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An Evaluation of Matching Unknown Writing Inks with the United States International Ink Library*

ABSTRACT: Utilizing a database of standards for forensic casework is a valuable resource. Undoubtedly, as more standards (and corresponding information about the specimens) are collected, there is a greater certainty of identification when a questioned and a known item cannot be distinguished after a series of analyses. The United States Secret Service and the Internal Revenue Service National Forensic Laboratory jointly maintain the largest known forensic collection of writing inks in the world, which is comprised of over 8500 ink standards collected worldwide, dating back to the 1920s. This study was conducted to evaluate the reliability of matching arbitrarily purchased pens with known inks from a database. One hundred pens were randomly obtained from a variety of sources and their respective ink compositions were compared with standards. Eighty-five of the inks were determined to be suitable for comparison utilizing optical examinations and thin-layer chromatography. Three of the inks did not match any of the specimens on record; one of these inks was similar to an ink from an identical brand of pen that was in the database, but had a modified formulation.

KEYWORDS: forensic science, questioned documents, ink, writing ink, ink dating, writing instruments, chromatography, TLC, ink database

The forensic analysis of writing inks can prove to be critical in cases involving the examination of questioned documents. Requests for ink analysis typically comprise three types. The first may involve comparing two or more inks to determine whether the formulations match each other, as defined in Sections 9.3.1 and 9.3.2 of the American Society for Testing and Materials (ASTM) Standard Guide E 1422-01 (1). This may help to ascertain whether any of the writing was added or altered. The second is to attempt to identify the writing ink on a questioned document and provide investigative information regarding the possible source of the ink. The third, and most challenging, request is to establish when the written entries were created to help determine whether they are authentic with respect to the purported date on which the document was prepared. The latter two tasks can be achieved by comparing the questioned ink(s) with an adequate collection of standards as described in ASTM Standard Guide E1789-04 (2).

Cantu (3,4) has outlined two analytical approaches for determining the age of an ink on a questioned document. The dynamic approach includes methods that incorporate procedures for the purpose of measuring the physical and/or chemical properties of an ink that change with time. The changes that occur over a given period of time can generally be referred to as aging characteristics. Different approaches to measuring the age of an ink, once it has been placed on a document, have been discussed in the literature by Brunelle (5,6), Cantu (7), Aginsky (8–11), Gaudreau and Brazeau (12), Brazeau et al. (13), Andrasko (14,15), Andermann and Neri (16), Humecki (17), and Hofer (18).

The second, or static, approach to ink dating generally applies to methods that are based on the comparison of various ink components with a standard reference collection of inks to determine the first date of production. Because of a variety of manufacturing logistics (e.g., changing the ingredients of a formulation for cost savings), marketing factors, and variations in consumer demand regarding the color, type of writing instrument (e.g., fountain, ballpoint, fiber tip, gel), and other personal preferences (e.g., fine point, medium point), numerous ink formulations have been commercially introduced in the past several decades. With such a vast number of writing inks and documented information relating to formulation changes, a database of inks can be used to discriminate and identify questioned entries forensically.

Cantu (3) and Harget (19) provide a comprehensive historical perspective of the United States International Ink Library. The United States Secret Service (USSS) and the Internal Revenue Service (IRS) jointly maintain the largest known forensic collection of writing inks from around the world. The collection includes more than 8500 inks, which date back to the 1920s, obtained from various manufacturers throughout the world. The pen and ink manufacturers are contacted on an annual basis and requested to submit any new formulations of inks, along with appropriate information, so that the new standards can be chemically tested and added to the reference collection. In addition, writing pens are obtained on the open market and compared with the library of standards to identify additional inks that may not have been formally submitted by a manufacturer. Maintenance of the library is a formidable task that obviously requires significant resources which may not be practical for most forensic laboratories. Indeed, this is not always a practical solution for every forensic facility to achieve. Consequently, the USSS generally

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(consideration is made on a case-to-case basis) provides assistance to law enforcement agencies throughout the world with cases involving the physical and chemical analyses of writing inks.

Writing inks mainly consist of colorants (dyes and/or pigments) and vehicles (solvents and resins). There is also a wide array of other ingredients, which can include antioxidants, preservatives, and trace elements, but these typically form a small fraction of the overall ink composition. Nevertheless, their importance should not be undermined. It is the combination of all of the ingredients that allows forensic examiners to differentiate inks using optical methods, such as examination under infrared reflectance (IRR) and infrared luminescence (IRL) illumination with an instrument like the Foster & Freeman Video Spectral Comparator (VSC). In 1999, Roux et al. (20) conducted studies on black and blue ballpoint inks using a filtered light examination (FLE), thin-layer chromatography (TLC), and reflectance visible microspectrophotometry (MSP). The authors concluded that "the power of the individual techniques to discriminate inks between and within brands, models and batches varied, the most informative techniques being TLC > FLE > MSP." They showed that FLE of blue inks ($n = 49$) and black inks ($n = 42$) resulted in a discriminating power (DP) of 0.83 and 0.96, respectively, where

$$\mathrm{DP} = \frac{\text{Number of discriminating pairs}}{\text{Number of possible pairs}}$$

TLC is one of the most widely used and generally accepted scientific methodologies used to compare and help characterize ink formulations. TLC has been discussed extensively by Witte (21), Brunelle and Pro (22), Brunelle and Reed (23), Brunelle and Crawford (24), Kelly and Cantu (25), and Aginsky (26). TLC analysis begins by removing an ink sample from a document, and subsequently extracting the ink in an appropriate solvent. The extract is then applied to a specially coated TLC plate (e.g., glass or plastic surface coated with silica), and placed in a solvent-equilibrated glass chamber containing a solvent or mixture of solvents. The sample components then migrate up the plate via capillary action. Typically, the colorants (e.g., dye components) that are present in the ink sample will separate into colored bands or spots. As described in the aforementioned study conducted by Roux et al. (20), "thin layer chromatography had the highest discriminating power for the individual techniques at 0.98 for blue and 0.99 for black."

The focus of this paper will be to evaluate the static approach of comparing unknown writing inks with inks in the U.S. International Ink Library. The study was conducted using 100 pens that were randomly obtained from various sources. Some of the pens were purchased from retail stores and others were collected on the open market (e.g., trade shows and hotels). As a matter of consideration, the authors have chosen to limit the discussion with regard to naming the manufacturers as technical information pertaining to writing inks is often proprietary. An open market sample includes any writing ink that is gathered from throughout the world and does not come directly from the manufacturer as a result of an annual petition for newly formulated inks. As noted in ASTM Standard Guide E 1789-04 (2), a questioned ink(s) and a known ink(s) are determined to match each other when "... optical and chemical analyses reveal no significant, reproducible, inexplicable differences and there is significant agreement in all observable aspects of the results." It should be noted that at the level of analysis utilized in this study, i.e., an optical examination and TLC, ink formulations are not chemically identified with 100% certainty; instead, the questioned and known inks are ascertained to be indistinguishable based on a comparison with all the inks in the collection (> 8500).

Typically, open market samples are chemically analyzed and compared with library specimens. If the sample matches an ink(s) on file, a notation is made in the database. If a match is not made, further information is then obtained, as appropriate, to determine the manufacturer and the first commercial date of introduction. Making continual open market purchases is important because such purchases function as a check-and-balance system to ensure that the library is as comprehensive as possible.

Materials and Methods

Extraction

One hundred pens were randomly purchased and/or collected from various sources. A summary of the types and colors of ink specimens can be found in Table 1. A writing sample from each pen was made on Whatman® filter paper # 2 (Catalog Number 1002-917, Whatman Ltd., Maidstone, Kent, U.K.). Five to 10 hole punches (*c.* 1.0 mm in diameter), or plugs, were removed from each ink line using a hypodermic needle-like apparatus (Harris™ micro-punch, Electron Microscopy Sciences, Fort Washington, PA). The plugs from each of the inks were placed into a glass vial and allowed to extract with an appropriate solvent. Ballpoint inks were extracted with approximately 5 μL of pyridine. Nonballpoint inks (e.g., fiber tip, roller ball, gel) were extracted with approximately 5 μL of a 1:1 solution of ethanol and water. In all cases, the inks were manually agitated for 20–30 s to promote better extraction of the colorant components.

TLC

TLC analysis was conducted in accordance with section 7.7 in ASTM Standard Guide E 1422-01 (1), and comparisons were made with reference specimens from the U.S. International Ink Library as described in Section 7 of ASTM Standard Guide E 1789-04 (2). The TLC plates were allowed to develop in a solvent system composed of ethyl acetate, ethanol, and water in a ratio of 70:35:30, respectively.

Optical Examination Using the Video Spectral Comparator 2000 High Resolution (VSC 2000 HR)

The VSC 2000 HR (Foster and Freeman, Ltd., Evesham, Worchestershire, U.K.) was used following the TLC examination to ensure that there were no significant differences in the IRL and IRR properties of the questioned and known inks. A comparison was made between the samples, and as per Section 9.3.1.1 in ASTM Standard Guide E 1789-04 (2), if there were any significant, reproducible, and/or inexplicable differences, the questioned and referenced inks were determined to be different.

TABLE 1—*A total of 100 inks that were randomly obtained are categorized by type (e.g., ballpoint and nonballpoint) and color.*

	Black	Blue	Red	Green	Total
Ballpoint	37	21	6	0	64
Nonballpoint*	16	10	8	2	36
Total	53	31	14	2	100

*Fiber tip, fountain, gel, and rollerball.

Results and Discussion

The colorants in 15 of the writing inks did not extract into solvents and/or migrate on the TLC, which indicates that they are pigment based. These inks were not feasible for comparison with the library of standards based on their lack of a colorant profile on a TLC plate; however, this would not preclude additional comparative testing using alternate methods such as Fourier transform-infrared spectrometry (FT-IR), gas chromatography-mass spectrometry (GC-MS), liquid chromatography-mass spectrometry (LC-MS), and/or scanning electron microscopy (SEM) coupled with energy-dispersive X-ray analysis (EDXA). It is noted that 14 of the 15 inks that were not extractable were gel inks (eight produced by the same manufacturer). The remaining 85 writing inks (64 ballpoint and 21 nonballpoint) were used to conduct the assessment based on TLC and optical examination results.

After conducting intercomparison examinations on the 85 inks, it was determined that there were at least 44 different formulations, i.e., 44 different families of inks that could not be further discriminated at the aforementioned level of analysis. The fact that there were fewer formulations ($n = 44$) than the number of pens ($n = 85$) is not surprising for several reasons. For example, some companies commonly sell different pens with the same formulation of ink. Oftentimes, the only difference in such pens is in the construction of the barrel (these writing instruments may be assigned different brand names) or the size of the tip (e.g., fine and medium point). Also, some of the pens in the study were acquired from tradeshow vendors or hotels. These pens may incorporate the same ink formulation that was purchased from a manufacturer, which, in turn, produced another pen in this study (e.g., Bic Corporation [Milford, CT] may produce pens for a hotel chain). One other reason for possible ink duplication is that some pen manufacturers may purchase ink formulations from each other or from a common source. Figure 1 depicts a classification scheme of the extractable inks and the number of different formulations within each ink type and color in the respective writing instruments.

After comparing inks from the collected pens with comparable standards maintained in the U.S. International Ink Library, it was determined that 100% of the black ballpoint, the blue nonballpoint, and the red nonballpoint inks matched corresponding inks in the collection. One blue ballpoint pen that was acquired in Berlin, Germany, in March 2005, did not match any reference standards. Two red ballpoint pens, which had consistent formulations, did not match any ink in the database. Finally, one of the black nonballpoint pens (felt tip marker) did not match any of the known specimens; however, it is very similar to a formulation on record that is used in a similar felt tip marker produced by the same company, i.e., the markers were the same brand name. Additional information from files maintained at the USSS (based on conversations with the manufacturer) indicated that this ink formulation had been slightly altered multiple times over the past 25 years. Table 2 represents a summary of the number of matches made after the unknown inks were compared with inks in the reference collection.

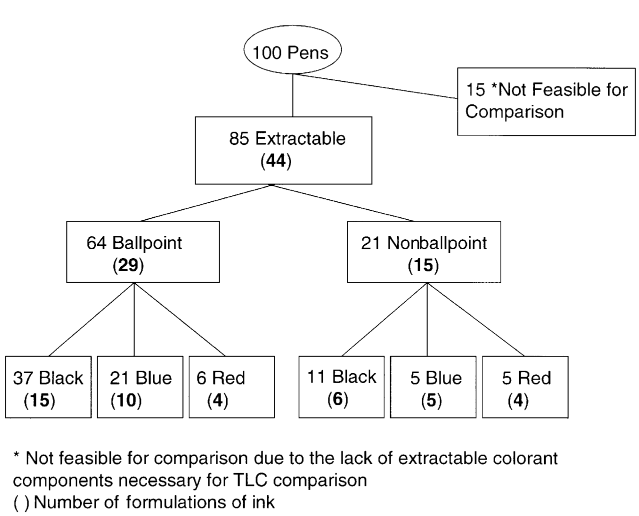

FIG. 1—*A total of 85 inks that were determined to be feasible for optical and thin-layer chromatography examinations are categorized by type (e.g., ballpoint and nonballpoint) and color of ink. The numbers in parentheses indicate the number of formulations, or families, of inks.*

TABLE 2—*The percentage of randomly obtained pens that were determined to match a specimen in the United States International Ink Library are categorized by type and color. The number in parentheses indicates the number of matches/sample size.*

	Black	Blue	Red
Ballpoint	100% (37/37)	95% (20/21)	80% (4/5)*
Nonballpoint	91% (10/11)	100% (5/5)	100% (5/5)

*Two of the pens were determined to have matching formulations. Therefore, the total number of pens was changed from 6 to 5.

When an unknown ink does not match any of the reference standards, this may be due to one of several factors. First, the manufacturer may not have participated in the submission process when annually petitioned. Second, the manufacturer may be an active participant, but may have neglected to send a known standard one or more times. Third, the ink formulation might be relatively new to the market (typically less than 1 year) and the manufacturer may not have had the opportunity to submit the new sample, as requests are normally submitted at the beginning of the year.

Conclusion

Utilizing appropriate reference collections in many disciplines of forensic science is a valuable resource if the intended users understand the inherent capabilities and limitations. The U.S. International Ink Library has long been considered to be the largest known forensic collection of writing inks in the world. While it is nearly impossible to be certain that a database such as this one is truly complete, there are some measures that can be taken to increase the reliability of a match to the exclusion of all remaining inks in the library. In addition to circulating an annual solicitation to all known pen and ink manufactures to submit new ink formulations, pens are also procured from the open market and compared with known standards on a regular basis. In this study, 100 pens were collected randomly from various sources in order to evaluate the comprehensiveness of the collection. Fifteen of the 100 inks evaluated were determined unsuitable for comparison, as they lacked any extractable colorant components necessary for comparison with standards in the collection, based on the parameters set forth in this study. The remaining 85 pens examined were categorized into 44 different ink formulations. Three of the inks did not match any of the specimens on record; one of these inks was similar to an ink from an identical brand of pen that was in the database, but had a modified formulation.

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