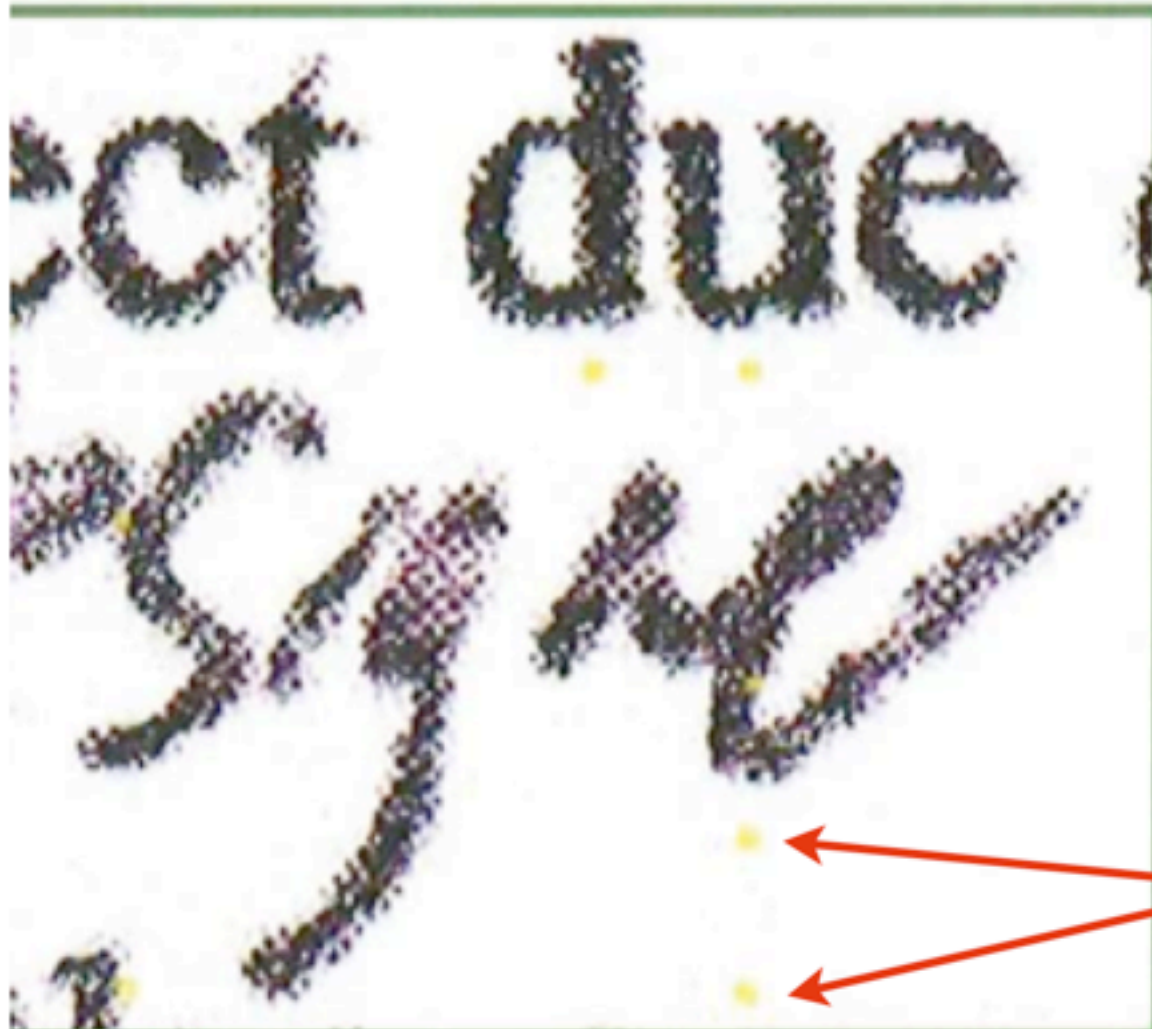# Exhibit 14

Declaration of Larry F. Stewart

Image used by Lesnovich as his Q1 document.

Note the yellow dots, indicative of printing on a color printer or copier. These aren't found on the original.
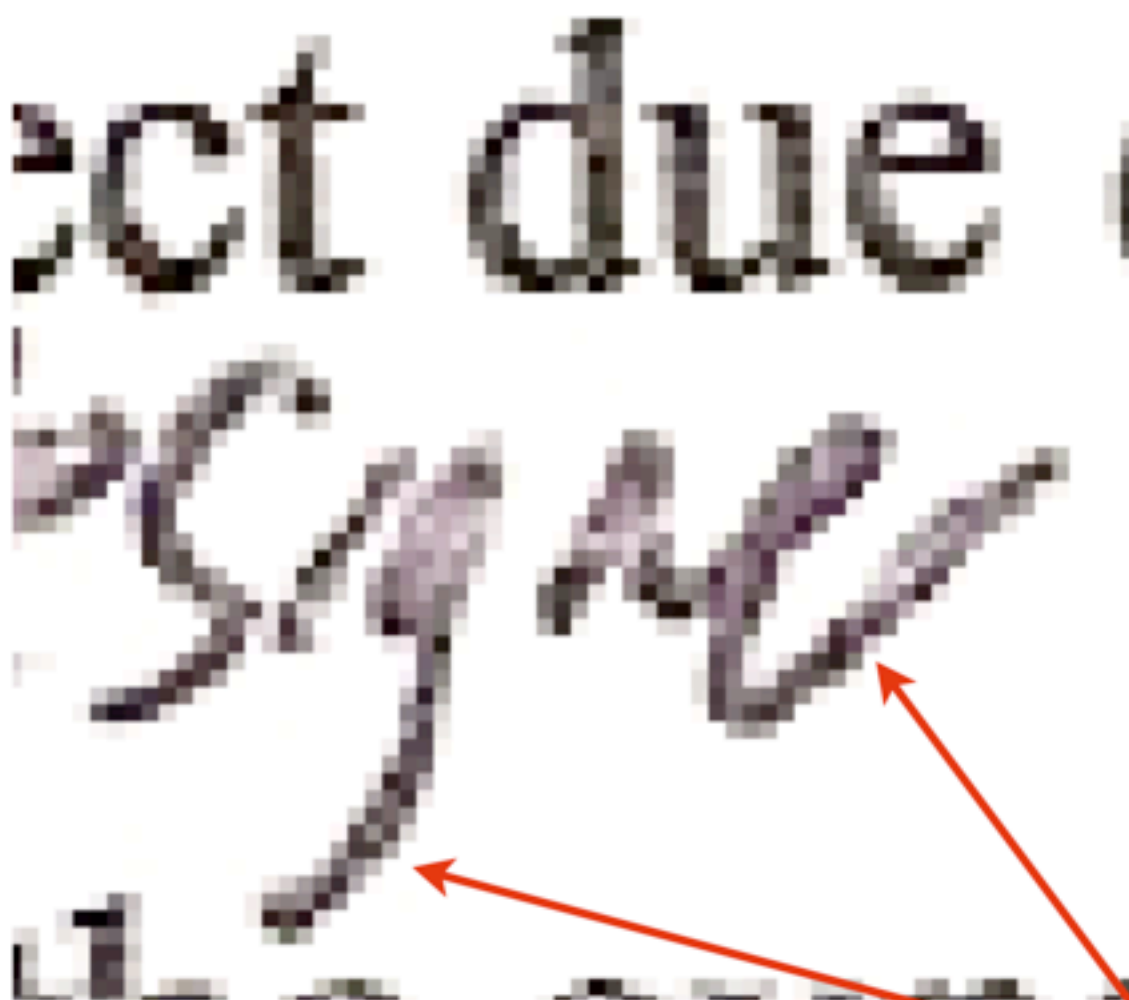
Image obtained directly from Argentieri of the original of the "Q1" document.

Note the differences in the shapes of the letters, thicknesses of lines, and edge detail. The original image has "stair-stepping." When a color computer printer or copier tries to interpret stair-stepping it causes changes in the appearance of the edges of the characters.

Exhibit 15

Lesnovich has implied that there was some change in the pages of the WFH document sometime between his Q1 and Q2 images and his Q3 and Q4 images. Following is an experiment comparing the position of the interlineation writings to the printed document on the best (clearest) sample of each of his two groups.

Q1 from Lesnovich. Tif sent by Ceglia to Argentieri 6/27/10.

Q3 from Lesnovich. Aginsky scan from 1/13/11 examination.

Exhibit 16

Comparison of poorly resolved scanned image of the WFH Pg1 to high resolution scanned image taken after forensic testing began and the document was in secure storage:

Here we have two images that were simply scanned at different settings creating similar anomalies to what Lesnovich is pointing out. This doesn't imply wrongdoing, but instead computer scanner setting differences.
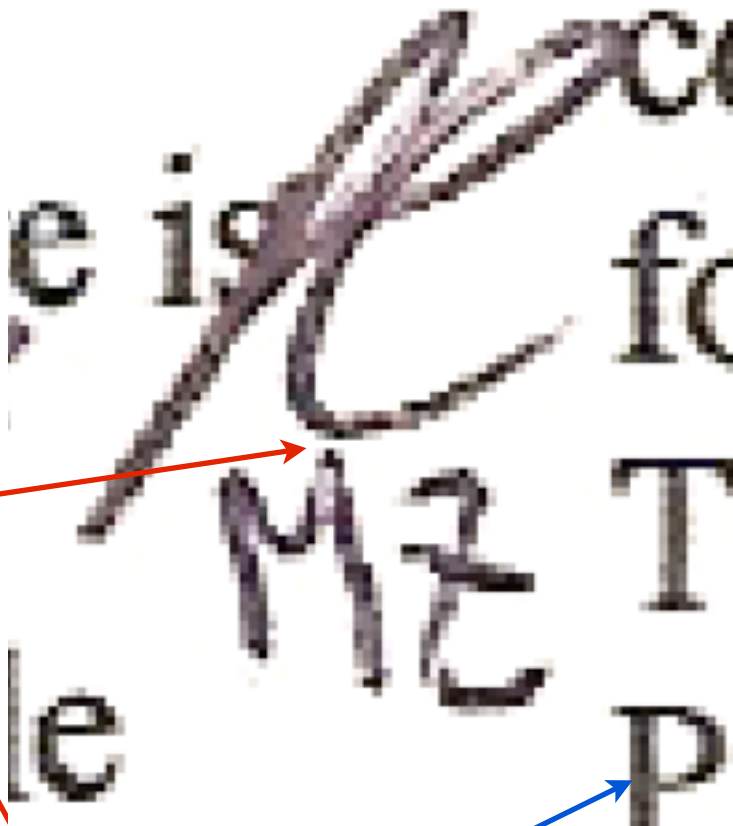
Lesnovich's Q1 - Image from Ceglia email to Argentieri 6/27/10 (Note: Poor resolution)

High resolution scanned image taken 7/15/11

Look at the difference in thickness within the vertical staff of the printed "P" in the lower right corner. The difference in thickness can cause the letters to merge or appear to close in on each other.
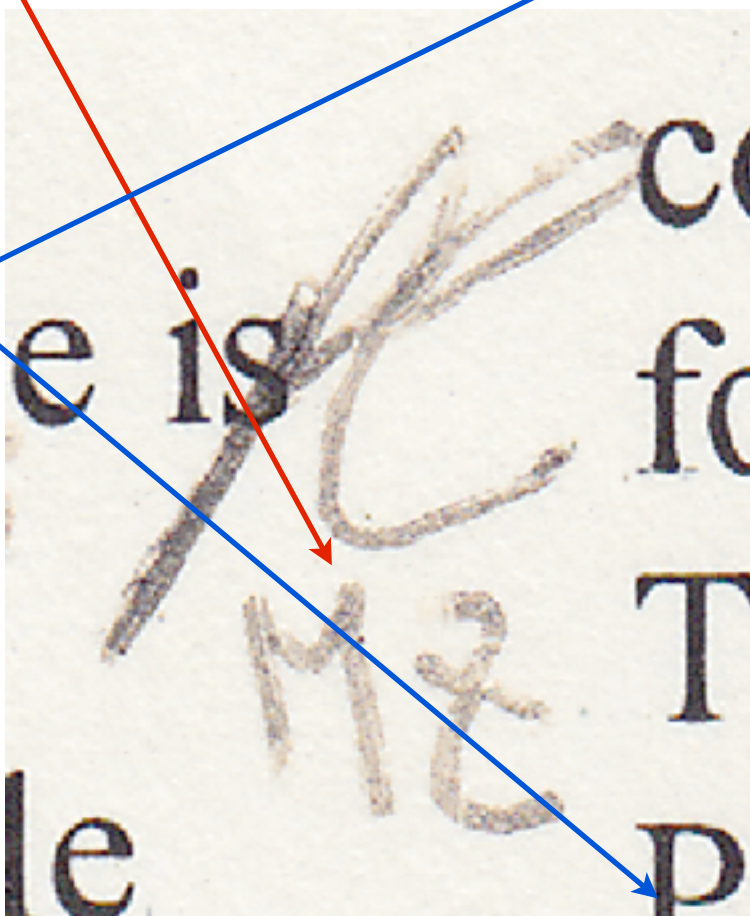
Exhibit 17

Exhibit Q-1
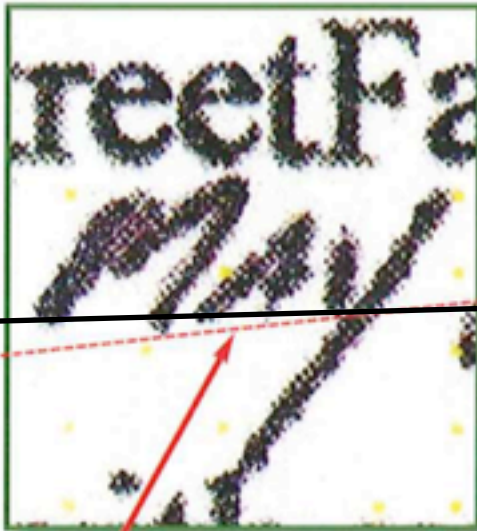
LETTER "A"
SLANTS UPWARD

Exhibit Q-2

LETTER "A"
SLANTS UPWARD

"WORK FOR HIRE" CONTRACT
LETTERS "A" FROM THE WRITTEN WORD "MAY"

Exhibit Q-3
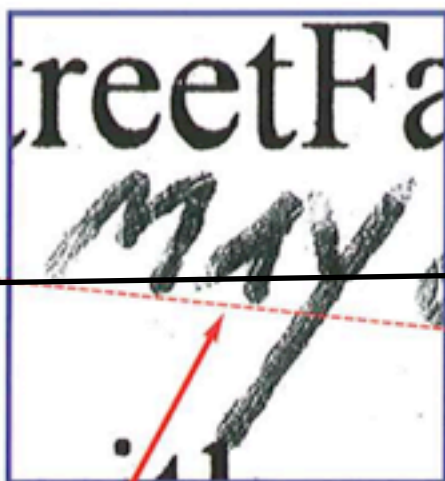
LETTER "A"
SLANTS DOWNWARD

Exhibit Q-4
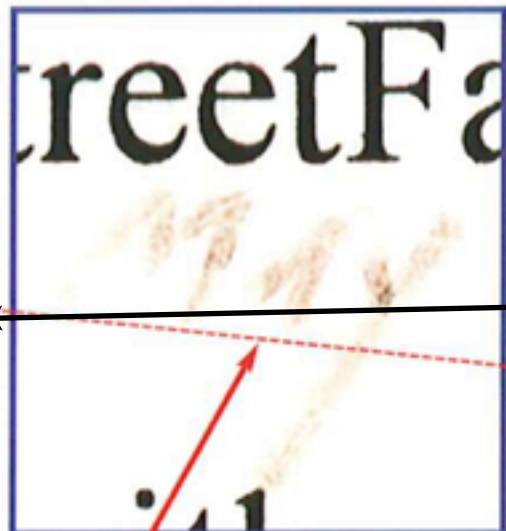
LETTER "A"
SLANTS DOWNWARD

Exhibit 18

![IPS TESTING EXPERTS logo]

Report to: Larry Stewart
              Stewart Forensic Consultants
              793 A East Foothill Blvd.
              San Luis Obispo, CA 93405

Sample identification: 2 Vials

Date received: November 1, 2011

Test requested: Fiber Identification

Purchase Order: Credit Card

Report of Fiber Analysis

Enclosed are the results of the analysis performed on the sample we received with your Test Services Request Form.

If you have any questions concerning this work, please do not hesitate to contact us.

Authorized By: _Gregory J Fox_   Signed _Walter J. Rantanen_____
              Gregory J. Fox   Walter J. Rantanen
              Lab Manager   Technical Leader, Fiber Science
                                          (920) 749-3040 Ext. 127

WJR/jml

Fiber Identification

The paper samples did not have any detectable mechanical (high lignin) pulp fibers which would be effected by photodegredation from UV light. There is a strong UV fluorescence in both samples, which indicates optical brightening agents. In the small punch outs, significant fluorescence differences were not detected. It could not be determined if these samples were effected by contact with UV light, but long exposure to UV light has been known to lower the whiteness of paper. A noticeable particulate material was observed on one side of the punch outs. This particulate may also affect the UV fluorescence of paper. The main inorganic substance in these particulates was found to be iron. The EDS spectra are enclosed. The nature of this material implies contact on one surface of the papers.

Spot tests show the same consistent reactions for starch and pH levels between the two samples. The fiber content of the two vials is consistent with coming from the same mill and production run.

Table 1. Fiber Identification of Vial 7
_____

Hardwood Bleached Kraft – Principally Redgum and Oak with some Blackgum, Yellow-
                                   Poplar, Cherry, Southern Magnolia
Softwood Bleached Kraft – Hard Pine (Except Red & Pine)

_____

Table 2. Fiber Identification of Vial 9
_____

Hardwood Bleached Kraft – Principally Oak and Redgum with some Yellow-Poplar,
                                   Blackgum, Cherry
Softwood Bleached Kraft – Hard Pine (Except Red & Pine)

_____

Method: TAPPI Test Method T 401 om-03 "Fiber Analysis of Paper and Paperboard."

Analyzed by WJR
Quality review by JML, KTM
Date(s) of testing November 8, 2011

Notes: These results relate only to the item(s) tested. This test report shall not be reproduced, except in full, without written consent of IPS. See the TAPPI test method(s) cited for estimates of measurement uncertainty.

IPS
TESTING EXPERTS
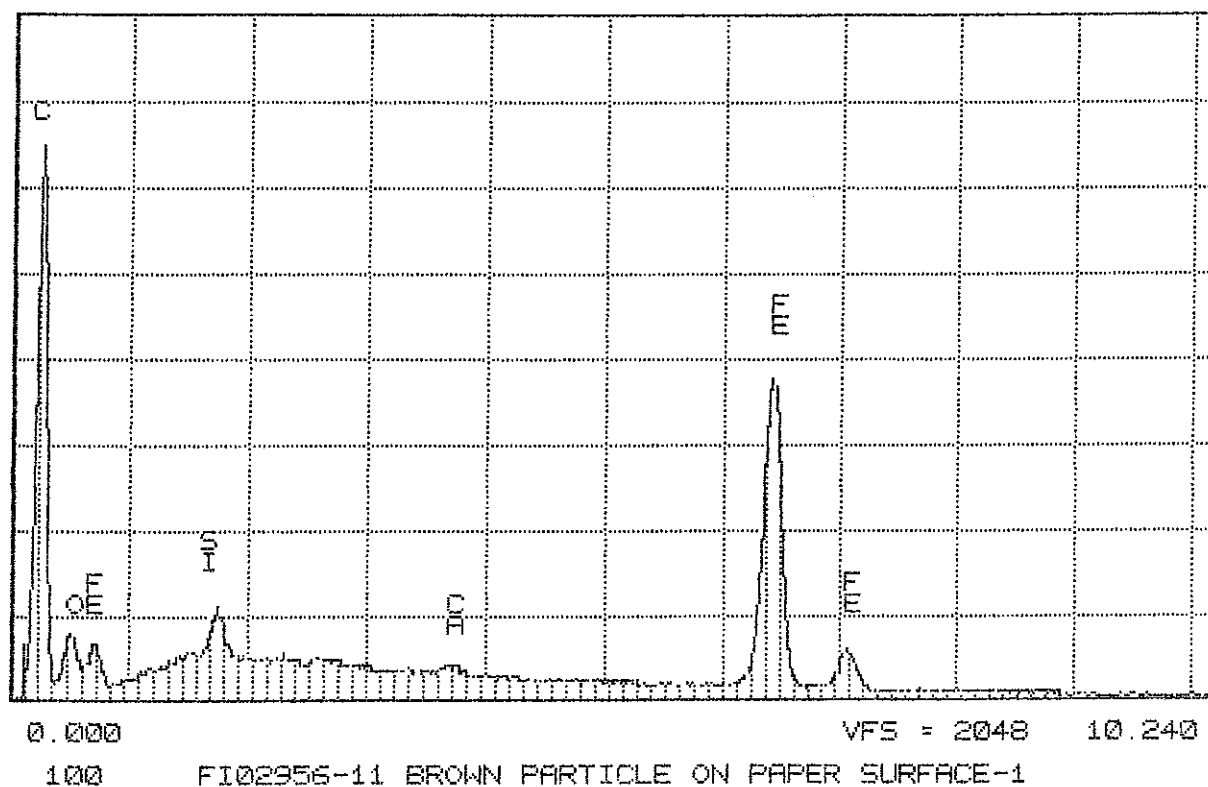
0.000   VFS = 2048   10.240
100   FIO2956-11 BROWN PARTICLE ON PAPER SURFACE-1

0.000   VFS = 2048   10.240
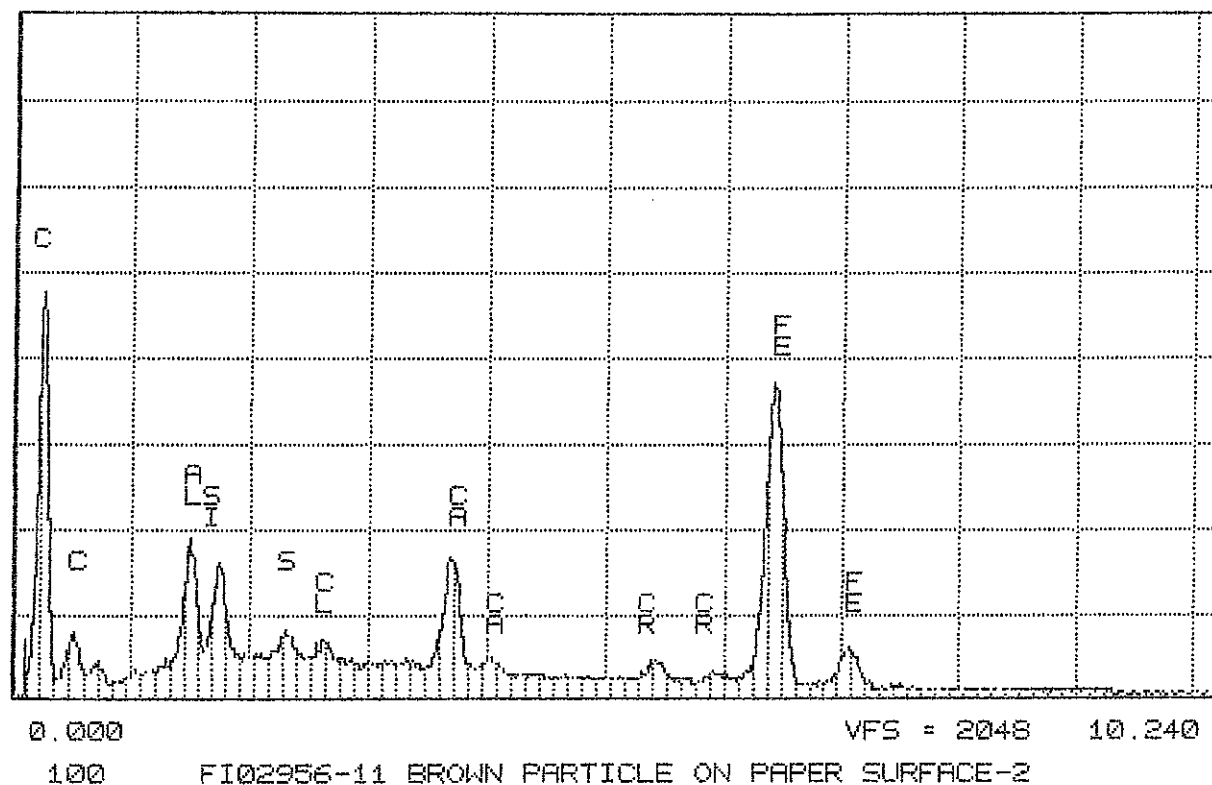
100   FI02956-11 BROWN PARTICLE ON PAPER SURFACE-2
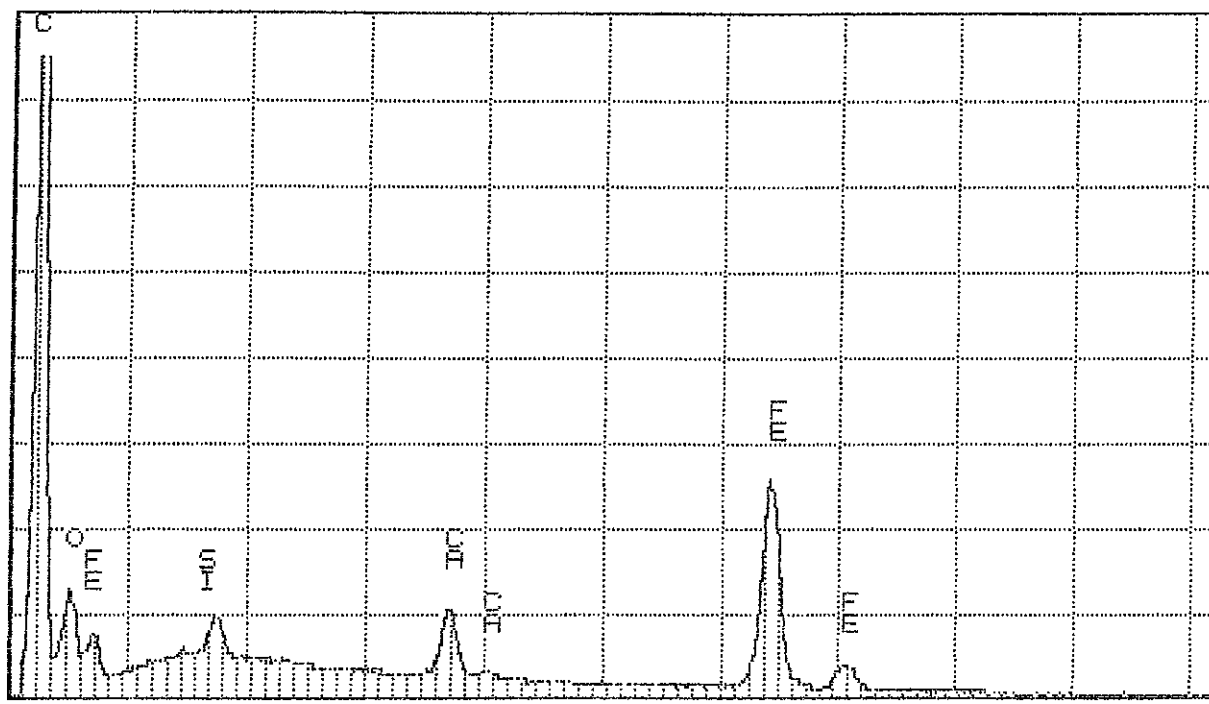
0.000   VFS = 4096   10.240

100   FI02956-11 BROWN PARTICLE ON PAPER SURFACE-3

Exhibit 19

Larry F. Stewart,[1] *M.F.S.*

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

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-

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.

[3]A. A. Cantu, private communication, 1982.
[4]Private 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 μL
- Ice bath
- High purity vehicle standards
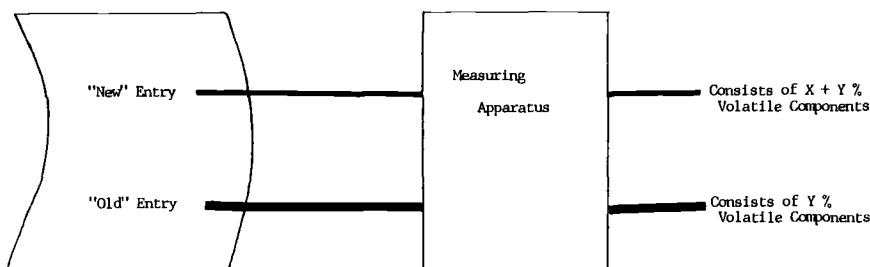- ×20 gauge hypodermic needle
- Plunger
- Timer

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 μL 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-μL 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])
N_2 gas flow at 25 cm^3/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 μL using methanol as the extracting solvent
Attenuation: $\times$2 K till methanol peak, then $\times$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.

GC COMPARISION OF TWO INKS
OF THE SAME FORMULATION
WRITTEN AT DIFFERENT TIMES

b

a

fresh writing

two month old
writing

b

a

FIG. 2—*Aging curve for each ink.*

RATIO

RATIO = (Peak A) / (Peak B)

DAYS
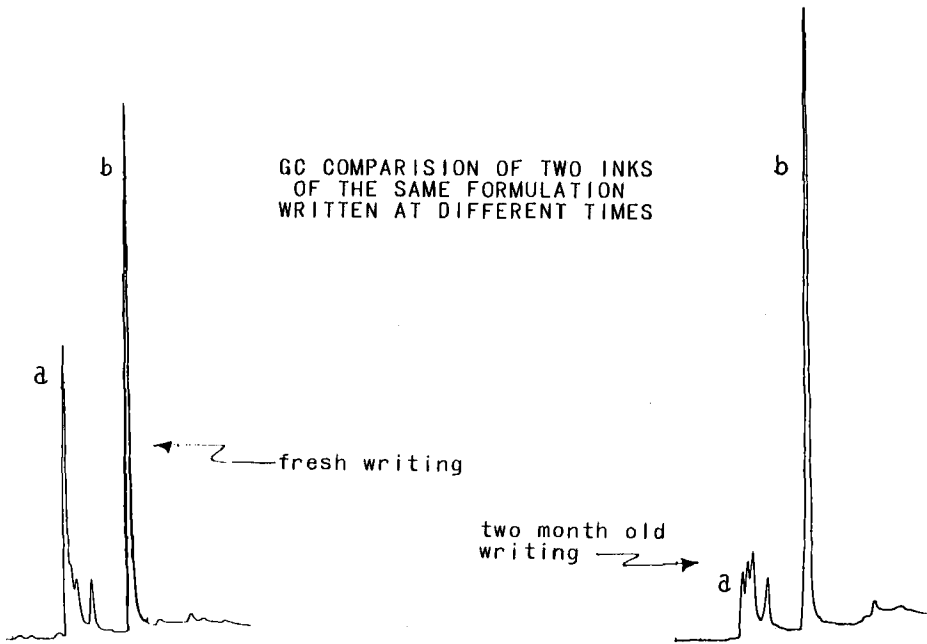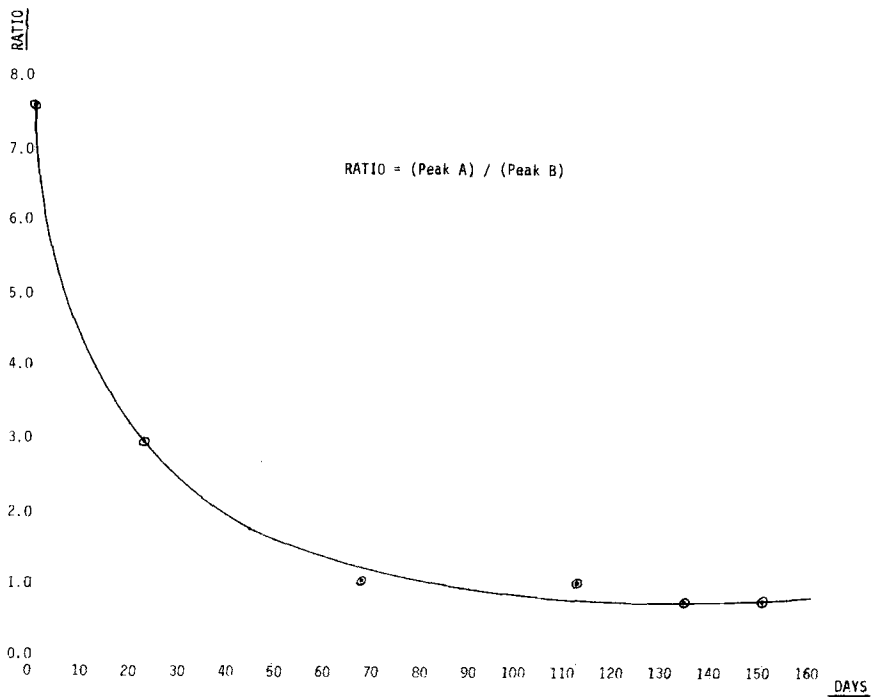
FIG. 3—*Aging curve calculated from the ratio of Peak A/Peak B versus actual age.*
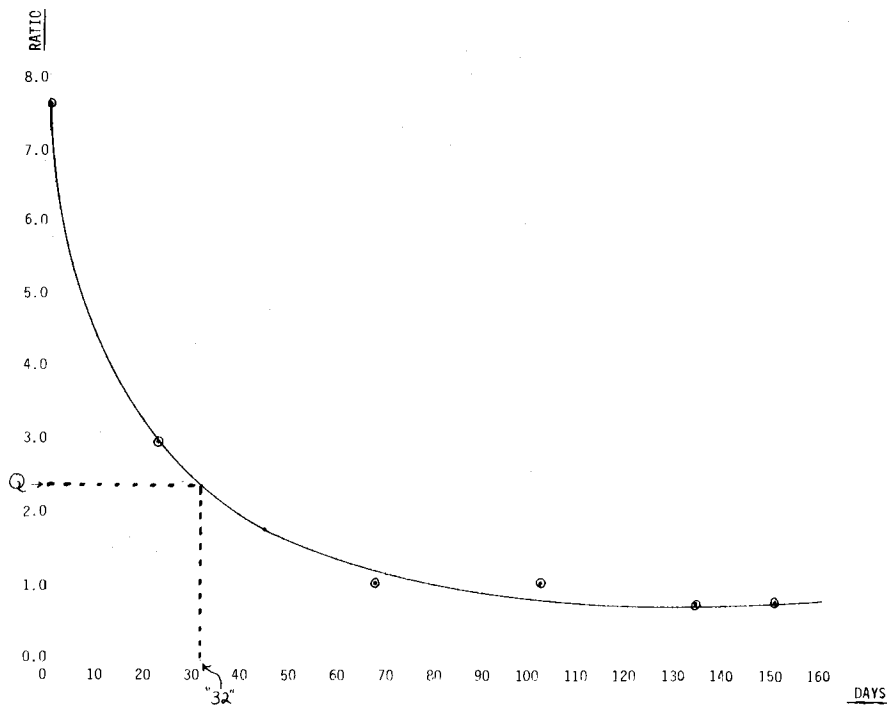
FIG. 4—*Aging curve for the Q entry.*

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,

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

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.

References

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[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.
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[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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United States Secret Service
Forensic Services Division
1800 G St., N.W., Room 929
Washington, DC 20223

Exhibit 20

Determination of the age of ballpoint pen ink by gas and densitometric thin-layer chromatography*

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(First received October 8th, 1993; revised manuscript received March 31st, 1994)

Abstract

Two procedures for dating ballpoint inks are considered that use gas chromatography (a combination of the technique for determining the extent of extraction of ink volatile components and of the accelerated ageing technique) and densitometric thin-layer chromatography (separation of ink components and evaluation of the resulting chromatograms using a specially developed mass-independent technique that is also a very effective tool for the comparative TLC examination of similarly coloured inks, paints, fibres and other materials of forensic interest). The procedures have been used in many real case situations and the results of the examinations were accepted as conclusive evidence by courts of law.

1. Introduction

Gas chromatography (GC) and densitometric thin-layer chromatography (TLC) have been demonstrated to be useful tools for the solution of many problems frequently encountered in ink analysis, including ink dating problems [1–4]. Recently, five new procedures for dating ballpoint inks have been described [5,6]. Two of them, based on using chromatographic methods, are as follows.

(1) A GC method is used to determine the extent of extraction of ink volatile components, which decreases as ink ages on paper. The procedure considered in this paper combines the capabilities of this method and of the accelerated ageing technique. The procedure allows discrimi-

nation between "fresh" (age less than several months) and "old" ballpoint ink entries and it does not need dated reference entries written with ink having the same formula as that of the questioned ink.

(2) A TLC method is used for determining age changes in resins and other colourless non-volatile ballpoint ink components; these changes are detected by observing the resulting thin-layer chromatograms under UV illumination and evaluated by using scanning densitometry. The modified TLC procedure described in this paper includes a new, mass-independent approach to evaluating thin-layer chromatograms that allows one to obtain the values of an "ink ageing parameter" [7] directly proportional to the ratios of the masses of the separated ink components (dyes, resins, etc.). For this reason, the proposed procedure gives more reliable results for ink age determination than those obtainable with the

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* Presented in part at the *13th IAFS Meeting, Düsseldorf, Germany, August 1993.*

widely used peak signal-to-peak signal ratio technique. The described approach is also a powerful tool for the comparative examination of similarly coloured inks, paints, fibres and other materials of forensic interest as its discriminating power is much greater than that usually produced by the peak ratioing technique [8–10].

2. Experimental

2.1. Materials

Up to 15-year-old entries written with Soyuz ballpoint inks of different colours having similar compositions of colourless components were analysed by GC. Entries of known ages (1 day, 1 month, 1, 2, 3 and 6 years old) written with a Parker blue ballpoint ink were analysed by TLC.

Camag N-11 polypropylene micro vials with cone-shaped interiors and a 10-μl Hamilton syringe were used.

2.2. Gas chromatography

A Hewlett-Packard Model 5890 gas chromatograph equipped with a flame ionization detector and an HP split–splitless injection system was used. A SCOT column containing SP-1000 (polyethylene glycol 20M terminated with nitroterephthalic acid) (Supelco) (25 m × 0.5 mm I.D.) was used with nitrogen (4 p.s.i.) as the carrier gas at a flow-rate of 40 ml/min. The column oven temperature was programmed from 50°C (held for 0.5 min) at 10°C/min to 220°C (held for 6 min). The injection volume was 2 μl (splitless) at 250°C. A flame ionization detector was used at 250°C.

Each sample was obtained by cutting out a ca. 1-cm sliver of ink of approximately equal thickness from the paper using a safety razor and placed in a micro vial. A 10-μl volume of carbon tetrachloride as a "slowly extracting weak solvent", containing 10 μg/ml of benzyl alcohol as an internal stranded (if benzyl alcohol is detected in ink samples in significant amounts, another appropriate substance can be used as an internal

standard) was added and the vial was capped. After 30 min a ca. 2-μl aliquot of each sample was removed and analysed by GC.

The samples were removed from the extraction solutions, dried and placed into other micro vials. A second extraction was carried out for 1 min, stirring with a needle, with 10 μl of chloroform ("fast-extracting strong solvent") also containing benzyl alcohol in the same concentration. About 2 μl of each extract were removed and analysed by GC.

The masses of a vehicle component determined in each of the two extracts analysed (M_1 and M_2 for the first and second extractions, respectively) were calculated by means of the internal standard method. The percentage extraction [1,5], that is, the percentage of the mass of the ink vehicle component, $\%M$, extracted in the "weak" solvent (relative to its total amount contained in the sample analysed), was calculated as follows:

$$\%M = [M_1/(M_1 + M_2)] \cdot 100$$

The values of $\%M$ obtained for all samples analysed were plotted against the age of the known ink entries (see Fig. 1).

2.3. Thin-layer chromatography

To obtain an "ageing curve", samples as two 1-cm slivers of ink of approximately equal thickness were taken from five entries of known ages (X_1–X_5). Three more samples were taken from a 2-year-old entry that was analysed as a questioned (Q) entry. Each sample was placed in a micro vial and extracted for 2 min with 15 μl of chloroform, stirring with a needle. A calibration standard solution was prepared by the treatment of eight 1-cm slivers taken from a 1-month-old entry with 60 μl of chloroform. Volumes of 10 μl of the obtained extracts and 5,8,11 and 15 μl of the calibration standard solution (calibration standards, S_1–S_4) were applied to a 20 × 10 cm precoated Merck HPTLC silica gel 60 F_{254} plate as 8-mm bands by means of a Camag Linomat-3 applicator. One-dimensional ascending development was performed with ethanol–acetone–hex-

ane (1:5:20, v/v/v). The development distance was 50 mm.

The resulting chromatograms contained zones of two ink components, A and B. For five samples, X_1–X_5, the relative proportion of these components was obviously linked with the age of the ink (see Fig. 2). The chromatograms were scanned densitometrically by reflectance in the absorbance mode for fluorescence quenching at 254 nm using a Camag TLC/HPTLC scanner (with a mercury lamp, monochromator band-width 30 nm, slit dimensions 0.3×5 mm and scanning speed 1 mm/s) connected to an SP4100 integrator (Spectra-Physics). The densitometric data obtained were evaluated with external standards in the following way.

For the calibration standards S_1–S_4, it was assumed that the contents of components A and B per zone (their real values are unknown, as follows from the procedure used for preparing the calibration standard solution) were equal to the corresponding values of the volumes of the calibration standard solution applied to the plate (see Table 1).

For each calibration standard component, A and B, a logarithmic (this function gave the best correlation coefficient in all non-linear calibrations that were tested in the given case) approximated calibration graph was constructed and then the contents C_A and C_B of components A and B per zone were determined for the chromatograms of the samples taken from the known and Q aged entries.

The ratio C_A / C_B was calculated for each

sample. The values obtained were plotted against the actual age of the known ink entries and the age of the Q ink entry was determined (see Table 3 and Fig. 3).

3. Results and discussion

3.1. Gas chromatography

Figure 1 shows ageing curves obtained for Soyuz ballpoint inks of different colours having similar compositions of colourless components. The curves show that significant ageing taking place over a period from about 6 months to more than 2 years for different inks. After this period until the age of 15 years the extent of the extraction of the volatile component, phenoxy-ethanol, from the ink entries remained at about $20 \pm 10\%$.

An explanation of this result characterizing the mechanism of evaporation of volatile components (such as phenoxyethanol, phenoxy-ethoxyethanol and other high-boiling vehicles frequently used as the ingredients of ballpoint inks) from ageing inks has been given previously [5]. It was considered that the evaporation process includes a limiting stage of diffusion of a vehicle from the interior layers of the ink body

Table 1
Contents of components A and B in the chromatographic zones of the calibration standards

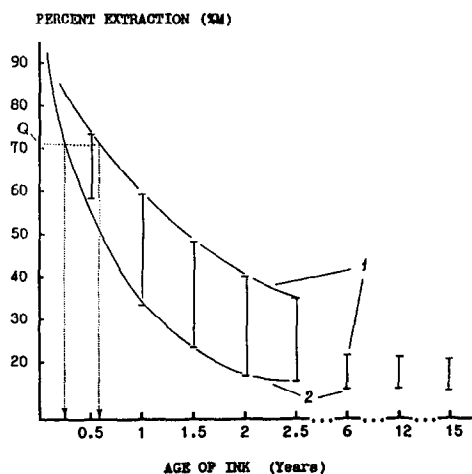| Standard[a]	Volume applied (μl)	Component content (mg per spot)	
		A	B
S_1	5	5	5
S_2	8	8	8
S_3	11	11	11
S_4	15	15	15

[a] Extract from the 1-month ink entry.

Fig. 1. Ageing curves obtained for violet, blue, green and black Soyuz ballpoint inks: 1 and 2 relate to the maximum and minimum values of %M obtained for the inks analysed.

to the surface of the film. For the same vehicle and thickness (depth) of the ink film, the efficiency of the diffusion process is mainly a function of the nature of ingredients of inks such as resins and polymers. Moreover, if the resin is capable of polymerizing, i.e., of cross-linking, the diffusion process slows as an ink ages on paper, and at a certain stage of ageing it can virtually stop. For this reason the remaining ink volatile components can be detected in the ink line even after a long period of time; this is shown in Fig. 1 for up to 15-year-old entries written with Soyuz ballpoint inks.

In such situations, a "weak" solvent (with regard to hardened ink resins), being unable to penetrate inside an old ink line, extracts the ink volatile components only from its exterior layers. However, the newer the ink, the more exterior layers of the ink become available to the weak solvent, and hence a greater amount of the volatile components is extracted.

Fig. 1 is a good illustration of the above observation that the extraction efficiency of a "weak" solvent decreased from about 90% for fresh writings to about 20% for old writings.

It should be noted that the proposed method includes also an important stage that is carried out if the values of %M determined for the Q ink entry are larger than ca. 60%. In this event, another sample (1-cm sliver) is taken from the ink entry, heated moderately, e.g., at 80°C for 5 min, and analysed as described under Experimental. The percentage extraction value, $\%M_t$, is calculated for the heated sample and compared with the value of %M that was determined for the unheated sample. If the difference between %M and $\%M_t$ is ca. 10% or larger, it can be concluded that the ink entry analysed is a fresh one. If the difference is less than 10%, it means that a more suitable "weak solvent" should be chosen for a given ink.

For example, as a result of studying the ageing process of many ballpoint inks of different formulae by using the proposed method, it has been established that if, for a given ink, the analytical results are $\%M > 70\%$ and $\%M - \%M_{t=80°C, 5 min} > 10\%$, then the age of the ink analysed is less than ca. 6 months (depending on

the ink formula, this value may decrease to ca. 2 months).

As an example, Fig. 1 shows the results of the age determination obtained for the Q entry (in fact, it was a 3-month old entry written with a Soyuz blue ballpoint ink) using the proposed method.

The method demonstrated high efficiency in many actual case situations when it was necessary to determine whether the age of the Q entry was less than several months or not less than 1 year. Such cases are fairly typical when the investigator suspects that the given entry or signature was made after the time the investigation began. Some similar examples have been presented by Cantu [11].

3.2. Thin-layer chromatography

Fig. 2 demonstrates the view under UV illumination of the fragment of the thin-layer chromatogram (without the chromatographic zones of the paper's ingredients) and corresponding densitograms obtained for samples taken from entries written with Parker blue ballpoint ink. A and B represent separated colourless components of interest in the ink analysed.

It is clearly seen in Fig. 2 that there is an
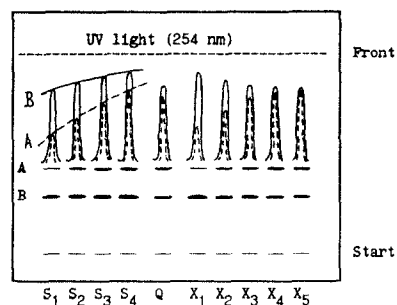

Fig. 2. Fragment of the thin-layer chromatogram (UV detection at 254 nm) and corresponding densitograms obtained for Parker blue ballpoint ink entries of different ages. S_1–S_4 are calibration standards; Q relates to an entry of questionable age; X_1–X_5 relate to known ink entries: X_1 = 1 day, X_2 = 1 month, X_3 = 1 year, X_4 = 3 years, X_5 = 6 years old.

obvious link between the relative proportion of substances A and B and the age of the ink writings examined: the substance A/substance B ratio gradually increases as the ink ages (it is a minimum for a fresh, 1-day-old entry, the X_1 track, and maximum for a 6-year-old entry, the X_5 track).

As a rule, the relative proportions of the components separated by TLC are evaluated by obtaining related densitometric data and further by calculating the ratios of the components' peak signals [1–3,8,9]. However, this approach has been shown to produce erroneous results because, in densitometric TLC, when chromatograms are scanned by reflectance in the absorbance mode, the relationship between signal output (peak height or peak area) and the content of a separated zone is hardly ever a directly proportionality [10,12,13].

In this connection, a more reliable approach is offered here. It can be considered as a version of the external standard method for evaluating thin-layer chromatograms for cases typical in forensic analysis when information on the quantitative and even qualitative composition of samples to be analysed is not available and, therefore, calibration graphs cannot be obtained for the analytes. (Another way to avoid erroneous results produced by the signal-to-signal ratio technique includes the application of the approach based on the mass-independent version of the peak ratioing technique [10,13].)

The proposed method allows one to obtain the actual mathematical functions of signal versus content for any two components, A and B, of the materials analysed within a certain calibration range of the contents of these components, C_{min}–C_{max}. This calibration range is formed by applying at least four or five calibration standards on a TLC plate as follows.

If samples are sprayed on as narrow bands, different volumes of only one standard solution can be applied to form a calibration range, C_{min} – C_{max}. An important characteristic of the method is that the real values of C_{min} and C_{max} can be unknown to the examiner: only the values of C_{max}/C_{min} and C_i/C_{min} (where i relates to a calibration standard characterized by the content

of a component per zone that is less than C_{max} and larger than C_{min}) must be known, as was described under Experimental.

If samples are applied as spots, calibration standards should be prepared in different concentrations and spotted as a fixed constant volume: multiple spotting of a single standard solution to generate a calibration graph is not acceptable for accurate quantification as there is no simple correlation between signal response for a constant amount of substance and spot size in scanning densitometry [12]. In this case, the contents of components A and B per zone are assumed to be equal (or directly proportional, if only dilution factors, not real concentrations, are known for the calibration standard solutions) to the corresponding concentrations of the calibration standard solutions. Hence the value of the ratio of the contents of any component in the chromatographic zones corresponding to any two prepared calibration solutions will be equal to the value showing how many times one of these solutions is more (or less) concentrated than the other.

Further, for each component A and B, an appropriate approximation function is found and used as a calibration function for calculating the contents, C_A and C_B, of components A and B per spot of the samples taken from the entries of the known and questionable ages. Although these content values are not real, this is not sufficient for the considered method: the main point is that the ratios of these values, C_A/C_B, are independent of mass, in contrast to the peak ratioing technique that is based on using the mass-dependent values of $signal_A/signal_B$ (see Table 2).

Tables 2 and 3 show peak-height values calculated by an integrator for the separated components of the Parker ink analysed, PH_A (for component A) and PH_B (for component B), and the values characterizing the relative proportions of the components A and B calculated by using the peak rationing technique (fourth column) and the proposed "content" ratioing method (last column).

Fig. 3 shows ageing curves obtained for the Parker ink by plotting the values of the ratios

Table 2
Data obtained for calibration standards

Standard	Integrator reading[a]		Ratio of peaks, PH_A/PH_B	Ratio of contents[a], C_A/C_B
	PH_A	PH_b		
S_1	31 032	90 506	0.34	1.02
S_2	51 716	99 126	0.52	0.98
S_3	73 261	107 745	0.68	0.96
S_4	88 782	112 056	0.79	1.04
Mean			0.58	1.00
R.S.D.			0.34	0.04

[a] Peak heights, PH_A and PH_B, were plotted against the contents C_A and C_B (see Table 1). As a result, the following regression equations and correlation coefficients (r^2) of the logarithmic calibration graphs were obtained: $PH_A = -56\,496 + 53\,529 \log C_A$ ($r^2 = 0.9929$) and $PH_B = 57\,816 + 20\,258 \log C_B$ ($r^2 = 0.9894$). Using these equations, the values of C_A and C_B were recalculated for each standard, S_1–S_4, and used for calculating the content ratio values listed in the last column.

listed in the last two columns of Table 3 against the actual age of the known ink entries.

The results of determining the age of the Q entry (in fact, the age of this entry was 2 years) are also shown in Fig. 3 and presented in Table 3.

It is clearly follows from Fig. 3 and the data in Tables 2 and 3 that, in comparison with the peak ratioing technique, the proposed mass-independent content ratioing method gives a significant increase in the accuracy and precision of ink age determination.

It should also be noted that this method can be successfully applied to a comparative TLC examination of similarly coloured inks, paints, fibres and other materials of forensic interest, as

Table 3
Data obtained for ink entries

Ink entry	Integrator reading		Ratio of peaks, PH_A/PH_B	Ratio of contents, C_A/C_B
	PH_A	PH_B		
X_1	39 659	110 334	0.36	0.45
X_2	64 644	103 435	0.63	1.01
X_3	79 735	94 817	0.84	2.04
X_4	84 472	94 388	0.89	2.27
X_5	88 351	93 093	0.95	2.60
Q	81 887	93 529	0.88	2.26
	87 963	96 975	0.91	2.14
	80 168	93 394	0.85	2.20
Age determined for the Q entry (years)			1.3	1.4
			2.6	2.4
			4.1	3.0

MASS-INDEPENDENT

RATIO OF "CONTENTS" (a)

MASS-DEPENDENT
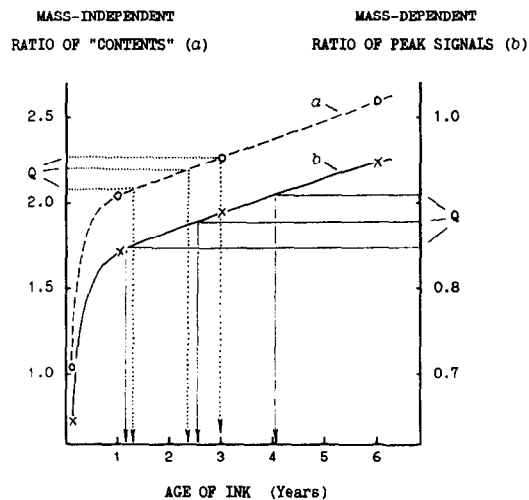
RATIO OF PEAK SIGNALS (b)

Fig. 3. Ageing curves obtained for the Parker ink using (a) the content ratioing method and (b) the peak ratioing technique.

its discriminating power is much greater than that usually produced by the widely used mass-dependent signal-to-signal ratio technique.

4. Conclusions

Two complementary methods for dating ball-point inks have been considered. The method using GC allows discrimination between fresh (age not greater than a few months) and old ballpoint inks, including inks with formulae unknown to the examiner. It is effective for analysing ballpoint inks that contain phenoxy-ethanol, phenoxyethoxyethanol or similar high-boiling vehicles.

The method using TLC allows the detection of age changes in resins and other non-volatile ink components. It includes a new procedure for evaluating thin-layer chromatograms of sepa-rated ink components. Being mass-independent, this procedure gives much more correct results for dating inks than those obtained with the aid of the widely used signal-to-signal ratio tech-nique.

Both methods, together and separately, have been used in many actual case situations and the results of the examinations have been accepted as conclusive evidence by courts.

Further work is necessary to evaluate the limits of the applicability of the methods to numerous inks that are on the market.

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Exhibit 21

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Some New Ideas for Dating Ballpoint Inks—A Feasibility Study

ABSTRACT: This paper introduces four techniques developed with the goal of estimating the age of ballpoint inks. These techniques are based on using the microspectrophotometric determination of the rates of color changing in inks as a result of the reaction with chemicals—the older the ink the less the rate (procedure 1); a combination of gas chromatographic (GC) and spectrophotometric methods for determining the masses' ratios "volatile component/dye component" in ink that decrease with the age of inks (procedure 2); a GC method of determining the extent of extraction of ink volatile components that decreases as ink ages on paper (procedure 3); a thin-layer chromatographic method for determining age changes in resins and other colorless nonvolatile ballpoint ink components: these changes are detected by observing the resulting thin-layer chromatograms under UV illumination and can be evaluated by using scanning densitometry (procedure 4). Suggestions for further work are proposed.

KEYWORDS: questioned documents, ballpoint inks, relative aging, chemical reagents, microspectrophotometry, thin-layer chromatography, densitometry, gas chromatography, spectrophotometry, solvent extraction, paper, dyes, resins, volatile components, ratios

Ink age determination is one of the very complex forensic problems. Recently, the state-of-the-art in the field of ballpoint ink dating has been critically evaluated by Brunelle and Cantu in their comprehensive reviews [1,2]. In these reviews, special attention was paid to several approaches determining the dynamic characteristics of ballpoint ink aging [3–9].

This paper also deals with the dynamic characteristics of ink aging. It introduces four techniques (described in the following sections) for estimating the length of time an ink has been on a document.

All examples described in this paper deal with determining the relative age of ballpoint ink entries that had been placed periodically on paper sheets during a certain period of time (over six years, maximum) and stored under controlled environmental conditions (the ambient temperature of the metal safe in which samples were stored ranged between 17° and 23°C).

Theory

Ballpoint inks are complex mixtures of vehicles, dyes, synthetic resins, polymers, and other organic compounds that begin changing or evaporating as soon as the ink is placed on a paper. The rates of these processes are significantly different. Thus, it is evident that evaporation of volatile components is very intensive initially and then it decreases quickly in the first hours and days after a ballpoint ink have been applicated on a paper while oxidation, cross-linking and other similar processes go slowly, with more or less steady rates (provided ink is not heated [10] or exposed to light [11]). These rates depend on many factors—environmental ones, formula and nature of the components of ballpoint ink analyzed, an ink line thickness (depth of the film of the writing), etc. All this must be under consideration when determining the age of questioned ink is performed. So an analyst should have a working knowledge on peculiarities of ballpoint ink manufacture, nature of ink components and their possible behavior during the aging process (this aspect of the ink dating problem has been described completely by Brunelle and Cantu [12]).

Ink Age Determination by Using Volatile Chemicals

One of the first techniques using chemical tests for ink dating was introduced by Mitchell [13], who investigated reactions of iron gallotannate inks with some chemicals. In particular, he showed that when using a reducing agent—oxalic acid—the rate of bleaching of freshly written inks was much higher than that of inks that were several years old.

In 1983, Dr. Tamara I. Saphronenko supplied the author with the technique for dating ink that was based on Mitchell's approach. Her method used a water solution of a mixture of iodine, potassium iodide, and magnesium chloride, as a reagent allowing discrimination between "fresh" (about one month old) and "old" writings made by blue and violet fountain pen inks produced in the former Soviet Union. The procedure included spotting of the reagent micro drop onto a questioned ink line, removing that drop in approximately a minute, and observing an ink color: fresh inks were becoming deeply black, whereas old ones were showing moderately gray color.

These works provided the basis for the reagent–photometric technique presented in this paper. This technique uses comparatively volatile strong organic bases like benzylamine or piperidine as reagents capable to cause reversible bleaching or changing the color of ballpoint inks, and microphotometric detection of corresponding changes of ink reflectivity at a certain analytical wavelength preliminary determined for the ink analyzed.

Experimental Procedure

Ink Samples—Lines of a "Soyuz" (produced in the former Soviet Union) blue-violet ballpoint ink have been placed on a white paper for notes during about six years.

Instruments and Measuring Conditions—A Leits (Germany) MPV-SP spectral photometer with a current-stabilized light source (tungsten-halogen lamp, 12 V/100 W), measurement grating monochromator (1200/mm), Hamamatsu-type R928 photomultiplier, dark-field "Ultropak" condenser and objective "UO-6.5 × 0.12"; wavelength range— 400 to 700 nm; monochromator half bandwidth—3 nm; lamp current—7A; photomultiplier output—500 V. A Goerz Metrawatt (Austria) SE-120 chart recorder; chart speed— 1 cm/min.

Homemade Tools—A reaction chamber specially designed for examining color changing reactions of inks with volatile chemicals. The chamber has a hole in its bottom, a transparent cover made of glass, and two, inlet and outlet, vents.

Choice of Reagents—A lot of acidic, basic, reducing, and oxidizing agents were tested with the aim of finding such chemicals that would allow discrimination between "old" and "fresh" ballpoint ink entries. Some of them that gave more or less positive results follow.

Iodine Fumes—after several minutes of exposition in the reagent fumes most of blue and violet ballpoint inks analyzed were becoming black. After the reagent was removed the initial color practically recovered but it took a long period of time (several hours). This reagent does not seem a satisfactory one to be used in the procedure described.

Nitrogen Dioxide and Hydrogen Chloride—in small concentrations they reversibly change colors of some ballpoint inks. However, these substances are too toxic and corrosive to be used as routine reagents for ink analysis.

Benzylamine and Piperidine—these organic bases were chosen from a wide range of amines (some of those, like triethylamine, dipropylamine, or butylamine, showed unsatisfactory effects of reactions with inks, the others like 25% ammonia or dicyclohexylamine did not change the color of many tested ballpoint inks at all). They seem to be the most promising ones as agents for using in the procedure of ink age determination described below (though unfortunately they are toxic and so corresponding precautions should be taken when working with them). Their action is based on reversible decolorizing ink dyes (mainly, triarylmethane compounds) or perhaps, on changing color and/or brightness of some ink dyes as a result of the formation of "dye-reagent" charge transfer complexes.

A Procedure—The procedure based on using a comparatively volatile strong organic base (like benzylamine or piperidine) as a ballpoint ink color changing reagent includes the following operations.

At first, the questioned (Q) ink formulation is established by using TLC (see, for example [14,15]) and the formulation information obtained from the ink's manufacturers.[2] If such an ink with the same formula as that of the Q one is available it is used to apply a "fresh" entry on a paper that is then examined as follows.

A piece of paper with a fresh ink entry is placed into a colorless transparent flask, for example, into a 10 mL Pierce (The Netherlands) Reaction Flask, after a drop of a basic reagent had been spotted onto a bottom of the flask. The flask is capped and possible ink color changes are observed. The best candidate (for which the most satisfied effect of the reaction has been obtained) is used as a reagent for carrying out the following ink age determination procedure.

Reflectance spectra of the "fresh" known ink entry are recorded before (spectrum 1) and after (spectrum 2) reaction with the reagent using a microscope photometer. A wavelength is chosen as the analytical one at which the maximal change of reflectance intensity has been detected for compared spectra 1 and 2 (see Fig. 1).

At the next step of the procedure the rates of chemical reaction between colored components of the known ink entries written during a certain period of time and the reagent are determined using the equipment shown in Fig. 2.

For this a piece of paper with every known ink entry (5) is mounted on the stage of a microscope photometer (6) and a site of the entry chosen by an examiner is brought into focus (care should be taken to avoid obvious faults in the measuring sites of the ink surface). A chamber (4) like the one described above, is placed on the paper and the site is refocused. Then a carrier gas (nitrogen or helium are preferable) is supplied from a reservoir (1) with a predetermined velocity (it is very important to stress that this velocity should be kept constant during the analysis and optimal for given setup, tem-

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[2]These operations are to be done at the beginning of all the procedures described in this paper.

REFLECTANCE (%)
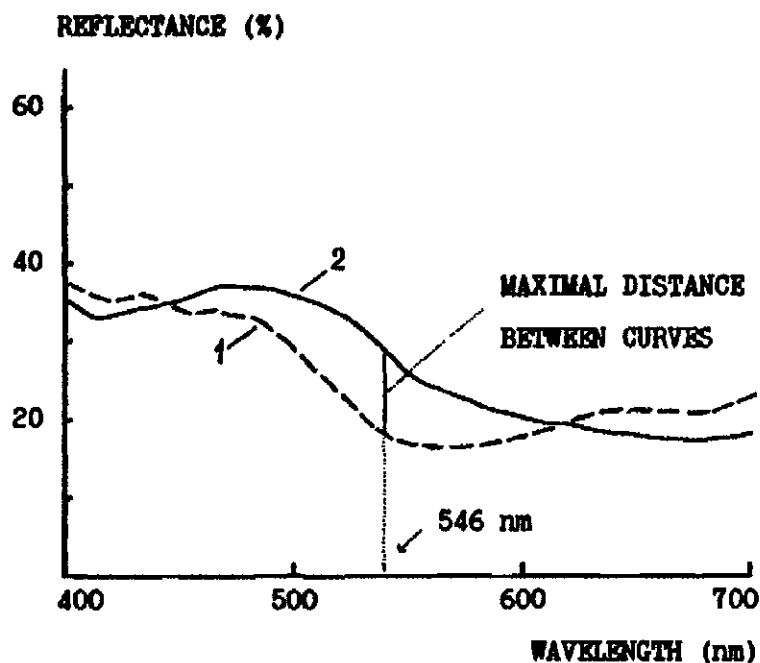
FIG. 1—*Visible spectra of a Soyuz blue-violet ballpoint ink before (1) and after (2) reaction with piperidine.*
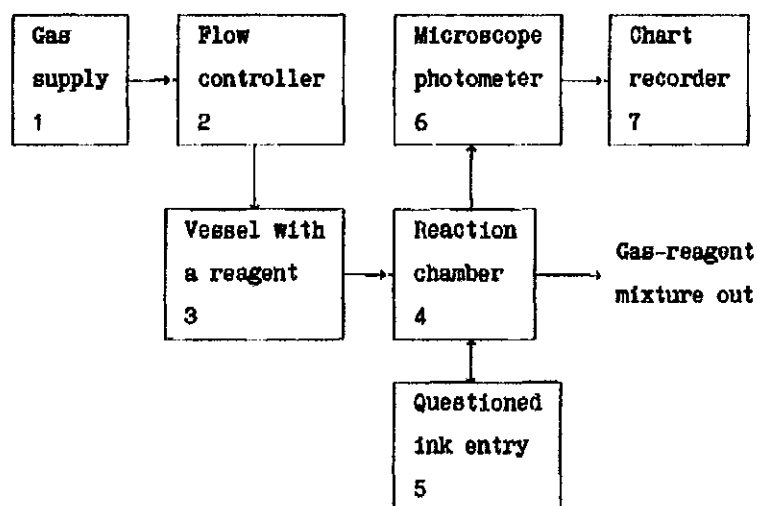
FIG. 2—*Basic assembly for the reagent-photometric technique.*

perature, and nature of the dye components of the ballpoint ink analyzed) into a vessel (3) where it is mixed with the reagent. The obtaining mixture goes through the chamber causing the color changes of the ink analyzed. These changes are being measured at the previously chosen analytical wavelength by the photometer system of the microspectro-photometer and depicted on the diagram of a chart recorder (7) as it is shown in Fig. 3.

The values of the rate of the reaction with the reagent determined for all known ink entries are plotted versus the age of these entries (as it is shown in Fig. 4). Using this "aging curve" the age of the Q entry analyzed by the same way described above, is determined as it is indicated in Fig. 4.

FIG. 3—"Reaction curves" obtained for the Soyuz ink writings of one-day (1) and one-month (2) ages.

FIG. 4—Aging curve obtained for a Soyuz blue-violet ballpoint ink using the reagent-photometric technique.
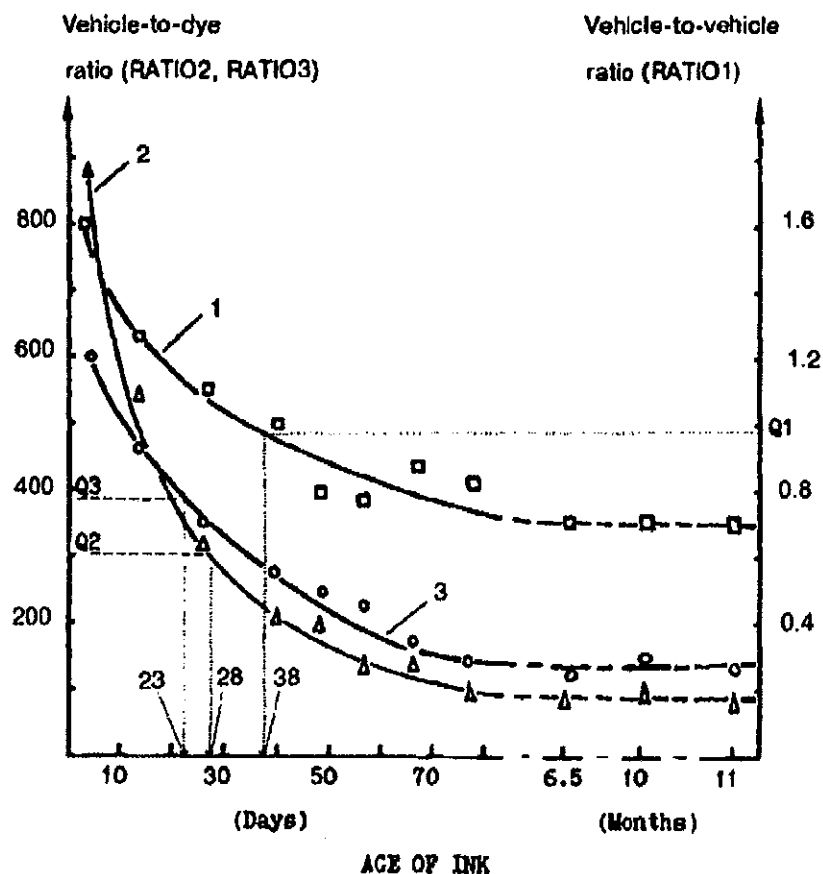
FIG. 5—*Aging curves for a violet ballpoint ink (made in Italy) and the Q entry age determination: the values of RATIOs 1–3 were calculated by using Eqs. 1–3.*

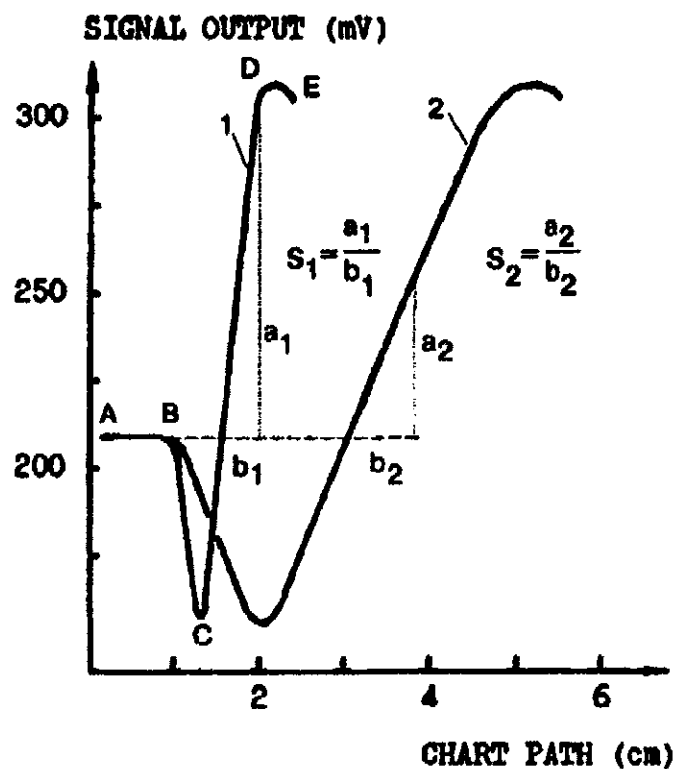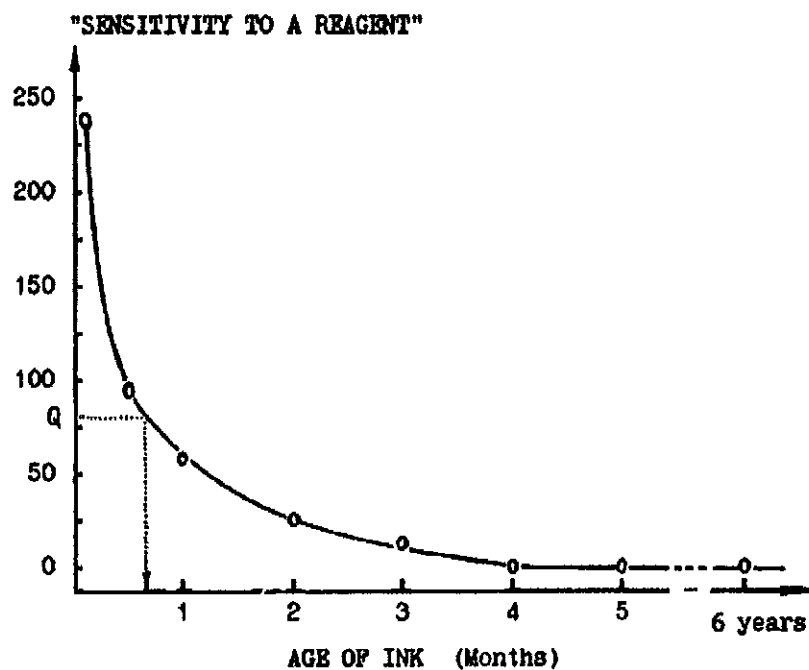*Example*—Entries known to have been written by a Soyuz blue-violet ballpoint ink during about six-year period were examined. The ages of these entries were 1 day, 1, 2, 3, 4, and 5 months, and 6 years. For these entries the "reaction curves" (like those depicted in Fig. 3 for one-day and one-month old entries) were recorded according to the above mentioned recommendations. For recording these reaction curves (at the previously chosen analytical wavelength, 546 nm; see Fig. 1) the measuring sites of the entries analyzed which seemed similar in thickness, homogeneity, and surface characteristics were selected under the microscope.

Then for every sample analyzed the value of "sensitivity (S) to a reagent" was calculated as the ratio of the change in the recorder signal (in mV) and the respective change in the chart path (in cm) within a linear portion of the recorder signal-vs-chart path graph (as it is shown in Fig. 3 for two samples analyzed: $S_1 = a_1/b_1 = 240$ mV/cm—for one-day old ink, and $S_2 = a_2/b_2 = 58$ mV/cm—for one-month old ink).

The calculated S-values were plotted versus the age of the corresponding ink entries analyzed (Fig. 4).

Results and Discussion

Figure 3 shows the "reaction curves" obtained for one-day (curve 1) and one-month old (curve 2) entries, respectively, written by a Soyuz blue-violet ballpoint ink.

These curves include four parts which can be characterized as follows (see curve 1 in Fig. 3):

A-B . . . reagent vapors do not contact with ink analyzed;

B-C and D-E . . . gloss of the ink surface is decreased and so reflectance goes down;

C-D . . . the ink is discolorated and so reflectance goes up.

It is clearly seen from Fig. 3 that the value of "sensitivity (S) to a reagent" characterizing the rate of the reaction between the reagent and ink's dye components, is higher for the newer, 1-day-old, writing as compared to that for the older, 1-month-old, one $(S_1 > S_2)$. As such a situation is a typical one for ballpoint inks containing dye components capable of changing their color in the presence of some reagents, the above mentioned sensitivity can be considered as an "aging parameter" (the term was introduced in [10]).

Fig. 4 represents the aging curve of a Soyuz blue-violet ballpoint ink using the described reagent-photometric procedure. The curve showed significant aging taking place over a period of about three months. It means that the age of questioned inks of the same formula could be accurately estimated up to 3 months if, of course, those inks have been stored under normal known conditions.

A lot of ballpoint inks of different ages have been analyzed by using the described technique. The technique has been found applicable to most of the inks examined except those which do not contain colored arylmethane compounds (and some other dyes capable of changing their color in the presence of the basic reagents), like a brilliant blue Bic ballpoint ink that contains only phthalocyanine dyes, which do not react with the basic reagents used in the described technique.

It should be also noted that this technique is non-destructive because inks being exposed to the reagent vapors recover their initial colors. Furthermore, the recovering rate is also a function of the age of ink: the older the ink, the less the recovering rate.

At the end of this section it is necessary to stress some things important for correct application of the discussed technique. In the first place, the color or texture of the support may influence drastically the results of microspectrophotometric measurements, and this should be remembered when placing fresh ink samples on a paper or choosing reference ink writings from an ink library file.

Secondly, the measuring sites of all ink entries that are to be analyzed, known and questioned ones, should be chosen as similar as possible with respect to their thickness (depth), homogeneity (homogeneous distribution of the ink substance), and surface characteristics (morphology, gloss, and so on).[3]

Ballpoint Ink Age Determination by Volatile Components Comparison. Vehicle-to-Dye Approach

In 1985, Stewart [9] proposed a technique for comparing the relative age of ballpoint inks. This technique included extraction and formulation identification of the questioned ink, qualitative determination of the volatile components of the ink using a method of gas chromatography (GC), calculation of the relative proportions of these volatile ingredients and age determination of the Q ink by comparison of the relative concentrations of its volatile components with those of known inks (age) of the same formulation.

Later, this method was modified for ballpoint inks that included phenoxyethanol and a phthalocyanine dye [16]. The main idea of that method was to measure the amount of phenoxyethanol using GC with thermodesorbtion of volatile components from ink entry followed by spectrophotometric determination of the phthalocyanine dye extracted from

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[3]Despite the fact that this technique can be considered as mass independent since it involves rates, it is highly dependent on these appearance factors. The other three techniques (also mass independent) described in this paper are less dependent on these appearance factors.

the same entry. However, that method cannot be applied to ballpoint inks containing solvents which boil higher than phenoxyethanol. For fast quantitative transmission of such solvents into vapor state ink samples removed from a questioned document have to be heated at the temperature higher than 200°C: in that case the resulting chromatogram profile would be distorted drastically by the paper's thermodecomposition products.

The technique proposed in this paper accumulates the advantages of the above mentioned methods [9,16] and does not depend on the nature of vehicles and dyes contained in dried ballpoint inks. It is based on measuring the amount of all available volatile components and of any colored one of dried ink, on determining all relevant vehicle-to-vehicle ratios (as it is suggested in [9]) and ratios of every vehicle and the colored component chosen, and on comparing the calculated ratios' values with those obtained for known ink of the same formula.

Experimental Procedure

Ink Samples—Lines of a violet ballpoint ink (made in Italy) have been placed on a white paper for notes during a year.

Sampling Devices—A safety razor and a syringe needle, 1 mm I.D., with a plunger to remove bored out samples.

Extracting Vessels—Camag (Switzerland) micro vials (N-11 polypropilene) with cone shaped interiors, a 10 μL Hamilton (USA) syringe.

Instruments—A Hewlett-Packard (USA) Model 5890 gas chromatograph equipped with a flame ionization detector (FID) and HP split/splitless injection system; a Carl Zeiss Jena (Germany) Model M-40 UV-VIS spectrophotometer.

GC Conditions—Column: SCOT, SP-1000 (polyethylene glycol 20M terminated with nitro-terephtalic acid; Supelco, Inc., USA), 25 m × 0.5 mm I.D. Carrier: Nitrogen, 4 psi, 40 mL/min. Oven: 50°C (0.5 min) + 10°C/min = 220°C (6 min). Injection: 2 μL, splitless, $T = 250°C$. Detector: FID, $T = 250°C$.

Procedure—The first step of the procedure includes the identification of a questioned ink formulation using methods of TLC and GC (or gas chromatography—mass spectrometry for unknown volatile components identification) and formulation information obtained from the ink's manufacturers. Then samples of the Q entry and entries written by the chosen ink of the same formula (with known ages) are removed by a micro-pellet technique [14] or cut out with a sharp razor blade (entries of about 2 cm in length[4]) and analyzed by using GC and spectrophotometric methods as follows.

Every sample is extracted in a vial with a solution of an appropriate substance used as an internal standard. At the end of the extraction process about 2 μL aliquot for every sample is removed and analyzed by GC. The mass (m) of any volatile components detected in the ink samples analyzed is calculated by means of the internal standard method.

The same samples are extracted in a strong solvent like dimethylformamide or pyridine, and the absorption spectra of the colored extracts obtained are recorded. The absorbance (A) measured at the absorption maximum of a dye presented in the ink analyzed is read for every sample, and the ratio of "m/A" is calculated.

If the chromatogram of an ink analyzed has at least two peaks corresponding to appropriate volatile components, X and Y, then three aging parameters can be estimated: the value (Ratio 1) directly proportional to the masses' ratio of those components that

[4]Samples of 1 cm in length of ink line can be used if the methods of microanalysis mentioned at the end of section on Ballpoint Ink Age Determination by Volatile Components Comparison are applied for quantitative determination of ink dyes.

is determined by ratioing one peak area to the other (as it was proposed in the work [9]):

$$Ratio\ 1 = (Peakarea_x)/(Peakarea_y) \qquad (1)$$

and, besides, the two following vehicle-to-dye ratios:

$$Ratio\ 2 = m_x/A \qquad (2)$$

$$Ratio\ 3 = m_y/A \qquad (3)$$

Finally, "aging curves" (like curves 1 to 3 in Fig. 5) for the known ink can be obtained from those three sets of Ratios plotted versus actual age, and using these aging curves, the age of the Q entry can be evaluated as a mean value of the three results obtained for this entry by means of the vehicle-to-vehicle [9] and vehicle-to-dye ratio techniques (like it is shown in Fig. 5).

The following example illustrates this procedure.

Example—Entries known to have been written by the violet ballpoint ink (made in Italy) were examined. The ages of these entries were 4, 13, 26, 40, 48, 57, 67, and 78 days, and 6.5, 10, and 11 months.

Every sample (2 cm slivers) was extracted in a vial with 15 µL of carbon tetrachloride containing methylstearate (25 mg/mL) as an internal standard). The extraction time was 60 minutes.

About 2 µL aliquot for every sample was removed and analyzed by GC. In each sample two volatile components of the ink—phenoxyethanol (component X) and phenoxyethoxyethanol (component Y)—were detected, and their masses (m_x and m_y) were calculated. The value of Ratio 1 was also calculated for each sample.

The samples were removed from the extracting solutions and dried. Then they were extracted with 1.2 mL of dimethylformamide and the absorption spectra of the colored extracts obtained were recorded. For every sample the absorbance (A) measured at $\lambda = 595$ nm (the absorption maximum of methyl violet—the main color ingredient of the ink analyzed) was read and the values of Ratio 2 and Ratio 3 were calculated.

The obtained three sets of Ratios were plotted versus actual age of the known ink entries (see curves 1 to 3 in Fig. 5).

After that the 29-day-old entry written by the same ink was analyzed (as a Q entry) in the same way as the known entries. The values of Ratio 1 ($Q1$), Ratio 2 ($Q2$), and Ratio 3 ($Q3$) were obtained for the Q entry, and using the previously plotted aging curves, the age of this entry (approximately 30 days) was determined as the arithmetic mean of 38 ($Q1$), 28 ($Q2$), and 23 ($Q3$) (see Fig. 5).

Results and Discussion

Figure 5 shows three "aging curves" obtained for a violet ballpoint ink (made in Italy) by using vehicle-to-vehicle (curve 1) and vehicle-to-dye (curves 2 and 3) ratio techniques and the way to use these curves to determine the age of Q entries.

The example described illustrates a case when two volatile components of the ink analyzed were determined.[5] In similar cases the use of three "aging curves" like those depicted in Fig. 5 can enhance the reliability of the results of dating inks. Moreover, the

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[5]Since sensitivity of the detector to one of the volatile component (phenoxyethanol) was a little bit more than that to the other (phenoxyethoxyethanol), the values of Ratio 1 were some more than corresponding values of Ratio 2/Ratio 3 (see Fig. 5).

use of the combination of these techniques can help to diminish possible misinterpretations of the results of dating ink, especially in cases when, as the author's own practice showed, bad correlation is observed between the ages of writings and corresponding values of vehicle-to-vehicle ratios obtained.

And of course, contrary to the vehicle-to-vehicle ratio technique [9], the proposed vehicle-to-dye ratio technique is applicable in frequently encountered cases when only one volatile component can be determined in an aging ink.

The obvious shortcoming of the described vehicle-to-dye ratio technique is the necessity to remove about 2 cm of inks from questioned documents (in order to obtain correctly measurable absorptivity values of dyes in the inks' extracts).

To overcome this shortcoming some other analytical methods for quantitation of dyes in ink extracts can be applied, such as microspectrophotometry, densitometic TLC, or spectrophotometry combined with beam condensing systems and micro cuvettes. With help of these methods samples of 1-cm of ink lines are quite enough to be examined by using the proposed vehicle-to-dye ratio technique.

Ballpoint Ink Age Determination by Volatile Components Comparison. Sequential Solvent Extraction Approach

The method of sequential solvent extraction of the colored (nonvolatile) components of aging inks has been developed by Cantu [3,4] and then comprehensively described by Cantu and Prough in the work [5].

A new ballpoint ink age determination technique described in this Section is based on the principles of the above mentioned method [5] and deals with ink's volatile components.

The technique includes the sequential extraction procedure in which one solvent ("weak") extracts volatile components of an aging ink with the extent of extraction depending on the ink age, while another solvent ("strong") extracts these volatile components practically completely from both, fresh and old, entries written by ballpoint inks of the same formula.

Experimental Procedure

Ink Samples—Up to 15-years old entries written by Soyuz blue-violet ballpoint inks of the same formula.

Tools, GC Equipment and Chromatographic Conditions—were the same as those described in the previous section.

Procedure—Approximately 10 micro discs (1 mm diameter) or about a 1-cm sliver of ink on paper are removed using a boring device or a safety razor, respectively, and placed in a micro vial with cone shaped interior. 10 μL of a "slowly extracting weak" solvent containing a certain substance as an internal standard is added and the vial is capped.

In a certain period of time (usually not more than 60 min) about 2 μL of the extract is taken for GC analysis.

The sample is removed from the extracting solution, dried and placed into another micro vial. The second extraction is carried out with 10 μL of a "fast extracting strong" solvent also containing an internal standard (the same or, preferably, another one). About 2 μL of the extract is removed and analyzed by GC.

Then the masses of a vehicle component determined in each of the two extracts analyzed (*M*1 and *M*2 for the first and second extractions, respectively) are calculated by means of the internal standard method, and "percent extraction" (see [5]), that in the present work means the percent of the mass of the ink vehicle component (%M) extracted in

the "weak" solvent (relative to its total amount contained in the sample analyzed), is calculated as follows:

$$\%M = M1/(M1 + M2) \times 100 \tag{4}$$

The values of %M obtained for all samples analyzed are plotted versus the age of these samples (as it is shown in Fig. 6). Using such a percent extraction aging curve the age of the Q entry analyzed by the described way, can be determined (see Fig. 6).

Example—Entries known to have been written by Soyuz blue-violet ballpoint inks of the same formula were examined. The ages of these entries were 2, 10, and 27 days, 2, 3, 4, and 5 months, 6, 12, and 15 years.

Every sample (1 cm slivers) was placed into a Camag micro vial with cone shaped interior and extracted for 60 min with 10 µL of carbon tetrachloride ("slowly extracting weak" solvent) containing methylstearate (25 mg/mL) as an internal standard. About 2 µL of every extract was taken for GC analysis.

The samples were removed from the extracting solutions, dried and placed into other micro vials. The second extraction was carried out for 2 min with 10 µL of chloroform ("fast extracting strong" solvent) also containing methylstearate in the same concentration. About 2 µL of every extract was removed and analyzed by GC.

Then the masses of phenoxyethanol (the only volatile component reliably detected in all ink samples analyzed) contained in each of the two extracts obtained for every sample analyzed were calculated, and the "percent extraction" of phenoxyethanol (%M) was determined by using Eq (4).
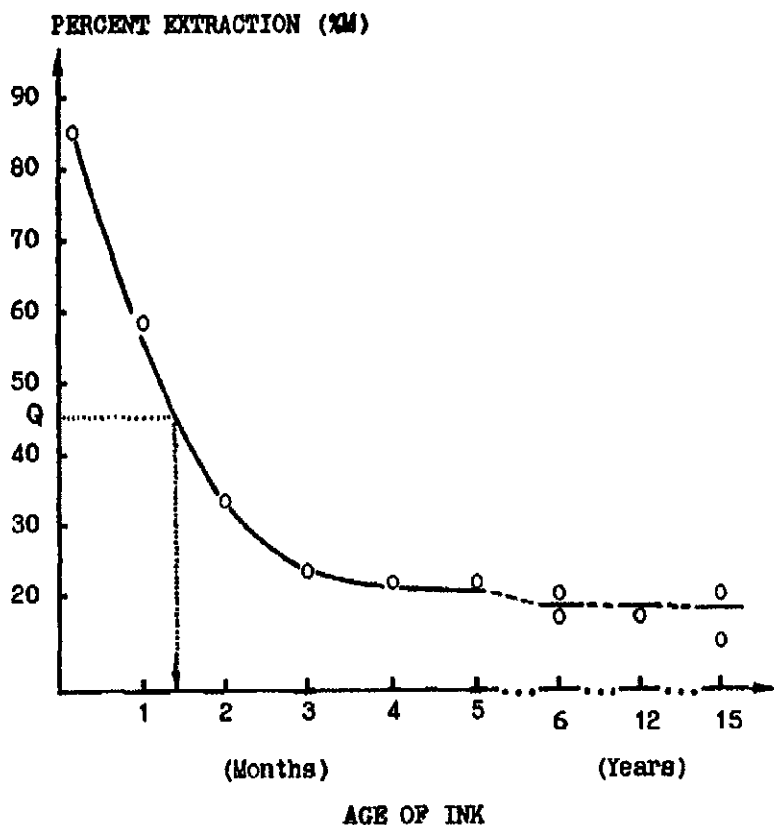

FIG. 6—*Aging curve obtained for Soyuz blue-violet ballpoint inks of the same formula using the sequential extraction procedure.*

The values of %M obtained for all samples analyzed were plotted versus the age of these samples (see Fig. 6).

Results and Discussion

Figure 6 represents the aging curve obtained for Soyuz blue-violet ballpoint inks of the same formula. The curve shows significant aging taking 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 of about 20%.

This experimental result characterizing the mechanism of evaporating volatile components (like phenoxyethanol, phenoxyethoxyethanol and so on high boiling vehicles frequently used as the ingredients of ballpoint inks) from aging inks can be interpreted as follows. The process of such evaporation is carried out from the surface of ink line placed on a paper. To reach the ink line surface a vehicle must diffuse from the inner layers of the line. However, resins and other viscous ballpoint ink ingredients limit a diffusion process (to some extent, of course). In addition, as soon as the reaction of cross-linking or polymerization of these ingredients has started, those diffusion processes are getting more and more slow, and at a certain stage of ink aging they stop completely "keeping" the remained micro drops of the ink volatile components inside the aging ink line for a practically infinite period of time (or until extracting by a solvent or heating[6] "frees" them).

So when using a strong solvent capable to dissolve hardened ink resins (like chloroform used in the example discussed), those vehicle remainders can be easily detected even in very old ballpoint ink writings (Fig. 6 demonstrates it for 12- and 15-year-old entries written by Soyuz blue-violet ballpoint inks of the same formula). Hence, by this way it can be possible to obtain additional information about formulations of old questioned inks or to try solving other forensic tasks, for example, like that mentioned in footnote 6.

A different situation takes place when a "weak" (with regard to hardened ink resins) solvent is used. It cannot penetrate into an old ink line, so it extracts ink volatile components only from outside layers of the ink line. But the newer the ink, the more outside ink layers (up to the whole ink material for fresh inks) become available for the weak solvent, and hence, the more quantity of volatile components is extracted.

Returning to Fig. 6 one can see that the above considered tendency, indeed, characterizes the behavior of a weak solvent: the extracting efficiency of carbon tetrachloride decreased from about 90% (fresh writings) to about 20% (old writings).

The proposed method has shown good efficiency for dating ballpoint inks which contain comparatively high boiling vehicles (those that boil higher than 200°C). At the same time, when using this technique one should remember that samples of approximately equal thickness (depth) of ink line are to be taken from questioned and known ink entries. It seems quite obvious because thicker lines "store" more ink volatile components than thinner ones.

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[6]The present author has found that high boiling vehicles cannot be completely removed from ballpoint inks by their heating (without damage of the paper on which the inks have been placed). Besides, it has been noted that heating (accelerated aging) of the inks often leads to much more extent of evaporation of their high boiling volatile components (approximately 10 to 100 times greater) than it takes place at the result of long natural aging of these inks. In this connection, a procedure has been developed that can enable discrimination between naturally and artificially aged inks of the same formula. The procedure (it will be described in the next publication) was successfully used in the author's expert practice to establish a fraudulent nature of questioned documents (those that had been artificially aged).

Determining Age Changes of Nonvolatile Colorless Components of Ballpoint Inks

As a rule, synthetic resins and polymers are mixtures of oligomers and other compounds of different stability. So it can be supposed that detectable changes in relative content of these components or even in their qualitative composition may occur when ink ages. This suggestion was confirmed in the present work by studying an aging process of several ballpoint inks of different formulations.

The proposed procedure is based on a TLC separation of colorless nonvolatile ingredients of ballpoint inks of known and Q ages and the assessment of the resulting chromatograms under UV illumination. (The procedure of densitometric evaluation of the resulting chromatograms is also being developed. The procedure includes the modified peak ratioing technique described partly in [17] that is less mass dependent and so more correct than the well-known peak signal-to-peak signal ratio technique [7,18]).

Experimental Procedure

Ink Samples—Lines of a Parker blue ballpoint ink and Soyuz blue-violet ballpoint ink have been placed on a white paper for notes for a period of six years.

TLC Materials—High-performance (HP) TLC silica gel 60-F_{254} (10 × 10 cm) precoated glass plates (Merck, Germany) and also thin-layer plates of 10 × 10 cm cut out from precoated Merck TLC silica gel 60-F_{254} aluminum backed 20 × 20 cm plates.

Procedure—Samples (4-cm slivers[7]) of the known ink having the same formula with the Q ink are placed into cone shaped micro vials and extracted with chloroform, carbon tetrachloride, or some other suitable solvent. The extracts obtained are applied onto a precoated TLC or HPTLC plate with fluorescent indicator. The plate is developed in an eluent capable, on the one hand, to separate colorless components of the ink examined and, on the other hand, to prevent overlapping of the zones of these components and of those extracted from a paper.[8]

The resulting chromatogram is observed under UV illumination (254 and 366 nm) to detect the location of the zones of colorless non-volatile components of the ink analyzed.

If not less than two such zones have been detected (within a chromatographic track corresponding to a sample of the ink entry of a certain age), then possible correlations between relative proportion of any two of these colorless components and the age of the analyzed ink entry is determined by means of visual "semiquantitative" assessment [18] or by evaluating the relative proportion of the two chosen components of the known and Q inks with the aid of scanning densitometry (some limitations of this technique are considered below).

After a correlation "relative content of two components—age of ink" has been established the second stage of the procedure is carried out. It includes the same operations described above but now samples (2 cm slivers, for HPTLC, or 4 cm slivers, for TLC) are taken from the ink entries of known and Q age.

Finally, the age of the Q entry is determined by comparing the corresponding data obtained for the Q and known entries.

The capabilities of this approach are illustrated by the following examples.

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[7]Sample sizes can be sufficiently diminished if HPTLC plates are used instead of TLC plates and if a procedure for sensible visualization of separated zones of ink colorless components is applied.

[8]For several ballpoint inks from the collection of the author the mobile phases consisting of acetone and low boiling saturated carbohydrates, with or without low boiling alcohols, showed good efficiency and selectivity (see *Example*). But in general, the composition of an eluent depends on the nature of colorless components of the ballpoint ink analyzed.

Example—Entries of known ages (up to six-year-old) written by a Parker blue ballpoint ink and Soyuz blue-violet ballpoint ink were examined.

Every sample (4 cm slivers) were placed into a micro vial with cone shaped interior and extracted for 2 min with 20 μL of chloroform (extraction in carbon tetrachloride during about 60 min also gave good results). The obtained colored extracts (as chloroform dissolved the dyes of the ballpoint ink analyzed) were applied with the help of glass capillaries onto 10 × 10 cm TLC plates cut out from a precoated Merck TLC silica gel 60-F_{254} aluminum backed 20 × 20 cm plate.

The samples taken from the Soyuz blue-violet ballpoint ink entries were eluted in a solvent system of acetone—hexane (1:4, v/v), and the ones taken from Parker blue ballpoint ink entries were chromatographed in a mixture of acetone—hexane—ethanol (5:20:1, v/v).

The resulting chromatograms as viewed under UV light at 254 nm are depicted in Figs. 7 and 8.

Results and Discussion

Figures 7 and 8 demonstrate the view under UV illumination of thin-layer chromatograms of samples taken from the entries of known ages written by a Parker blue ballpoint and Soyuz blue-violet ballpoint ink, respectively. A to D point out separated colorless components of the inks analyzed. The other spots in the chromatograms correspond mainly to the substances extracted from the paper on which the analyzed inks had been placed.

For the Parker ink (Fig. 7) the link between the relative proportion of substances A (R_f value was about 0.4 in this development) and B (R_f value was about 0.25) and the age of the ink writings examined is quite obvious even by means of a visual assessment: ratio "substance A/substance B" gradually increases as the ink ages (it is minimum for the fresh, one-day old entry—the first track in Fig. 7, and maximum for the six-year old entry—the fifth track in Fig. 7).

This example shows that the eluting solvent applied is selective enough for the given "ink–paper" system.
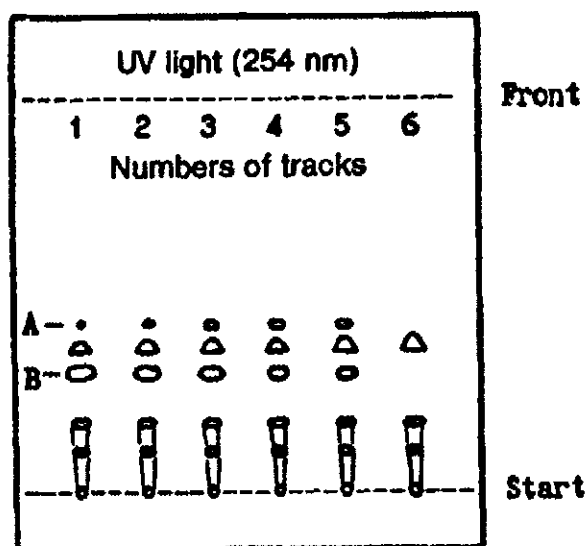

FIG. 7—*Thin-layer chromatogram obtained for the extracts from the Parker blue ballpoint ink entries of different ages (under UV 254 nm): 1—one day; 2—one month; 3—one year; 4—three years; 5—six years; 6—paper.*
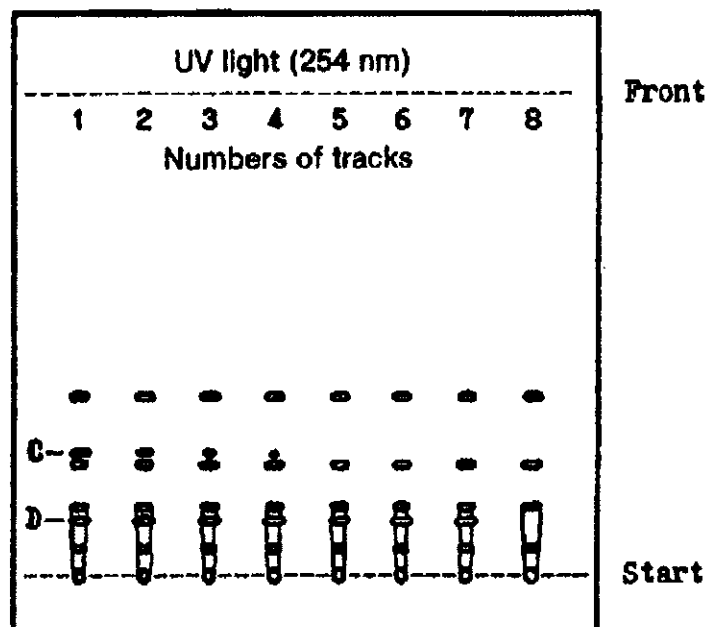
FIG. 8—*Thin-layer chromatogram obtained for the extracts from the Soyus blue-violet ballpoint ink entries of different ages (under UV 254 nm): 1—one day; 2—one month; 3—five months; 4—one year; 5—one-and-a-half year; 6—two years; 7—six years; 8—paper.*

The next example (Fig. 8) illustrates another situation. There are two colorless components, C and D, on the chromatogram which are the fractions of phenoloformaldehyde resin of the Soyuz ink analyzed. It is seen that the relative proportions of these components change as the ink ages leveling off after about a year and a half since the ink has been placed on paper. The problem is that only component C (R_f value was about 0.2 in this development) is located in a "pure" part of a chromatographic track, whereas a zone of component D (R_f value was about 0.1) is overlapped by the zones of the paper's ingredients.

In this particular case such overlapping is not too critical because the D zone dominates over less UV light absorbing tailed spots of the paper's extracted ingredients (furthermore, in this particular case the component D can be converted into a strongly light absorbing derivative by a reaction with diazotized amines). But, of course, in general such a situation is not desirable, especially in connection with the necessity of applying the densitometric evaluation of chromatograms for calculating relative contents of analyzed ink colorless components and subsequent obtaining corresponding aging curves (by plotting the ratios determined for each known dated ink sample versus age).

So the last example illustrates difficulties that may occur when using this technique and shows that preliminary studying of chromatographic behavior of the known inks' colorless components in the presence of substances extracted from the paper on which the ink had been placed, should be considered as a necessary and important part of this approach.

Another important thing should be mentioned in connection with using of densitometric thin-layer chromatography for evaluating the relative proportions of the ingredients of samples analyzed. The matter is that the widespread peak signal-to-peak signal ratio technique, though it sometimes seems quite applicable (see, for example, the works [7,18]), often produces statistically bad results [17-19].

In fact, using this technique an analyst must be confident that in his or her case of comparing separated samples the obtaining relationship between signal output (peak

height or peak area) and the content of a separated zone is well approximated either by the function

$$Signal = empirical\ constant \times content \qquad (5)$$

that is a form of Beer's law [20], or by the function

$$Signal = empirical\ constant/content \qquad (6)$$

because only in such cases the signal-to-signal ratio technique is, in fact, mass invariant.

However, in many works (see, for example [19,21] devoted to studying "signal-content" relationships in TLC it has been shown that this is not so and it was demonstrated that other functions like different polynomials or the Michaelis-Menten function gave much better results.

In connection to this an attempt of improving the signal-to-signal ratio technique has been made in the work [17].[9] Basing on the result of this work, a TLC method including an "improved" signal-to-signal ratio technique with the corresponding software is now being developed by the author and will be described in the next publication.

The procedure considered in this Section uses ink samples of more than 1 cm length of ballpoint ink line. Therefore, the work on improving the analysis' procedure is being carried out with the aim to increase the sensitivity of the detection of ballpoint inks' colorless non-volatile ingredients, for example by chemical reaction on the plate.

Conclusion

The four techniques considered in this paper can be used effectively for determining the relative age of entries written by ballpoint inks on the same piece of paper. In some cases (when the conditions of ink aging are known) these methods can also be applied to determining the absolute age of ink.

Of course, these techniques can be applied only to the ink entries aging in darkness and within the known temperature interval. Knowledge of aging conditions is extremely important and allows to avoid gross mistakes when interpreting the results of the examination of ink dating.

Further work is necessary for testing the application capabilities of the described techniques on a wide range of ballpoint inks that are in the market. Besides, some other works on ink aging problem which include a study of degradation of ink colored components as the ink ages and developing the above mentioned "improved signal-to-signal ratio technique" are now in preparation.

Acknowledgments

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Exhibit 22

REVIEW ARTICLES

DISTINGUISHING BETWEEN RELATIVE INK AGE DETERMINATIONS AND THE ACCELERATED AGING TECHNIQUE

A discussion of dynamic methods for determining the age of a writing ink on a document.
by Larry F. Stewart, M.S.F.S.[1] and Susan L. Fortunato, B.A.[2]

ABSTRACT: Methods for determining how long an ink entry has been on a sheet of paper have been evolving since the early 1900's. One of the latest endeavours in the field, accelerated aging, has been a recent topic of debate in the forensic science community as well as in the court system. In light of the recent fact that forensic ink examiners hold opposing viewpoints on this topic, a review was conducted in an attempt to identify the source of this opposition. Definitions for relative ink age determinations and the accelerated aging technique have been provided for clarity. All of the articles which appeared to have provided a platform for the accelerated aging approach were reviewed. Laboratories or individuals using these techniques will be able to consider advantages and limitations prior to utilization in casework.

Introduction

It would be ideal to forensically examine an ink entry on a document and determine if the document bears an authentic date. Although this is possible in a number of cases utilizing conventional ink analysis techniques [1-12], not every case has a definitive, scientific answer.

There seems to be an increase in the number of cases where ink testimony is requested on each side of the courtroom. Often, the experts' opinions are diametrically opposed in these cases. With all of the advances that have been made in the area of ink analysis over the past few decades, one would anticipate that there would be consistency between techniques of choice and opinions in these matters.

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. The problems may be compounded by a misunderstanding of previously reported definitions, incomplete research and validation studies, and improper use of techniques. To clarify these disagreements a reevaluation of some

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of the published practices in the field is in order. 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. Once validation studies are complete then precise protocols must be documented before the use of any new technique as a primary tool in casework.

Historical

Distinguishing Between Relative Age Determinations and Accelerated Aging

It is important to make the distinction between the techniques which are known as "relative ink age determination" and "accelerated aging."

Relative ink age determination techniques were first developed in the early 1900's by Mitchell [13,14] in England and later by Hess [15] in Germany. At that time they were studying the effects of the aging on fluid iron gallotannate inks while they were still on the document. In 1959, Kikuchi [16] furthered the research by noting variations in the time taken for an ink line to disperse when solvents were applied to the ink on the paper. He detected a correlation between the dispersion rates and age of ink. In 1963, Witte [17] reported on the examination of ballpoint pen inks and observed that as inks age, their "copying power" decreases. Copying power referred to the ease of removing the ink from an ink line (transferability). The extent of transfer was shown to be affected by the length of time the ink had been on the paper.

In the early 1980's, further research began that has led to the latest advances in the area of relative ink age determination. The developed techniques include methodologies in the areas of Fourier Transform Infrared Spectrometry [18,19], Gas Chromatography [20,21], Thin Layer Chromatography [22,23,24], High Performance Liquid Chromatography [25] and microspectrophotometry [26]. While the techniques are still evolving, some basic definitions, methods, parameters, and their associated criteria, have since developed.

A relative ink age determination is, by *definition*, an examination performed on two or more ink entries of the same formula on the same paper. The preparation date of at least one of the entries must be known in order to determine whether the questioned entries were written on or about their purported dates. These examinations are performed for the purposes of determining the order of the preparation of the entries. Advances in the area of

relative ink age determination have undergone independent review and the methods have been shown to be reproducible. These advances have provided answers to previously asked questions on determining the age of a document through ink analysis.

Accelerated ink age determination is a technique which utilizes many of the analysis methods described in relative ink age determinations; however, a key difference is that this procedure is accomplished without known, dated comparison entries. This technique was developed as a result of cases where conventional ink analysis dating methods could not be applied in the absence of known identifiable and dated ink samples. Consequently, validated accelerated aging techniques could potentially assist document examiners in determining the authenticity of documents in cases where the relative ink aging criteria were not met. In the accelerated aging technique, the "standards" that are used for comparison are samples of the questioned entry which are heated to a point where the ink is now said to mimic an ink that has undergone aging. Comparison of the questioned ink before and after age inducement is said to yield information regarding the age of the entry.

Because of the many contributing factors (e.g. heat, humidity, paper, etc.) associated with accelerated ink aging determinations, it is important to continue to consider relative ink age determinations and accelerated aging as two separate techniques until the basis for the accelerating age technique has been independently evaluated and reproduced. A review of the research that has led to accelerated aging techniques will underscore the concerns and the necessity for follow-up work.

Review of the work leading to the accelerated age technique

In 1982, "Artificial Aging of Documents," [27] reported a case where a particular Bic black ballpoint ink was found to degrade when exposed to extreme heat. Initial comparisons of the questioned ink against a reference library collection yielded no match; however, one ink was chemically close in composition. It was noted that it was not possible to match the questioned ink to the library of standard writing inks without first heating the most consistent library comparison ink. This library standard chromatographically appeared as a "unique two dye component system". Interestingly, after heating the library standard ink at 204°C for 1 hour, the standard ink was again developed and resulted in a chromatogram containing four areas of difference from the original unheated ink. (It was the heated form of the library standard that matched the questioned ink.) Also, as a note, the author credited Browning's notation [28] that previous reports concluded that paper aging at 100°C for three days is approximately equal to 25 years of normal aging.

In 1985, "Ballpoint Ink Age Determination by Volatile Component Comparison - A Preliminary Study," [20] described a potentially viable approach using gas chromatography to quantify the ratio of volatile vehicle components in an ink. The work showed that the volatile vehicles in an ink evaporate at different rates and this difference could be quantified for some inks. This ink aging was noted over the first few months after the ink was placed on paper. The conclusion proposed that further work should be performed including "testing the paper independence theory" and alludes to the accelerated aging technique by mentioning "developing a laboratory technique for controlled *artificial aging of ink* standards to obtain immediate aging curves for known standard inks".

In September of 1987, "On the Relative Aging of Ink - The Solvent Extraction Technique," [22] the dynamic characteristics of ink aging and the principles of relative ink age determination. The authors reported their analysis of one "Fisher pressurized black ballpoint ink on Nashua (photocopy) paper". Heat was used (100°C for time periods of up to 165 minutes) to create known ink samples of increasing age. They did not report the time, humidity and temperature necessary to achieve the appearance of a specific age of ink, however their work allowed them to validate well documented theories pertaining to heat inducement and extraction effects. Specifically, the authors were able to document an effect where the more heat that was introduced, the less the ink extracted.

In November of 1987, two publications emerged which set out guidelines for the use of the relative ink age analysis technique. Since accelerated aging had not yet been conceived, this technique was not mentioned in either publication. However, the guidelines that were established in 1987, are considered today when utilizing either relative ink aging or accelerated aging. Some of them are mentioned here. In the first article "Critical Evaluation of Current Ink Dating Techniques" [7], the following criteria were established:

• the inks compared must have the same formula;

• the inks compared must appear on the same paper;

• when comparing the age of one ink to another, the parameter compared must be independent of the amount of ink sampled;

• accuracy of the aging techniques must be determined; and

• reliability measurements must be conducted.

The second publication of November 1987, was entitled "Training Requirements and Ethical Responsibilities of Forensic Scientists Performing Ink Dating Examinations" [8]. This publication set forth the requirements that were necessary in order to report sound conclusions. It discussed "unethical" practices with respect to ink dating examinations and conclusions. The reported unethical behaviours included:

• a conclusion as to the age of ink by any technique where the accuracy, reproducibility and experimental error have not been scientifically established (if accuracy, reproducibility and experimental error are not known, conclusions will be misleading.);

• conclusions on the basis of data that are within or even close to the range of experimental error of the procedure used (These conclusions would be based on misrepresentations of data and would be technically incorrect. Conclusions of this type also suggest partisanship or special interest in a case.);

• conclusions that state or infer the absolute age of an ink without sufficient proof;

• testimony involving ink dating that does not state the significance of results obtained and the limitations of what can be concluded from the results of the examination; and

• conclusions made on the age of inks found on different documents (unless the effects of different paper have been proven to have no effect on the age determination).

At any stage in the development or implementation of a

technique, it is important to strictly adhere to these criteria until proven otherwise.

In 1988, "Comments on the Accelerated Aging of Ink" [29] ` `s published and again, the "Fisher pressurized black ballpoint ink Nashua (photocopy) paper" was studied. This time, the natural ses accelerated aging curves of the Fisher ink were compared in an attempt "to determine if scaling was possible to make them equivalent". A scaling factor indicating that "90 days of natural aging at 25°C is equivalent to 4 minutes of artificial aging at 100°C" was developed. This calculation was qualified in that "the scaling factor obtained applies at least to the Fisher ink on Nashua paper and for the method used for measuring the percent extraction." Credit was given to the extensive work done on the aging of paper which notes that "three days of aging paper at 100°C is equivalent to 68 years of natural aging at 22°C."

In 1992, "Ink Dating - The State of the Art" [30] reviewed the ink dating techniques being used, discussing their value and the limitations of the various techniques. It reiterated that all relative age comparison procedures require that the questioned and known dated inks consist of the same ink formulation and that they be on the same paper to eliminate storage condition variables. The author noted that since 1988, when the feasibility of accelerated aging was reported, he had been working in this area of ink analysis. The article goes on to say:

"Because of the obvious potential benefits of the accelerated aging technique, the author has been working with [another author's] ideas in this area. The premise behind this work is based on observations from several natural aging curves and is that changes in certain solubility parameters of most ballpoint ⁱnks are not detectable in inks two to three or more years old. ɔnversely, significant changes in the solubility parameters of ᴜks in solvents occur with age and are usually detectable in inks less than two to three years old. This has been established with natural aging curves of numerous ballpoint ink formulations. The assumption is that inks that are not completely dry will undergo changes in solubility parameters when subjected to heat. Inks that have reached the end of their natural aging curve (point of complete dryness) will not undergo changes in solubility when heated. This theory was validated by heating ballpoint inks of known date (from fresh up to four years old) at 100°C for 15 minutes In every case, changes in the dye ratios were observed if the ink in question had not reached the asymptote of its natural aging curve. Naturally, different ink formulations have different natural aging curves. Therefore, any attempts to estimate the age of ink using the accelerated aging procedure must consider the natural aging curve of the ink in question."[3]

In a 1994 presentation entitled "Relative Aging of Ball Pen Ink: Natural Aging vs. Artificial Aging"[31], the results of the testing of six different ink formulations were reported. Each ink was tested through natural aging over a five year span and after heating the ink on paper and in a vial. This was the first time that data and calculations of the results were published. The author was unable to achieve consistent, reliable results and called the technique of accelerated aging "unreliable and possibly misleading."

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ₛ Important to note that none of the research results which were mentioned appear in this publication, therefore these observations and conclusions cannot be independently validated.

In fairness to the technique, the author indicates an absence of a full understanding of the technique for heating of writing samples (accelerated aging) in the introduction. As a result of the study, it was the authors' opinion, regarding the use of heated samples to mimic aged writing "to not do so at this time".

The most recent article (1995) entitled "A Sequential Multiple Approach to Determining the Relative Age of Writing Inks"[32], outlines a procedure combining three commonly used thin layer chromatography methods for performing relative age determination. Four techniques are described which include the accelerated aging approach. Under the accelerated aging section, the article indicates that after heating the ink, if "a significant difference [is] obtained by any one of the three methods [it will] indicate the ink is not completely dry and therefore is most likely less than three years old, but definitively less than four years old." This is based on the "fact" that no inks have been found to continue to dry after four years using all three relative age determination methods described. A case is described where no entries of known date were available for comparison. Accelerated aging of the ink was conducted (in this case, by heating the ink for 20 minutes at 100°C) to create known standards for comparison. It was concluded that the questioned ink was still drying (aging) and could not have been written in 1989, as the date on the document purported. This conclusion was based on the natural aging curve of the questioned ink which showed no further drying after approximately four years. The result was confirmed through the identification of a dating tag. In the summary, it is noted that the storage conditions of the document and the type of paper involved must be considered and that only inks of the same formulation can be compared.

Discussion

The relationship between accelerating the age of paper and accelerating the age of an ink.

Although the reported induced age characteristics of paper have been helpful in obtaining a starting point, it is doubtful to these authors if papers and inks age consistently. Assuming they do not, then the effects of the paper must be further considered before adoption of accelerated aging techniques.

In "Artificial Aging of Documents," it was reported that paper heated to 100°C for three days is approximately equal to 25 years of normal aging. "Comments on the Accelerated Aging of Ink" reported that the heating of paper at 100°C for three days was equivalent to 68 years of natural aging (22°C). The authors qualify these figures and admit that they may vary depending on the type of paper and the type of testing method utilized. By using the two reported calculations for age inducement of paper, one would have to heat the paper at 100°C for either approximately 43 or 16 minutes to mimic 90 days of natural aging (see Figure 1). Given this range between reported findings it was interesting to note the scaling factor that was created for an ink and paper *combination*. With the scaling factor it was concluded that for one particular ink, 4 minutes of artificial aging at 100°C was equivalent to 90 days of natural aging (25°C). Using simple ratios, it is apparent that in this case, the ink and paper together do not age along an equivalent scale. The ink has been shown to be an influencing factor in the aging process. As noted by the author, the findings were for one ink formula, on a particular type of paper, for the method used. It must be assumed that each ink ages at a different rate on each different type of paper until proven otherwise.

The origin of the time and temperature parameters.

The 1992 article, "Ink Dating - The State of the Art," stated that after heating a particular ink for 15 minutes at 100°C it had reached the end of its aging curve. In "Relative Aging of Ball Pen

Ink: Natural Aging vs. Artificial Aging," the author reported the use of 10 minutes at 100°C for all of the inks examined and was unable to get consistent results. The 1995 article, "A Sequential

There are 4320 minutes in 3 days

There are 9125 days in 25 years and 24820 days in 68 years

$$\frac{4320 \text{ mins.}}{X} = \frac{9125 \text{ days}}{90 \text{ days}} \quad \text{or} \quad \frac{4320 \text{ mins.}}{X} = \frac{24820 \text{ days}}{90 \text{ days}}$$

X= appx. 43 mins.   X = appx. 16 mins.

Figure 1: Two reported calculations for age inducement of paper.

Multiple Approach to Determining the Relative Age of Writing Inks" describes heating any questioned ink entry for 20 minutes at 100°C to induce age. It is clear that to date there has been no consistent result that has led multiple examiners to utilize a given procedure. This must be due to the fact that no reported studies exist which examine the effects of various time and temperature parameters on numerous ink formulations. Research of this type may determine not only the maximum time and temperatures that may be applied to inks without fear of degradation, but also the conditions necessary to assure that the heated sample is now representative of itself at the end of its natural aging curve.

Consider heat degradation of ink

The article "Artificial Aging of Documents," found extensive damage to an ink after heating the ink in an oven at 204°C for 60 minutes. Granted that the temperature used in this experiment was twice the heat intensity as others that have been reported, it still has not been established whether inks chemically degrade at temperatures of less than or equal to 100°C. The origin of the time/temperature combinations currently being used are unclear. The practice of using unverified method parameters could lead to an erroneous conclusion unless further studies are conducted and reported which determine if other inks also degrade with induced heat. If it is determined that other inks do degrade, then studies should be conducted to determine the contributing cause for the degradation (e.g. dye composition, vehicles, etc.). If, for instance, a particular dye (i.e. dye X) is found to be a dye which degrades with heat, then it would be useful to establish criteria which state that any ink containing dye X should not be selected for examination by the accelerated aging technique. The exclusionary criteria could be further developed with information regarding the temperature and humidity required to induce degradation of a variety of inks. This information would supply examiners with values for extreme threshold conditions which could then be avoided when examining particular ink formulations.

A discussion of "significant difference"

Before the most recent accelerated aging technique can be independently evaluated, it is necessary to define the term "difference". In "A Sequential Multiple Approach to Determining the Relative Age of Writing Inks" the author states that *a significant difference* obtained by *any one of the three* methods indicates the ink is not completely dry and therefore is most likely less than three years old, but definitely less than four years old." The article indicates the examiner must look for a "significant

difference" between heated and unheated sample results. It does not state what is meant by "significant". It is necessary to know what criteria are being required of the results in order to determine if the questioned and induced aged samples are behaving in a "significantly different" way. The authors assume there must be data that has led to this determination. If the data were published, the findings could then be independently verified.

There should also be an explanation regarding why one of the three techniques might indicate a significant difference when presumably the other two techniques do not. The authors presume this is based on knowledge that for some ink formulas one of the techniques may be more resolving than the others. If this is so, this data would also be useful for independent reproducibility studies.

Conclusions

Based on the frequent courtroom opposition of qualified experts, it seems obvious there is a misunderstanding of some of the techniques useful in determining the age of a document. It has become all too routine for ink experts to oppose one another in court with alarmingly different opinions when each is assumed to be a competent examiner basing their analysis on scientific principles. Hopefully, the definitions that have been provided will clarify and assist all who encounter questions regarding the age of an ink entry.

Relative ink age determination historically has required known standards for comparison. It has been well documented that the criteria for the standards is very strict. These comparison standards must be of the same ink formulation, on the same paper and stored under the same conditions as the questioned entry. (As a note, these are commonly asked questions when testimony of this type is rendered.) The relative ink age determination technology is commonly used in cases involving journals, diaries and calendars. Results in these cases are generally limited to either 1) the questioned entry is consistent with having been placed on the document concurrently with the known entries *or* 2) the questioned entry is not consistent with being placed concurrently and appears to have been placed on the document much more recently. In some instances, based on the data, it is possible to suggest a time frame within which an entry is believed to have been written. On the other hand, the accelerated aging technique does not require known entries for comparison, instead it uses a heated sample of the questioned entry as a comparison. Yes, this technique is much simpler, faster and has much more lenient criteria. This technique could therefore be applied to many more ink dating cases. There are, however, many unanswered questions with respect to the impact and the effect of applying heat to an ink entry. The influence from the paper type, the time and temperature parameter selections, heat degradation and significant differences are all in need of our attention.

Every forensic scientist should agree that before applying a new technique to casework, it is important to validate the work, procedures, limitations and to illustrate the soundness of the technique through the close scrutiny of your peers. Techniques for performing writing ink comparisons, identifications and relative age determinations have undergone extensive scrutiny and have been shown to be viable methods. The creation of new and better methodologies based on these procedures which lead us toward the answer regarding the age of a document will be an unending process.

Before routine utilization of the accelerated aging technique,

the authors are requesting more data regarding the number of inks tested, the types of ink formulas tested, the reasoning for the temperature, humidity and time choices as well as the limitations of the conclusions. Only then can this new technique be properly scrutinized by other experts in the field. The accelerated aging technique is still in its infancy and as such it is hoped that with time, the technique will be shown to be solidly based and reproducibility tests will underscore any limitations. A wonderful addition to the forensic arsenal would be an effective method for analyzing the age of an ink entry when no comparison entry is available. If the limitations and effectiveness of an accelerated aging technique were proven, it would certainly assist these endeavours.

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Exhibit 23

TECHNICAL NOTE

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

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

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

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

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

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

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

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Chemical Abstract Services (CAS) Number: 122-9-6
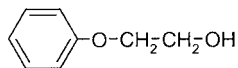Molecular Weight: 138.17

$$C_6H_5OCH_2CH_2OH$$

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

Extraction

Liquid inks were sampled utilizing a disposable capillary glass pipette in order to minimize sample handling. The pipette was then placed into a glass vial containing 1 mL of acetonitrile. The ink and solvent were agitated/stirred to ensure a homogenous mixture. Dried ink samples from scribble sheets were sampled using a 5-mm hole punch. The punches were taken from a highly dense area and allowed to extract in a vial with 1 mL of acetonitrile for approximately 1 min. The solvent was decanted and placed into a separate vial.
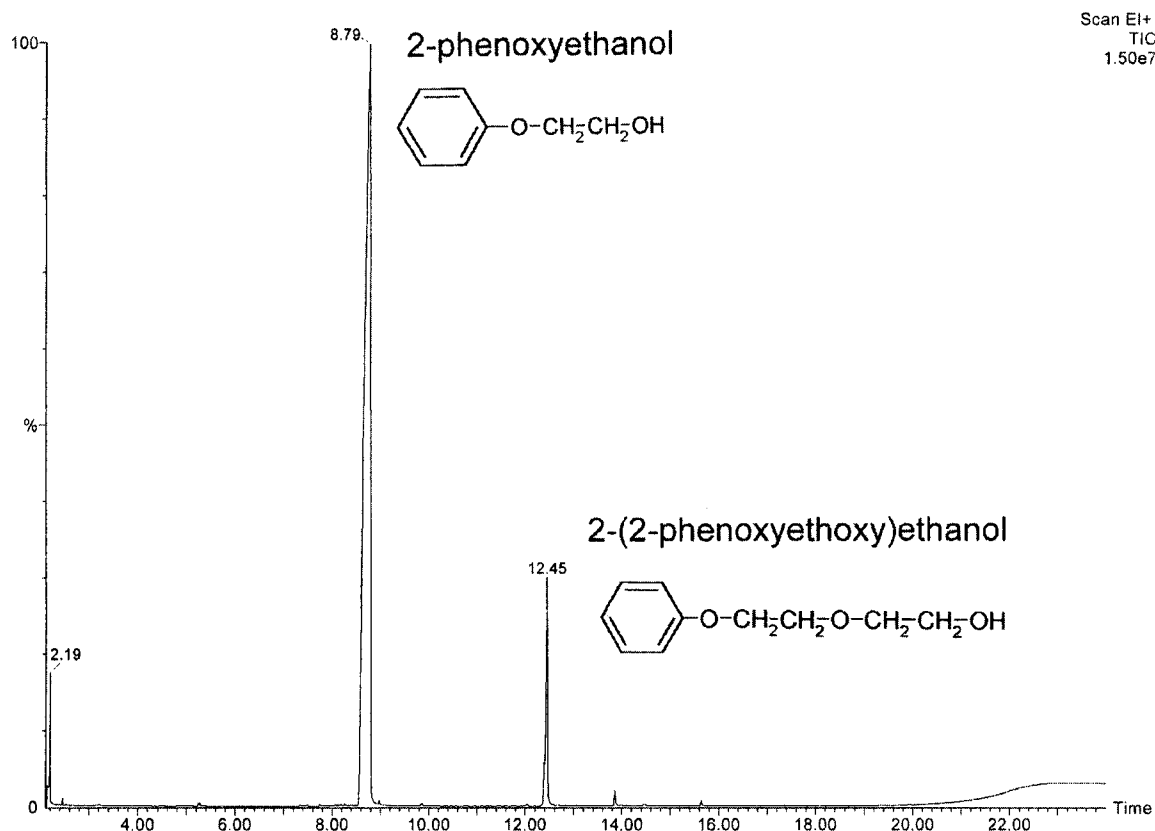
FIG. 2a—*The total ion chromatogram for 2-phenoxyethanol standard (J.T. Baker* [TM] *product No. T-319-07).*

Gas Chromatography/Mass Spectrometry (GC/MS)

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

Results and Discussion

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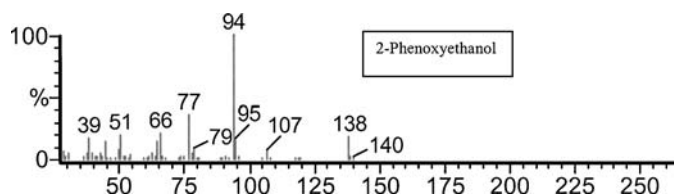

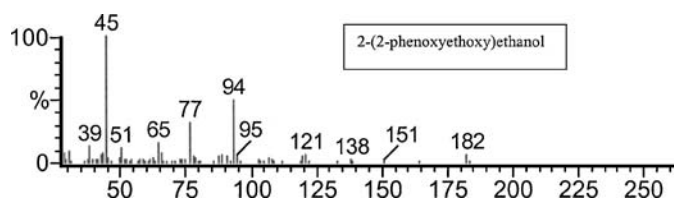FIG. 2b—*The mass spectrum for Peak 1 at retention time (RT) = 8.79 min.*

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

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

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

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

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

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

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

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

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

Conclusion

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

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