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## Determining the Relative Age of Ballpoint Inks Using a Single-Solvent Extraction Technique

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**ABSTRACT:** A new single-solvent extraction technique was developed to estimate the relative age of ballpoint inks. The procedure involves extracting the inks with weak solvents, spotting the ink extract onto a thin-layer chromatographic plate and measuring the amount of ink extracted densitometrically. By comparing the amount of questioned ink extracted with the amount extracted by known dated inks, it is possible to estimate the date the questioned ink was written. Success in using this technique depends on finding suitable weak solvents for extracting the ink. It also depends on the ability of the analyst to remove nearly equal amounts of ink from the document for each ink sample tested. This paper describes the results of several experiments for determining the relative age of ballpoint inks using a single extraction technique. Reproducibility measurements, experimental variations, and the limitations of the technique are also reported. Suggestions for further work are proposed.

**KEYWORDS:** questioned documents, inks, extraction, relative age, solvent extraction, densitometry, ink library, solubility, thin-layer chromatography, Fourier transform infrared spectroscopy, reproducibility, ballpoint ink

Over the past 18 years, the primary method used for dating writing inks on questioned documents has been the "Standard Ink Reference Library" approach developed by Brunelle [1] at the Bureau of Alcohol, Tobacco and Firearms in 1968. This method involves matching a questioned ink to an ink in the Standard Ink Reference Library. Parameters for comparison include dye and fluorescent components by thin-layer chromatography (TLC), solubility, color of writing, color of ink in solution, infrared reflectance, ultraviolet and infrared luminescence properties, and identification of unique additives to inks such as taggants. When a match between questioned and known dated inks is found, a conclusion is made that the questioned ink is not older than the date the matching standard ink formulation was first manufactured. If a taggant is found, then the actual year the ink was manufactured can be determined.

There are several limitations to the ink library approach to dating inks: many ink formulations remain unchanged for years, and the life cycle of a writing instrument from initial production to final sale can be short for inexpensive, mass marketed pens but quite long for

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quality, refillable pens. To be useful for the detection of backdating, the ink library approach requires frequent ink formulation changes.

An ink dating approach is needed to supplement the first production ink library approach for determining the age of writing on a document. In 1979, Cantu began experimenting with determining the relative age of ballpoint inks on questioned documents [2]. He found that as an ink ages on paper, the ink becomes more difficult to extract with organic solvents. Cantu established that a relationship exists between the age of an ink and the rate and extent of extraction of the ink.

Other work to date ballpoint ink using the relative age approach was done by Kikuchi [3] and Humecki [4]. Humecki's method was based on the measurement of changes in the infrared spectrum with the age of the ink. We have also made some preliminary studies of this approach; however, because of difficulties in sample preparation and reproducibility of measurements, we have sought a better approach. Stewart [5] measured ratios of ink vehicle components that remain in dried ink by gas chromatography. A limitation of this technique is that ink vehicles are not detectable after a few months. On the other hand, Kikuchi's observations that freshly written inks dissolve easier than older inks provided the basis for Cantu's research and the method described in this paper. A description of all major ink dating methods up to 1983 is given in *Forensic Examination of Inks and Paper* [6]. Brunelle and Cantu have published a comprehensive discussion of the limitations of current ink dating techniques [7].

This paper describes the results of several experiments for determining the relative age of inks using a new, single-solvent extraction technique. The inks tested ranged in age from freshly written samples to samples over three years old. Reproducibility measurements and experimental variations of the method are also reported. All inks tested were written with nearly equal pressure of the pen on Whatman Paper No. 2.

### *Theory*

As ink ages on paper, oxidation, cross-linking, polymerization, and solvent evaporation take place. These factors cause the components in the ink to become less soluble in organic solvents as the ink gets older. This phenomenon can be used to estimate the age of ballpoint ink as long as

- the ink is on the same type of paper and has had the same storage conditions and
- there are known dated inks of the same formulation for comparison.

### **Experimental Procedure**

The procedure is simple in principle, but requires careful use of the measurement pipets and removal of the ink samples from the documents. The method involves measuring the amount of ink extracted into specific organic solvents. The fresher the ink, the greater amount of the ink will be extracted. The older the ink, the less will be extracted into the solvent. The most difficult part of the method is finding a suitable solvent that will only partially extract even fresh ink from the paper. The amount extracted should be in the range of about 10 to 70% of the total ink. If all of the ink is extracted into the solvent, then no meaningful differences will be observed. If too little ink is extracted, the concentration is difficult to measure reproducibly. The amount of ink extracted is formula dependent, so a suitable solvent must be found for each different formula ink.

### *Procedure*

*Sample Size*—Take 1 cm length of ballpoint ink line or ten plugs of ink (1-mm diameter), removed with a blunted syringe needle (microplugs). The same amount of ink must be taken

for each sample of ink compared. To do this, take triplicate samples of each ink from areas where the amount of ink deposited on the paper appears to be the same (if enough ink is available). Average the three results when calculating the amount of ink extracted.

#### *Steps of the Procedure*

1. Place the ink sample into Kontes (or equivalent) cone-shaped vials (2-dram size). If a 1-cm line is used, cut the line into 2-mm size pieces so they all fit at the bottom of the vial.
  2. Quantitatively add 25  $\mu\text{L}$  of a suitable weak solvent to the ink sample in the cone-shaped vials (a Centaur automatic pipet was used in this study). To find the correct solvent, place a minute portion (1  $\mu\text{L}$ ) of the candidate solvents on the written ink line to see how much of the ink dissolves. The best solvent will only slightly dissolve the ink line.
  3. Cap the vials to prevent evaporation and allow the ink to extract for 10 min. To ensure comparable extraction, tap the vial frequently to make sure all of the ink is constantly exposed to the solvent. An ultrasonic vibrator is best for this.
  4. Quantitatively remove 5  $\mu\text{L}$  of the extracted ink and spot onto a clean E. Merck silica gel thin-layer chromatographic (TLC) plate, without fluorescent indicator. The solvent must be spotted with one smooth deposition of the ink extract on the plate to get the same size, uniform spots.
  5. Repeat Steps 1 to 4 with all inks compared. Spot all samples in a direct line on the same TLC plate.
- (Note: Each ink sample should be run in duplicate or triplicate, if enough sample is available. This will establish the range of variation in the amount of ink removed from the document for analysis.)
6. Dry the ink spots on the TLC plate for 10 min in an oven at 50°C.

#### *Measurement of the Amount of Ink Extracted*

Different age inks can sometimes be distinguished with the naked eye, if the amounts extracted are significantly different. To quantitate, a recording densitometer (Shimadzu Model CS-930 or equivalent) can be used to record the precise amounts of ink extracted. To do this, scan the spots on the TLC plate in the linear mode. Use a wavelength setting of 580 nm for blue and black inks. Choose a slit width that approximates the diameter of the ink spot. Use the reflectance mode.

#### *Calculations*

Average the densitometer readings for each different ink sample. If the ages of just two ink samples are being compared, the lower reading will be the oldest ink. The higher reading will be the newest ink. If three or more inks are being compared, for example, one questioned and at least two or more known, then the age of the Q ink can best be estimated by plotting *amount extracted versus age* of the known dated inks.

Note that if the formula of the questioned ink is known, then a sample of this ink should be written on the questioned document and then extracted according to the same procedure described above. This will provide a standard for the amount of ink extracted with freshly written ink (age zero). If time permits, this same ink standard can be analyzed at 1, 4, 8, 12, and so forth week intervals to provide additional points for the "age versus amount extracted" curve. The limitations to this approach have already been described [2].

#### **Results and Discussion**

Success in determining the relative age of ballpoint inks depends on finding a suitable solvent for the extraction. It also depends primarily on the ability of the analyst to remove

nearly equal amounts of ink from the document for the questioned and known dated inks. This is because the single extraction technique is mass dependent.

### *Choice of Extracting Solvent*

Choice of the optimum solvent to use for extracting the inks must be determined for each different ink formula tested. This is because solubility is formula dependent.

Table 1 shows a list of potential solvents to consider for dissolving ballpoint inks. The ideal solvent is one that will only partially extract the ink from the document. Extractions in the range of 10 to 70% appear to be satisfactory for the technique described. Of course, the older the ink, the less the amount of ink that will be extracted into the solvent selected. The aliphatic alcohols were the most satisfactory for the inks tested in this study; however, toluene is satisfactory for certain ink formulations. For the experiments described in this paper, *n*-butanol, 2-propanol, and toluene were used.

Table 2 shows the results of Kikuchi-type tests on 15 different ink formulations. These tests involve spotting about 1  $\mu$ L of the solvent tested on the ink line and observing the amount of spread of the ink line. In this table the number zero represents no spread (zero solubility) of the ink. The number five represents complete solubility (complete removal of the ink from the ink line). Numbers one to four represent varying degrees of solubility between zero and five. These numbers were arbitrarily assigned as a way to quantify ink solubility in different solvents. Solvents with a rating of 1, 2, and 3 should be acceptable for the relative age test. Ratings of 4 and 5 should be avoided.

### *Reproducibility Tests and Measurements*

1. To determine the reproducibility of spotting the ink on the TLC plates, a sample of freshly written Formulabs 587 black ballpoint ink was dissolved in pyridine and five successive aliquots of the extract were spotted on an E. Merck silica gel TLC plate. The results are

TABLE 1—Potential solvents for ballpoint inks.

ALIPHATIC ALCOHOLS	MISCELLANEOUS ORGANIC LIQUIDS (continued)
1. Methanol	5. Tetrahydrofuran
2. Ethanol	6. Ethylene glycol-monomethyl ether
3. <i>n</i> -propanol	7. "Cellosolve"
4. 2-propanol	
5. <i>n</i> -butanol	AROMATICS
6. Ethylene glycol	1. Benzene
7. Glycerol	2. Toluene
8. 3-methyl-1-butanol (Isoamyl alcohol or isopentyl alcohol)	3. Benzyl alcohol
9. 2-methyl-1-propanol (Isobutyl alcohol)	4. 1,4-dimethyl benzene (xylene)
ALIPHATIC HYDROCARBONS	CHLORINATED HYDROCARBONS
1. Hexane	1. Dichloromethane
2. Petroleum ether	2. 1-chlorobenzene
	3. Carbon tetrachloride
	4. 1-2 dichloroethane
	5. Chloroform
MISCELLANEOUS ORGANIC LIQUIDS	
1. Pyridine	1. Water
2. Carbon disulfide	
3. Ethyl acetate	
4. Acetone	

TABLE 2—Ink solubility chart.

	METHANOL	ETHANOL	n-PROPANOL	2--PROPANOL	n--BUTANOL	ETHYLENE GLYCOL	BENZYL ALCOHOL	GLYCEROL	WATER	TOLUENE	HEXANE	XYLENE	PET. ETHER	CHLOROFORM	METHYLENE CHLORIDE	CHLOROBENZENE	PYRIDINE	ETHYLENE GLYCOL MONO METHYLETHETHER	ETHYL ACETATE	
0 = NOT SOLUBLE																				
5 = TOTALLY SOLUBLE																				
PILOT FIBER TIP	3	2	1	1	0	5	4	5	5	0	0	0	0	0	0	0	4	4	—	
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	—	0	—	—	—	—	5	5	—	

given in Table 3. The average percent deviation was 2.3%. These measurements were performed on a Shimadzu Model CS-930 densitometer at 580 nm, using the reflectance mode and linear scanning.

2. The reproducibility of the densitometer readings was determined by conducting repetitive scans of a single ink spot prepared as described in No. 1 above. These results are given in Table 4. Here, the average percent deviation was only 1.8%.

3. To determine the optimum method of extracting the ink from the paper, ultrasonic agitation was compared with manual stirring of the ink sample in the solvent. Table 5 reveals that ultrasonic agitation provided a more complete extraction of the ink from the paper (one-minute ultrasonic agitation). Thirty-eight percent more ink was extracted using this method.

*Effect of Densitometer Light Source on Extracted Dyes*—In this experiment, four different ink extracts were spotted on a TLC plate and scanned in the densitometer four times over a 2-h period. The results indicate a significant decrease in the densitometer area readings. This decrease is attributed to fading of certain dyes caused by the densitometer light source.

TABLE 3—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 4—*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 5—*Effect of ultrasonic agitation on amount of ink extracted (Formulab 587 black ballpoint ink and solvent n-butanol).*

Densitometer Readings		
With No Ultrasonic	With Ultrasonic	% Change
28 400	39 100	+37.7
31 300	43 100	+37.7

An average reduction of 10.5% was observed (see Table 6). Therefore, it is important to minimize exposure of the ink spots on the TLC plate to the densitometer light source. For this experiment, freshly written Anja M-311 black ballpoint ink was used.

*Sample Size Reproducibility*—Because the technique described is mass dependent, it is essential to remove nearly equal amounts of each ink sample to be compared for relative age. While it is impossible to remove exactly the same amount of ink every time, with practice the difference in sample size can be minimized. Table 7 gives the densitometer area readings for six different ink extractions—two extractions for each age of ink. As can be seen, the readings for the duplicate samples are in good agreement. In this experiment, a 3-cm ink line written with nearly equal pressure was measured for each sample. The same degree of sampling reproducibility was observed when ten microplugs of ink (again written with nearly equal pressure) were removed for testing (see Table 8). For both types of sampling, the amount of ink removed for extraction was within 10% average deviation. When dealing with ink entries written with varying line pressures, extreme care must be taken in the sampling procedure.

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

TABLE 7—Amount of ink extracted  
Anja M-311 black ballpoint ink  
(2-propanol) reproducibility.

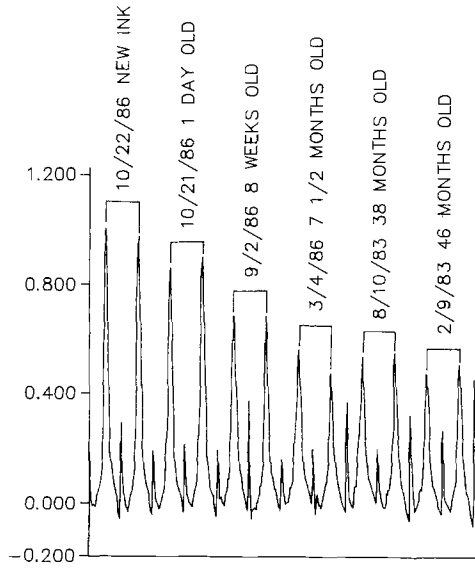
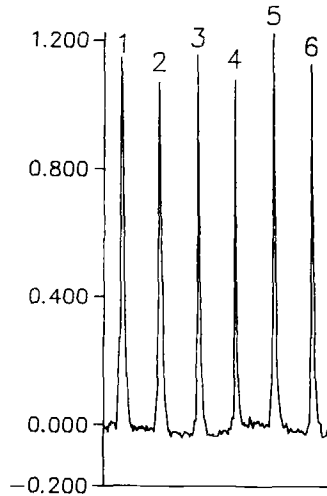


TABLE 8—Sampling  
reproducibility: replicate samples  
of the same ink (ten microplugs in  
each sample).



*Relative-Age Experiments*—Once all of the experimental parameters were optimized, relative age experiments were performed on three different ballpoint ink formulations. The age of the inks tested ranged from freshly written inks to inks over three years old. The ink samples tested were written on Whatman No. 2 qualitative filter paper that was free of fillers and binders.

The first ink tested was an Anja M-311 black ballpoint ink formulation. The extracting solvent used was 2-propanol. Table 9 gives the relative amounts of ink extracted for the different age inks. The results demonstrate a definite relationship between age of the ink and the amount of ink extracted. Figure 1 shows a plot of the data in Table 9. Figure 1 also shows the results of a test on the same ink conducted a day later. The two curves show excellent reproducibility of the aging technique.

Figure 1 shows that the Anja M-311 ink ages rapidly during the first seven months. After seven months, the aging process levels off. This means for this particular ink, fairly accurate

TABLE 9—Relative age of Anja M-311 black ballpoint ink (single solvent extraction).

Date Ink Applied to Substrate	Age of Ink	Areas from Densitometer 2-propanol Extract
9 Feb. 1983	44 1/2 months	5 350
10 Aug. 1983	38 1/2 months	5 950
4 March 1986	7 1/2 months	6 200
2 Sept. 1986	1 1/2 months	8 050
21 Oct. 1986	1 day	10 600
22 Oct. 1986	fresh	11 250

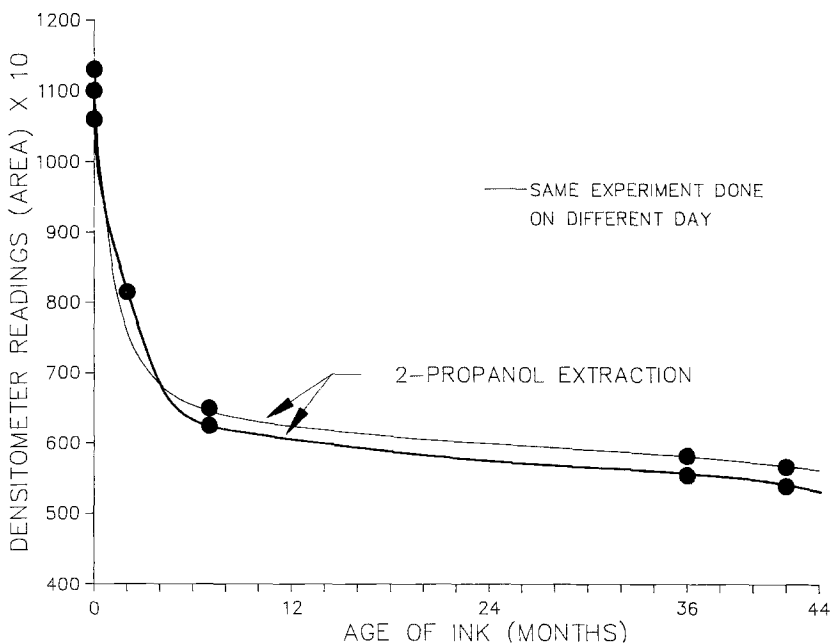


FIG. 1—Aging of Anja M-311 black ballpoint ink (single-solvent extraction).



age estimates are possible for about seven months; however, after seven months, the aging is too slow to measure. On the other hand, the Formulab 587 black ballpoint ink formulation, using *n*-butanol as the extracting solvent, can provide fairly accurate measurements up to three years (see Fig. 2). This demonstrates that the aging process is definitely formula dependent. Using different solvents it may be possible to detect changes in the age of ink for longer periods of time, but this needs to be verified.

Figure 3 shows the results of a relative age experiment on a Formulab 904 blue ballpoint ink, using toluene as the extracting solvent. With this ink, the age can be accurately measured up to about one year. After one year, the age estimates would be within the range of experimental variation so no accurate age estimations are possible using toluene as the extracting solvent.

The results of the tests described clearly demonstrate a relationship between the age of ink and the amount extracted using three different solvents on three different ink formulations. This finding can be used to estimate the age of questioned ballpoint inks under certain conditions. These conditions are:

- The inks compared must consist of the same formula.
- The inks compared must be on the same paper.
- The inks compared must have been subjected to the same storage conditions. This is assumed to be the case when the inks appear on the same document.
- The inks compared must be only partially soluble in the extraction solvent used.
- There must be enough ink available to remove at least duplicate samples for testing to minimize sampling variation. (Triplicate samples are preferable.)
- The inks tested must still be aging at a significant rate to enable accurate age estimates.

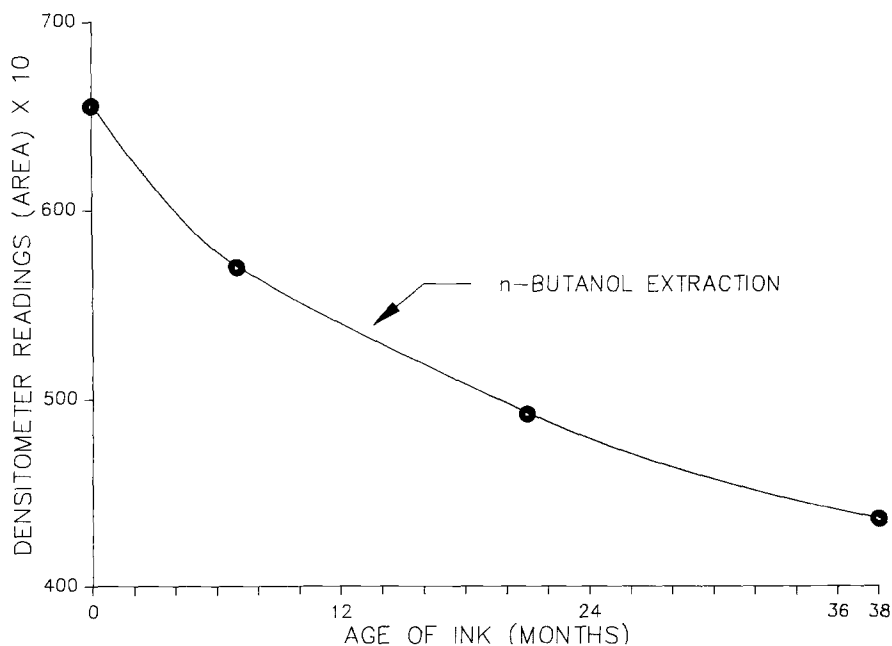


FIG. 2—Aging of Formulab 587 black ballpoint ink (single-solvent extraction).

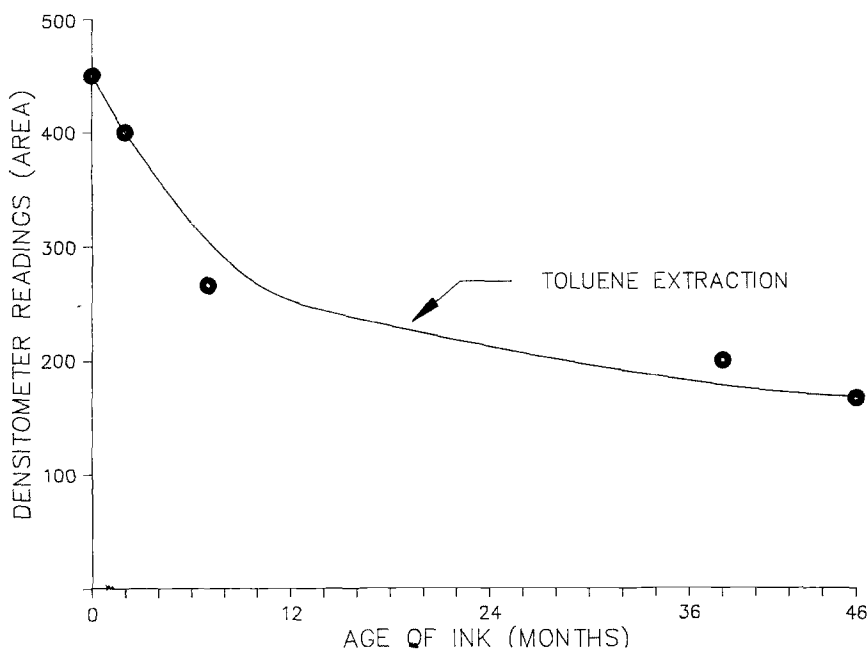


FIG. 3—Aging of Formulab 904 blue ballpoint ink (single-solvent extraction).

#### Further Work Needed

The authors intend to extend this study to determine the effects of paper and storage conditions on the relative aging technique. We also want to identify solvents that might enable age estimates to be made on inks older than the three-year maximum described in this paper. The ability of this technique to determine the relative age of nonballpoint inks should also be explored. Lastly, ways to make this technique mass independent should be explored. One approach would be to determine the ratios of the dye components of each ink separated by TLC. These ratios would be mass independent. This procedure may also reveal that some dyes age slower than other dyes. If this is the case, then the single-solvent extraction technique might work on inks up to ten years old or more on some ink formulations. Obviously, sufficient ink sample must be available to enable the separated dyes to be measured by densitometry.

When the limiting requirement that equal amounts of ink be sampled is satisfied, the proposed procedure provides a valuable initial aging trend for those procedures that are followed by further extractions (in the same or different solvents) as described in the several mass independent procedures [2].

#### Conclusions

Experiments have been described that demonstrate the feasibility of determining the relative age of ballpoint inks using a single extraction procedure. This capability is based on a relationship between the age of ink and the amount of ink extracted into an appropriate organic solvent as indicated by measurement of dye level. Finding a suitable solvent to extract the different inks is time-consuming, and the sampling procedure requires meticulous

care. Nevertheless, the technique described has been demonstrated to work effectively on three ballpoint inks, and the authors are convinced the technique will work on all ballpoint inks once more work has been done to identify those types of solvents best suited to extracting particular ink formulations.

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