of Police Science and Administration*, Vol 1, 1973, pp. 175–181.
- (28) Aginsky, V. N. "Dating and Characterizing Writing, Stamp Pad and Jet Printer Inks by Gas Chromatography/Mass Spectrometry," *International Journal of Forensic Document Examiners*, Vol 2, No. 2, April/June 1996, pp. 103–115.
- (29) Fanali, S. and Schudel, M. "Some Separations of Black and Red Water-Soluble Fiber-Tip Pen Inks by Capillary Zone Electrophoresis and Thin Layer Chromatography," *Journal of Forensic Sciences*, Vol 36, 1991, pp. 1192–1197.

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Designation: E 1789 – 04

Standard Guide for Writing Ink Identification¹

This standard is issued under the fixed designation E 1789; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

INTRODUCTION

This guide is intended as a general outline for use in forensic ink examinations, where the intention is to identify an ink formula or type. It is designed both for the experienced document examiner (see Guide E 444) and for those unfamiliar with previously reported procedures. The aim is to describe those techniques that will provide the most information about an ink with the least damage to the document. This guide refers to well-reported and thoroughly tested techniques currently in use by forensic document examiners, chemists, and other scientists.

Following the procedures as outlined, an examiner can accurately discriminate between ink formulas; as well as significantly reducing the possibility of reporting false matches of ink samples from different sources or incorrectly differentiating ink samples from a common source.

Identifications of ink formulas may be accomplished through the use of an adequate collection of standards. The necessary completeness of a comparison collection and limitations of conclusions will be addressed in the guide.

1. Scope

1.1 This guide covers assisting forensic examiners in identifying writing inks. Included in this analysis scheme are the necessary tools and techniques which have been successfully utilized to reach conclusions as to the common or different origin of two samples of ink.

1.2 This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2. Referenced Documents

2.1 ASTM Standards: ²

E 444 Guide to Descriptions of Scopes of Work Relating to Forensic Sciences for Questioned Document Area

E 1422 Guide for Test Methods for Forensic Writing Ink Comparison

2.2 NIST Standards:

- NBS Standard Sample No. 2106 ISCC-NBS Centroid Color Charts³
- NBS Special Pub. 440 Color: Universal Language and Dictionary of Names³

3. Terminology

3.1 *Definitions*—Terminology has been defined in Guide E 1422, with the following addition:

3.1.1 *ink library*—an organized collection of reference samples of inks and related materials.

3.1.1.1 *Discussion*—For maximum effectiveness in identification of questioned ink, an ink library should at minimum include the following elements: reference samples of ink in unused form, either in bulk samples from the manufacturer or in distribution form such as bottles, pens, or cartridges; dried ink specimens of each reference sample of ink placed on paper (scribble sheets); analysis results of each reference sample of ink, for example, TLC sheets/plates; and an ink information file for each reference sample of ink containing available relevant data. All elements of the collection should be as complete, comprehensive, and up-to-date as possible, although this will vary between ink libraries.

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¹ This guide is under the jurisdiction of ASTM Committee E30 on Forensic Sciences and is the direct responsibility of Subcommittee E30.02 on Questioned Documents.

Current edition approved Dec. 1, 2004. Published January 2005. Originally approved in 1996. Last previous editon approved in 1996 as E 1789–96.

² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

³ Available from U.S. Department of Commerce, National Bureau of Standards, Office of Standard Reference Materials, R. B311, Chemistry Building, Gaithersburg, MD 20899.

4. Significance and Use

4.1 The reasons for identifying writing inks are to obtain information about: the origin; relative availability; distribution; and first and last (if applicable) production dates. It is this valuable information available from the manufacturer and through the use of a collection of standards that differentiates this guide from Guide E 1422.

4.1.1 The procedure set forth in this guide are applicable in determining the significance of a match obtained by performing the examinations set out in Guide E 1422 (by showing how rare or common an ink formula may be), or in determining the source of an ink. The identification of a specific ink formula can facilitate the determination of the first date of production and the discontinuance date of that ink.⁴

4.1.2 In addition to proficiency in the use of the necessary analytical procedures, specialized knowledge and experience on the part of the examiner are required.⁵ Also required is a comprehensive collection of reference samples of ink and related materials (ink library). The ink reference standards are cataloged, analyzed, and stored according to the procedures described in Section 7.

4.2 Even with access to a comprehensive ink library, it is not always possible to positively identify a questioned ink sample. This is because some ink formulations are very similar; usually only non-volatile ingredients such as dyes and pigments are compared; and no matter how comprehensive the ink library is, the collection will never be complete.⁶

4.2.1 Some ink formulas are not distinguishable; they behave in the same manner under various examinations because they have similar formulas with the same nonvolatile components. Thus, it is not always possible to find a single reference ink sample in the ink library that matches a questioned ink. Even if one is found, it may not provide an identification unless the ink formula is shown to be unique because it contains a specific component. For these reasons, it will not be possible to identify every questioned ink. There is not always a forensic answer to a question at hand.

4.2.2 It must also be understood that it is not possible to create an all inclusive ink library, just as it would not be possible to obtain every fingerprint, or every paint, soil, or glass sample. Conclusions as to the identity of an ink are dependent on the completeness of the ink library used. Thus, it is possible that there are one or more inks not in the ink library that would be indistinguishable from the questioned ink.

4.3 In spite of these limitations, questioned inks can be associated with reference ink samples with a high degree of confidence using the systematic approach in this guide. The analytical procedures given here, such as TLC and TLC Densitometry, are sufficient to distinguish most inks, and therefore to match most questioned ink samples to a reference sample of ink or a relatively limited group of reference samples in an ink library.

4.3.1 Just as with other forensic tools, for example, FTIR, GC, HPLC, etc., pattern profile matching with reference samples is often sufficient to yield an identification. Individual component identification through an internal standard approach may be used, but is not usually necessary.⁴

5. Interferences

5.1 Most interferences with ink examinations and subsequent identifications are a result of variables interacting with the ink. These variables can usually be attributed to the writing process or storage conditions, or a combination thereof, and are discussed in Guide E 1422. Evaluation of these variables can avoid problems examinations.

5.2 Other interferences can be caused by changes to the TLC diffusion of fluorescent components, differences in the paper controls, differences in color due to fading either of the inks or of the components on the TLC sheet/plate, solvent depletion, or a combination of these and other factors. Evaluation of these variables, use of paper blanks, and proper storage and maintenance of the reference samples and related material in the ink library can avoid problems in examinations.

5.3 Large batch-to-batch variations in the manufacturing process can also lead to problems in evaluating a match.

6. Reagents and Equipment

6.1 Appropriate reagents and equipment for the required techniques have been listed in Guide E 1422, with the following additions:

6.1.1 Low Resolution Precoated Plastic or Glass Sheets/ Plates of Silica Gel, without fluorescent indicator (60 angstrom pore size).

NOTE 1—Low resolution sheets/plates are generally not as sensitive to external effects, for example, temperature, humidity, and development conditions. They have the quality of exhibiting excellent reproducibility and as such are an appropriate choice for storage media of the ink library TLC plates.

6.1.2 High Resolution Precoated Plastic or Glass Sheets/ Plates of Silica Gel, without fluorescent indicator (60 angstrom pore size).

NOTE 2—It is recommended that the TLC sheets/plates be kept in a desiccator.

7. Procedure

7.1 Collection, Preparation, and Analysis of Reference Materials for the Ink Library:

7.1.1 Reference Samples of Ink:

7.1.1.1 The core of the ink library consists of reference samples of ink formulas, usually obtained from ink manufacturers. Additionally, ink and pens should be purchased at retailers on a regular basis (at least once a year), because it is not always possible to obtain samples directly from all manufacturers of ink. Because of international trade and travel patterns, reference samples of ink should be obtained on a world-wide basis.

7.1.1.2 Accession information for each reference sample of ink should be recorded, such as date of acquisition, source, etc.

⁴ Brunelle, R. L. and Pro, M. J., "A Systematic Approach to Ink Identification," *Journal of Official Analytical Chemistry*, Vol 55, 1972, pp. 823–826.

⁵ Brunelle, R. L. and Cantu, A. A., "Training Requirements and Ethical Responsibilities of Forensic Scientists Performing Ink Dating Examinations," Letter to the Editor, *Journal of Forensic Sciences*, November, 1987.

⁶ Crown, D. A., Brunelle, R. L., and Cantu, A. A., "Parameters of Ballpoint Ink Examination," *Journal of Forensic Sciences*, Vol 21, 1976, pp. 917–922.

For an assembly of reference samples of ink to be considered a collection rather than an accumulation, it must be organized and cataloged. If a computerized database is used, searching can be on any criteria; if not, the features noted in a light examination performed in accordance with Guide E 1422 can be used to organize the collection.

7.1.1.3 Reference samples of ink should be stored under optimal laboratory conditions (sealed containers, darkness, temperature and humidity controlled) to retard drying, oxidation, and other changes related to aging.

7.1.2 Dried Ink Specimens:

7.1.2.1 Prepare a specimen by making lines or marks on a sheet of paper (scribble sheet). Record the date of preparation. Allow the ink to dry for up to 1 h under ambient conditions before storing.

NOTE 3—Dried ink specimens can be effectively stored on filter type paper that does not contain optical brightener additives. A sample of any paper being considered for a library storage media should be analyzed following the laboratory procedures as indicated in this standard. This will determine if the paper will interfere with the examination procedure.

7.1.2.2 Dried ink specimens should be stored under optimal laboratory conditions (darkness, temperature and humidity controlled) to retard fading and other changes.

7.1.3 *Results of Analysis of Reference Samples*—Because questioned ink samples will be analyzed in accordance with Guide E 1422 for comparison with the ink library (see 7.2), the reference samples in the library should undergo the same analyses with results preserved for future searching.

7.1.3.1 Perform the light, ultraviolet (UV), and infrared (IR) examinations in accordance with Guide E 1422.

7.1.3.2 Perform the spot testing and solubility testing in accordance with Guide E 1422.

7.1.3.3 Perform the thin layer chromatography TLC examination in accordance with Guide E 1422.

7.1.3.3.1 Note and record the extraction solvent used. Where appropriate, prepare duplicate extractions using all the different solvents likely to be employed in extraction from various substrata. Prepare a TLC of each extract, recording the solvent used. Appropriate TLC sheets/plates will then be available for comparison with questioned samples.

7.1.3.3.2 The TLC analysis should be conducted on low resolution type sheets/plates. Low resolution sheets/plates are generally not as sensitive to external effects, for example, temperature, humidity, or development conditions. They have the quality of exhibiting excellent reproducibility and as such are an appropriate choice for storage media of the ink library TLC sheets/plates.

NOTE 4—Plastic backed 60 angstrom size silica gel without fluorescent indicator sheets/plates has been found to be satisfactory.

7.1.3.3.3 Ink library TLC sheets/plates should be stored under optimal laboratory conditions (darkness, temperature and humidity controlled) to extend the useful life of the sheets/plates. TLC sheets/plates have a limited useful life: the sheets/plates themselves will degrade after 10 to 20 years, and the band colors and fluorescence characteristics may fade or undergo other changes sooner. Deteriorating TLC sheets/plates should be replaced as needed.

7.1.4 Ink Information Files:

7.1.4.1 All available relevant data on each reference ink sample should be collected and maintained. This can include information on the manufacturer; ink formula; manufacturer's designation(s) and marketing name(s); other user's (for example, pen manufacturers) and their designation(s) and marketing name(s); volume of ink manufactured; area(s) of distribution; first production date; date first released to the public; last production date; etc.

NOTE 5—Some information may be considered proprietary by the ink manufacturer or other source. Such information should be treated with the appropriate confidentiality.

7.1.4.2 Analytical results and other data from 7.1.3 should be maintained. Efficient organization of this information can facilitate searches of the ink library.

7.2 Ink Identification—Ink identification is a two step process. The first step involves comparative analysis techniques described in Guide E 1422. The second step includes comparison of any resulting TLC plate from the initial analysis to an ink library.

7.2.1 Perform the light, ultraviolet (UV), and infrared (IR) examinations and record results in accordance with Guide E 1422.

7.2.2 Perform the spot testing and solubility testing and record results in accordance with Guide E 1422.

7.2.3 Perform the thin layer chromatography TLC examination in accordance with Guide E 1422.

7.2.3.1 The comparison reference inks in the ink library must have been extracted using the same solvent. If there is no TLC plate in the ink library that meets this requirement, prepare one in accordance with Guide E 1422 using the appropriate solvent before proceeding.

7.2.4 First TLC Interpretation:

7.2.4.1 Samples of ink with qualitatively different colorant compositions can be easily distinguished by comparison of the characteristics described in Guide E 1422.

7.2.5 Comparison Against a Library of Standards:

7.2.5.1 Where comparison against a library of standards is desired, the initial TLC analysis should be conducted on low resolution type sheets/plates of the same type used to prepare the TLC sheets/plates in the ink library.

7.2.5.2 Using the results of the light, ultraviolet (UV), and infrared (IR) examinations (see 7.2.1) search the library for samples known to produce these results. Physically compare the questioned ink sample in situ with the dried ink samples from the ink library. Note and record all ink library reference samples that are consistent with the questioned ink at this stage.

7.2.5.3 Physically compare the chromatogram of the questioned ink with the chromatograms of all the reference samples in the ink library that were not eliminated in 7.2.5.2. Observe the band colors, Rf separations, and fluorescence characteristics. Note and record all ink library reference samples that are consistent with the questioned ink at this stage.

7.2.5.4 Those reference samples that match at every level of the examination are selected as possible matches in preparation for the second TLC comparative examination.

7.2.5.4.1 Reference samples from the ink library having explicable differences should also be selected as possible matches. Such over-selection of standard inks reduces the possibility that a true match is not eliminated from consideration. Explicable differences include characteristics arising from diffusion of fluorescent components, differences in the paper controls, differences in color due to fading either of the inks or of the components on the TLC sheet/plate, solvent depletion, or a combination of these and other factors.

7.2.6 Second TLC Analysis:

7.2.6.1 Begin a second TLC comparison between the questioned ink and the potential matches from the ink library. This examination may further reduce the number of standard library inks that could match the questioned ink.

NOTE 6—The TLC sheets/plates used at this stage should be very high resolution. TLC sheets/plates that are high resolution are generally very sensitive both to their surroundings and to development conditions. The reproducibility within a plate is extremely good; however, plates should not be inter-compared due to potential variations.

7.2.6.2 Remove a suitable amount of sample from each of the reference ink samples in the ink library whose physical and chemical TLC results are consistent with the questioned ink's. There may be many potential library matches at this stage of the examination. Every potential match should be sampled.

7.2.6.3 Perform a TLC analysis in accordance with Guide E 1422.

NOTE 7—Glass backed 60 angstrom size silica gel without fluorescent indicator plates has been found to be satisfactory. Variations within plates of the same type and manufacturer have been noted.

NOTE 8—Spot all inks and the paper control samples (blanks) on the same plate. This is necessary based on the sensitivity of the high resolution TLC plates. If more than one plate is needed (one 20 by 20 cm plate can accept approximately 18 spots 2 to 3 mm wide) respot the questioned ink(s) and paper control(s) on each additional plate.

7.2.7 Second TLC Interpretation:

7.2.7.1 Physically compare the chromatograms of the questioned and selected standard ink(s). Note and record the consistencies in band colors, Rf values, and any fluorescence characteristics. Also note and record any inconsistencies.

7.2.7.2 These comparative examinations between the questioned and standard inks provide the necessary information to eliminate non-matching inks and to locate one or more matching reference ink samples in the ink library (if any matches are present).

8. Additional Analyses

8.1 To date, most forensic analyses of writing inks involve thin layer chromatography. TLC provides a reproducible method that allows for storage of standards and for subsequent comparisons with unknowns. Sometimes, optical techniques along with TLC are insufficient to narrow the field of possible matches to a single reference sample in the ink library. The previously described analysis methods are not by any means the only techniques that can be used, nor are they represented to be the best of all possible methods. Each examination should be considered as an individual matter involving decisions regarding the best method(s) of analysis. The analyst must use the best analytical techniques available, be aware of advantages and shortcomings and determine as many identification criteria as necessary. If more information is needed regarding a particular ink, the additional techniques listed in Guide E 1422 can be tried.

9. Reporting Conclusions

9.1 In reporting conclusions of comparative examinations with an ink library, three necessary elements should be included: (1) a listing of the examinations performed; (2) the matches found; and (3) the conclusions drawn.

9.2 *Examinations Performed*—The report should include a listing of the laboratory examinations conducted. This section should discuss, but does not need to be limited to, the techniques found in Sections 7 and 8.

9.2.1 *Examples*—"Optical (physical) and chemical examinations were performed on the questioned ink from exhibit (give exhibit designation) and the results were compared with those from inks in our ink library. The examinations conducted include (list examinations performed)."

NOTE 9—If the exhibit bears several questioned inks, the report should state their location on the document and that the results of their individual examination were compared with each other. The report should identify questioned inks that are different from each other by sorting the questioned inks into distinct groups consisting of inks that match each other.

9.3 *The Matching Standard Ink(s)*—The cumulative set of comparative examinations (see Sections 7 and 8) will determine the number of reference ink samples (if any) that match a questioned ink. Depending on the level of analysis, a questioned ink can be said to match one or more reference samples in the ink library.

9.3.1 Differentiation:

9.3.1.1 If significant, reproducible, inexplicable differences between the questioned ink sample and a reference sample are found at any level of the physical, or chemical analyses, or both, it may be concluded that the inks do not have a common origin.

9.3.1.2 However, when inks give differing test results, the possibility of batch-to-batch variation within an ink formula must be considered; this kind of slight variation may be detectable utilizing sophisticated instrumentation, generally limited to FTIR, GC/MS, HPLC and/or XRF. The potential influences of interfering factors that can alter the composition of an ink sample must also be considered (see Section 5).

9.3.2 *Matches*—When the comparison of the questioned ink sample and a reference sample by optical and chemical analyses reveal no significant, reproducible, inexplicable differences and there is significant agreement in all observable aspects of the results, it may be concluded that the ink samples match at that level of analysis and that the results of the examination indicate that the ink samples are of the same formula or of two similar formulas with the same components.⁶The possibility that other analytical techniques might be able to differentiate the samples should be considered.

NOTE 10—Each comparative examination has its own criteria for determining if a match exists. These are determined by the examiner, based on the examiner's training and experience. Matching criteria should not include inexplicable differences that are too vague (since this may unnecessarily increase the number of matching possibilities) or too specific (since this may eliminate an actual match).

Note 11-When a comparative examination yields no inexplicable

differences, the items compared may be said to match or to be indistinguishable at that level of analysis. These terms are not synonymous with the term similar, a term sometimes used for near matches where the results are close but do not meet all the necessary criteria.

9.3.3 An important concern when reaching a conclusion regarding ink matches is whether the matching inks are the same to the exclusion of all other inks. The possibility that the questioned ink matches an ink formula not in the ink library must be assessed based on the experience of the examiner, who evaluates the characteristics of the questioned ink, the examinations performed, the comprehensiveness of the ink library, and information from the ink manufacturer. Based on the above cited factors, this possibility can range from highly probable to extremely unlikely.

9.4 *Single Library Match*—The questioned ink matches only one reference ink sample in ink library to the exclusion of all other reference ink samples.

9.4.1 The matching reference ink sample must be the only one in the library that matches (see 9.3.2) when compared by each examination with the questioned ink sample.

9.4.2 Furthermore, it must be possible to differentiate (see 9.3.1) the questioned ink sample from each of the other (nonmatching) reference ink samples in the library by at least one comparison, thereby eliminating all other reference samples in the ink library as a possible match for the questioned ink.

9.4.3 In the absence of a unique component in the ink formula or some other reason to discount the possibility that the questioned ink may also match one or more additional inks not in the ink library, conclusions should not be reported in absolute terms as an identification, even though based on the comprehensiveness of the standard ink library, the level of examinations performed, and the characteristics determined, this possibility can be remote.

9.4.3.1 *Examples*—"These findings suggest that the questioned ink matches only one standard reference ink from the ink library." Alternatively, "these findings suggest that the matching standard ink is the only standard ink that could not be eliminated as being, the questioned ink." An equivalent statement can be substituted.

9.4.4 If it is determined that the questioned ink sample matches a reference sample that is unique, the report of the findings and of the conclusions should reflect this.

9.4.4.1 *Examples*—"The questioned ink was found to uniquely match a reference sample ink." The conclusion should also state that "The questioned ink is (identified as) the matching standard ink."

9.4.5 Depending on the information requested by the submitter, the report may include the ink manufacturer's name; the manufacturer's designation for the formula; the first production date and last production date; the area(s) of distribution; the brand and type of pens using the formula. If a first commercial production date of the questioned ink was requested, report that the questioned ink matches a reference sample in the ink library that was first manufactured on (state first production date of the matching reference sample ink). Identification of specific dyes, components, and ratios should be avoided as this information may be considered proprietary to the manufacturer.

9.5 *Multiple Library Match*—The questioned ink matches a group of two or more reference ink samples in the ink library to the exclusion of all other reference ink samples outside the group.

9.5.1 The matching reference ink samples must be the only ones in the library that match (see 9.3.2) when compared by each examination with the questioned ink sample.

9.5.2 Furthermore, it must be possible to differentiate (see 9.3.1) the questioned ink sample from each of the other (nonmatching) reference ink samples in the library by at least one comparison, thereby eliminating all other reference samples as a possible match for the questioned ink.

9.5.3 Conclusions should be reported in a manner similar to a single library match (see 9.5.3), while reflecting the multiple matches found.

9.5.3.1 *Example*—"These findings suggest that the questioned ink is one of these matching standard inks or another ink with the same determined characteristics."

9.5.4 Reporting these findings may also include informational items regarding the inks (see 9.5.3). If a first commercial production date of the questioned ink was requested, then it is necessary to report the earliest first production date found within the group of matching reference samples. As noted above, no information should be reported that may be deemed proprietary to the manufacturer.

9.6 *No Match*—The questioned ink does not match any reference samples of ink in the ink library.

9.6.1 Inability to find a matching reference sample in the ink library could be due to one or more of several causes: The ink formula of the questioned ink sample exists outside of the library; but a reference sample of that ink formula is not in the ink library. A reference sample of the ink formula is in the ink library but does not match the questioned ink sample because of significant batch to batch variations in the manufacturing process. The questioned ink sample has changed to the point that it no longer will match a reference sample of the same ink formula in the library.

9.6.2 The report can list some of the possible reasons for these results.

9.6.2.1 *Examples*—"The questioned ink was not found to match any reference sample ink in the ink library. The questioned ink's appearance and characteristics may have changed (have been altered) due to storage conditions, contamination, etc. Another possibility is that the questioned ink may be one that is not in the ink library."

10. Keywords

10.1 forensic sciences; ink identification; questioned documents



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Exhibit 13

http://en.wikipedia.org/wiki/HP_LaserJet

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http://www.hparchive.com/seminar_notes/HP_LaserJet_The%20Early %20History_by_Jim_Hall_110512.pdf

http://www.hp.com/hpinfo/abouthp/histnfacts/museum/imagingprinting/0018/index.html

Stewart Forensic Consultants, LLC

United States-English



As the primary printer for a small business or company department, the LaserJet printer was ideal for letterhead correspondence, memoranda, financial spreadsheets and other applications. It had high print quality, could print horizontally or vertically in a variety of character fonts and could produce graphics. The printer employed a disposable print cartridge capable of printing about 3,000 pages, and the print speed was 8 pages per minute. In addition, the LaserJet was virtually silent; office personnel could talk on the telephone while sitting next to the laser printer as it produced documents.

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HP LaserJet – The Early History

Jim Hall

Introduction

Why write a LaserJet History? Over the past 15 years, various books and articles have given bits and pieces of HP LaserJet history and dissected the reasons for its market and business success. Most^{1,2,3} have been reasonably accurate, while one was mostly inaccurate. Still I don't feel any of them gives the reader a complete understanding of the facts behind HP LaserJet's success. My goal here is to try to give a complete, early (admittedly R&D centric) history⁴, plus offer a few thoughts as to why LaserJet continues to be successful after more than 25 years. As you will see, many, many factors came together to develop the remarkable LaserJet story.

Why should I be the one to write a LaserJet history? Mostly because I was the R&D project/section manager for HP's first laser printer (HP 2680A) during most of its development. After that I was R&D section manager for all laser/LaserJet products until 1989 and all Personal LaserJet products until 1995. So I was in the middle of most of the history that follows.

Computers and Printing in the Late 70's and Early \$0's

In the late 1970's and early 1980's computers and computer printing was in the stone age compared to today. Operating systems were rudimentary and performance was often lacking. No wireless connections or Internet. Graphics was crude or nonexistent and fonts were fixed in size and spacing. WYSIWYG (what-you-see-is-what-you get), color and digital pictures were only dreams in minds of the technically sophisticated. Almost all of what we take for granted today with computers and printing was still the stuff of scientific fiction.

In the mid-70's mainframe computing was starting to fade and the minicomputer market (Digital Equipment, HP, Data General) was exploding. Minicomputers made it possible for even mid-sized companies to finally own a computer. But computers and computer printing remained centralized and behind glass walls. Computer printers utilized impact print technology which had poor print quality and was extremely noisy. Laser xerographic printers costing \$500,000 or more had been introduced by IBM and Xerox for mainframe computers but there was nothing comparable for the minicomputer market. There was an opportunity for HP to offer a better printing solution for our rapidly growing HP 3000 minicomputer line.

Then in 1981, IBM introduced their personal computer and the world of computing began an even more dramatic transformation. Having a computer running "killer apps" like Lotus 1-2-3, WordPerfect and MS Word on your very own desk was personallyenabling in a way no one could imagine. But without a printed page, a PC was a bit like a 2-legged stool, something was missing. You could do wonderfully creative work, but in the end, the job was not finished until you could print your results onto a permanent page. The only personal printing solutions available were slow, noisy daisy wheel printers, slower thermal printers requiring expensive, special paper or slow, noisy dot matrix impact printers with poor print quality. This proved to be an even greater printer market opportunity for HP.

The HP Boise Division

In the fall of 1973, the Boise Division was established with Ray Smelek as Division General Manager. The original charter of the division was to design, manufacture and market printers for HP minicomputers (HP 3000, HP 1000). In addition, the division was responsible for manufacturing the HP 7970 tape drive, another HP minicomputer peripheral. At that time it was felt that tape drives were becoming obsolete and there was no need to invest in developing new ones. Therefore Boise Division could use the revenue from the HP 7970 to fund the division but focus all new product development on printers, a growing market and product needed for HP computers.

The first printer Boise Division put into production was the HP 2607A line dot matrix printer, introduced in 1974. Its design and manufacturing rights had been purchased from another company. It was a relatively poor product so Boise Division immediately started the design of a replacement printer (HP 2608A).

The Canon/HP Relationship

The Canon/HP relationship is a key part of LaserJet history. The relationship between the two companies started while HP was working with Yokogawa Electric Works to form the YHP Division in Japan as our entry into the Asian market. In the early 1960's, Bill Mewlett met with various Japanese companies to develop a better understanding of HP's Japanese YHP partner. In those meetings, Bill Hewlett became friends with Dr. Takeshi Mitarai, the person who resurrected Canon after WWII and became its first post-WWII president. Both companies were high tech and known for empowering young engineers to quickly develop innovative products. In addition, Dr. Mitarai was a medical doctor as was Bill Hewlett's father.

Several years later, in an interesting side story, when Dr. Mitarai's son (Hajime Mitarai) applied to Stanford University to pursue a PhD in electrical engineering, he was at first turned down. Dr. Mitarai told this to YHP president Ken Sasaoka, who in turn phoned Bill Hewlett to see if he could find out why. When Hewlett inquired, the responsible Stanford dean couldn't understand why Hajime hadn't been admitted, and accepted him on the spot for the PhD program. After obtaining his PhD, Hajime worked in the US semiconductor industry for a couple of years before returning to Japan to head up Canon's Central Research Laboratory (CRL). Interestingly, Canon's CRL was where the Canon's laser printer was developed and "mothered" for several years before finally becoming a successful commercial product line within the company.

HP's First Laser Printer – HP 2680A (EPOC)

In the mid 1970's Canon developed a prototype laser printer based on their NP5000 45 page-per-minute (ppm), dry toner copier and demonstrated it at the fall 1975 National Computer Conference (NCC). They were hoping to find a partner to bring their technology to market. At that time John Young was HP's Executive VP for computer, instrument and component groups and was at NCC. So when Canon asked Bill Hewlett to look at their laser printer, Hewlett had Young do just that. Young was intrigued by the product and quickly involved Hewlett and Paul Ely (Computer Group Manager). Ely contacted Ray Smelek in Boise. After reviewing the product, they all supported buying the technology from Canon.

Bill Hewlett put together a team to purchase the technology. Don Hammond of HP Labs led the team. Other members were John Chognard (HP General Counsel), Jim Boyden (HP Labs) and Jim Barnes (Boise Division R&D Manager). After two or three days in Japan, viewing the prototype and negotiating, Hammond and team were able to work out an agreement with Canon. This agreement, launching HP into laser printing, was another example of Bill Hewlett's vision and willingness to gamble on new technology and business opportunities. Design of HP's first laser printer commenced with the formation of a Boise Division R&D design team in early 1976. I was the initial project manager. When Ray Smelek and Jim Barnes interviewed me for the job I told them I didn't know anything about laser printers (My background was in microwave communications (13 years at GE) and instrumentation (4 years at HP)). They said: "Don't worry, no one else in HP does either." I was gratified and yet somewhat intrigued when they hired me anyway.

Our project was code named EPOC (Electrophotographic Printer On Computer), a play on "epoch" or new era of printing (It is traditional within HP to let the R&D team pick the code name for their project.). The actual product model number became the HP 2680A. Our vision (and the one that convinced Hewlett and team to invest in the technology) was to commercialize the Canon NP5000 copier based prototype by simply adding an HP print controller and laser optics. However it turned out this was only the tip of the iceberg as far as the amount of effort ahead of us.

When we tested Canon's prototype in the summer of 1976 we found its MPBF (mean pages between failures) was only around 250 printed pages. This was clearly unacceptable for a computer peripheral. Even if we improved the MPBF by a factor of 10 or even 100 it would still be too troublesome and expensive to maintain. Part of the problem was that HP mostly employed engineers to support our mini-computers and peripherals. They were expensive (\$100 per hour) and mostly experts in computers, not the technologies used in a laser printer (mechanics, high voltage electrostatics and lasers).

Service wasn't as big a problem for companies in the copier business (like Canon) who employed less expensive service technicians with their training focused on copier technology. However it was sure to be a computer-room stopper for HP or anyone trying to support both computers and laser printers with the same service staff. For a successful HP minicomputer laser printer, we felt we needed to achieve an MPBF of at least 100,000 pages. This drive for reliability was founded on business reality but also came naturally from HP's historical obsession with quality in our instruments. Meeting our reliability goal required a complete redesign of Canon's prototype concept and implementation of an extensive MPBF testing program.

For EPOC design details, look at the HP Journals of June and July 1982. The June issue includes a good description of the laser printing process. LaserJet products were able to simplify some steps but the basic process has remained the same. On-line copies of these HP Journal articles can be found at:

http://www.hpl.hp.com/hpjournal/pdfs/IssuePDFs/198 2-06.pdf

http://www.hpl.hp.com/hpjournal/pdfs/IssuePDFs/198 2-07.pdf



When you read the HP Journal articles, you will gain some appreciation for the size and complexity of the EPOC project. For example, the completed product had some 10,000 parts. 3,500 of these were designed specifically for EPOC. Not only did we have to completely redesign Canon's concept, we had to conquer multiple technologies and design new solutions encompassing many dimensions of physics, mechanics, electronics, computers, software and systems. One particularly daunting challenge was the printer controller/formatter which had to support EPOC's 45 ppm print speed. Jim Langley designed an innovative "linked list" bit slice microprocessor architecture and programming language that solved this problem.

The HP Labs (Palo Alto) team and the HP 3000 (Cupertino) software division helped us a lot. However most of the design responsibility for this huge undertaking still resided with the young, relatively inexperienced group of engineers in Boise. The whole design team rose to the challenge, driven by a fear that either IBM or Xerox would scoop us with a comparable product. Everyone was extremely motivated and felt proud to be part of making a breakthrough product like EPOC successful.

In early 1980, I became Boise Division R&D manager and Bill Robison assumed responsibility for the EPOC project. He successfully released EPOC to manufacturing in late 1980 and on December 7, 1980, after almost 4 years of development, we finally introduced the HP 2680A Laser Printing System. It was extremely reliable (many machines demonstrated an MPBF approaching a million pages), fast at 45 ppm, had excellent print quality and supported multiple type faces and complex graphics. It worked seamlessly with the HP 3000 and included software which allowed users to design their own custom fonts, logos and electronic form overlays. Nothing on the market came close to matching the price/performance or features of the HP 2680A. The only problem was that it only worked with the HP 3000 minicomputer and sold for almost as much (\$120,000).

To give you a better feel for the HP 2680A's place in HP's laser printer history, here's what the Boise Division marketing manager had to say about it on the tenth anniversary of its market introduction (By this time LaserJet had established a dominant worldwide market position.):

> "Friday, December 7, 1990. Ten years ago today. HP introduced its first laser printer, the HP 2680A Laser Printing System. We had a "pool" in marketing on how many we would sell in that first month; the forecast was 75, actual sales were zero. We also sold zero in January and in February. Finally in March we sold our first unit to a company in Washington D.C. This was the struggling beginning of the laser printer revolution within HP. A sequence of events that have lifted us to a leadership position in the world. The HP 2680A, from this humble beginning, is still part of our product line. It has become a cornerstone of many HP 3000 data centers and the source of many innovative ideas."

So the HP2680A was a great technical achievement and a solid product (It stayed in the HP product line for 12 years and we sold approximately 1200 units) but it didn't become the huge market success we had hoped.

The revolutionary HP 2680A made many contributions to our eventual LaserJet successes.

• During its development we established a strong working relationship with Canon, including Hajime Mitarai, Takashi Kitamura, Junji Ichikawa and several others who became key members of the Canon management team during the early LaserJet years and into the late '90s.

- We learned about laser printer technology from the inside out.
- The EPOC controller/formatter taught us a lot about controller design and printer control languages. We learned about the design and use of high quality proportional fonts.
- We internalized the value customers placed on the ability to mix multiple fonts and graphics on the same page.

In spite of being disappointed by the lack of early market success with the HP 2680A, we (Boise Division) were still convinced that laser printing was the future for high speed, high quality printing. However we also internalized that only companies (like Canon) who could leverage their huge copier investments, "know how", patents, manufacturing capability, etc. could be successful in building laser print engines. HP was just too far behind and lacked the resources to realistically catch up. Therefore our "next generation" strategy focused on buying a smaller, lower cost, lower speed laser print engine from one of the copier companies. This would give us the right price/performance to match the needs of our HP minicomputers (Remember this was the early '80s and the PC market was in its infancy.).

Canon was easily our #1 choice to supply our next generation printer. However the only print engine they could offer was the LBP-10. The LBP-10 was a 10 ppm, solid state laser, liquid toner print engine that Canon had introduced in 1979. The price/performance was acceptable, the reliability good but the liquid toner was a killer. Paper coming out of the printer was saturated with the liquid (which smelled like kerosene) that carried the toner. Besides smelling bad the liquid was flammable and Underwriter Laboratories would not approve its use in a computer room environment. (This seemed to be a strange anomaly in the UL regulations. They allowed flammable chemicals like kerosene in the office but not in computer rooms!). I kept insisting that Canon needed to come up with a "dry toner" print engine. Canon kept insisting that HP should buy the LBP-10. Finally it became obvious that we would have to use a different engine supplier.

HP buys our Second Laser Print Engine from Ricoh

During 1981 and early 1982 I traveled throughout Japan in search of a suitable laser print engine we could purchase. Finally I chose Ricoh, who had almost completed development of a desktop 12 ppm laser printer (engine and controller), as our supplier.

We named this HP project "Bonsai" which was the smallest tree we could imagine (Admittedly it's a bit of a stretch, paper is made from trees, paper is what comes out of a printer). Side note: The Ricoh folks were upset when they heard the project name we had chosen. Turns out that depending on how you pronounce Bonsai, it can come out as the tree or the cry "banzail" that had unpleasant WWII implications. We intended the former but pronounced it like the latter. After explanations, everything turned out OK! Another lesson for us in Japanese culture!

Mr. Kitamura headed Canon's Laser Beam Printer Business Division at this time. Although his group utilized much of Canon's copier technology and know-how, it was a completely separate business from copiers. He was devastated when I told him of HP's decision to go with Ricoh. Ricoh was Canon's largest Japanese copier competitor and our choice resulted in a major loss of face for Canon. Mr. Kitamura railed against HP's decision all through dinner the night I told him, repeatedly telling me that HP would deeply regret our decision. This was clearly a low point in the Canon/HP relationship!

HP introduced the Bonsai laser printer (HP 2687A) in 1983. Although desktop and dramatically less expensive, it turned out to still be too expensive (\$12,800) for its 12ppm performance and the reliability proved to be poor. The technology used in the printer was just too complex to have a reasonable chance of meeting our reliability goals or customer expectations. So unfortunately, once again we didn't achieve any serious market success.



HP 2687A Desktop Laser Printer

Printer Command Language (PCL)

By the early 1980s Boise Division had active projects for a whole family of computer printers. These included daisy wheel, serial dot matrix, line dot matrix and laser printers. Each product tended to have its own unique set of computer commands for printing. This meant that each of the host computer systems had to have different software to control each of the multiple printers. As a result, the effort to provide the necessary system software was growing exponentially. Clearly, something had to be done.

Von Hansen (Formatter Project Manager) and his team in Boise Division developed a uniform Printer Command Language (PCL) for all our printer products. The language needed to be scalable since at one end, simple products like our serial dot matrix printers had a limited set of features while on the other end, laser printers had a very broad set of features. For that reason PCL was developed to have a range of capabilities. PCL 1 for the simplest printers, with higher levels of PCL having greater capability for printers with a wider range of printing features.

A key attribute of PCL was that each higher level of the language was a true superset of all lower levels. For example if you sent out PCL1 commands, all PCL printers (PCL1, PCL2, PCLn) would successfully print that information, just the way a PCL1 printer would. You might not be able exercise some higher level features but at least you could successfully print. If you sent out PCL2 commands, all PCL2 and higher printers would print your information just like a PCL2 printer and so forth.

This PCL approach allowed us to implement PCL2 in Bonsai, then move to PCL3 for the first LaserJet, then PCL4 for LaserJet II, etc. System software developed for Bonsai worked on all future LaserJets. Software developed for the first LaserJet worked on all later LaserJets and so forth. If you had a later generation PCL printer and software for an earlier generation PCL printer, you were still OK so long as you only needed the older set of PCL features.

So PCL had three key strategic advantages for LaserJet:

- It allowed us to grow the capability of PCL in step with the decreasing cost of printer memory and processing power. This let us to keep costs low in the early days when customers were happy with limited functionality but to grow functionality as semiconductor costs came down.
- It let HP spread out our PCL development investment over multiple years allowing us to add functionality one step at a time.

• It maintained customer satisfaction with computer software. For example, if a customer got a new printer with PCL4 capability but had computer software supporting only PCL3, he could still print with all PCL3 features. Later when PCL4 software was available he could take advantage of his new printer's new features. Customers really liked this "backward compatibility" feature of PCL.

Bonsai was the first HP laser printer to use PCL. So although Bonsai wasn't very successful in the market, it provided us the requirement and platform to develop PCL2 and 300 dots per inch (dpi) font families (EPOC was only 180dpi). We also developed print engine, environmental and regulatory specifications for Bonsai and utilized our experience from the HP 2680A to set goals and participate in print engine testing and qualification. These added to the building blocks at our disposal for the fast track LaserJet product that followed!

Back to Canon for our Third Laser Printer Product

1. **

On April 7, 1983 Canon's Mr. Kitamura came to Boise and (finally) demonstrated their dry toner print engine (CX). Not only did it use dry toner and a solid state laser leveraged from the high volumes used in CD players, but most importantly, it utilized the "allin-one" cartridge concept Canon had recently invented and implemented for the first time in their desktop personal copier (PC-20), introduced in 1982. The concept was to package the printer toner with all the other components that tended to wear out and require service (e.g. photoconductive drum, charging and cleaning systems) in a customer replaceable cartridge. Thus when the toner was depleted, the customer plugged in a new cartridge and in effect had an almost new printer. The cartridge tends to be called the "toner cartridge" since the customers signal to change the cartridge is when the toner runs out. However this name isn't a good representation of the other major engine components contained in a cartridge. For more detail see the Canon video showing how laser printing works with the "all-in-one" cartridge at: http://www.canon.com/technology/canon_tech/catego ry/output.html#lp Click on: "Special features of Canon products, All-in-one-cartridges".

Canon sold the CX engine to several other companies including Apple. We beat Apple to market with the CX engine by almost a year and at a price much lower than their product. Canon also sold the CX to a few small companies but they didn't have the volumes to compete and quickly dropped out of the market. I imagine Canon also offered the CX to IBM and maybe even Xerox but evidently neither of them was interested.

Canon's "all-in-one" toner cartridge was a breakthrough concept, finally achieving "electronics like" reliability with a simple, straightforward design. In addition, since the CX print engine was largely leveraged from Canon's hugely successful, high volume personal copier, the manufacturing cost was relatively low. We were all tremendously excited when we saw the printer. We felt we finally had the product and partner we had wanted all along!

We chose Sprout as our project name for the first LaserJet. What's a "tree" smaller than a Bonsai? Of course, just a Sprout!

Schedule and trade-offs

When Canon visited us in April 1983, they told us they would be ready to begin mass production of the CX engine by February 1984. We were determined to a control canon's schedule for our HP product. This meant we would have had only ten months to develop a controller for the product. For that reason, we elected to use the controller Canon had already developed for their CX based product.

PCL (again)

For the print controller, there was much internal pressure to just emulate the Diablo 630 Daisy Wheel Printer (good text quality) or the Epson Dot Matrix Printer (good graphics) for Sprout since both of those products already had good software support across the industry. However, based on our HP 2680A experience, we knew business users wanted to print mixed text and graphics. For that reason we decided to use HP PCL since it had that capability plus all the other advantages mentioned earlier. So Von Hanson and his team worked with Canon to specify and implement PCL3 in their controller for Sprout.

PCL3 offered all the features early PC customers could realistically utilize (especially since at that time PCs lacked a graphical user interface) at a much lower price than the much more complex page description language (Postscript) chosen by Apple. By using our already largely-developed PCL, we were able to deliver LaserJet for a street price about \$1,000 less and almost a year before Apple's CX based product.

Software support was critical to making PCL and LaserJet successful. One opportunity came on an airplane departing the Softcon computer software show in New Orleans in February 1984. Von Hansen and Roger Archibald "just happened" to be seated on the plane beside Bill Gates of Microsoft. They told Gates about HP's exciting new laser printer and how it was the ideal output device for Microsoft products like *Word* and *Excel*. We were never sure how much this helped to get Microsoft support for LaserJet and PCL but it surely didn't hurt! How is THAT for serendipity?

A few weeks later Von carried a LaserJet prototype to Microsoft to solicit their software support. Initially the Microsoft folks gave the HP team a rather cool reception. But then Von took LaserJet out of its box and printed some demo pages. This got the Microsoft people really excited and they immediately called for their managers to come look at the printer. From that point forward, Microsoft tended to offer good software support for LaserJet and other PCL products.

In addition to Microsoft, we worked with other major independent software vendors (ISVs) to ensure excellent application software support for PCL. However during development of the first LaserJet we didn't have enough resources to do much. Later, Janet ' Buschert in the lab and then Cathy Lyons in marketing led major efforts that dramatically grew PCL application software support.

Fonts were a challenge for the first LaserJets. Semiconductor memory was very expensive and customer font requirements very fragmented. For those reasons, we elected to offer a limited number of "built-in" fonts and supply the rest in optional font cartridges. This satisfied mainstream users, kept the printer cost low and still gave customers a way to satisfy their special font requirements. Font cartridges (and fonts) became another responsibility for Janet Buschert. Through her efforts, this soon became a major business in its own right with more than 25 different cartridges at prices ranging from \$150 to \$330 each. It remained a good business for us into the early '90s when Microsoft started bundling fonts with their Windows operating system.

When Microsoft started bundling fonts with Windows, they basically gave them away. This was a huge advantage to HP in that it mostly solved our font problem and made WYSIWYG much better by ensuring matching screen and printer fonts.

Piggybacking on the Dealer Demos

Late in 1983 HP instigated a major push to participate in the PC market. A key part of this strategy involved development of a PC dealer channel to sell the new HP 150 Touch Screen PC (to be introduced in May 1984 along with LaserJet). The computer part of HP had the management support, money, resources and (hopefully) the PC to drive development of this channel. As the PC market exploded, several individuals associated with the LaserJet development (Roger Archibald, Von Hansen and Alan Armstrong) sensed that (just maybe) there could be a PC market for LaserJet. So we begged the HP 150 marketing folks to let us go along with them when they demonstrated their product to the major PC dealers. Finally they agreed to let us go with them to visit a few of the dealers but reserved the majority of time to demo the HP 150 (e.g. $1 \sim 1.5$ hours) while letting us have 10 or 15 minutes at the end to demonstrate LaserJet.



HP LaserJet

The dealer visits were a real eye opener for Boise Division. Typically the meeting started with dealer upper management in attendance. As the HP 150 demonstration dragged on, most of the dealer managers left and only a few subordinates stayed. When the LaserJet demo started, a subordinate would suddenly say "Wait a minuté" and dash out of the room. Soon they returned with their managers to watch the LaserJet demo. Needless to stay, all of the dealers we visited wanted to carry the LaserJet in their stores and thought it would be a good seller.

The HP PC Division still hesitated to let Boise Division sell LaserJet through the dealer channel. They thought it would defocus efforts to sell HP PCs. But after repeated urging by Roger Archibald they finally gave in at the last minute. Access to the PC dealer channel proved to be a key contributor to LaserJet's market success. It quickly proved to be the overwhelming vehicle for LaserJet sales.

Dealer visits plus the PC Division's agreement to let us use "their" dealer channel, convinced those of us in Boise Division that the LaserJet market was likely to be much bigger than just that required for HP minicomputers. This in turn gave us the confidence to forecast higher sales volumes when we priced the product. Paul Ely (Dick Hackborn's⁴ boss) was the person who bought into our sales volume vision and gave the final OK to price the first LaserJet at an aggressive \$3,495.

When we began development of Sprout (spring 1983), our market focus was still as a peripheral for HP minicomputers. HP's sales channel was largely direct sales and we were just beginning to develop a dealer channel. In addition, we estimated the first LaserJet would need to be priced at between \$3,500 and \$4,000. This was about equal to what an IBM PC sold for. PC sales were beginning to ramp up but we guessed that few customers would be willing to pay so much for a printer to go with their PC. We thought 1/2 or 1/3 of the cost of a PC was more likely what customers would expect.

Of course our prediction of customer expectations turned out to be wrong. We discovered that business customers were willing to pay much more for the break through print capability Sprout offered than we had imagined.

Because of our early focus on HP minicomputers as our market, the first LaserJet was designed with only a serial interface. By the time we knew we could sell through the dealer channel and that business PC customers might pay what a LaserJet would sell for, it was too late to change the design and add a parallel interface. We corrected this shortcoming in LaserJet+.

Naming LaserJet

In the natural order of things, the first LaserJet should have been the HP 2686A. HP had always named our products by their model number so why should this product be different? Our Boise marketing people heard that the first HP thermal inkjet printer was going to be called "ThinkJet" (for "THermal INK JET) so they said "That's catchy. Why don't we name our product the "LaserJet"?" We lab engineers thought this was a dumb idea. Our printer had a laser but it certainly didn't have a "JET". Fortunately marketing prevailed and LaserJet was born!

LaserJet Time to Market

We couldn't have achieved the short schedule for Sprout without our two earlier "failures." With the HP 2680A we established a strong working relationship with Canon. We also learned about the features customers wanted, fonts and the technologies involved in laser printing. With Bonsai we developed 300dpi laser fonts, implemented PCL2 and determined that significant HP engine testing was required to identify and cure failure modes. We had also developed the engine, environmental and regulatory specifications necessary for the product to meet HP's worldwide market requirements.

We were determined to (and did) make the LaserJet's schedule match that of Canon's print engine and product. So it turned out that we were the first company to have a CX engine based product in the PC dealer channel in the USA and Europe. Canon's product had some presence but it was small compared to HP. Canon's marketing strength was more with copier dealers and not the newly emerging PC dealers.

Reliability

HP played a significant role with Canon in the testfail-fix process of product development. Canon supplied HP with early prototypes and HP ran them until they failed. Of course Canon ran a similar process in parallel with HP. However we often found failure modes and usability problems Canon didn't see (or recognize) in their testing. About 15% or 20% of the failures found during the design process were unique to MP's testing. When problems were found, fixes were incorporated in later prototypes. Then we did more testing, failures and problems were analyzed and more fixes incorporated. This process went on throughout the development cycle. Together with Canon we discovered that joint testing resulted in a customer friendly product with superior reliability.

Not Everyone was a LaserJet Booster

There were forces working against LaserJet's initial (and longer term) success:

Limited resources and time – In early 1982 Dick Hackborn⁵ recruited a new R&D manager for Boise Division. The new manager changed our focus from laser printing to an investigation of high speed thermal ink jet TIJ) printing. As a result, by the middle of 1983 Boise Division had 5 engineers working to specify/qualify the Sprout engine and 15 engineers working on high speed TIJ technology. This reflected the feeling by much of upper management at this point in time. They weren't confident in LaserJet and believed TIJ had a good shot at replacing it in the midrange and high end markets. That still hasn't happened, twenty-five years later.

Besides limited resources, we had less than ten months between the time Canon showed us the CX prototype and the date Canon would start production of the print engine. In spite of limited support, we were still able to match Canon's engine schedule and full LaserJet production began in February 1984. Historically HP was a vertically integrated company. Corporate culture tended to believe HP had to control the technology used in our products. So from the beginning, HP upper management was inclined to discourage investment in laser printers based on a purchased engine and there was certainly some logic in that historical perspective. They were convinced the engine supplier would eventually take the market away from us with their own product using the same engine. This belief was still alive even after LaserJet was wildly successful and we had already sold several million units.

For example I remember Dick Hackborn interacting with us during a quarterly review when we were demonstrating the LaserJet II prototype. I expressed our excitement about the product and our belief that its market potential was even greater than the first LaserJet. We also explained our short schedule and need for additional resources to stay on track. Dick's response was something like: "It (LaserJet business) looks OK now but don't get used to it because it won't last." Everyone who heard this received it like a dash of cold water. In spite of this, the project team wasn't deterred and if anything worked even harder to make LaserJet II a success.

7. NC

Another example was around 1990 when HP's CEO told HP Labs they shouldn't support LaserJet with their research because it was probably not a sustainable business.

Finally, in January 1984 Boise Division General Manager Ray Smelek attended the annual HP general managers meeting in Napa, California. He told HP's top leaders from around the world that Boise Division was ready to launch a remarkable product in four months and we were convinced we could potentially sell as many as fifty thousand a year. Ray was almost laughed off the podium. Everyone in the room knew HP Computer Group had never sold fifty thousand of anything. Clearly hardly anyone in HP believed in laser printing or LaserJet. Only Ray and a small group of us in Boise Division kept the faith.

Successful LaserJet Market Introduction

We introduced the HP LaserJet on schedule at the National Computer Conference (COMDEX) in May 1984. It was a huge success at that show with long lines of attendees waiting to look at the LaserJet and find out how they could buy one. In May we received orders for about 1500 printers. December 1984 orders were for almost 8,000 printers. We ended up shipping 250,000 over its life.

LaserJet Follow-On Products Offer "More for Less"

It is with considerable pride that we can look at the following list of follow-on LaserJets. Each built on the success of the first LaserJet by continually offering "more for less". New product generations offered more features and capability for less cost, obsoleting the previous generation. This classic business strategy was implemented to near perfection with the early LaserJet products.

New capabilities are highlighted in **Bold Italics.** In general once a new capability was incorporated into a product, it was incorporated in all subsequent products. For example LJ II and all following products had correct order (face down) output, LJ IIP and all following products had "No Ozone" print engines, PCL was continually enhanced from product to product with higher levels of functionality. This gave customers "more" capability with each new product:

- LaserJet: 8 ppm, 300 dpi, \$3,495, Spring 1984. Price reduced to \$2,995, September 1985.
- LaserJet+: LaserJet with more formatting features, memory, fonts and a *Centronics parallel interface*. 8 ppm, 300 dpi, \$3,995, September 1985.
- LaserJet D+: LaserJet print engine and formatter but with 2 paper trays, 8 ppm, 300 dpi, \$4,995, Spring 1986.
- LaserJet II: Preceding LaserJets were leveraged from the Canon PC-20 personal copier. However LaserJet II was designed from the ground up as a laser printer with correct order paper output. (Correct order means when you pick up the pages out of the printer they are in the same order as in your software file.) HP's version had a unique HP industrial design to differentiate it from Canon's version. PCL4 Language with improved features, more memory and fonts. 8 ppm, 300 dpi, \$2,695, Spring 1987.





- LaserJet IID: Same as LaserJet II except 2
 paper trays and first desktop laser printer
 with duplex (2 sided) printing. First LaserJet
 with an HP designed and manufactured
 Formatter. 8 ppm, 300 dpi, \$4,295, Fall 1988.
- LaserJet IIP: Worlds first "personal" laser printer, "No Ozone" print engine. 4 ppm, 300 dpi, \$1,495, Fall 1989.
- LaserJet III: New version of LaserJet II engine with PCLS, scalable fonts, REt (Resolution Enhancement Technology), HPGL and all new industrial design. REt gave perfectly (to the eye) smooth characters and graphics although the basic printer resolution remained 300 dpi. 8 ppm, 300 dpi, \$2,395, Spring 1990.
- LaserJet IIID: Same as LaserJet III with the addition of 2 paper trays and duplex printing.
 8 ppm, 300 dpi, \$4,995, Fall 1990.
- LaserJet IIISi: Higher speed, high duty cycle, LAN connectivity with MIO. 17 ppm, 300 dpi, \$5,495, Fall 1990
- LaserJet IIP+: Higher performance, lower price version of LaserJet IIP. 4 ppm, 300 dpi, \$1,249, Spring 1991.
- LaserJet PostScript Cartridge PostScript printing for the LaserJet III and LaserJet IIP, \$695, Fall 1991
- LaserJet 4: New Canon engine with 600 dpi resolution and Microfine toner. Supports Microsoft TrueType scalable fonts. 8 ppm, 600 dpi, \$2,199, Fall 1992.
- LaserJet 4Si: 600 dpl resolution. 17 ppm, 600 dpi, \$3,749, Spring 1993.

• LaserJet 4L: New low cost print engine with *"Instant On" fusing.* 4 ppm, 300 dpi, \$1,229, Spring 1993.

I could go on but I think by 1993 you can clearly see the following "more for less" trends:

- Midrange (8 ppm) LaserJets From the first LaserJet to LaserJet 4, prices decreased from \$3,495 to \$2,199 while both software and hardware features increased dramatically.
- The LaserJet product line expanded to encompass two new market segments:
 - Personal (4 ppm) LaserJet -Prices as low as \$1,249
 - Network (17 ppm) LaserJet Higher speed and duty eyele, network connected, priced almost as low as the original LaserJet but with much, much greater capability

LaserJet sales greatly expanded as we drove prices down, performance up and entered new market segments. We shipped 1 million LaserJets by 1988. Sometime after the introduction of LaserJet II our order processing system came to a halt. Orders for that month had exceeded 99,999, the largest number Computer Group's order processing system would accept! The computer glitch was fixed and orders continued to climb. Total LaserJet sales had reached 100 million by 2006.

HP Printer Formatters/Controllers and LaserJet IID

The printer formatter (or controller) translates commands generated by the user's software application, describing what is to be printed, into the dots the laser actually puts on the page. We designed our own formatter for the HP 2680A, however the lack of resources and short schedules made this impractical for the next few laser products. For that reason Canon designed and manufactured the controllers for all LaserJet products up to and including LaserJet II.

By 1986 (LaserJet II) it had become increasingly clear that Canon's control over formatter design was greatly constraining HP's ability to add new features (e.g. higher levels of PCL, memory, processing power) at the rate we desired. At that time Doug Carnahan was Boise Division General Manager. He initiated a program to overcome this shortcoming by having HP design and manufacture all future LaserJet formatters. This was a bold step in that our next product (LaserJet IID) was scheduled to be released to manufacturing only 18 months later.

Fortunately LaserJet IID offered a relatively good entry point for HP designed and manufactured controllers. Although the schedule was short, the IID was projected to sell at only a few thousand per month. This would allow HP to exercise and perfect our design and manufacturing processes before we took on very high volume products like the follow-on LaserJet III.

The plan was that HP would manufacture controllers in Boise then ship them to Canon in Japan where they would be installed in the print engine to make a complete product. Canon required that our formatters have 99.97% reliability as delivered to their factory in Japan. This was an extremely aggressive goal and sometimes we wondered if they were just using it as a way to discourage us from supplying the formatters!

Doug Carnahan challenged Von Hansen and his team to complete the project in 18 months. Von and team took on the challenge even though the high performance PCL4 graphics in LaserJet IID required a new microprocessor plus a complex custom integrated circuit (The first one ever designed by Boise Division.). The formatter project was named 3A (Version 3A of multiple potential hardware architectures). To meet the schedule, Von's engineers took extreme measures such as canceling family vacations and in one case, a team member dropping out of graduate school. Von managed the project in the most organized fashion I've ever experienced. Detailed progress was measured on a weekly basis and resources reallocated as necessary to keep everything on track. Von's whole team pitched in and gave the effort everything they had.

To meet Canon's reliability goal Von implemented a rigorous design review process plus a special form of environmental testing that subjected the formatter to temperatures ramped from -50 to +100 degrees C and then back to -50 degrees over just a few minutes. The formatter was operating during all this so any failure could be detected and corrected. This test process proved extremely effective at exposing basic semiconductor as well as circuit design flaws.

While Von's team was scrambling to design the formatter, a similar crash program was taking place in manufacturing led by Steve Hager and his team. There was no precedent within HP for a factory that could manufacture printed circuits at the quality levels and volumes required for 3A. Steve's team did a lot of intense, pioneering work and was finally able to meet or beat all their manufacturing goals. LaserJet IID was the first LaserJet where we had to integrate HP formatter development and manufacturing with Canon's engine development and manufacturing. To match Canon's aggressive engine schedule we needed a new way to coordinate HP R&D, manufacturing and marketing activities. So we formed a Program Management Team (PMT). This team was composed of one manager from each major part of the program who was able to make decisions for their group without normally having to consult a higher authority. This helped maximize overall coordination and shortened the schedule. The LJIID PMT approach proved to be so successful that we adopted it for all future LaserJet programs.

Through the hard work of Von's and Steve's teams, the LaserJet IID and 3A formatter programs were a complete success. Our formatter matched Canon's engine schedule, we met all quality, cost and performance goals and LaserJet IID shipped on schedule. From this point forward HP designed and manufactured all formatters used in LaserJet products, providing FIP the following advantages:

- Gave HP more control over the timing and implementation of key differentiating features such as higher levels of PCL and REt..
- Significantly increased HP's added value and resulting profit.

The Consumables Business

In the early LaserJet days we were focused on selling printers. To do this, we felt we needed low cost toner cartridges to make the printer "cost per page" as competitive as possible. Canon did not agree with our strategy. They tended to charge HP more for toner cartridges than we thought prudent for selling printers. Canon's strategy was based on their years of experience selling copiers. They understood, much better than we did, that the toner business was an important part of the overall printer profit model.

It wasn't until about 1990, after we had sold several million LaserJets, that we formed an Operation (later a Division) responsible for our consumables business. From that point forward we put more emphasis on making money on toner even if it made printers a bit less competitive. The consumables group then expanded their product line to include paper. Their focus on making consumables a strong business for HP became an important part of the LaserJet evolution and overall business success.

Competition

Remember the management worry that HP's initial LaserJet success was just a "flash in the pan" and our business would evaporate as soon as Canon wanted to take it away? Well in more than 25 years Canon hasn't taken the business away from HP. One reason was that the LaserJet brand and market leadership was so commanding, that by the time Canon developed a dealer channel, there was almost no way to catch up with us. Another reason was that ongoing MP PCL enhancements and software support meant Canon's products were always at least one step behind ours. All this meant Canon could make more money selling print engines to HP than fighting us in the marketplace.

Actually the closest we ever came to losing significant LaserJet market leadership was probably from Lexmark. Lexmark was a spinoff from IBM in 1991 but kept the legal right to use the IBM-logo for a number of years. The Lexmark engineers had years of experience in designing IBM copiers and had access to IBM copier technology and know-how. IBM had a patent cross license with Canon which was retained by Lexmark for all patents issued prior to the spinoff date. This meant Lexmark had access to many key Canon patents including the "all in one" toner eartridge. Lexmark engineers combined parts of an earlier design with the Canon "all-in-one" toner cartridge concept, made further improvements and introduced a very competitive series of products. The Lexmark products were well designed, had the IBM logo and were a very serious competitive threat for a number of years. An overview of Lexmark's version of the "All-In-One" cartridge can be seen at: http://www.youtube.com/watch?v=PHxXmjxcAIo Since Lexmark's cartridge concept is similar to Canon's, the video is quite applicable to LaserJet.

Dick Hackborn's View

An excerpt from a manuscript in the HP Company Archives based on a conversation with Dick Hackborn in *Print Unchained*³ page 164 gives his view of how the LaserJet business evolved:

> "By the early 1980s, the Boise Idaho team had already gained a lot of experience in laser printers based on their own minicomputer system products. It was through their insight that the huge potential of a desktop laser printer was first recognized and subsequently turned into an immensely successful new business for HP. There was no backseat driving from me or Bill Hewlett or any of the corporate executives in Palo Alto. Boise set its own agenda with Canon, negotiated its own contracts, jointly did product

definition with Canon, developed its own printer controllers, planned its marketing strategy (including distribution, a not uncontroversial item) and made the business happen."

Summary - Key Factors Shaping the LaserJet Business Success

Initial Business Success

- Timing Canon: Reliable, low cost laser engine with toner cartridge leveraged from Canon's personal copier, availability of low cost CD player solid state lasers; PC market explosion; HP: Development of a PC dealer channel, HP Boise: PCL language (low cost, good performance, "just enough" functionality for the typical office user), technology and processes leveraged from earlier laser printer projects. - All these pieces came together at just the right time to design the right quick, quiet, quality product customers wanted for PC printing.
- Strong Canon/HP relationship. Starting with Bill Hewlett and Dr. T. Mitarai and including Hajime Mitarari and Don Hammond, T. Kitamura and the HP engineers/managers who interacted with Canon during HP2680A development.
- Canon culture Many similarities with HP culture (ethics, honesty, quality, innovation, dedicated work force, people focus, respect, citizenship). This made for an excellent working relationship.
- HP Organizational/Divisional Structure:
 - Enabled/forced Boise Division to purchase a very significant portion of the LaserJet product. Although the traditional HP business model historically suggested vertical integration, Boise Division had neither the resources nor time to design and manufacture our own print engines. We had to purchase them from an outside company.
 - Boise Division was hungry for a successful printer product. It is unlikely that a division with a large, successful business would have gambled as much as we did on a new, unproved technology like laser printing. In our eyes, non-impact laser

printing was the obvious technology for the print speeds, duty cycles and office environment required by our customers. During this time, Thermal Ink Jet was still too slow and had too many other problems (e.g. water fastness) to be viable. Being small and largely invisible to upper management probably helped us in successfully pursuing our laser printing vision.

Longer Term Business Success

- Canon/HP mutual dependence In a relatively short period, the HP LaserJet had the brand recognition, market share and sales channel allowing us to move higher product volumes than anyone else. Canon would have had a hard time walking away from such a high volume customer. At the same time, Canon had by far the best laser print technology, reliability and manufacturing capability. HP could not have found another partner with the ability to deliver such a competitive product (except for those very brief periods when Canon fell behind).
- Continued HP investment (PCL: improved functionality, keep it a moving target), formatter (controller) hardware, software support, fonts, industrial design, innovative features, reliability, usability and "time-tomarket." Constantly striving to deliver "more for less" and always keeping our product development in step with Canon's engine development (We called this "drinking from the Canon fire hose.")
- Continued strong Canon investment in laser engine technology and manufacturing, driving engine costs down and performance up. Major innovations such as "instant-on" fusing, roller charging and transfer, 600 dpi resolution, micro-fine toner.
- The right business model at both HP and Canon for a successful non-vertically integrated business.

Acknowledgements

I wish there were some way to list all the people who contributed to HP's success in laser printing. Ray Smelek clearly played a major role by continuing to support laser printer development even after our first two failures. Don Hammond consistently supported our efforts and worked to strengthen the Canon/HP relationship.

Key architects for the HP 2680A included Jim Langley, Bob Hay, Bill Robison and Phil Gordon. I've already mentioned Von Hansen's leadership with PCL/formatters, Roger Archibald's role as project manager for the first LaserJet and Steve Hager's leadership in formatter manufacturing. However there are literally hundreds of other people who played key roles in LaserJet's success over the years and it is downright impossible to name all of them. So all I can do is to just say "Thank you for a job well done. Your dedication and hard work allowed us to accomplished what most "pundits" said was impossible"

A special vote of thanks to John Minck who encouraged me to write this history and edited the final result. John was a long time HP employee (joined HP long before me), knew Bill Hewlett and Dave Packard personally, served in multiple management and marketing roles including the LED Dept. Manager in the HPA Division that supplied LED displays for HP calculators and instruments in their early days. John and I crossed paths at HP Microwave Division in 1975 and have remained friends since.

Jim Hall Boise, 2011

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- 1) Charles House and Raymond Price, The HP Phenomenon – Innovation and Business Transformation (Stanford University Press, 2009)
- 2) Ray Smelek, Ray Smelek Making My Own Luck (Claxton Printers, Caldwell, ID)
- 3) Edward Webster, Print Unchained (DRA of Vermont, Inc, 2000)
- 4) Good additional historical information on the early LaserJet product line can be found at the HP Museum web site: http://www.hpmuseum.net/exhibit.php?class=5& cat=19
- 5) Dick Hackborn was General Manager of Disc Memory Division (DMD) when it moved to Boise in 1976. In 1980 he became responsible for the Computer Peripherals Group which included Disc Memory, Vancouver, Greeley and Boise Divisions. In 1984 his role was expanded to also include San Diego, Corvallis and Bristol – (UK) Divisions.

13

HP LaserJet

From Wikipedia, the free encyclopedia

LaserJet as a brand name identifies the line of dry electrophotographic (DEP) laser printers marketed by the American computer-company Hewlett-Packard (HP). The HP LaserJet was the world's first desktop laser printer.^[1]

Contents

- I Technology
- 2 History
 - **2.1** 1980s
 - **2.2** 1990s
 - **2.3 2000s**
 - 2.4 Evolution of the LaserJet control panel
 - 2.5 Key innovations
 - 2.6 Industry firsts
 - 3 Models
 - 3.1 Mono
 - 3.2 Color
 - 3.3 Model suffixes
 - 4 Upgrading memory of older models
 - 5 See also
 - 6 References
 - 7 External links

Technology

HP LaserJet printers employ xerox electro-photographic laser-marking engines sourced from the Japanese company Canon. Due to a very tight turnaround schedule on the first HP LaserJet, HP elected to use the controller already developed by Canon for the CX engine in the first HP LaserJet.^[2]



The LaserJet 500 Plus (model 2686D) was ... the largest of the early LaserJet series.

Laser head from HP LaserJet 5L printer

The first HP LaserJet and the first Apple LaserWriter used the same print engine, the Canon CX engine.^[3] HP chose to use their in-house developed Printer Control Language (PCL) as opposed to Apple, which adopted the PostScript language, as developed by Adobe Systems. The use of a less-ambitious and simpler Page Description Language allowed HP to deliver its LaserJet to the market about a year before Apple's CX based product, and for \$1000 less.^[2] The sharing of an identical Canon engine in two competing products continued with the HP LaserJet II/III and the Apple LaserWriter II, which both used the Canon LBP-SX print engine.

[•]History

1980s

HP introduced the first laser printer for IBM compatible personal computers in May 1984 at the National Computer Conference (COMDEX). It was a 300-dpi, 8 ppm printer that sold for \$3,495 with the price reduced to \$2,995 in September 1985,^[2] and featured an 8 MHz Motorola 68000 processor and could print in a variety of character fonts.^[1] It was controlled using PCL3. Due to the high cost of memory, the first LaserJet only had 128 kilobytes of memory, and a portion of that was reserved for use by the controller.

The HP LaserJet printer had high print quality, could print horizontally or vertically, and produce graphics.^[1] It was ideal for printing memos, letters, and spreadsheets. It was quiet compared to other contemporary printers, so people could talk on the phone while sitting next to the HP LaserJet printer as it was printing.^[1]

The first LaserJet was a high-speed replacement for text-only daisy wheel impact printers and dot matrix printers. By using control codes it was possible to change the printed text style using font patterns stored in permanent ROM in the printer. Although unsupported by HP, because the Laserjet used the same basic PCL language (PCL Level III)^[3] spoken by HP's other printers it was possible to use the Laserjet on HP 3000 multiuser systems.

The LaserJet Plus followed in September 1985, priced at US\$3,995.^[2] It introduced "soft fonts", treatments like bold and italic and other features including a parallel (Centronics) interface. It also included 512 kilobytes of memory, which was just enough to print graphics at 300 dpi that covered about 70% of the letter-size page area.
In March 1986 HP introduced the LaserJet D+, which included the LaserJet print engine and formatter but with 2 paper trays.^[2] The original MSRP was \$4,495.^[3] In 1986, desktop publishing came to the world of IBM PCs and compatibles, after its origin on the Apple Macintosh and Apple LaserWriter. The HP LaserJet family, along with Aldus PageMaker and Microsoft Windows, was central to the PC-based solution and while the design was more plebeian than Apple's product, this multi-vendor solution was available to a mass audience for the first time.

HP introduced the mass-market laser printer, the LaserJet series II, in March 1987. The HP LaserJet II was designed from the ground up as a laser printer with correct order page output as opposed to being leveraged from the Canon PC-20 personal copier.^[2] The HP LaserJet II used PCL4, improved features, more memory and fonts for a market price of \$2,695.^[2]

Also in March 1987, the LaserJet 2000 was launched. A high-end, networkable printer, the LaserJet 2000 offered a duty cycle of 70,000 pages per month and the standard 300-dpi output, initially priced at \$19,995.^[citation needed]

The HP LaserJet IID was released in the fall of 1988, It was the first desktop laser printer capable of duplexing.^[2] It was also the first HP LaserJet with an HP designed and manufactured formatter.^[2]

In September 1989, HP introduced the first "personal" version of the HP LaserJet printer series, the LaserJet IIP. Priced at US\$1,495 by HP, and half the size and price of its predecessor, the LaserJet II, it offered 300-dpi output and 4 ppm printing with PCL 4 enhancements such as support for compressed bitmapped fonts and raster images. It was also the first **no ozone** print engine.^[2] Retailers predicted a street price of \$1000 or less, making it the world's first sub-\$1,000 laser printer. The LaserJet IIP (and its very similar successor, the IIIP) were extremely reliable except for scanner failures, diagnosable by the lack of the familiar "dentist drill" whine and a "52" error displayed on the control panel; aftermarket replacement scanner assemblies remain readily available to this day.

1990s

In March 1990 HP introduced the LaserJet III, priced at US\$2,395, with two new features: Resolution Enhancement technology (REt), which dramatically increased print quality, and HP PCL 5.^[2] Thanks to PCL 5, text scaling became easy, and thus customers were no longer restricted to 10- and 12-point type sizes. This had a dramatic effect on word processing software market.

The HP LaserJet IIID was the same as the HP LaserJet III except it had 2 paper trays and duplex printing. It sold for \$4,995 in the fall of 1990.^[2]

The first mass-market Ethernet network printer, the HP LaserJet IIISi, d Priced at \$5,495, it featured a high-speed, 17 ppm engine, 5MB of memory, 300-dpi output, Image REt and such paper handling features as job stacking and optional duplex printing. The LaserJet IIISi also was HP's first printer to offer onboard Adobe PostScript emulation as opposed to the font-cartridge solution offered on earlier models.

In October 1992 HP introduced its first printer with 600-dpi output and Microfine toner, the LaserJet 4, bringing publication-quality printing to the desktop for a cost of US\$2,199. This model also introduced TrueType fonts to Laserjets; this ensured that the

printer fonts exactly matched the fonts displayed on the computer screen. (TrueType fonts could print on an original LaserJet Plus or later, but they would be printed as graphics, making the printing slow and restricted to a limited page area or reduced resolution.)The HP LaserJet 4 had a new Canon engine to enable the 600dpi.^[2]

Instant on fusing was introduced with the HP LaserJet 4L in the spring of 1993. It included a new low cost print engine.^[2] It sold for \$1,229.

In April 1994 HP shipped its 10-millionth LaserJet printer.

In September 1994 HP introduced the Color LaserJet, the corporation's first color laser-printer. The printer had an average cost per page of less than 10 cents. The Color LaserJet offered 2 ppm color printing and 10 ppm for black text, 8MB of memory, 45 built-in fonts, a 1,250-sheet paper tray and enhanced PCL 5 with color. Priced at \$7,295.

In March 1995 HP introduced the LaserJet 5 family of printers. They supported HP PCL 6, a printer-language which gave noticeably faster output – especially with complex, graphics-intensive documents. They also featured 600-dpi output with REt, and a 12 ppm engine. Prices started from \$1,629.

In 1996 HP introduced the network-ready LaserJet 5Si, a major revision and upgrade to the 3Si (IIISi) and 4Si, which had used the Canon NX engine. The 5Si, based on the Canon WX engine, could thus provide 11"x17" printing at an unprecedented 24 pages per minute and at 600 dpi with resolution enhancement. An internal duplexer enabled full-speed double-sided printing. Automatic personality switching (between PCL and PostScript), a feature that first appeared on the 4SiMX, was standard on the 5SiMX. The 5Si series were true workhorses, but initial models were somewhat hobbled by a vulnerability to slightly low voltage (i.e. crashing if mains voltage was less than 120 Volts) as well as a weak clutch in Tray 3 (thus resulting in paper jamming for Tray 3 as well as the optional 2,000-sheet Tray 4), and also a weak solenoid in the manual feed tray (Tray 1).



These paper-handling issues were easily dealt with. Many 5Si LaserJets remain in service today.

In 1997 HP introduced the HP LaserJet 4000 family of printers. They included features from the HP LaserJet 5 plus higher resolution of 1200 dpi. These are mostly used in offices, and most recently in people's homes mainly to replace the HP LaserJet 4/5 series if the user had them previously. In 1999 HP released the HP LaserJet 4050 series, which was identical to the HP 4000 but with a faster formatter and an easily accessible paper-registration area (where the paper is stopped, registered, and then advanced for printing; a flip-up cover here made clearing of this component easier.) The 4000 series, as well as the 4050 and the 4100, used partly external duplexers.

The world's first mass-market all-in-one laser device, the HP LaserJet 3100, debuted in April 1998. Users could print, fax, copy, and scan with a single appliance.

In July 1998 HP shipped its 30-millionth LaserJet printer.

In February 1999 HP introduced the LaserJet 2100 printer series^[citation needed] – the world's first personal laser printers in their class to offer high-quality 1200x1200-dpi resolution without significant performance loss.

In the network laser-printer market, the 5Si series was succeeded by the 8000, and later by the 8100 and 8150. The 8000 brought 1200x1200-dpi resolution, which was continued in the 8100 and 8150. The 8100 and 8150 brought faster printing (32 pages per minute), but this speed was only realized for single-sided (simplex) printing; double-sided printing remained at 24 pages per minute. These models, which used the Canon WX engine, provided excellent durability and good maintainability.

2000s

In December 2000 HP shipped its 50-millionth LaserJet printer.^[4]

In September 2001 HP entered the low-end laser printer market with the introduction of the LaserJet 1000: the first sub-\$250 LaserJet and the lowest-priced monochrome (black and white) HP LaserJet printer to date. It offered 10 ppm, an HP Instant-on fuser, 600 dpi with HP REt boosting output effectively to 1200 dpi, a 2.5-cent cost per page, and a 7,000-page monthly duty cycle.

In 2002, the 8150 was discontinued and was replaced by the 9000 series, which produced 50 pages per minute and used an internal duplexer. Meanwhile, the 4100 was replaced by the 4200 (later



HP LaserJet 1012, a low-end personal laser printer

4250) and 4300 (later 4350), which brought speeds of up to 55 pages per minute.

In 2003 HP shipped its 75-millionth LaserJet printer.

In November 2003, HP entered the \$24-billion copier market with the LaserJet 9055/9065/9085 MFPs(multifunction printers), a copier-based line of high-volume multifunction printers.

In 2006, total HP LaserJet sales had reached 100 million.^[2]

As of 2007 HP has several lines of monochrome and color printers and multifunction products (copy, scan, and/or fax included) that range from 20–55 ppm and range in price from \$149 to several thousand dollars.

Evolution of the LaserJet control panel

The 1992 LaserJet 4L marked the transition between a control panel evolved for an informed operator and one evolved for a casual user. The 4L's predecessor, the IIIP, had an array of buttons and a cryptic numerical LCD. The 4L shipped with 4 LEDs, each with an icon to indicate a different condition, and a single pushbutton whose purpose varied depending on context (i.e. Hold down during printing, the printer will cancel the job. Hold down when off, the printer will power up and print a test page including total number of pages printed. A short press would provide a form feed or tell the printer to resume from a paper jam or out-of-paper condition. The actual application of the button is far more intuitive than any possible written description – basically, the button tells the printer "Whatever you're doing now, do the next most logical thing".). This interface is easier for new and casual users to understand and use, but it is also much less powerful, as in any case there is only one thing you can make the printer do, and until you become familiar with the printer's behavior, you have to guess what that one thing is, or else consult the manual.

A 4L's four status LEDs will also light in unusual patterns to indicate service requirements; for example, a lit error light and a lit ready light would indicate a fuser problem (usually just needs to be reseated – most 4L problems can be resolved by simply disassembling the printer, cleaning it, then reassembling it).^[citation needed] This was much more cryptic than the alphanumeric display of earlier models like the II/IID, III/IIID, IIP, and IIIP, as it was impossible to determine the meaning of the patterns of LEDs without comparing them against a manual (or

HP LaserJet 500 Plus Control Panel: the original LaserJet two-character display provides a wide range of feedback, status, and error messages



HP LaserJet 4 Control Panel: the two-character ready code "00" is a carryover from the original LaserJet display shown above, but the display now features 16 alphanumeric characters, allowing 13character descriptive messages (after the number and a space). Many options, such as font selection, paper

size and tray selection, I/O settings, and test prints are also available at this control panel through a menu system.

and in fact upgraded from the LCD displays of earlier models by using a 16-character alphanumeric dot-matrix vacuum fluorescent display. To this day, professional-grade LaserJets retain more comprehensive displays.

Before the 4L, the control panel typically had buttons with names like **Online**, **Menu**, **Shift**, **Continue**, **Reset**, +, -, and **Form Feed**. It also included status indicators like **Online** and **Ready**. Users without a technical background, especially those who has not used a printer before the late 1990s, might not understand these indicators, or might think they are conflicting or ambiguous. It may not be intuitive to new users that a printer that is ready but offline does not print, and while being able to take the printer off line (effectively disconnecting it from the computer) without shutting it down can be very useful, this distinction may appear as an extra complication to users who want to casually use the printer merely as an information appliance.

When a Windows PC controls a LaserJet, the "Form Feed" button seldom does anything when pressed. It has a small indicator light, and was usually used with very simple DOS programs that did not eject the last page after sending data to the printer, though it could also be useful to print the data in the printer's memory if a program failed in the middle of sending a page to be printed. (In certain cases, this might be the only way to recover one's data in the event of a system crash that occurred while printing.) The Form Feed button would print whatever was remaining in memory and prepare the printer to accept any new data as the start of a new page. Note that for at least some LaserJet models, notably the LaserJet 4[M][Plus], the printer must be switched off-line before the Form Feed button will work. Most users of dot-matrix printers in the 1980s probably found the Online and Form Feed functions obvious, as most dot-matrix printers had these buttons and they worked similarly. The indicator on the Form Feed button illuminates when there is received data in the printer's buffer; this makes it much easier to predict what will happen if the printer is put online and a new job is sent to it, or if sending of a job in progress is resumed.

Also, the "Online" button is actually a toggle switch, such that if the printer is already online, pressing Online makes the printer go offline and can be used to stop a runaway print job. Pressing Shift-Reset will then reset the printer, clearing the remainder of the unwanted document from the printer's memory, so that it will not continue to print it when brought back on line. (Before resetting the printer, it is necessary to make the computer stop sending data for the print job to the printer, if it hasn't already finished sending that job, through the computer's software. Otherwise, when the printer is put back online, it will start receiving the job from somewhere in the middle, which will likely cause the same runaway problem to recur.)

HP LaserJet - Wikipedia, the free encyclopedia

With the advent of the HP LaserJet 4000 in 1997, the control panel was completely redesigned. The

Shift button, which might have been confusing, was gone. There was a Menu, an Item and a Value button. Each of these might be clicked left of right. There was a Select button, a large green Go button, and a small orange Cancel Job button. Configuration through the control panel was easier and more intuitive: you navigate in the menus with the Menu button. Then, you navigate in the items within the menu with the Item button. To change an item's value, you use the Value button which had - (decrease) and + (increase). You could use the Select button to select a particular choice. Also the display was adapted too, it was a blue-backlit two-line LCD display.

But by 1999 personal computers had embraced the Windows 95 era and many of the original manual control buttons like Form Feed were no longer necessary, because the Windows 95 printspooler subsystem offered even simple Windows applications a much greater control over the printer than was available to DOS applications, which had to each independently rebuild and reengineer basic printer management systems from scratch. This new



HP LaserJet 4000 Control Panel. Notice the backlit LCdisplay and the more intuitive user interface.

Windows-oriented interface was highly intuitive and obvious to the casual user, who needed little familiarization with the printer to use it effectively.

Raw, unformatted, text-only support still exists, but the professional LaserJet printers keep it hidden away. Most professional LaserJet printers include a PCL menu where the number of copies, the font style, portrait or landscape printing, and the number of lines-per-page can be defined. These settings are ignored by graphical PCL/Postscript print drivers, and are only used for those rare situations where a LaserJet is used to emulate a lineprinter.

Key innovations

- Spring 1984 First HP LaserJet
- Fall 1991 First HP Color LaserJet
- Spring 1997 First printer-based multifunction device
- Spring 2006 World's smallest-footprint LaserJet
- Summer 2011 HP Extraordinary Colors

Industry firsts

• Spring 1984 – Personal laser printing

- March 1991 Ethernet network printing
- April 1993 Web Jetadmin
- November 2005 Universal Print Driver

Models

The model numbers do not necessarily have anything to do with the order of product development or the type of print-engine technology. For example, the LaserJet 1018 printer has newer, smaller, and more energy-efficient technology than the LaserJet 4000. The 1018 also features USB while the older 4000 does not.

Mono

- HP LaserJet Original Printer series
 - HP LaserJet Printer (March 1984)
 - HP LaserJet Plus Printer (November 1985)
 - HP LaserJet 500 Plus Printer (March 1986)
- HP LaserJet II Printer series (March 1987)
 - HP LaserJet Series II Printer
 - HP LaserJet IID Printer (1988^[5])
 - HP LaserJet IIp Printer (1989)
 - HP LaserJet IIp Plus Printer (1989^[5])
- HP LaserJet III Printer series (March 1990)
 - HP LaserJet III Printer (1990^[5])
 - HP LaserJet IIID Printer (1990^[5])
 - HP LaserJet IIIp Printer (1991^[5])
 - HP LaserJet IIISi Printer (March 1991)
- HP LaserJet 4 Printer series
 - HP LaserJet 4 (October 1992) / 4M Printer series
 - HP LaserJet 4 Plus / 4M Plus Printer series
 - HP LaserJet 4L / mL Printer series
 - HP LaserJet 4p / mp Printer series
 - HP LaserJet 4Si Printer series
 - HP LaserJet 4v / mv Printer series (1994^[5])
- HP LaserJet 5 Printer series
 - HP LaserJet 5 / m / n Printer series
 - HP LaserJet 5 (April 1996)
 - HP LaserJet 5L Printer series

- HP LaserJet 5p / mp Printer series
- HP LaserJet 5Si Printer series
- HP LaserJet 6 Printer series
 - HP LaserJet 6L Printer series
 - HP LaserJet 6L Pro Printer
 - HP LaserJet 6p/mp Printer series
- HP LaserJet 1000 Printer series
 - HP LaserJet 1000 Printer (2001)
 - HP LaserJet 1005 Printer
 - HP LaserJet 1010 Printer series
 - HP LaserJet 1012 Printer
 - HP LaserJet 1015 Printer
 - HP LaserJet 1018 Printer
 - HP LaserJet 1020 Printer series
 - HP LaserJet 1022 Printer series
 - HP LaserJet 1100 Printer series
 - HP LaserJet 1150 Printer
 - HP LaserJet 1160 Printer Series
 - HP LaserJet 1200 Printer series
 - HP LaserJet 1300 Printer series
 - HP LaserJet 1320 Printer series
- HP LaserJet 2000 Printer series (March 1987)
 - HP LaserJet 2000 Printer series
 - HP LaserJet 2100 Printer series (February 1999)^[citation needed]
- HP LaserJet 2200 Printer series (2001)
 - HP LaserJet 2300 Printer series
 - HP LaserJet 2400 Printer series
- HP LaserJet 3000 Printer series (2006)
 - HP LaserJet 3100 Printer series
 - HP LaserJet 3200 Printer series
- HP LaserJet 4000 Printer series (1997)
 - HP LaserJet 4000 Printer series (1997)
 - HP LaserJet 4050 Printer series (1999)
 - HP LaserJet 4100 Printer series (2001)
 - HP LaserJet 4200 Printer series (2002)
 - HP LaserJet 4240n Printer
 - HP LaserJet 4250 Printer series
 - HP LaserJet 4300 Printer series

- HP LaserJet 4350 Printer series
- HP LaserJet 5000 Printer series
 - HP LaserJet 5000 Printer series
 - HP LaserJet 5100 Printer series
 - HP LaserJet 5200 Printer series
- HP LaserJet 8000 Printer series (1998)
 - HP LaserJet 8000 Printer series
 - HP LaserJet 8100 Printer series
 - HP LaserJet 8150 Printer series
- HP LaserJet 9000 Printer series (2002)
 - HP LaserJet 9000 Printer series
 - HP LaserJet 9040 Printer series
 - HP LaserJet 9050 Printer series
- HP-LaserJet P2001 Printer series
 - HP LaserJet P2015 Printer series
- HP EaserJet P3000 Printer series (2006)
 - HP LaserJet Enterprise P3010 series (2009)
- HP LaserJet P4010 Printer series
- HP LaserJet P4500 Printer series
- HP LascrJct Companion the LaserJet Companion is a sheet-fed monochrome scanner that connected to the parallel port of a LaserJet and provided copy functionality; as well as software scanning and fax functions.

Color

- HP Color LaserJet Original Printer series
 - HP Color LaserJet (September 1994)
- HP Color LaserJet CP4000 Printer series
 - HP Color LaserJet CP4005 Printer series
- HP Color LaserJet 5 Printer series
 - HP Color LaserJet 5/5m Printer series
- HP Color LaserJet 1000 Printer series
 - HP Color LaserJet 1500 Printer series
 - HP Color LaserJet 1600 Printer
- HP Color LaserJet 2000 Printer series
 - HP Color LaserJet 2500 Printer series
 - HP Color LaserJet 2550 Printer series
 - HP Color LaserJet 2600n Printer

- HP Color LaserJet 2605 Printer series
- HP Color LaserJet 2700 Printer series
- HP Color LaserJet 3000 Printer series
 - HP Color LaserJet 3000 Printer series
 - HP Color LaserJet 3500 Printer series
 - HP Color LaserJet 3550 Printer series
 - HP Color LaserJet 3600 Printer series (2004)
 - HP Color LaserJet 3700 Printer series
 - HP Color LaserJet 3800 Printer series
- HP Color LaserJet 4000 Printer series
 - HP Color LaserJet 4500 Printer series (1998)
 - HP Color LaserJet 4550 Printer series
 - HP Color LaserJet 4600 Printer series
 - -HP Color LaserJet-4610n Printer
 - HP Color LaserJet 4650 Printer series
 - HP Color LaserJet 4700 Printer series
- HP Color LaserJet 5000 Printer series
 - HP Color LaserJet 5500 Printer series
 - HP Color LaserJet 5550 Printer series
- HP Color LaserJet 8000 Printer series
 - HP Color LaserJet 8500 Printer series
 - HP Color LaserJet 8550 Printer series
- HP Color LaserJet 9000 Printer series
 - HP Color LaserJet 9500 Printer series

(Source: HP.com (http://www.hp.com/))

Model suffixes

Printers with factory-installed options have different model-numbers to denote the different options included and to differentiate a specific model from others in its series. These suffixes include:

- **D** for a duplexer, enabling automatic double-sided printing.
- T for an additional paper-tray (enables two different paper types to be kept available, or in certain models, to load paper while the printer is printing). (Some D models, with no T suffix, had two trays built in, as did the LaserJet 500 Plus.)
- S for a Paper Stacker, a device which increases the output bin capacity.
- N for built-in, MIO or EIO slot JetDirect (network) card
- W for built-in wireless network card

- *H* for High-capacity (heavy-duty model, sometimes combined with M to indicate Heavy Media)
- *L* for Light (only 1 paper tray)
- *P* for Personal, meant for "personal or small workgroup" use
- *ph+* for Paper handling (e.g. Stapler-stacker), or S/SL for stapler/stacker.
- *M* for Macintosh (PostScript module present); (sometimes?) also extra memory to support PostScript (as in 4M/4M Plus)
- V for 11-inch wide paper path, to support 8.5x11R and 11"x17" paper. (as in 4MV)
- X for combination duplexing, networkable printer with additional tray. Replaced the DTN suffix.
 - Example: A LaserJet 4000X would come with a duplexer and a built in JetDirect card, as well as an extra paper tray.

Upgrading memory of older models

Many older LaserJets and other HP printers (including LaserJet 4+, 4MV, 4MP, 4P, 5, 5M, 5MP, 5N, 5P, 5se, 5Si MOPIER, 5Si, 5Si NX, 6MP, 6P, 6Pse, 6Pxi, C3100A; DesignJet 330, 350C, 700, 750C, 750C Plus; DeskJet: 1600C, 1600CM, 1600CN; and PaintJet XL300) used proprietary 72pin HP SIMMs for memory expansion. These are essentially industry-standard 72-bit SIMMs with non-standard Presence Detect (PD) connections. One can often adapt a standard 72-pin SIMM of appropriate capacity to support HP PD by soldering wires to pads, a simple task.^[6] HP printers of this type specify that RAM not faster than 70ns be used; this is probably due to a limitation of the PD decoding, and faster RAM can actually be used so long as the PD encoding indicates a speed of 70ns or slower. All printers will work with FPM (Fast Page Mode) memory; many, but not all, will work with EDO memory.^{[7][8]}

Even older models, such as the LaserJet II, IID, III, IIID, and 4/4M (i.e. not 4 Plus), used proprietary memory expansion boards. For example, the II and IID models used a roughly 4" square memory expansion board populated with DIP DRAM chips and a two-row header connector (with pins on standard 0.1" centers).

See also

- Laser printer
- List of Hewlett-Packard products
- PC Load Letter

References

1. ^ a b c d "HP LaserJet Printer 1984"

(http://www.hp.com/hpinfo/abouthp/histnfacts/museum/imagingprinting/0018/index.html) . http://www.hp.com/hpinfo/abouthp/histnfacts/museum/imagingprinting/0018/index.html. Retrieved 6 June 2011.

2. A a b c d e f g h i j k l m n o Jim Hall (2011). "HP LaserJet-The Early History" (http://www.hparchive.com/seminar_notes/HP_LaserJet_The%20Early%20History_by_Jim_Hall_11051
2.pdf).

http://www.hparchive.com/seminar_notes/HP_LaserJet_The%20Early%20History_by_Jim_Hall_110512. pdf. Retrieved 6 June 2011.

- 3. ^ *a b c* "TPW CX Printers- Hewlett-Packard" (http://www.printerworks.com/Catalogs/CX-Catalog/CX-HP_LaserJet.html) . Printerworks.com. http://www.printerworks.com/Catalogs/CX-Catalog/CX-HP_LaserJet.html. Retrieved November 2, 2010.
- * "HP Virtual Museum: Hewlett-Packard LaserJet printer, 1984" (http://www.hp.com/hpinfo/abouthp/histnfacts/museum/imagingprinting/0018/index.html) . Hp.com. http://www.hp.com/hpinfo/abouthp/histnfacts/museum/imagingprinting/0018/index.html. Retrieved November 2, 2010.
- 5. ^ *a b c d e f* "Printers" (http://www.hpmuseum.net/exhibit.php?class=5&cat=19) . *HP Computer Museum*. Working Communications P/L. http://www.hpmuseum.net/exhibit.php?class=5&cat=19. Retrieved November 11, 2009.
- 6. ^ "Making Standard SIMMs Work Memory Upgrade on the HP LaserJet 6MP/5MP" (http://www.keycruncher.com/blog/2003/12/14/making-standard-simm-s-work-memory-upgrade-on-thehp-laserjet-6mp-5mp/). Keycruncher.com. http://www.keycruncher.com/blog/2003/12/14/makingstandard-simm-s-work-memory-upgrade-on-the-hp-laserjet-6mp-5mp/. Retrieved November 2, 2010.
- 7. ^ Page on memory upgrades for HP printers (http://www.hpprintermemory.com/index.html#y)
- 8. ^ List of HP printers and their memory options (http://www.shawnbehrens.de/hplist.htm)

External links

- HP Virtual museum: LaserJet printer (http://www.hp.com/hpinfo/abouthp/histnfacts/museum/imagingprinting/0018/index.html)
- Twenty Years of Innovation: HP LaserJet and Inkjet Printers 1984–2004 (http://h41131.www4.hp.com/uk/en/stories/20_years_LaserJet__proven_satisfaction.html)

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