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EXHIBIT E

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Standard Guide for Test Methods for Forensic Writing Ink Comparison[1]

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INTRODUCTION

This guide is intended to be a general guide for forensic ink examinations, both for the experienced document examiner (Guide E444) 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]

D1535 Practice for Specifying Color by the Munsell System

E131 Terminology Relating to Molecular Spectroscopy

E284 Terminology of Appearance

E444 Guide for Scope of Work of Forensic Document Examiners

2.2 *NIST Standards:*

NBS Standard Sample No. 2106 ISCC-*NBS Centroid Color Charts*[3]

NBS Special Pub. 440 *Color: Universal Language and Dictionary of Names*[3]

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. **(E284)**

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. **(E284)**

3.1.5 *light*—electromagnetic radiant energy that is visually detectable by the normal human observer, radiant energy

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[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.

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having wavelengths from about 380 nm to about 780 nm. **(E284)**

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. **(E131)**

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. **(E284)**

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. **(E284)**

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

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

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part of the examiner, as well as access to a collection or *library* of ink reference samples is also required.

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, 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, 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, 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

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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 µL or smaller suggested.

6.7.5 *Precoated Plastic or Glass Sheets/Plates of Silica Gel,* without fluorescent indicator (60 Å pore size[5]).

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

[5] Merck Silica Gel, Whatman PE SIL G, and Merck HPTLC Silica Gel 60 have been found satisfactory.

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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)*:

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 µL 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

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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 D1535, 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**).

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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

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