TECHNICAL NOTE

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A Microspectrophotometric Method for Dating Ballpoint Inks—A Feasibility Study

ABSTRACT: A new approach to estimate the age of ballpoint ink-written texts has been offered. It is based on using the microspectrophotometric determination of the ratios of comparatively unstable and stable dyes in the surface layer of the questioned ink and in the whole ink film by comparing reflectance values measured in natural (specular reflection) and polarized (diffuse reflection) light, respectively. The older the ink, the less the mentioned dyes' ratio in the surface layer of the ink.

Limitations of the technique and of the equipment's accessories used are discussed. Suggestions for further work are proposed.

KEYWORDS: questioned documents, ballpoint inks, relative aging, dyes, ratio, microspectrophotometry, reflectance, polarized light, irregular distribution of ink, distributional error

Determination of the age of an ink—and, in particular, ballpoint ink—written text is a complex and topical forensic problem. Several approaches for dating ballpoint inks published in 1970s and 1980s have been critically evaluated by Brunelle and Cantu [1,2].

In 1993, four new ideas for dating ballpoint inks were reported [3]. Based on this study, the following two procedures have been developed (they both have been used in many actual cases with the subsequent acceptance of the results of the examinations as conclusive evidence by courts of law) [4].

1. A procedure combining a thin-layer chromatographic (TLC) method for determining age changes in nonvolatile ballpoint ink components with a new, mass-independent, approach to densitometric evaluating thin-layer chromatograms[2] that allows one to obtain the values of an "ink aging parameter" [8] that are directly proportional to the ratios of the masses of the separated ink components (resins, dyes, etc.) The procedure gives more reliable results

of ink age determination than those obtainable with the mass-dependent peak signal-to-peak signal ratio technique.

2. A procedure combining a gas chromatographic method for determining the extent of extraction of ink volatile components with the accelerated aging technique. The procedure is very effective when two entries that are to be compared by their age have been written with ballpoint inks of the same formula including such ingredients as phenoxyethanol, phenoxyethoxyethanol or similar high boiling vehicles and a resin capable of polymerizing (namely, of cross-linking) as the ink ages on paper. The great advantage that this procedure has over traditional ones is that in a case where it is necessary to determine whether a questioned entry is a fresh one (age less than a few months),[3] it does not require dated reference entries be written with ink that has the same formula as that of the questioned ink (for detail see [4]).

In this work, another approach to dating ballpoint inks that is based on the presumption that maximum changes due to aging of the ink composition (as a result of oxidative destruction and other transformations of ink dyes, resins and polymers) must occur most intensively in the ink surface level that contacts with the ambient medium was studied. The proposed technique includes the microspectrophotometric determination of the ratios of the masses of comparatively unstable and stable dyes in the surface layer of the questioned ink and in the whole ink film by comparing reflectance values measured in natural (non-polarized) light and in polarized light (with the analyzer and polarizer crossed to eliminate the gloss of the ink surface), respectively, the older the ink the less the above mentioned dyes' ratio in the surface layer of the ink.

Preliminary Study

Generally, blue, violet, and black ballpoint inks contain phthalocyanine blue (a very stable component, dye 1) and triphenylmethane violet (significantly less stable component that is usually methyl violet or crystal violet, dye 2) dyes.

In this work, it has been ascertained that the masses' ratio of dye 2 to dye 1 for all inks analyzed decreases gradually as the ink ages: approximately 0.5 to 1.5% of dye 2 (in comparison with the content of dye 1 in the same ink) is decomposed per year

[3] Such cases are fairly typical when the investigator suspects that the given entry or signature was made after the time the investigation began. Some similar examples have been presented by Cantu [9].

of the natural aging process.[4] At the same time, no satisfactory correlation was established between the age of the analyzed inks and the contents' ratios of dye 2 and the main products of the natural aging of dye 2 in the inks (see [10] and footnote 4 for details).

Further, it has been supposed that maximum changes due to aging of an ink composition (as a result of oxidative destruction and other transformations of ink dyes, resins and polymers) must occur most intensively in the ink surface level that contacts with the ambient medium. The method used to check this idea included the following operations.

1) separating of surface (sample 1) and internal (sample 2) layers of a ballpoint ink line by copying the substance of the surface layer onto another support or by erasing this substance, for example, with the help of an eraser.

2) extracting of the dyes from both samples obtained.

3) recording absorption spectra of the extracts, calculating the ratios of the absorbances measured at the absorption maxima corresponding to dye 1 and dye 2, respectively.

4) comparing of these ratios obtained for the samples.

However, contrary to the expectations, the described approach gave no statistically significant differences between the obtained ratios even for up to six-year-old ballpoint ink writings stored in darkness at normal temperature. These results lead to suppose that *determinable changes of dyes ratios may take place only in a very thin exterior layer of the ink line that practically cannot be removed for analysis.*

In this connection, a new approach that includes measuring and comparing of the masses' ratio of dyes in the surface and interior layers of an ink line and that does not require separation of the layers has been studied. According to the technique developed on the base of this approach, each ink site chosen is microphotometrically measured by two modes (see Fig. 1)

• in natural, non-polarized, light with such illumination of the ink surface that the ink site to be measured looks completely glossy: in this mode (further with the abbreviated name *"spec"*) only light specularly reflected from the surface of the ink site goes through the objective to a photomultiplier of the microscope photometer.
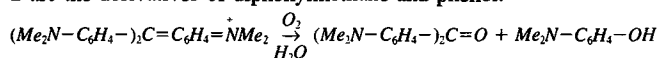
• in polarized light when a polarizer and analyzer are crossed to eliminate the gloss of the surface of the site to be measured: in this mode (further with the abbreviated name *"dif"*) only light diffusely reflected from both surface and interior layers of the ink site, is measured.
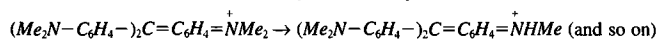
Experimental Procedure

Ink Samples

Entries known to have been written by a Parker blue ballpoint ink during about six-year period were examined. The ages of these entries were one month, one and six years.

[4] It has been found that the main products of the natural aging of dye 2 are the derivatives of diphenylmethane and phenol:

$$(Me_2N-C_6H_4-)_2C=C_6H_4=\overset{+}{N}Me_2 \overset{O_2}{\underset{H_2O}{\rightarrow}} (Me_2N-C_6H_4-)_2C=O + Me_2N-C_6H_4-OH$$

whereas the successive demethylation of dye 2

$$(Me_2N-C_6H_4-)_2C=C_6H_4=\overset{+}{N}Me_2 \rightarrow (Me_2N-C_6H_4-)_2C=C_6H_4=\overset{+}{N}HMe \text{ (and so on)}$$

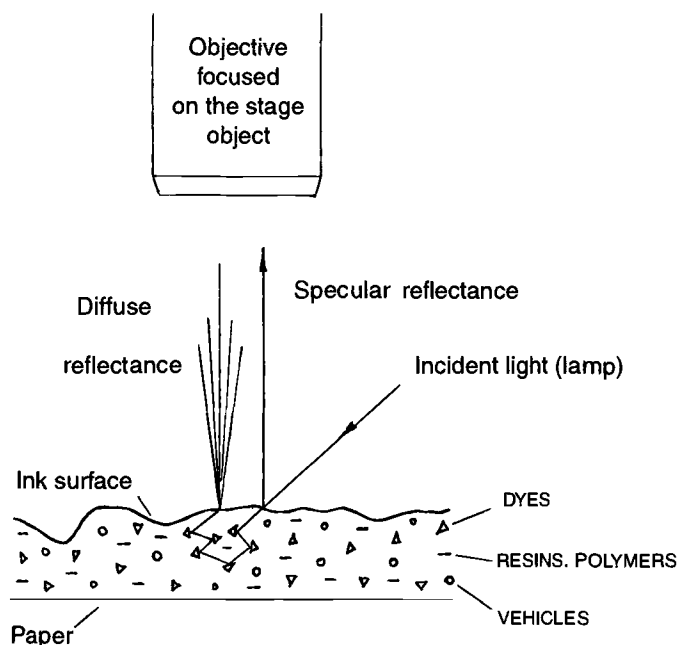is not a significant process for the analyzed inks.

FIG. 1—*Specular and diffuse reflectance measurements of inked lines.*

Instruments and Measuring Conditions

A Leits (Germany) MPV-SP. spectral photometer with a current-stabilized light source (tungsten-halogen lamp, 12 V/100 W), measurement grating monochromator (1200/mm), Hamamatsu-type R928 photomultiplier, dark-field "Ultropak" condenser and objective "UO-6.5 × 0.12"; wavelength range — 400–700 nm; monochromator half bandwidth — 3 nm; Leitz polarizing filters.

For every ink entry, eight sites that looked apparently similar in thickness (depth of ink), surface characteristics (morphology and so on) and homogeneity (more of less even distribution of the ink in the measuring sites) were chosen. These sites were located under the microscope (in polarized light with the polarizer and analyzer crossed) and the reflectance spectra of them were recorded in the polarized light (series "dif") and in natural, non-polarized light (series "spec").

For each series, two analytical wavelengths, λ_1 and λ_2, were chosen at which absorption maxima were located relating to two main dye components of the Parker ink analyzed—copper phthalocyanine blue ($\lambda_1^{dif} = 685$ nm and $\lambda_1^{spec} = 670$ nm) and methyl violet ($\lambda_2^{dif} = 615$ nm and $\lambda_2^{spec} = 580$ nm).

Then for every site analyzed the value of the ratio, Z, of the reflectance values, R, taken at the wavelength chosen was calculated for the series "dif" and "spec" by using Eqs 1 and 2, respectively:

$$(Z_{dif})_i = [R(\lambda_1^{dif})_i - C] / R(\lambda_2^{dif})_i \qquad (1)$$

$$(Z_{spec})_i = [R(\lambda_1^{spec})_i - K] / R(\lambda_2^{spec})_i \qquad (2)$$

where i is the site index; C and K are coefficients (determined by using an iterative technique), which change the respective reflectance values, $R(\lambda_1^{dif})_i$ and $R(\lambda_1^{spec})_i$, so that for every series the sum of the ratio values' dispersion measures, calculated for each entry analyzed, becomes minimum (detailed description of the calculation procedure is given in [11]).
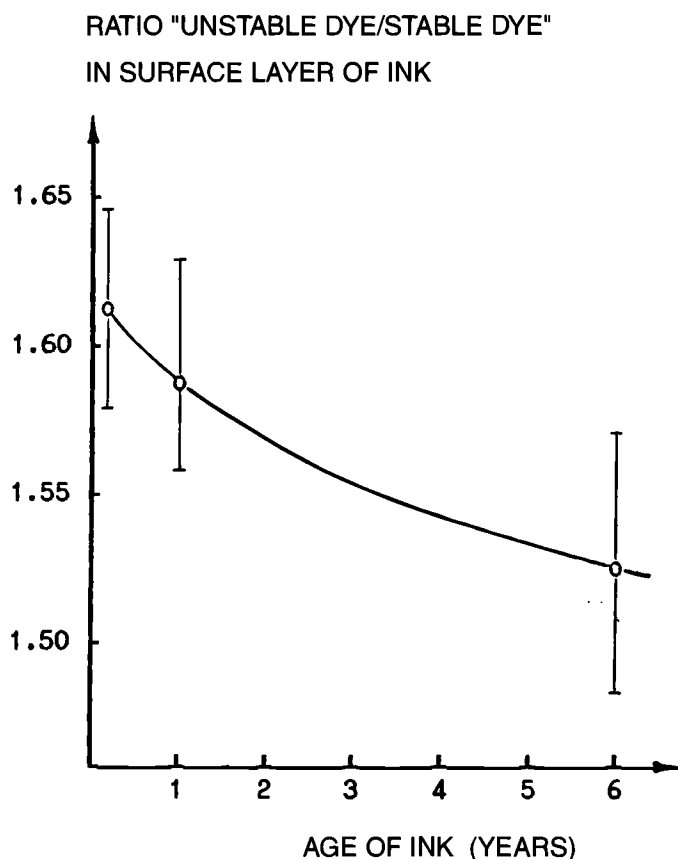
RATIO "UNSTABLE DYE/STABLE DYE"

IN SURFACE LAYER OF INK

FIG. 2—*"Aging curve" obtained for the Parker blue ballpoint ink.*

Finally, for each measured site, i, the value of Z_i was calculated that characterizes the masses' ratio of the comparatively unstable and stable dyes in the surface layer of the ink entry analyzed:

$$Z_i = (Z_{dif})_i / (Z_{spec})_i \qquad (3)$$

The calculated Z_i values were plotted versus the age of the corresponding ink entries analyzed (Fig. 2).

Results and Discussion

Table 1 shows the results of the relative age determination for one-month, one-year and six-year old entries written by the same Parker blue ballpoint ink.

An "aging curve" obtained for these entries is depicted in Fig. 2. The curve shows that the *median* of Z_i values (the arithmetic mean was not used since the received Z_i values were not normally distributed) taken as an aging parameter for each entry analyzed, *decreases monotonically* as the ink ages.

At the same time, it is seen in Fig. 2 that the deviation of Z_i values from the median value is so large that in this particular case it became possible to differentiate only between 1-month and 6-year old writings analyzed, that is between very fresh and very old writings.

The reason for so large dispersion of Z_i values received in the given example, is explained by the following. The measuring areas of all ink entries analyzed were chosen as similar as possible with respect to their thickness (depth), surface characteristics (morphology, gloss, etc.) and distribution of ink substance per area. This was done since there was always a so-called "distributional" error [12] in the measured reflectance due to the inherently irregular distribution of the mass of ballpoint ink across the photometrically measured area in an ink line (the ink deposits on the microscopic ridges of the matted paper fibers rather than on the crevices between them). The present author's experience shows that when the reflectance of different areas of a ballpoint ink line is being measured, this error dominates over the standard deviation of the measuring result due to overall statistical uncertainties including, namely, instrumental errors and errors of repetition measurements.

Of course, the distributional error can be decreased with the decrease in size of the photometric field. However, in this case the signal-to-noise ratio will decrease rapidly since the optical flux in the microspectrophotometer, and hence the measuring value, is proportional to the second term of the radius of photometric field [12].

In this study, it was noted that the distributional error increases with the increase of the magnifying power of the objective used for measurements, and vice versa. In this connection, it seems that the most effective way to decrease this error involves the use of objectives of as low power as possible (with large free working distances) that would not allow the photosensor of the microspectrophotometer to "see" the real image of the fine texture of the non-uniform field of a ballpoint ink line on which photometry is being done. The use of such objectives that, unfortunately, were not available for this study, would allow one to decrease the interval of the ratio values calculated for each ink writing analyzed according to the proposed method (see Fig. 2) and hence to increase the efficiency of the method.

Summing up, it is necessary to stress the following.

(1) The method proposed is non-destructive to the sample, contrary to, for example, the techniques [4–6] using TLC densitometry that require semi-destructive testing.

(2) This method has merit only if it is somehow known or shown as a result of an appropriate examination that the two inks being compared are of the same formula. At the same time, one should bear in mind that there are some inks (some Bic inks, for example) that are very identifiable with a given formula regardless of the degree of ink fading, and in such case only a TLC analysis of the ink colored components may not allow one to prove that

TABLE 1—*The results of the spectrophotometric analysis of the ink writings.*

Age of ink	Z_i values calculated by Eq 3								Median of Z_i values
	Number of ink site measured								
	1	2	3	4	5	6	7	8	
1-month	1.590	1.581	1.628	1.611	1.619	1.593	1.632	1.645	1.615
1-year	1.569	1.618	1.596	1.584	1.579	1.557	1.628	1.609	1.590
6-year	1.483	1.508	1.544	1.563	1.570	1.516	1.519	1.492	1.518

two inks—which contain the same dyes but in different proportions (due to fading)—are of the same formula. So, in such situation, other analytical methods are to be used for more complete characterizing the compositions of the inks to be compared. Among these methods are gas chromatography/mass spectrometry (enables identification of ink vehicles and other ink ingredients which are volatile at temperatures used in gas chromatographic analysis, as it was mentioned in [3]), diffuse reflectance infrared spectrometry (enables characterization of dye components, resins and other additives of ink; see [13]) and high performance liquid chromatography/mass spectrometry (enables identification of nonvolatile ink components, as it was offered in [14]).

Conclusion

A new non-destructive method for estimating the relative age of entries written with ballpoint inks of the same formula has been considered. The method as described has yet limited capabilities to distinguish the age of inks and hence further work to increase the efficiency of the technique must be performed: in particular, this can be achieved by using the low-power objectives with large free working distances in other to decrease the distributional error in the reflectance of the photometrically measured areas of ink lines due to inherently irregular distribution of ink per area.

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