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

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

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

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

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

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

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

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

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
- $\times$20 gauge hypodermic needle
- Plunger
- Timer

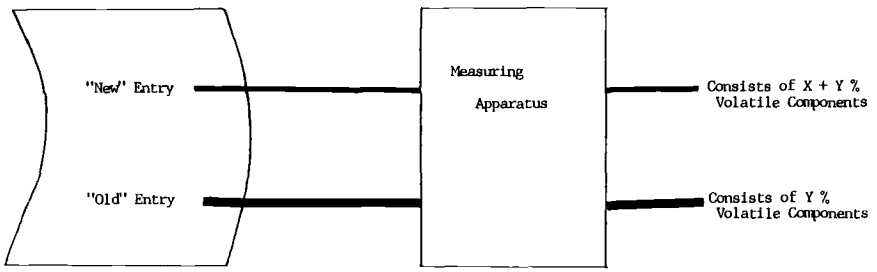

FIG. 1—*Theory of work.*

Method

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

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

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

Samples of ink were removed from the paper by a micro-pellet technique. This technique utilizes a blunted 20-gauge hypodermic needle fitted with a shortened "syringe type" plunger. The micro-plugs of ink and paper (= 15 plugs) are placed in tapered microvials. Approximately 10 to 15 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.

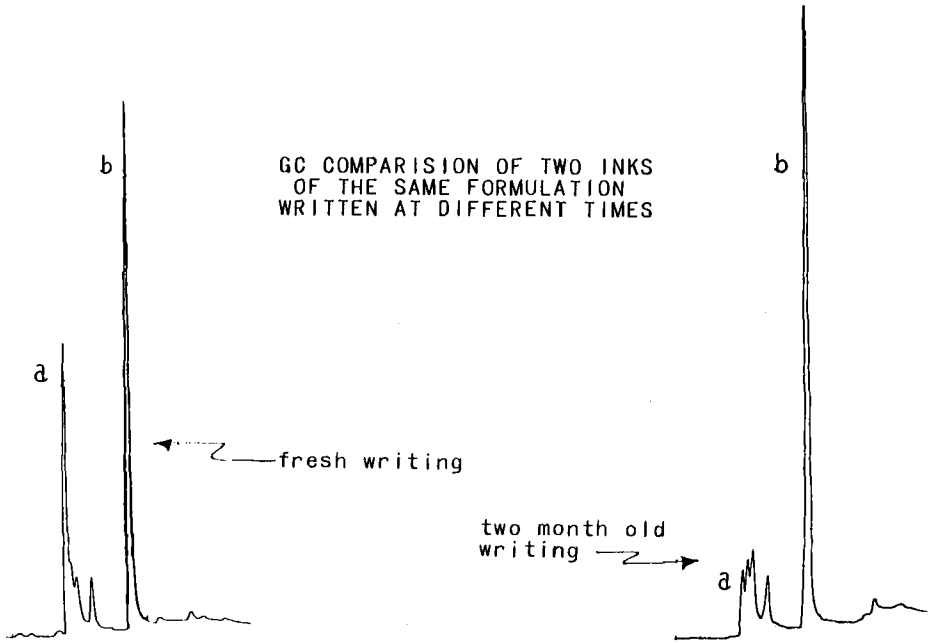

FIG. 2—*Aging curve for each ink.*

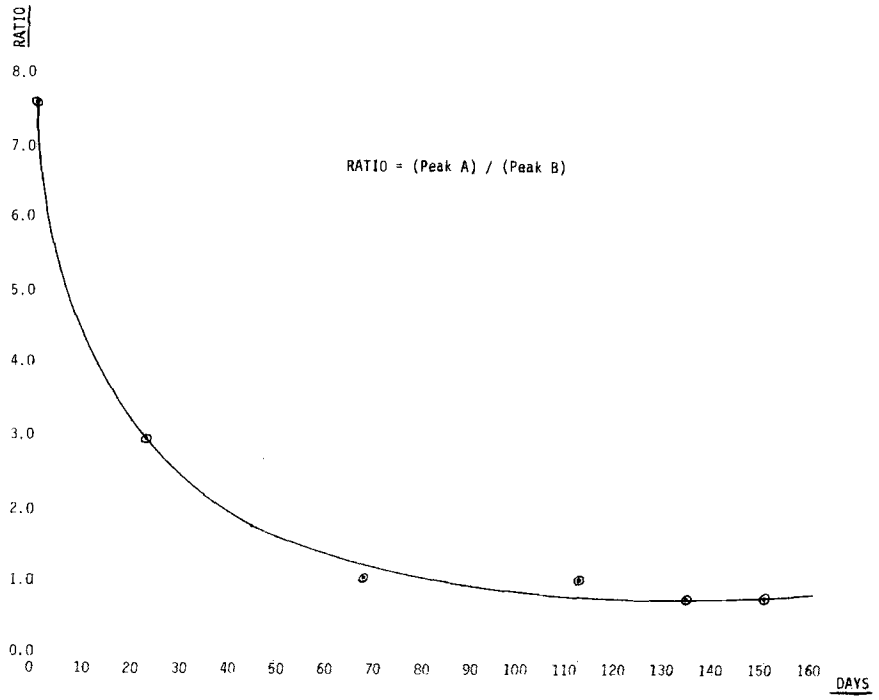

FIG. 3—*Aging curve calculated from the ratio of Peak A/Peak B versus actual age.*

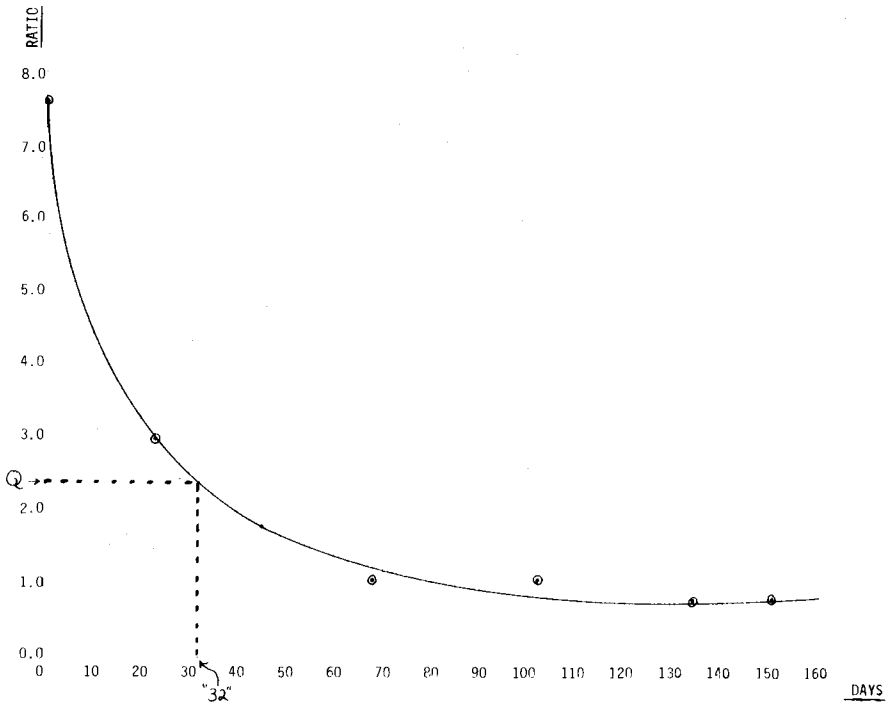

FIG. 4—*Aging curve for the Q entry.*

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,

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

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.

Acknowledgments

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