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A Critical Evaluation of Current Ink Dating Techniques

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ABSTRACT: Advances in ways to date inks have been publicized over the past 17 years. As a result, Government agencies and the private sector now rely heavily on these techniques in criminal and civil litigations. As new procedures have become known, more forensic scientists are asked to perform ink dating examinations. While the capabilities of these techniques are generally known, their limitations are not. This paper evaluates the current approaches used for dating writing inks and takes a critical look at conclusions that can be made on the basis of the different laboratory techniques.

KEYWORDS: questioned documents, inks, extraction, tagging, ink library, relative aging, solvent extraction, solubility, thin-layer chromatography, densitometry, fluorescence spectroscopy, gas chromatography, Fourier transform infrared spectroscopy

There has been a long-standing interest in the ability to determine the age of writing inks on various kinds of documents. Over the past 17 years, much has been done to improve the forensic science laboratory's ability to date these questioned inks. One method involves the compositional comparison of the unknown ink with inks in a standard reference library having known production dates. In some cases, inks can be dated by the identification of tags or other unique components added by the manufacturer. Most recently, techniques have been developed to estimate the length of time an ink has been on a document. This may be done if inks of the same formulation and of known dates of writing are present on the same document for comparison.

These developments have been widely publicized or reported in the literature [1-5,9-14]. Government agencies and the private sector have relied heavily on these techniques in both criminal and civil litigation as these capabilities have become better known. Understandably, this has prompted great interest among scientists who are asked to perform these examinations.

There is a need to present a critical evaluation of developments in any discipline, and it is timely to do so with ink dating techniques. Forensic science examiners and attorneys should be aware of the pros and cons of methods used to examine evidence, and ink evidence is no exception. Also, persons performing these examinations should be aware of the training and experience requirements for conducting ink dating examinations.

This paper discusses the current methods used for dating writing inks. It takes a critical look at conclusions that can be made on the basis of the different examinations.

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Evaluation of Ink Dating Methods

Before 1968, methods for dating writing inks were limited. The methods used involved knowing the date when new inks were introduced or when major changes occurred in manufacturing. Examples include the introduction of soluble blue dye in iron gall inks in 1838 (in the United States), the development of the ballpoint ink in 1939, the change from oil based to glycol based ballpoint ink around 1950, the introduction of the green copper phthalocyanine dye in ballpoint inks around 1955, and the introduction of the fiber tip pen in 1963 (in the United States from Japan).

Before the origin of ballpoint inks, there were at least three techniques used to perform relative aging of fountain pen inks (iron gallotannate) [6]: one measured the color change, the second monitored the migration of chloride ions and sulfate ions, and the third involved the extraction of the ink into a solvent. These techniques provided the basis for the relative aging techniques in use today and discussed in this paper.

Ink Library Approach

In 1968, a new approach for dating writing inks was developed by Brunelle et al. at the Bureau of Alcohol, Tobacco and Firearms (ATF) laboratory [1]. This approach involved the chemical and physical comparison of questioned inks with inks in the laboratory's standard ink reference library. With the excellent cooperation from the ink manufacturers in the United States, Japan, and Europe, the ATF lab was successful in compiling a comprehensive standard ink reference collection. This collection now consists of over 5000 different ink formulations and is complete for inks first manufactured since 1958. Many ink standards were obtained dating back to as early as 1900 from some ink companies.

Methods used for the chemical and physical comparison of inks include thin-layer chromatography (TLC) combined with visual, microscopic, and solubility tests. Infrared reflectance and luminescence and ultraviolet (UV) fluorescence characteristics are also determined. A complete description of the ink library approach to ink dating is described in several publications [1,3,5].

The situation that permits writing inks to be dated by the ink library approach is that no two ink formulations are the same. Most ink formulations differ in their nonvolatile dye components which TLC readily separates. Those that differ only in their volatile components sometimes cannot be distinguished with the methods described. These "equivalent" formulations make up a class which must be treated as a single formulation whose earliest date of production is that of the earliest formulation in the class.

By comparing the chemical and physical characteristics of a questioned ink with those from inks in the standard ink library, a unique match with a standard ink is often found. The formula designation and first date of production of the standard ink is provided by the ink manufacturer.

The major limitation of the ink library approach to dating inks is the infrequency of formulation changes. It is the changes in ink formulations that permit the examiner to identify the first production date of the ink in question. A process for tagging inks was developed to alleviate this limitation.

It may seem at first that dating inks is a simple matter of matching or differentiating inks, but ink dating using the ink library approach has pitfalls for the inexperienced examiner. Some questions the examiner must be prepared to address are:

- Is it necessary to have a sample of every ink formula produced in the world to be certain the questioned ink has been matched with the correct standard?
- (or equivalently) Is it possible that there exists an ink not in the library which uniquely matches a standard ink? How does this possibility depend on the discriminating method used, the extent of the library, and the particular standard ink formula identified?

- What does it mean when a questioned ink cannot be matched to a standard?
- Is it possible for a questioned ink to change its chemical and physical characteristics, for example, through fading, and end up being matched to a wrong standard?
- What is the significance of batch variations when matching questioned and standard inks?
- How is it possible to keep an up-to-date standard ink library with the influx of foreign inks into the United States?

There are answers to all of these questions, but too much space would be required to answer them here. However, these questions do bring out the complexity of ink dating using the ink library approach. Obviously, before anyone attempts to conduct ink dating examinations using this approach, they must have a complete ink reference collection, working knowledge of manufacturing practices of ink formulations, and the experience to tell differences in ink formulas using TLC and other standard tests. For this reason, the ATF lab requires that an examiner receive comprehensive, full-time, on-the-job training under an experienced forensic ink chemist before presenting testimony in court.

Tagged Inks

In 1975, some ink manufacturers began adding unique tags to their inks during the manufacturing process. The tags are changed every year at the request of ATF to enable the determination of the exact year the ink was made. This allows dating of inks that have the same formula year after year. By 1978, approximately 50% of all writing inks produced in the United States were tagged. Because the tags are unique to inks and change every year, the actual year of production of the ink can be positively determined. It is not essential to identify the manufacturer or formula of the ink. The ATF ink tagging program greatly increased the ability to date inks on questioned documents.

Since 1978, there has been a great influx of foreign produced inks (mainly from Japan and other Asian countries) into the United States. The effect of this was to reduce the percentage of inks on the market in the United States that contained tags. This reduced the number of times tags were encountered in casework situations. When tags are not detected, the ink library approach or methods described later in this paper must be used to date inks.

Relative Age Determinations

Techniques to estimate the relative age of inks on documents were developed in the 1930s by Mitchell in England and Hess in Germany who studied the aging of the fluid iron gallotannate inks. Witte [7] provides the work of these and other researchers in his discussion of age determination of writing inks. With ballpoint pen inks, he observed that as ink ages, its "copying power" decreases. Kikuchi's work [8] provided the basis of the solvent extraction procedures described in this paper. This excellent work discusses the time it takes for inks to disperse when solvents are applied to the dried ink on paper. It was observed that older inks disperse slower than newer inks.

Relative age determinations are examinations performed on two or more ink entries of the same formula and on the same document to establish the order of their preparation. If the date of one of the entries is known, then it may be possible to state if the other entries were written before or after the known entry. No significant work was done on the relative aging of ink since about 1959 until the 1980s. Then, almost simultaneous developments were made at the ATF, FBI, and McCrone laboratories. It is this aspect of ink dating that is the subject of most current research and where future developments will probably occur. A comprehensive discussion of Cantu's solvent extraction techniques is in the *Journal* [14].

The ability to compare the relative age of inks on documents under a wide variety of circumstances is an important breakthrough in the field of questioned document examination.

However, relative aging techniques are widely misunderstood and have the potential for the most error by forensic scientists performing these examinations. For these reasons, a clear understanding of the relative aging procedures, limitations, interpretation of results, and how results can be misinterpreted is needed.

Limitations of All Relative Aging Determinations

Several limitations must be considered before any relative aging test can be applied [14].

1. The inks compared must have the same formula.
2. The inks compared must appear on the same paper. It is assumed that whatever exposure the paper has had over time has been uniform on all of the paper. If inks of the same formula are on different papers, but have the same composition and age, knowledge of their storage conditions is essential to make valid age comparisons. When the composition and age of the separate documents are not the same, extreme caution has to be taken. The effects of paper aging, if any, have to be tested by determining how ink ages on different papers when placed on them at different times.
3. When comparing the age of one ink with another, the parameter compared must be independent of the amount of ink sampled. This is because there is difficulty assuring that the same amount of ink is being sampled all the time. Measurement of ratios meets this requirement. Attempts should still be made to sample similar amounts of ink to minimize any possible error.
4. Accuracy of the aging techniques must be determined. Relative aging is a monotonic process which slows down and levels off with time, like an "exponential" behavior. Therefore, the accuracy decreases dramatically as the aging process levels off. It may be impossible to distinguish two inks with a small age difference between the time either was written and their time of analysis. Also, if two inks being compared show no difference in their relative age, then they are of the same age only if they still continue to have measurable aging, that is, their aging has not leveled off yet.

The ink aging process eventually reaches an age after which no differences can be detected. Because the process behaves "exponentially," this leveling off age is related to the rate of aging. This rate or leveling off age is dependent on the ink formulation. This is why some ink formulas, under the same storage conditions, age faster than others and why inks of the same formula are required for comparison.

5. Reliability measurements must be conducted. Whatever technique is used to determine the relative age of an ink, the reliability of the measurement must be determined. Triplicate measurements should be taken if enough sample is available, and then the standard deviation should be calculated. This will show how reproducible or reliable the measurement is.

General Approaches to Relative Aging

There are three different techniques to determine the relative age of inks on documents. Each of these measure some kind of change in a particular property of the ink with age. Because of their basic composition—volatile components, resins, and dyes—ballpoint inks potentially have more measurable changes with age than fluid inks. Aging of fluid inks have not been studied with current technology and is the subject of future research. The following sections describe these three techniques as applied to ballpoint inks.

Solvent Extraction (Rate Determining Procedures)

The solvent extraction procedure [4,5,14] is based on the premise that the longer an ink has been applied to paper, the more difficult it is to dissolve into (weak) solvents. Conversely,

the fresher the ink, the easier it will dissolve. As the ink dissolves with time, the amount of ink in the extracting solvent increases as does its color. Therefore, by measuring the rate ink extracts into solvents, it is possible to compare relative ages of questioned and known dated inks. In the R ratio procedure, sequence of ink entries can be determined by dividing the amount of ink extracted at time (t_1) by the amount extracted at the time of complete or near complete extraction (t_2). R , therefore, is the fraction of ink extracted at time t_1 , where the fraction is of the amount of ink extracted at the later time t_2 . This amount is the total amount extracted to the solvent when t_2 is the complete extraction time. The ink that has the lowest ratio (R) value will usually be the oldest ink. Originally the inverse of R was considered [4,5].

Time measurements can be made at more than two extracting times. If this is done, each measurement is divided by the longest extraction time to get ratio values. R is a measure of rate of extraction and is expected to decrease with the age of ink; however, increases with some ink formulations have been observed. Therefore, the direction for a particular ink must be tested by artificially aging the ink or comparing with inks of known age, if these are present on the document being examined.

In the L th extraction time procedure, the time it takes for $L \times 100\%$ of the ink to extract in the given (weak) solvent is measured. (Here L is less than 1, which means less than 100% extraction.) Clearly, to determine this, enough points on the extraction curve (extraction concentration versus extracting time) are necessary. This can be accomplished by taking several R ratios, for example, five evenly spread out over the total extraction time. (See also the fluorescence procedure below.) The resulting curve (R ratios versus extracting time) is simply the normalized extraction curve.

For L close to 1, this procedure is quite sensitive to aging [15]. This corresponds to Kikuchi's dissolution time (time taken until no more ink dissolves in the solvent), and is the basis of her successful observations on the aging of fluid inks [8].

The L th extraction time, for a given ink in a specified solvent, is expected to increase with age. However, the reverse has been observed [14]. Consequently, as in the case of the R ratio, the direction has to be tested.

Limitations of the Rate Determining Procedures

Problems with the R ratio solvent extraction relative aging procedure involve the experimental methods used and the fact that it only addresses the rate of extraction. The direction or the rate of extraction must be checked because the ratio sometimes increases with age and other times it decreases. Extreme care must be taken in recording the extraction times, pipetting the extracting solvent into the ink sample, and measuring the aliquot of ink spotted onto the TLC plate. The choice of the extraction solvent is critical (see below). Each of these facets of the test (experimental procedure, solvent choice, and so forth) can produce large errors if extreme care is not taken. In a typical test, 10 μL of extracting solvent is added to the ink sample and a 1- μL aliquot is taken for a spotting on a TLC plate. A small error in these measurements may produce large errors in the final age estimate. Failure to remove the aliquot at precisely the correct time interval (for example, 1, 5, and 15 min) can also produce large errors, especially at the 1-min time when the ink is extracting at its fastest rate. Spotting of the extracted ink must be uniformly applied on a TLC plate if results are to be reproducible. This takes considerable practice. Furthermore, performing densitometry requires considerable skill to assure that the actual concentrations are being measured (see below). The type of instrument and the way it is used is critical.

The major limitations of the L th extraction time procedure is that it is necessary to work with an extraction curve that has more than two or three points unless L is limited to be around one (as Kikuchi did). Sometimes not enough ink is available to obtain sufficient R ratios to get a workable curve.

Another limitation of the *L*_{th} extraction time procedure is the problem of direction (increase or decrease of extraction time with age of ink). Kikuchi [8] never observed this problem, perhaps because she dealt only with blue-black iron gallotannate inks and one solvent (oxalic acid solution). Cantu [14] observed this with one ink component (rhodamine) extracted in water, but not in aqueous solutions of methanol. This directional problem in both the *R* ratio and *L*_{th} extraction time procedures may be identified and alleviated by monitoring the extraction of the separated ink dyes. This may be accomplished by developing the TLC spots and measuring the density of the separated dyes [14].

Detection of Volatile Components of Ink by Gas Chromatography

This technique of determining the relative age of inks depends on the gradual disappearance of the major vehicles contained in the ballpoint ink formulations with time [9]. Typically the vehicles (solvents) include glycols and methyl or ethyl derivatives of glycol ethers. The vehicles are solvents for the dyes and other nonvolatile ingredients of ballpoint ink. Preliminary research has demonstrated these vehicles will remain in the dried ink on the paper for up to one year and perhaps longer in some inks. This technique involves the use of strong solvents to extract totally the volatile components from an ink. A comparison is then made of the relative concentrations of volatile vehicle components which are detected by gas chromatography using peak height or peak area methods. The older the ink, the lower is the relative concentration of a pair of volatile components where the first is more volatile than the second. As with the previously described technique, only inks having the same formulation can be compared. This technique can only be used if the ink being studied contains at least two measurable volatile components.

A possible advantage of the volatile components approach to ink dating is that it may eliminate the effect different papers may have on the ink aging [9]. However, this "paper independence theory" has not yet been proven and may not be valid if it can be shown that volatile components placed on a different paper, for example, papers of very different porosity, evaporate at different rates.

The rate at which volatile components disappear from the dried ink differs with each ink formulation, and lifetimes of the volatile components can range from three months to over a year. The extreme time limits have not yet been determined and may only be limited by the sensitivity of measurement techniques. As always, reproducibility of results and experimental error must be established, and significance of difference found between questioned and known inks must be carefully evaluated before conclusions are drawn.

Fourier Transform Infrared Techniques (FTIR)

Relative age determinations have been reported [10] using FTIR to detect changes in dried ink with age. In this work the hydroxyl (OH) and methyl (CH) infrared (IR) absorption bands were used. Humecki [10] found a decrease in the ratio of the hydroxyl to methyl bands in 1 ink formulation up to 22 years old with the leveling off beginning around 10 years.

Humecki used micro FTIR techniques since he was working with micro samples of ink (1 to 5 mm). Becker et al. at ATF attempted to verify the usefulness of this technique using micro samples of ink [11]; however, they did not use an IR microscope attachment as used by Humecki. Their results have been unsuccessful so far, perhaps because the optimum experimental procedures were not attained. However, the general trend of aging-versus-several ratios of IR absorbance peaks was observed.

In all these cases, the ink extract is placed on a KBr window, although ATF also tried mixing KBr and making a pellet. It appears that the success of this technique depends on the extreme care that must be taken in sample preparation and on the use of an IR microscope. The setting of the apertures and placement of the sample in the microscope is critical [10].

Recent Research

Recent research by Cantu and Prough [14] has addressed some of the problems inherent in the original rate determining procedures. This work is summarized in the next sections.

Extraction Rates by Fluorescence Analysis

Fluorescence measurements are extremely sensitive because emitted light relative to a nonemitting (black) background is measured. If a TLC plate of an ink shows that it has a fluorescent component, then this fluorescence can be observed and measured using a fluorescence spectrophotometer. Typically about 15 micro discs or 1 cm of ink line is placed in a conventional fluorescence cuvette with 1 mL of solvent. This method produces more complete extraction curves. Consequently, there is more flexibility in finding the optimum rate determining parameters for comparing inks of different age. Monitoring the extraction of fluorescent components is helpful because it involves larger volumes of extracting solvent and there is no need to remove successively samples of extracting solution for measurement.

Limitations

The fluorescence method works well when there is no interference from paper fluorescence. Paper fluorescence occurs when UV light is used as an excitation source, so the desired ink component should be one that fluoresces when other excitative sources are used. Fortunately, there is a series of these dyes that are used in the ink industry. Rhodamine-type dyes are excited by UV light but more efficiently by particular visible wavelengths. Excitation around 525 nm causes fluorescence around 552 nm. Solvents that exhibit interfering fluorescence must be avoided.

For inks without any fluorescence components a different approach is taken. The extracting solution is *spiked* with a premeasured amount of a rhodamine-type dye. An extraction procedure is carried out but the measurement is that of fluorescence "robbing" by the extracting color. For this approach to work the extracting species must have absorption either at the excitation wavelength or the emission wavelength, or preferably, both. Sensitivity increases when the extracting species absorbs both excitation and emission wavelengths. In this method possible oxygen fluorescence quenching has to be considered.

Extents of Extraction—Sequential Extraction Procedure

With this sequential extraction procedure, the ink is extracted in a weak solvent for a given time (for example, until the ink stops dissolving) [14]. The ink remaining in the residue from the first extraction is extracted in a second strong solvent until all the remaining ink is extracted. If the two extracting volumes are the same, then the absorbance of the first extraction divided by the sum of this absorbance and the absorbance of the second extraction $\times 100$ becomes the *percent of extraction* of the ink (for a given time in the first solvent). In the case of monitoring a fluorescent component, absorbance measurements are replaced by fluorescent measurements.

Absorbance measurements in this procedure are taken at two times: when the first partial extraction is complete (C_1) or nearly complete and when the second (total) extraction is complete (C_2). Concentration of ink extracts is determined using a spectrophotometer or fluorimeter for fluorescence analysis. As an alternative, the extracted inks can be spotted on a TLC plate and its concentration measured by a densitometer.

Then [14],

$$(\text{Percent extracted in weak solvent after } t \text{ min}) = P = \frac{C_1}{C_1 + C_2} \times 100$$

(Both extractions must be done with the same volume of solvent.)

The age of inks tested is estimated by comparing the percent of questioned ink extracted into the weak solvent with the amounts extracted from inks of known dates. The higher the percent of ink extracted, the fresher the ink is. When several known dated ink entries are available for testing, the age of a questioned ink entry can best be estimated by plotting an age of ink versus percent extraction curve. Table 1 and Fig. 1 show how this technique works on a Fisher pressurized black ballpoint ink on government note pad paper [14].

TABLE 1—Percent extraction in natural aging (Fisher pressurized black ballpoint ink).

Age in Months	Densitometric Readings			Percent Extraction
	Solvent 1 Toluene	Solvent 2 Benzyl Alcohol	Sum	
25	2.8	20.8	23.6	11.9
	2.7	20.7	23.4	11.5
	2.7	20.1	22.8	11.8
Average 20	2.7	20.5	23.2	11.7
	4.0	22.4	26.4	15.2
	3.8	21.2	25.0	15.2
Average 15	3.7	17.7	21.4	17.3
	3.8	20.4	24.3	15.9
	4.5	19.1	23.6	19.1
Average 10	4.4	18.3	22.7	19.4
	3.9	16.0	19.9	19.6
	4.3	17.8	22.1	19.4
Average	5.5	16.0	21.5	25.6
	5.3	15.6	20.9	25.4
	5.1	14.8	19.9	25.6
Average	5.3	15.5	20.8	25.5

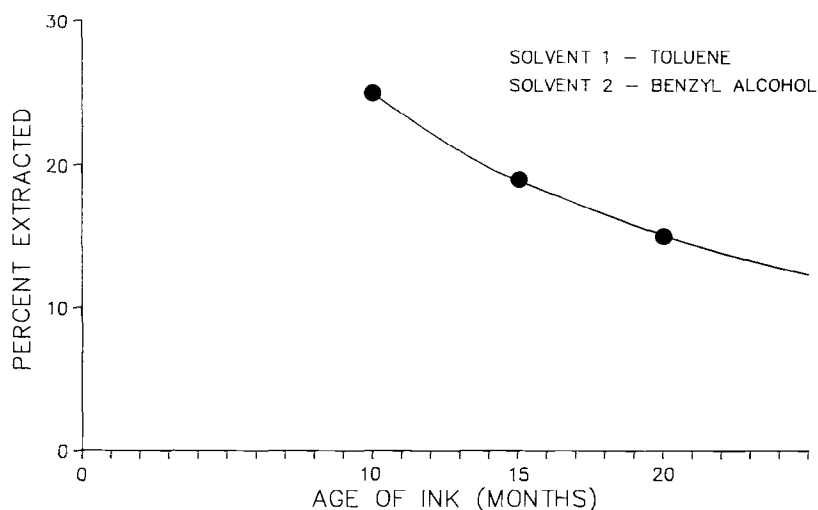


FIG. 1—Aging of ballpoint ink (double sequential solvent extraction) with Fisher pressurized black ballpoint ink.

Limitations

Choice of Weak Solvent—The key feature of the sequential extraction approach to relative aging (as in the rate determining procedures) is the choice of the first (weak) solvent since the percent extraction is in this solvent. It must discriminate inks of different age. Spotting techniques can help select the right solvent [14]: using a pipet, spot the inks being compared with various solvents and observe the speed and degrees of dispersion. A solvent which shows a difference in dispersion pattern is a candidate for the weak solvent. Pure solvents or mixtures of these, such as dilutions of strong solvents may be used as weak solvents. Table 2 shows the effect of spotting 15 different freshly written ballpoint and fluid ink formulations on Whatman paper No. 2 with several pure solvents. This table helps determine which solvents may be too strong or too weak to serve as the weak solvent. It also shows that there may not be a universal weak solvent that can be used on all ink formulations.

Choice of Strong Solvent—Even after a suitable weak solvent is identified, actual experimentation demonstrates the difficulty in selecting a workable strong solvent (see Fig. 2). This figure shows the results of extracting a Formulab 587 black ballpoint ink on Whatman paper No. 2 first with *n*-butanol (weak solvent) and second with pyridine (strong solvent). The *n*-butanol curve, obtained by keeping the amount of ink sampled as close as possible (discussed further below), reveals a definite relationship between age of ink and the amount of ink extracted into *n*-butanol. However, when the double sequential extraction is performed to obtain the percent extraction into the weak solvent, no clear relationship results between age of ink and percentage of extraction. This same lack of relationship also occurred when benzyl alcohol was used as the strong second extracting solvent. These examples lead to certain speculations: the choice of the second solvent may depend on the first solvent used (benzyl alcohol is not miscible with *n*-butanol and thus the residual *n*-butanol on the ink residue may impede the ink extraction into benzyl alcohol). Pyridine, one of the

TABLE 2—Ink solubility chart.

	0 = NOT SOLUBLE ↓ 5 = TOTALLY SOLUBLE																			
	METHANOL	ETHANOL	<i>n</i> -PROPANOL	2-PROPANOL	<i>n</i> -BUTANOL	ETHYLENE GLYCOL	BENZYL ALCOHOL	GLYCEROL	WATER	TOLUENE	HEXANE	XYLENE	PET. ETHER	CHLOROFORM	METHYLENE CHLORIDE	CHLOROBENZENE	PYRIDINE	ETHYLENE GLYCOL	BOND METHYLETHYL ETHER	ETHYL ACETATE
PILOT FIBER TIP	3	2	1	1	0	5	4	5	5	0	0	0	0	0	0	0	4	4	4	1
CROSS BLUE B.P.	4	4	4	4	4	4	5	1	0	0	0	0	0	3	4	4	5	5	—	—
FORMULAB 904 BLUE B.P.	4	4	4	4	4	1	5	1	0	3	0	3	0	4	4	4	5	5	—	—
PARKER BLUE B.P.	4	4	4	3	4	5	5	5	1	0	0	0	0	0	1	0	5	5	—	—
SKILCRAFT BLUE B.P.	4	4	4	2	4	3	5	1	0	0	0	0	0	1	2	1	5	5	—	—
SANFORD SHARPIE	4	4	4	4	4	4	5	1	0	—	—	—	—	—	—	—	—	—	—	—
SHEAFFER BLACK B.P.	2	1	1	0	1	0	4	0	0	0	0	0	0	1	2	1	5	4	—	—
BIC BLACK BALL POINT	4	3	3	0	3	1	5	0	0	0	0	0	0	0	0	0	5	5	0	—
ANJA M311 BLACK B.P.	4	3	4	2	3	1	5	0	0	0	0	0	0	4	4	1	5	5	—	—
FORMULAB 926 BLACK B.P.	4	4	3	4	4	2	5	0	0	0	0	0	0	4	4	1	5	5	—	—
BIC BANANA BLACK	4	2	2	1	0	5	1	5	5	0	0	0	0	0	0	0	4	4	—	—
PILOT BLACK B.P.	3	2	2	0	3	2	5	0	0	0	0	0	0	3	3	0	5	5	—	—
SKILCRAFT BLACK B.P.	4	3	5	4	5	1	5	1	0	0	0	0	0	4	4	1	5	5	—	—
BIC BLUE B.P.	3	4	3	1	3	4	5	—	0	0	—	—	—	0	—	—	5	5	5	—
FORMULAB 587 BLACK B.P.	4	3	4	1	4	—	5	—	0	0	—	—	—	—	—	—	5	5	—	—

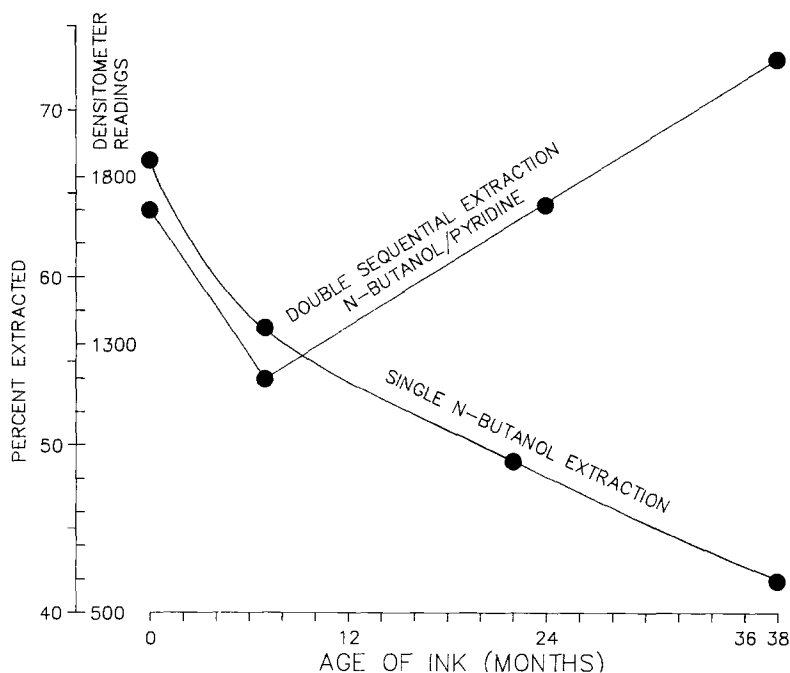


FIG. 2—Aging of ballpoint ink with Formulab 587 black ballpoint ink.

strongest Lewis bases and complexing agent, may complex with the residual *n*-butanol (reducing its extractability) and with dyes (possibly causing discoloration as has been observed).

Table 3 involves the same solvents as those in Table 1 and Fig. 1, that is, toluene and benzyl alcohol as the weak and strong solvent, respectively. In Table 3, the ink is the Formulab 904 blue ballpoint ink formulation on Whatman paper No. 2. The expected relation holds in this case. Note that even though there is an absolute percent difference of 6% in the percent of ink extracted in the weak solvent between the oldest and newest ink tested (45-month difference in age), the relative percent difference (absolute difference/average) of 30% is higher. Equivalently, one can say that there is a 27% decrease from 22% or 38% increase from 16%. The relative percent difference would be much lower if the percent ex-

TABLE 3—Percent extraction in natural aging (Formulab 904 blue ballpoint ink).

Age of Ink	Average Percent Extraction (Toluene) ^a
Fresh	22.0
1 month	19.5
6 months	19.3
40 months	17.8
45 months	16.1

^aBenzyl alcohol was used for the second strong solvent extraction.

tractions were higher and their absolute difference remained small. These differences would be too close to the range of experimental variation (see below) to draw any conclusion as to relative age.

Experimental Variation Problems—Experimental variation in both the TLC spotting technique and the densitometer area readings were evaluated [15]. Several aliquots of a solution of ink (extract of fresh Anja M-311 ink) were spotted separately on a TLC plate and each ink spot was scanned twice with a Shimadzu Densitometer Model CS-930 using the linear scanning mode. The average range of variations in the ink spotting procedure was 2.3% (see Table 4). The average variation of the densitometer scans was 1.8% (see Table 5). These low values of variation are only possible after considerable practice of the technique by the examiner. First attempts using this technique produced variations as high as 20%. It was also found that prolonged exposure of the same ink spots on the TLC to 580-nm light could cause as much as 14% lower densitometer readings after a 2-h period (see Table 6). The average percent variation for these two variables combined is 4.1%. Consequently, the extraction parameters (*R* ratio or percent extraction) must have relative errors within 4.1%.

Aging Rate Problems—Another problem lies with the rate in which some ink formulations

TABLE 4—*Reproducibility of spotting technique.*

Spot Number	Area	% Deviation from Average
1	1270	0.86
2	1269	0.94
3	1228	4.14
4	1314	2.58
5	1322	3.20
Average	1281	2.3

TABLE 5—*Reproducibility of Shimadzu TLC scanner CS-930.*

Scan Number	Area	% Deviation from Average
1	17 900	3.8
2	18 600	0
3	18 200	2.2
4	18 900	1.6
5	18 800	1.1
6	19 000	2.2
Average	18 600	1.8

TABLE 6—*Effect of 580-nm light on dyes extracted.*

Extracting Solvent	Original Area	Area After 4 Scans	% Change
Methanol	63 400	58 700	7.3
Benzyl alcohol	65 000	58 700	9.7
<i>n</i> -butanol	56 100	49 100	12.5
2-propanol	42 800	36 700	14.2

age using the sequential percent of extraction procedure. Figure 3 shows that using this technique on an Anja M-311 black ballpoint ink, the aging process stops after only two months. Here the weak solvent is 2-propanol and the strong solvent is methanol. For such rapid drying inks, the procedure applies only to recently written inks (within two months). Note that this quick leveling off is not true for the other two inks written on the Whatman paper No. 2 (see Fig. 2 (single extraction) and Table 3).

The age at which leveling off occurs is dependent on the ink formula (as seen above), on the choice of weak solvent, and on the paper bearing the ink. Cantu [14] found that as the solvent strength increases, so does the leveling off age; however, at the expense of lowering the relative difference between the top (zero age) and bottom (leveling off age) of the percent of extraction versus age curve. If the three inks on Whatman paper No. 2 discussed above were on less porous paper, the aging process would probably be slower.

An Alternative to Percent Extraction and Its Limitations [15]

Figure 2 plots the densitometric area (density) of the spots from *n*-butanol extraction against ink age. This parameter is related to C_1 in the equation above. It represents the amount of ink extracted in the first (weak) solvent and is proportional to the amount of ink sampled. In this case, extreme caution was taken to assure that the inks being compared were *equally sampled* so that C_1 and C_2 , which represent the total amount of ink sampled in the above equation, is always constant. This makes every single extraction parameter proportional to the percent extraction (obtained by the double sequential extraction procedure) with the same proportionality constant.

Thus, other than a proportionality constant, any discrepancies found between the single extraction plot, where equal sampling was successful, and the double (sequential) extraction (percent extraction) plot can only be due to problems or errors or both introduced with the choice of the second (strong) solvent and its extraction. The biggest such discrepancy we observed is that shown in Fig. 2. Figures 4 and 5 are the single extraction counterparts of the double extraction results in Fig. 3 and Table 3, respectively. Note the improved smoothness

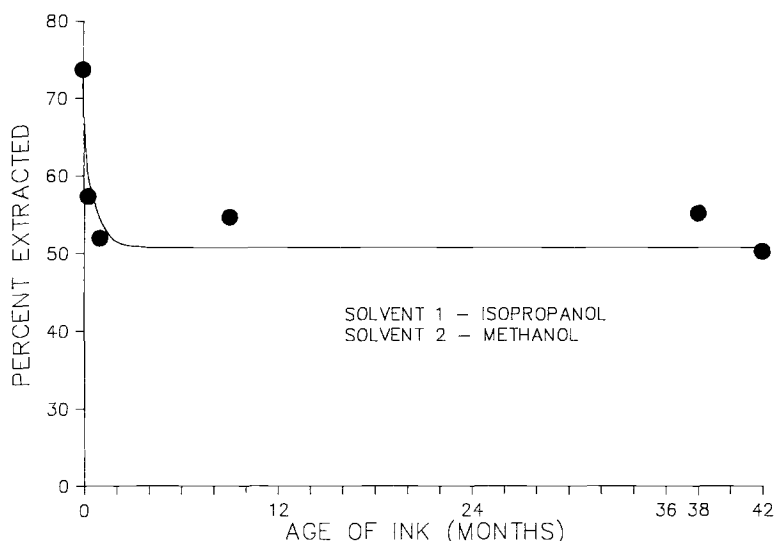


FIG. 3—Aging of ballpoint ink (double sequential solvent extraction) with Anja M-311 black ballpoint ink.

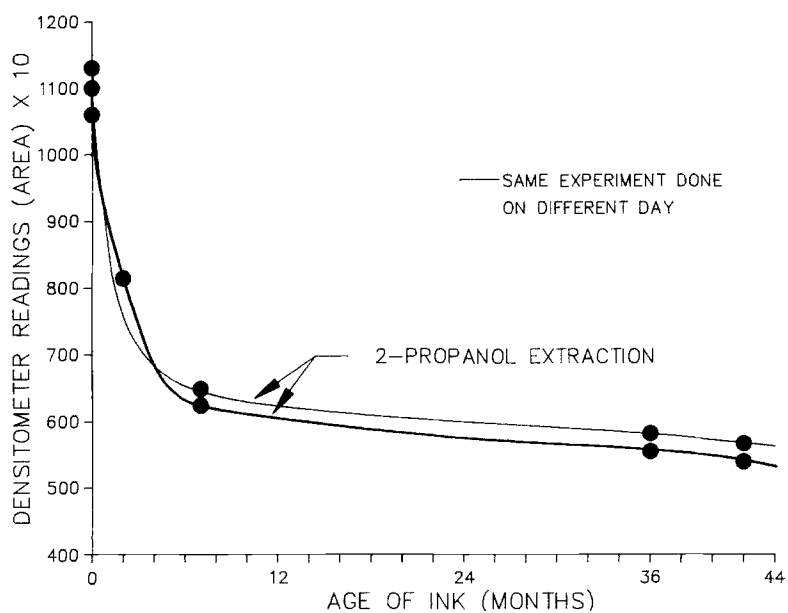


FIG. 4—Aging of ballpoint ink (single-solvent extraction) with Anja M-311 black ballpoint ink.

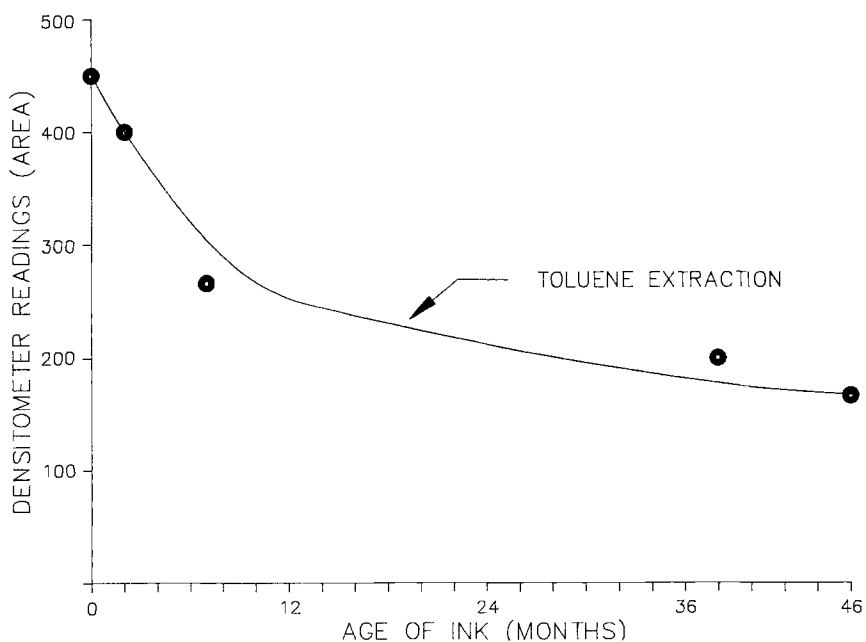


FIG. 5—Aging of ballpoint ink (single-solvent extraction) with Formulab 904 blue ballpoint ink.

found in the single extraction curves. In Fig. 4 there is good reproducibility and the leveling off age is more defined and longer (seven months rather than two months). Also, the percent relative differences are higher for the single extraction curves: 86 compared to 30% for the Formulab 904 blue ballpoint ink and 67 compared with 40% for the Anja M-311 black ballpoint ink. This single extraction approach is currently being evaluated by Brunelle at the ATF Laboratory and the results of the study will be published separately.

It may be possible to remove the requirement of equal sampling in the single extraction approach [14]. If the inks being compared contain at least two dyes and the ratio of the density of these dyes changes with age, then separating the dyes, using TLC, is necessary to determine this ratio which, by nature of it being a ratio, is independent of the amount of ink sampled.

Conclusions

In conclusion, all of the relative aging procedures discussed in this paper have many limitations. Therefore, if these procedures are used, they must be used with extreme caution. Any conclusions made on the basis of these procedures must consider the limitations described.

EDITORIAL COMMENT: *In Letters to the Editor of this issue of the journal (p. 1502), the authors discuss ethical responsibilities and qualifications as they relate to the performance of ink dating examinations.*

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