Richard L. Brunelle,[1] *M.S.*

Ink Dating—The State of the Art

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ABSTRACT: Over the past 20 years, no other field of forensic science has had greater impact on the detection of fraudulent documents than the scientific examination of writing inks. This paper traces the development of ink dating techniques from the 1930s to 1990. Techniques used during this period are described and, when possible, illustrated. The emphasis is on ink dating techniques used today, with discussion of the value and limitations of these procedures.

KEYWORDS: questioned documents, inks, aging, chromatographic analysis, ink aging, relative age of inks, accelerated aging, thin-layer chromatography, densitometry, solvent extraction, Auger microscopy, Fourier transform infrared spectroscopy, gas chromatography, high-performance liquid chromatography, dye ratios

Over the past 20 years, no other field of forensic science has had greater impact on the detection of fraudulent documents than the scientific examination of writing inks. Government agencies at all levels and lawyers in the private sector are using the dating of inks to establish the authentic or fraudulent nature of questioned documents. Settlements involving millions of dollars are made daily in cases involving medical malpractice, stock fraud, tax evasion, wills, copyright disputes, insurance fraud, divorce settlements, labor management disputes, and a wide variety of contractual disputes. This paper traces the development of ink dating techniques from the 1930s to 1990. Techniques used during this period are described and, when possible, illustrated. The emphasis is on ink dating techniques used today, with discussion of the value and limitations of these procedures.

Background

Methods for chemical and physical comparison of writing inks are abundant in the literature. Probably the most significant and comprehensive coverage of early work in the comparison of fountain pen inks is described in Mitchell's *Inks: Their Composition and Manufacture* [*1*] published in 1904. Mitchell updated this work in 1937, when he published another book with the same title [*2*].

Around 1950, research accelerated on methods of differentiating all types of writing inks. Paper chromatography [*3*], thin-layer chromatography [*4*], electrophoresis [*5*], chemical spot tests [*6*], gas chromatography [*7*], high-performance liquid chromatography [*8*], and Fourier transform infrared spectroscopy [*9*] have all been used for ink comparison. However, thin-layer chromatography remains the most widely used procedure for comparison and differentiation of writing inks.

In contrast to the numerous articles in the literature on differentiation of inks, only a few researchers have published procedures for dating inks. Witte [*10*] described the early work of Hess, Mitchell, and others in dating inks. These studies, developed around 1930, involved the relative aging of inks using such techniques as ion (chloride and sulfate) migration, fading, and extractability. None of these tests removed ink from the document.

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[1]Owner, Brunelle Forensic Laboratories, Fairfax, VA.

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In 1963, Witte developed techniques for removing microdiscs of ink on paper for chemical analysis. In 1968, the author of the present paper developed a similar microplug sampling technique at the U.S. Bureau of Alcohol, Tobacco, and Firearms. This procedure uses a 20-gauge needle and syringe to remove tiny needlepoint-sized microplugs of ink from the document. This sampling procedure, which does not destroy the legibility of the writing, has been accepted by the courts for over 20 years. Considerable interest in the dating of inks is reflected in the literature since this development and since the establishment of a comprehensive Standard Ink Reference Collection at the Bureau of Alcohol, Tobacco, and Firearms in 1968 [*11*]. The following discussion traces the development of ink dating techniques from 1937 to 1990.

Dating of Fountain Pen Inks (1937–1990)

Mitchell's 1937 book [*2*] describes chemical tests on iron gallotannate inks to estimate their age. His tests were based on the color of blue-black inks and the speed of reaction of the inks with certain chemicals. The color test required ink standards of known age so that the rate of disappearance of the blue color in the questioned inks could be matched with appropriate standards. The chemical tests involved the effect of oxalic acid on the pigment iron gallotannate. Mitchell found that the black pigment in freshly written inks bleached immediately and the blue color spread over the paper when the ink was treated with oxalic acid. Conversely, inks three or four years old reacted slowly to oxalic acid and the blue color showed little sign of diffusion in the paper.

Mitchell may also have been the first researcher to experiment with the measurement of the dryness of fountain pen inks on paper. He postulated that the tannate first formed is readily soluble in dilute acids; however, as oxidation proceeds, a resinous tannate is slowly formed until the tannate ink becomes difficult to dissolve in acids.

In 1959, Kikuchi's work provided the basis for the solvent extraction techniques in use today for estimating the age of writing inks. This work involves measurement of the time it takes for blue-black inks to disperse when solvents are applied to the ink on paper. Kikuchi observed that older inks disperse more slowly than newer inks [*12*].

In 1984, McNeil reported the use of scanning Auger microscopy for dating manuscript iron gallotannate inks [*13*]. This procedure is limited primarily to historical documents because its accuracy is plus or minus 22 years. Nevertheless, his procedure is valuable for dating inks on old documents, such as in the case involving the "Salamander Letter." McNeil's work on this case produced the only positive evidence of fraud. The technique measures the outward migration of iron atoms from the ink boundary along a fibril. The migration increases exponentially with the age of iron gallotannate ink, and absolute dating is possible because the procedure is not affected by temperature or humidity (see Fig. 1).

Dating of Ballpoint and Non-Ballpoint Inks (1945–1979)

Ladislao Biro is credited with the development of the ballpoint pen in 1939; however, marketing of this new writing instrument did not begin in the United States until around 1945, when 50 000 units were sold at Gimbel's Department Store in New York City. Writing in ballpoint ink is easily identifiable visually, microscopically, and chemically, and 1945 can be used as the first practical date on which a document could have been written with a ballpoint ink.

The first ballpoint inks were made with oil-based solvents such as mineral oil, linseed oil, recinoleic acid, and other similar substances. Around 1950, ballpoint inks changed from an oil base to a glycol base. Oil-based and glycol-based inks are readily distinguishable because oil-based inks are soluble in petroleum ether if the ink has been on paper

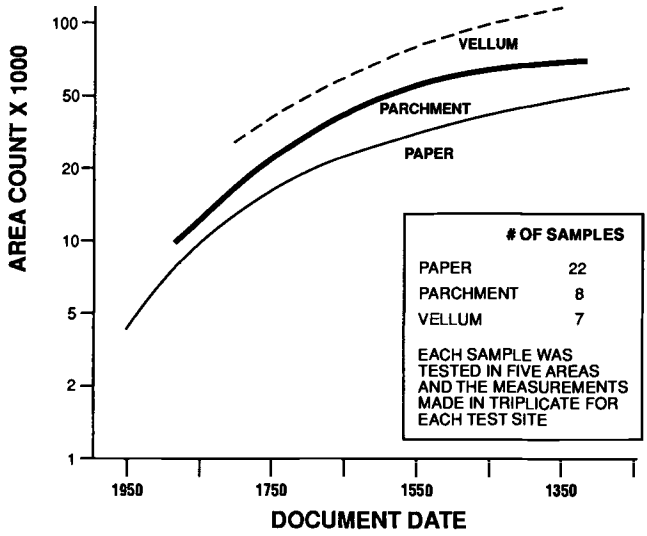

FIG. 1—*McNeil's aging curve.*

less than 5 to 10 years (Harrison test) [*14*]. With age, oil-based ink become insoluble. Therefore, 1950 is the first approximate date a document could have been written with a glycol-based ballpoint ink. Witte reports the year 1950 and Harrison reports 1951 as the date of change to glycol-based inks.

Another change in the composition of many ballpoint ink formulations occurred around 1955. This was the date when chelated metalized dyes were first used in ballpoint inks. The most popular of these dyes is the blue/green copper phthalocyanine dye. These dyes are stable to light and have excellent solubility properties. A simple solubility test using methanol can determine if an ink has the distinctive blue/green copper phthalocyanine dye.

In 1962, Pentel introduced the fiber tip writing instrument to the market, which was soon followed by plastic nib and porous tip pens. These inks are readily distinguishable from fountain pen and ballpoint pen inks because of their distinctive visual and microscopic appearance and dye compositions. Most of the inks used in this class of pens (fiber and porous tip pens) are water soluble except for the permanent markers, which are solvent based.

Paper Mate and Anja developed and marketed an erasable ballpoint ink in 1978. This ink has a rubber cement consistency and can be erased if erased soon after the writing occurs (within a day or so). Its visual appearance is not especially distinctive, but its dye composition is.

In approximately 1970, the roller ball pen was introduced to the marketplace. These pens usually contain water-based inks containing dyes similar to those in fiber tip and porous tip pen inks. Writing strokes made by roller ball pens are sometimes difficult to distinguish from those made by other fluid ink pens, such as fountain, plastic nib, and porous tip pens. Because the inks are fluid, shading is common. Striations usually visible in ballpoint inks are not normally seen in roller ball pen writing, because this type of ink flows freely over the fibers of the paper, filling in any striations that might otherwise be visible. Indentations of the ball in the paper are sometimes visible.

In the early 1960s, Werner Hofmann with the Zurich Cantonal Police Laboratory in Zurich, Switzerland, used a standard ink reference collection to identify inks and to

determine the first date of manufacture of ballpoint inks.[2] Hofmann used paper chromatography, thin-layer chromatography, spectrophotometry, spot tests, and the usual nondestructive tests to compare and match questioned and known inks.

Brunelle, the author of the present paper, established the first comprehensive standard writing ink reference collection in the United States in 1968. This collection of inks later became known as the Bureau of Alcohol, Tobacco, and Firearms (ATF) Standard Ink Library. Within one year, this library contained over 2000 different ink standards consisting of ballpoint, fountain pen, and other fluid inks. This ink library now is maintained by the U.S. Secret Service Forensic Laboratory and it contains well over 6000 different ink standards from countries all over the world.

The author dated inks by matching questioned inks with ink standards that have known first production dates. He used multiple thin-layer chromatography, solubility tests, chemical spot tests, infrared reflectance, infrared luminescence, and densitometry to compare questioned and known inks [*11,15*]. Occasionally, gas chromatography was used to identify resinous materials in ink. Electron diffraction was sometimes used to differentiate carbon, which is amorphous, from graphite, which is a crystalline material.

The value of the ink library approach to dating inks depends on the maintenance of a complete, up-to-date standard ink reference collection. To be effective in proving that documents have been backdated, this method also depends on frequent updating of ink formulations. The objective of the ink library approach to dating inks is to establish that the specific ink used on the questioned document was not commercially available on the date that appears on the document.

In spite of the limitations described for the ink library approach to dating inks, this procedure was the first systematic approach to dating inks in the United States and the procedure is still used today.

To overcome some of the limitations of the ink library approach for dating inks, an Ink Tagging Program was developed at ATF between 1975 and 1979. Some ink manufacturers volunteered to add unique chemicals (tags) to their inks and to change the tag every year. This procedure amounted to a change in the ink formulation every year by participating ink companies. When these tags are detected in questioned inks, the year of manufacture of the ink can be determined. The nature of the tags is proprietary and therefore cannot be documented in this paper; however, this ink tagging program has greatly increased the investigator's ability to detect backdated documents.

Dating of Ballpoint Inks Using Relative Age Solvent Extraction Comparison Techniques (1979–1990)

In 1979, Cantu used the principles applied by Kikuchi to develop a procedure for estimating the age of ballpoint ink [*16*]. He found that a relationship exists between the age of ballpoint ink and the rate at which ink can be extracted from paper using weak solvents such as toluene, isopropanol, and *n*-butanol. The longer the ink has been applied to paper, the drier it becomes and the slower the extraction process. By comparing the extraction rates of questioned inks with those of inks of known date having the same formulation, Cantu found it was possible to determine whether inks had been written at different times. If inks of known dates covering a span of years are present on the questioned document, then it is possible to estimate closely when a questioned entry was written by comparing the questioned and known ink extraction rates (see Fig. 2). This and all relative age comparison procedures require that the questioned and known-date

[2]Hofmann, W., "The Dating of Documents (with Particular Reference to Documents Written with Ballpoint Pens)," unpublished report, Zurich Cantonal Police Laboratory, Zurich, Switzerland, 1969.

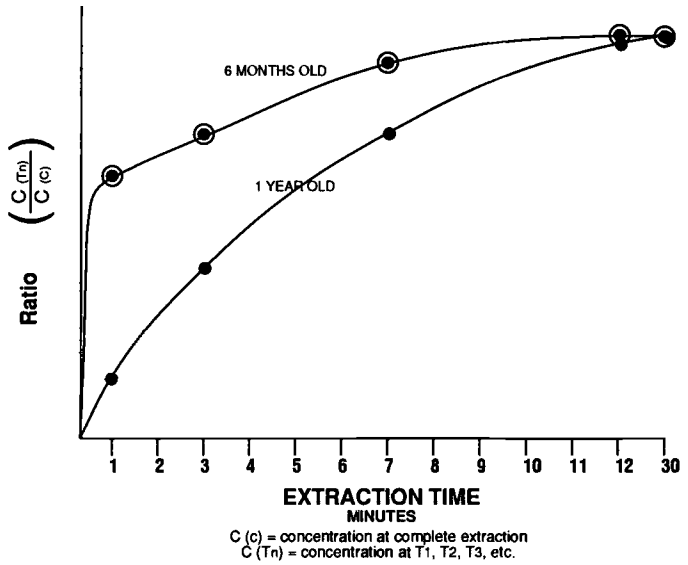

FIG. 2—R *ratio method (a model).*

inks consist of the same ink formulation and that they be on the same paper to eliminate storage condition variables.

Later Cantu developed a slightly modified relative age comparison procedure for estimating the age of ballpoint ink. This modified procedure measured the extent or percentage of ink extracted with solvents instead of the rate of extraction [*16*]. In cases of monitoring changes in a fluorescent component, absorption measurements are replaced by fluorescent measurements. Cantu states that *R* ratios (rates of extraction) and percentages of extraction can be measured by thin-layer chromatography (TLC) densitometry or by absorption spectrometry (see the following equation and Table 1).

$$\% \text{ extraction} = \frac{C_{(W)}}{C_{(W)} + C_{(S)}} \times 100$$

where

$C_{(W)}$ = concentration in weak solvent and
$C_{(S)}$ = concentration in strong solvent.

TABLE 1—*Percentage of extraction in natural aging.*[a]

Age, months	Densitometer Readings			Percent Extraction (Toluene/Total × 100)
	Toluene	Benzyl Alcohol	Total	
10	5.3	15.5	20.8	25.5
15	4.3	17.8	22.1	19.4
20	3.8	20.4	24.3	15.9
25	2.7	20.5	23.2	11.7

[a]Fisher pressurized black BP ink on notebook paper.

In 1985, Stewart reported a gas chromatography procedure for comparing the relative ages of ballpoint inks (see Fig. 3). This work was based on the gradual disappearance with time of the major vehicles (solvents) contained in ballpoint inks [7]. He reported that these vehicles remain in dried ink on paper for up to one year and longer for some ballpoint inks. This technique involves extraction of the dried ink on paper with strong solvents, such as pyridine, and then comparison of the relative concentrations of the vehicle components by gas chromatography.

Humecki reported yet another technique in 1985 for measuring the relative age of ballpoint inks using Fourier transform infrared spectroscopy [9]. In this work, changes in the hydroxyl (OH) and carbonyl (CO) infrared absorption bands were observed as ink aged. Humecki found a decrease in the ratio of the hydroxyl to carbonyl bands in ballpoint ink up to 22 years, with leveling off beginning at around 10 years. His observations were limited to just one ballpoint ink formulation (see Fig. 4).

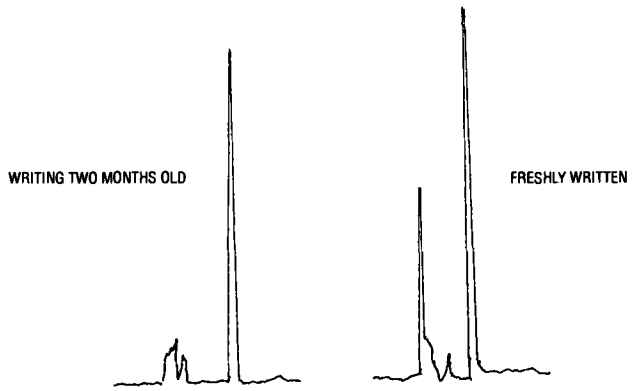

FIG. 3—*Gas chromatography comparison of relative age of the same ballpoint ink formulation written at different times.*

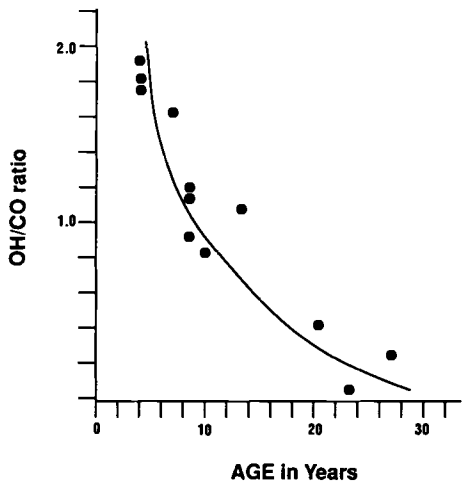

FIG. 4—*OH/CO peak heights in arbitrary units.*

In 1987, Brunelle, the author of the present paper, reported a single solvent extraction procedure to estimate the age of ballpoint inks [*17*]. This procedure involves the extraction of inks with weak solvents, spotting the extract onto a TLC plate, and measuring the amount of ink extracted densitometrically. The age of the ink is estimated by comparison with inks of known date. The difference between this procedure and Cantu's *R* ratio method is that the amount of ink extracted is measured directly without calculating ratios for amounts of ink extracted at different extraction times. The limitations of the procedure are that it is mass dependent and it requires that equal samples of questioned and known inks be removed for analysis (see Figs. 5 through 7).

In 1988, this author developed a mass independent technique to estimate the age of ballpoint inks. This revised procedure is called the "dye ratio" technique [*18*]. Using this

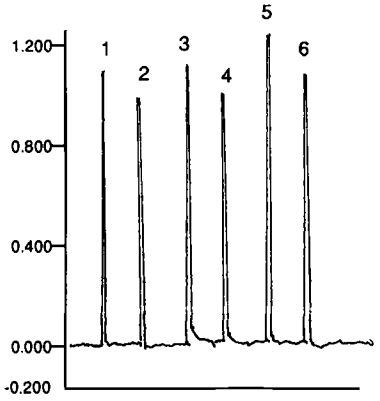

FIG. 5—*Sampling reproducibility: replicate samples of the same ink (ten microplugs in each sample).*

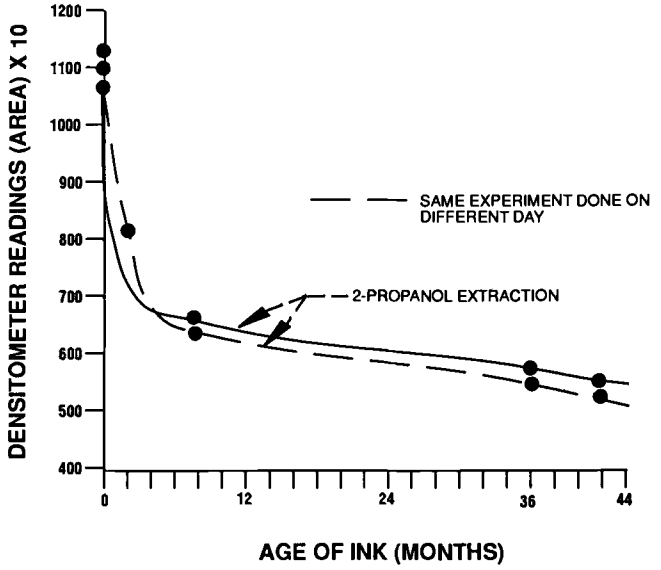

FIG. 6—*Aging of Anja M-311 black ballpoint ink (single-solvent extraction).*

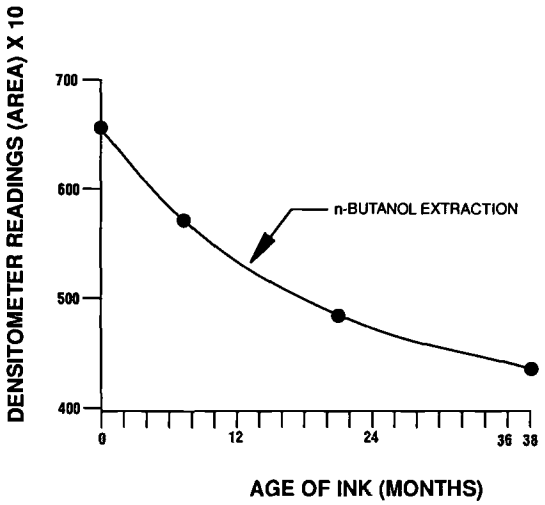

FIG. 7—*Aging of Formulab 587 black ballpoint ink (single-solvent extraction).*

technique, inks are extracted into either weak or strong solvents. The ink extracts are spotted onto TLC plates and the dye components are separated using a solvent system of ethyl acetate/alcohol/water (70:35:30). The relative concentrations of the dye components are measured using a TLC densitometer. The calculated ratios of the relative concentrations of the dyes are independent of the amount of ink taken for analysis. In this work, the effect of paper and extracting solvents on aging curves was described and the reproducibility of aging curves was determined. The feasibility of estimating the age of non-ballpoint inks was determined for the first time (see Figs. 8 through 12).

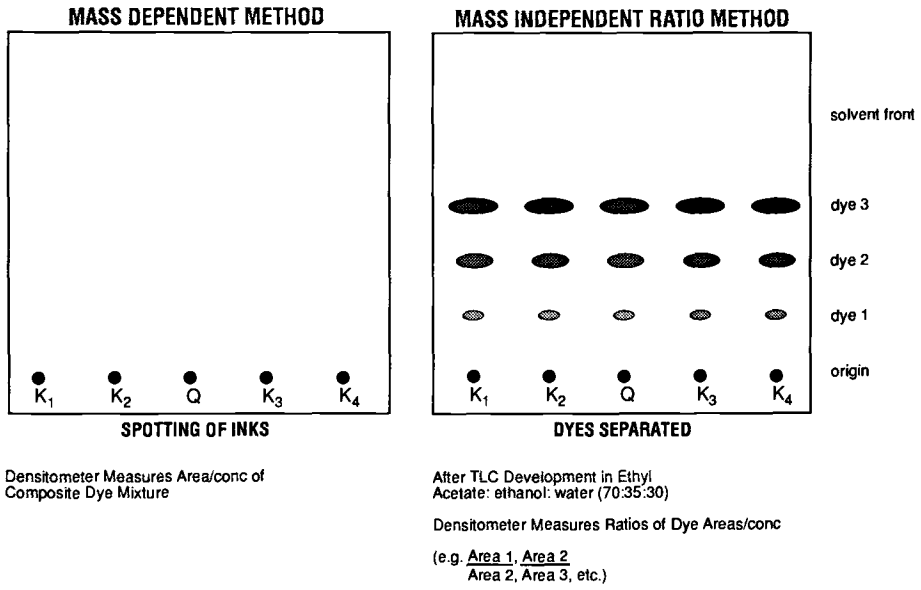

FIG. 8—*TLC procedure.*

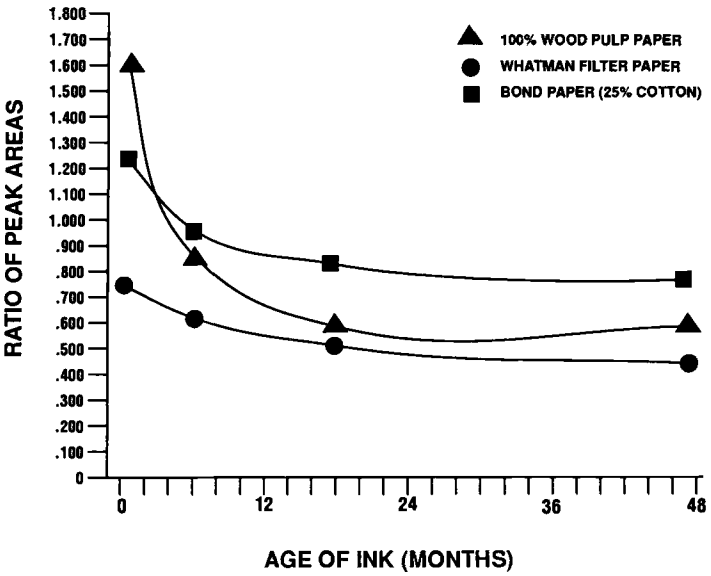

FIG. 9—*Effect of paper on aging curves. The experimental conditions included: Bic blue ballpoint ink,* n-*propanol extraction, and a TLC development time of 6 min (ratio of violet dyes at Rf 0.65 and Rf 0.70).*

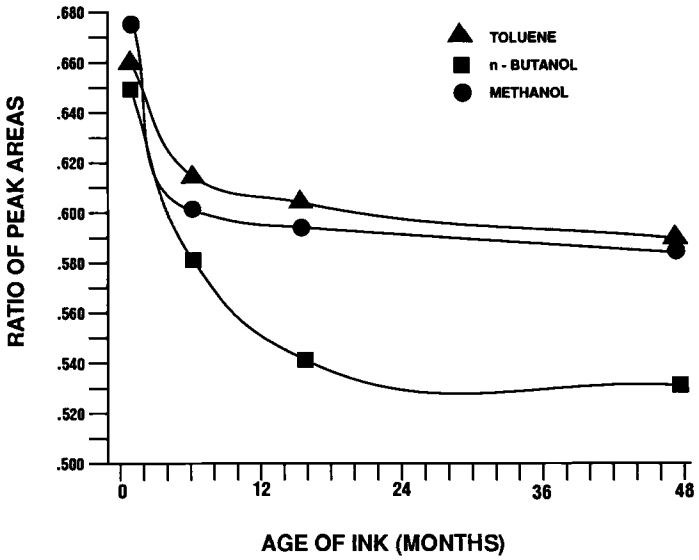

FIG. 10—*Aging curves using different extracting solvents. The experimental conditions included: Formulab 587 black ballpoint ink on 100% wood pulp paper and a TLC development time of 12 min (ratio of violet dyes at Rf 0.65 and Rf 0.70).*

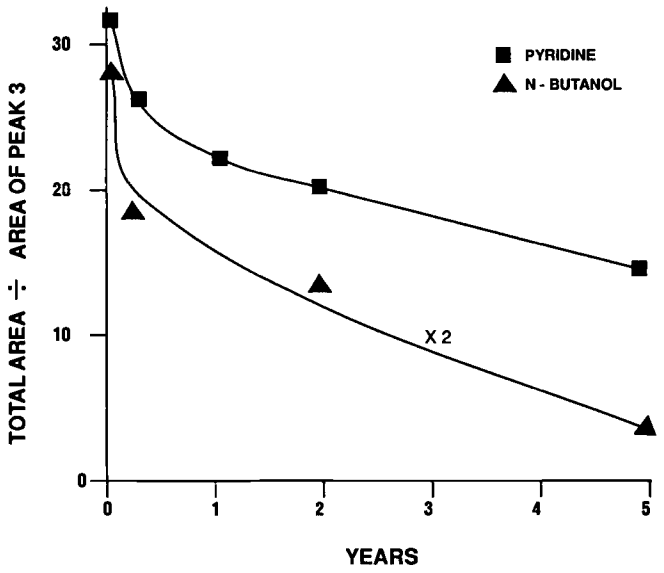

FIG. 11—*Aging curves for strong versus weak solvents. The experimental conditions included: Formulab 587 black BP ink on Whatman filter paper and a TLC development time of 14 min (Peak 3 corresponds to the violet dye at Rf 0.73).*

All of the relative aging techniques described up to this point require inks of known date for comparison, and the inks compared should be on the same paper so that the storage conditions for the questioned and known inks are the same.

In 1988, Cantu reported the feasibility of accelerating the age of ink to estimate the age without access to known-date inks [*19*]. He reported that heating a Fisher pressurized black ballpoint ink at 100°C for 4 min was equivalent to 3 months of natural aging at

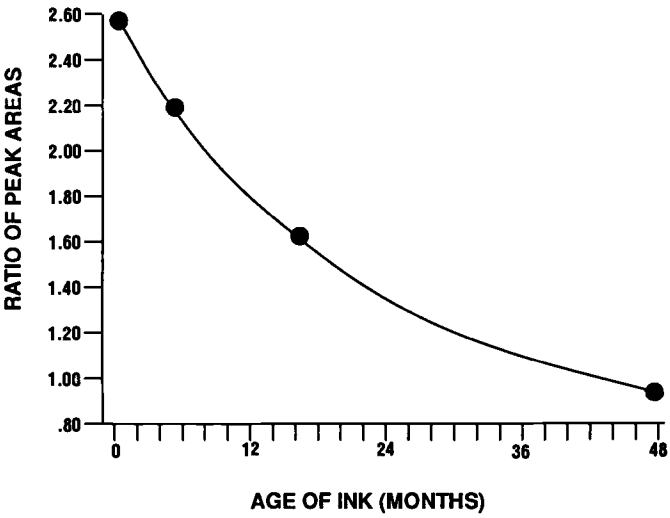

FIG. 12—*Aging curve for non-ballpoint ink. The experimental conditions include Sanford (Sharpie) black fiber tip ink on 100% wood pulp paper, ethanol extraction, a TLC development time of 5 min, and Scanning at 560 nm (ratio of two gray dyes, Rf 0.68 and Rf 0.77).*

20°C. His work was based on extensive work that has been done on the aging of paper, in which it was determined that the heating of paper at 100°C for 3 days was equivalent to 68 years of natural aging at 22°C. Cantu also reported that artificially aged ink samples can be used to determine whether extraction rates actually increase or decrease with the age of the ink.

Accelerated aging provides the opportunity to estimate the age of ink without access to writings of known date. This is important because, in many cases, known-date writings on the same paper using the same ink formulation are not available.

Because of the obvious potential benefits of the accelerated aging technique, the present author has been working with Cantu'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 2 to 3 or more years old. Conversely, significant changes in the solubility parameters of inks in solvents occur with age and are usually detectable in inks less than 2 to 3 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 4 years old) at 100°C for 15 min. In every case, changes in the dye ratios were observed if the ink in question had not reached the asymtote of its natural aging curve (see Fig. 13). 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. For example, if the natural aging curve levels off at 2 years, then estimates for the aging of this ink, using the accelerated aging procedure, are limited to less than 2 years if the ink is still drying or 2 or more years if the ink is totally dry.

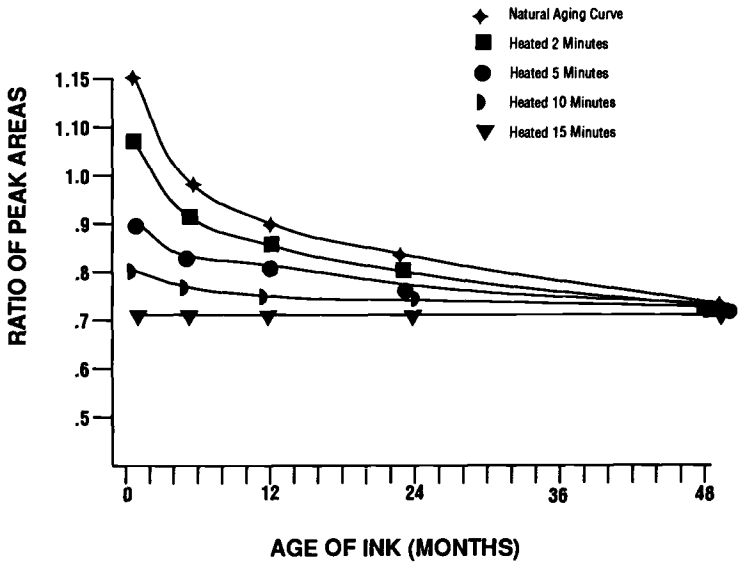

FIG. 13—*Accelerated aging (Samples heated at 100°C) of Bic blue ballpoint ink (extracted in* n-*butanol) of different ages by the dye ratio method. The dye ratios are the average of duplicate TLC spottings (methyl violet bands).*

Summary

Complete coverage of all the various ink dating techniques would require a textbook. Therefore, this paper only presents a brief discussion of advances in this field since about 1930 and up to 1990. The advances are many and the applications of these techniques to the detection of fraudulent documents are expanding constantly.

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Address requests for reprints or additional information to
Richard L. Brunelle
Brunelle Forensic Laboratories
3820 Acosta Rd.
Fairfax, VA 22031