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Some New Ideas for Dating Ballpoint Inks—A Feasibility Study

ABSTRACT: This paper introduces four techniques developed with the goal of estimating the age of ballpoint inks. These techniques are based on using the microspectrophotometric determination of the rates of color changing in inks as a result of the reaction with chemicals—the older the ink the less the rate (procedure 1); a combination of gas chromatographic (GC) and spectrophotometric methods for determining the masses' ratios "volatile component/dye component" in ink that decrease with the age of inks (procedure 2); a GC method of determining the extent of extraction of ink volatile components that decreases as ink ages on paper (procedure 3); a thin-layer chromatographic method for determining age changes in resins and other colorless nonvolatile ballpoint ink components: these changes are detected by observing the resulting thin-layer chromatograms under UV illumination and can be evaluated by using scanning densitometry (procedure 4). Suggestions for further work are proposed.

KEYWORDS: questioned documents, ballpoint inks, relative aging, chemical reagents, microspectrophotometry, thin-layer chromatography, densitometry, gas chromatography, spectrophotometry, solvent extraction, paper, dyes, resins, volatile components, ratios

Ink age determination is one of the very complex forensic problems. Recently, the state-of-the-art in the field of ballpoint ink dating has been critically evaluated by Brunelle and Cantu in their comprehensive reviews [1,2]. In these reviews, special attention was paid to several approaches determining the dynamic characteristics of ballpoint ink aging [3–9].

This paper also deals with the dynamic characteristics of ink aging. It introduces four techniques (described in the following sections) for estimating the length of time an ink has been on a document.

All examples described in this paper deal with determining the relative age of ballpoint ink entries that had been placed periodically on paper sheets during a certain period of time (over six years, maximum) and stored under controlled environmental conditions (the ambient temperature of the metal safe in which samples were stored ranged between 17° and 23°C).

Theory

Ballpoint inks are complex mixtures of vehicles, dyes, synthetic resins, polymers, and other organic compounds that begin changing or evaporating as soon as the ink is placed on a paper. The rates of these processes are significantly different. Thus, it is evident that evaporation of volatile components is very intensive initially and then it decreases quickly in the first hours and days after a ballpoint ink have been applicated on a paper while oxidation, cross-linking and other similar processes go slowly, with more or less steady rates (provided ink is not heated [10] or exposed to light [11]). These rates depend on many factors—environmental ones, formula and nature of the components of ballpoint ink analyzed, an ink line thickness (depth of the film of the writing), etc. All this must be under consideration when determining the age of questioned ink is performed. So an analyst should have a working knowledge on peculiarities of ballpoint ink manufacture, nature of ink components and their possible behavior during the aging process (this aspect of the ink dating problem has been described completely by Brunelle and Cantu [12]).

Ink Age Determination by Using Volatile Chemicals

One of the first techniques using chemical tests for ink dating was introduced by Mitchell [13], who investigated reactions of iron gallotannate inks with some chemicals. In particular, he showed that when using a reducing agent—oxalic acid—the rate of bleaching of freshly written inks was much higher than that of inks that were several years old.

In 1983, Dr. Tamara I. Saphronenko supplied the author with the technique for dating ink that was based on Mitchell's approach. Her method used a water solution of a mixture of iodine, potassium iodide, and magnesium chloride, as a reagent allowing discrimination between "fresh" (about one month old) and "old" writings made by blue and violet fountain pen inks produced in the former Soviet Union. The procedure included spotting of the reagent micro drop onto a questioned ink line, removing that drop in approximately a minute, and observing an ink color: fresh inks were becoming deeply black, whereas old ones were showing moderately gray color.

These works provided the basis for the reagent–photometric technique presented in this paper. This technique uses comparatively volatile strong organic bases like benzylamine or piperidine as reagents capable to cause reversible bleaching or changing the color of ballpoint inks, and microphotometric detection of corresponding changes of ink reflectivity at a certain analytical wavelength preliminary determined for the ink analyzed.

Experimental Procedure

Ink Samples—Lines of a "Soyuz" (produced in the former Soviet Union) blue-violet ballpoint ink have been placed on a white paper for notes during about six years.

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 "U0-6.5 × 0.12"; wavelength range— 400 to 700 nm; monochromator half bandwidth—3 nm; lamp current—7A; photomultiplier output—500 V. A Goerz Metrawatt (Austria) SE-120 chart recorder; chart speed— 1 cm/min.

Homemade Tools—A reaction chamber specially designed for examining color changing reactions of inks with volatile chemicals. The chamber has a hole in its bottom, a transparent cover made of glass, and two, inlet and outlet, vents.

Choice of Reagents—A lot of acidic, basic, reducing, and oxidizing agents were tested with the aim of finding such chemicals that would allow discrimination between "old" and "fresh" ballpoint ink entries. Some of them that gave more or less positive results follow.

Iodine Fumes—after several minutes of exposition in the reagent fumes most of blue and violet ballpoint inks analyzed were becoming black. After the reagent was removed the initial color practically recovered but it took a long period of time (several hours). This reagent does not seem a satisfactory one to be used in the procedure described.

Nitrogen Dioxide and Hydrogen Chloride—in small concentrations they reversibly change colors of some ballpoint inks. However, these substances are too toxic and corrosive to be used as routine reagents for ink analysis.

Benzylamine and Piperidine—these organic bases were chosen from a wide range of amines (some of those, like triethylamine, dipropylamine, or butylamine, showed unsatisfactory effects of reactions with inks, the others like 25% ammonia or dicyclohexylamine did not change the color of many tested ballpoint inks at all). They seem to be the most promising ones as agents for using in the procedure of ink age determination described below (though unfortunately they are toxic and so corresponding precautions should be taken when working with them). Their action is based on reversible decolorizing ink dyes (mainly, triarylmethane compounds) or perhaps, on changing color and/or brightness of some ink dyes as a result of the formation of "dye-reagent" charge transfer complexes.

A Procedure—The procedure based on using a comparatively volatile strong organic base (like benzylamine or piperidine) as a ballpoint ink color changing reagent includes the following operations.

At first, the questioned (Q) ink formulation is established by using TLC (see, for example [14,15]) and the formulation information obtained from the ink's manufacturers.[2] If such an ink with the same formula as that of the Q one is available it is used to apply a "fresh" entry on a paper that is then examined as follows.

A piece of paper with a fresh ink entry is placed into a colorless transparent flask, for example, into a 10 mL Pierce (The Netherlands) Reaction Flask, after a drop of a basic reagent had been spotted onto a bottom of the flask. The flask is capped and possible ink color changes are observed. The best candidate (for which the most satisfied effect of the reaction has been obtained) is used as a reagent for carrying out the following ink age determination procedure.

Reflectance spectra of the "fresh" known ink entry are recorded before (spectrum 1) and after (spectrum 2) reaction with the reagent using a microscope photometer. A wavelength is chosen as the analytical one at which the maximal change of reflectance intensity has been detected for compared spectra 1 and 2 (see Fig. 1).

At the next step of the procedure the rates of chemical reaction between colored components of the known ink entries written during a certain period of time and the reagent are determined using the equipment shown in Fig. 2.

For this a piece of paper with every known ink entry (5) is mounted on the stage of a microscope photometer (6) and a site of the entry chosen by an examiner is brought into focus (care should be taken to avoid obvious faults in the measuring sites of the ink surface). A chamber (4) like the one described above, is placed on the paper and the site is refocused. Then a carrier gas (nitrogen or helium are preferable) is supplied from a reservoir (1) with a predetermined velocity (it is very important to stress that this velocity should be kept constant during the analysis and optimal for given setup, tem-

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[2]These operations are to be done at the beginning of all the procedures described in this paper.
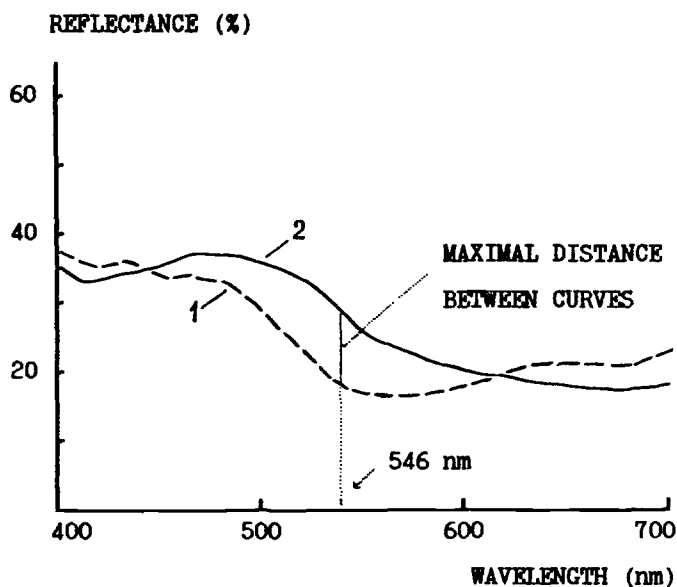
REFLECTANCE (%)

FIG. 1—*Visible spectra of a Soyuz blue-violet ballpoint ink before (1) and after (2) reaction with piperidine.*
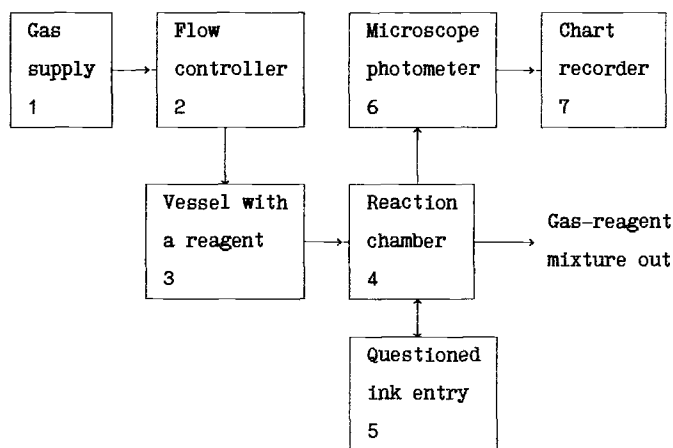

FIG. 2—*Basic assembly for the reagent-photometric technique.*

perature, and nature of the dye components of the ballpoint ink analyzed) into a vessel (3) where it is mixed with the reagent. The obtaining mixture goes through the chamber causing the color changes of the ink analyzed. These changes are being measured at the previously chosen analytical wavelength by the photometer system of the microspectro-photometer and depicted on the diagram of a chart recorder (7) as it is shown in Fig. 3.

The values of the rate of the reaction with the reagent determined for all known ink entries are plotted versus the age of these entries (as it is shown in Fig. 4). Using this "aging curve" the age of the Q entry analyzed by the same way described above, is determined as it is indicated in Fig. 4.

SIGNAL OUTPUT (mV)

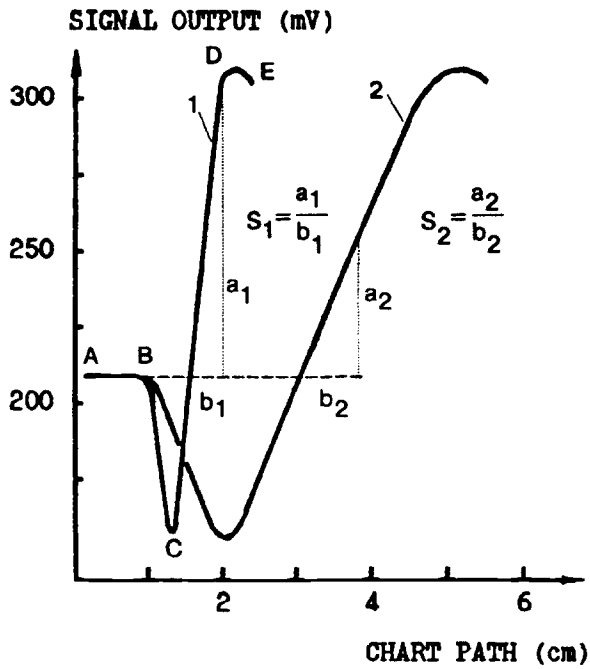

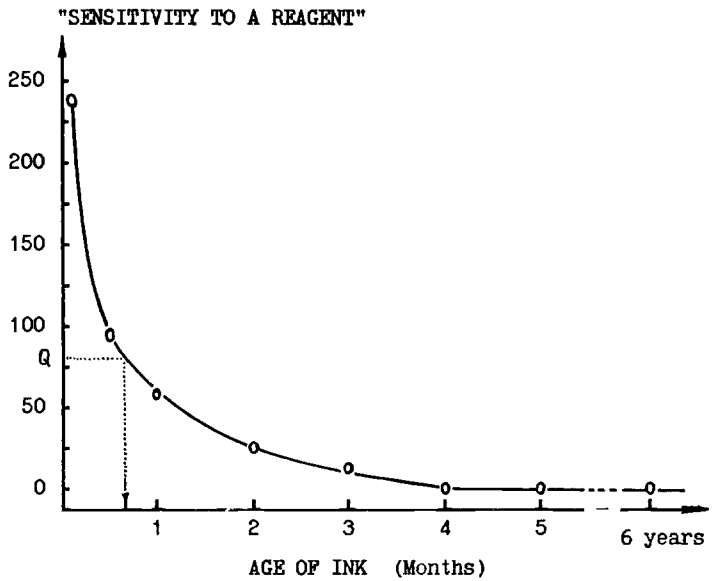FIG. 3—*"Reaction curves" obtained for the Soyuz ink writings of one-day (1) and one-month (2) ages.*

"SENSITIVITY TO A REAGENT"

FIG. 4—*Aging curve obtained for a Soyuz blue-violet ballpoint ink using the reagent-photometric technique.*

Vehicle-to-dye
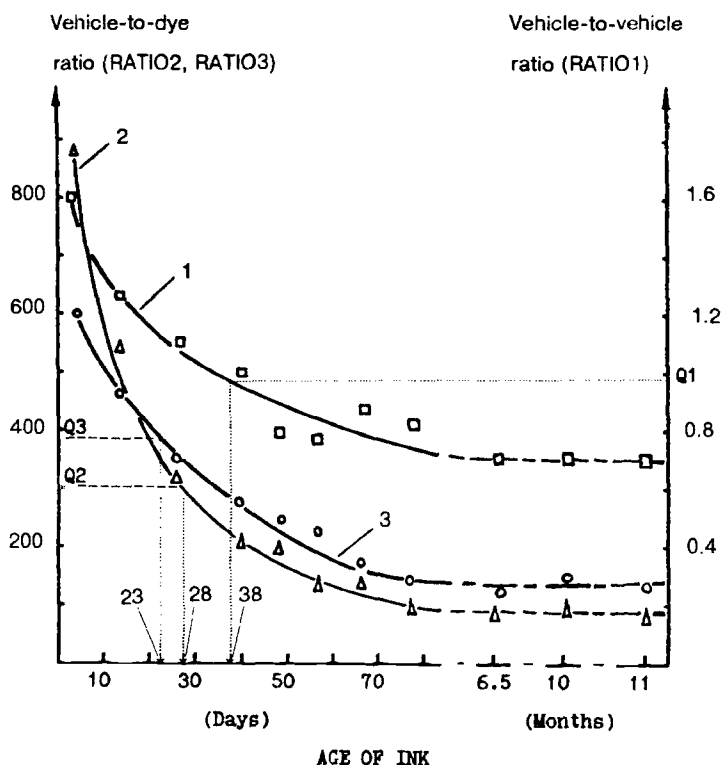
ratio (RATIO2, RATIO3)

Vehicle-to-vehicle

ratio (RATIO1)

FIG. 5—*Aging curves for a violet ballpoint ink (made in Italy) and the Q entry age determination: the values of RATIOs 1-3 were calculated by using Eqs. 1-3.*

Example—Entries known to have been written by a Soyuz blue-violet ballpoint ink during about six-year period were examined. The ages of these entries were 1 day, 1, 2, 3, 4, and 5 months, and 6 years. For these entries the "reaction curves" (like those depicted in Fig. 3 for one-day and one-month old entries) were recorded according to the above mentioned recommendations. For recording these reaction curves (at the previously chosen analytical wavelength, 546 nm; see Fig. 1) the measuring sites of the entries analyzed which seemed similar in thickness, homogeneity, and surface characteristics were selected under the microscope.

Then for every sample analyzed the value of "sensitivity (S) to a reagent" was calculated as the ratio of the change in the recorder signal (in mV) and the respective change in the chart path (in cm) within a linear portion of the recorder signal-vs-chart path graph (as it is shown in Fig. 3 for two samples analyzed: $S_1 = a_1/b_1 = 240$ mV/cm—for one-day old ink, and $S_2 = a_2/b_2 = 58$ mV/cm—for one-month old ink).

The calculated S-values were plotted versus the age of the corresponding ink entries analyzed (Fig. 4).

Results and Discussion

Figure 3 shows the "reaction curves" obtained for one-day (curve 1) and one-month old (curve 2) entries, respectively, written by a Soyuz blue-violet ballpoint ink.

These curves include four parts which can be characterized as follows (see curve 1 in Fig. 3):

A-B . . . reagent vapors do not contact with ink analyzed;

B-C and D-E . . . gloss of the ink surface is decreased and so reflectance goes down;

C-D . . . the ink is discolorated and so reflectance goes up.

It is clearly seen from Fig. 3 that the value of "sensitivity (S) to a reagent" characterizing the rate of the reaction between the reagent and ink's dye components, is higher for the newer, 1-day-old, writing as compared to that for the older, 1-month-old, one ($S_1 > S_2$). As such a situation is a typical one for ballpoint inks containing dye components capable of changing their color in the presence of some reagents, the above mentioned sensitivity can be considered as an "aging parameter" (the term was introduced in [10]).

Fig. 4 represents the aging curve of a Soyuz blue-violet ballpoint ink using the described reagent-photometric procedure. The curve showed significant aging taking place over a period of about three months. It means that the age of questioned inks of the same formula could be accurately estimated up to 3 months if, of course, those inks have been stored under normal known conditions.

A lot of ballpoint inks of different ages have been analyzed by using the described technique. The technique has been found applicable to most of the inks examined except those which do not contain colored arylmethane compounds (and some other dyes capable of changing their color in the presence of the basic reagents), like a brilliant blue Bic ballpoint ink that contains only phthalocyanine dyes, which do not react with the basic reagents used in the described technique.

It should be also noted that this technique is non-destructive because inks being exposed to the reagent vapors recover their initial colors. Furthermore, the recovering rate is also a function of the age of ink: the older the ink, the less the recovering rate.

At the end of this section it is necessary to stress some things important for correct application of the discussed technique. In the first place, the color or texture of the support may influence drastically the results of microspectrophotometric measurements, and this should be remembered when placing fresh ink samples on a paper or choosing reference ink writings from an ink library file.

Secondly, the measuring sites of all ink entries that are to be analyzed, known and questioned ones, should be chosen as similar as possible with respect to their thickness (depth), homogeneity (homogeneous distribution of the ink substance), and surface characteristics (morphology, gloss, and so on).[3]

Ballpoint Ink Age Determination by Volatile Components Comparison. Vehicle-to-Dye Approach

In 1985, Stewart [9] proposed a technique for comparing the relative age of ballpoint inks. This technique included extraction and formulation identification of the questioned ink, qualitative determination of the volatile components of the ink using a method of gas chromatography (GC), calculation of the relative proportions of these volatile ingredients and age determination of the Q ink by comparison of the relative concentrations of its volatile components with those of known inks (age) of the same formulation.

Later, this method was modified for ballpoint inks that included phenoxyethanol and a phthalocyanine dye [16]. The main idea of that method was to measure the amount of phenoxyethanol using GC with thermodesorbtion of volatile components from ink entry followed by spectrophotometric determination of the phthalocyanine dye extracted from

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[3]Despite the fact that this technique can be considered as mass independent since it involves rates, it is highly dependent on these appearance factors. The other three techniques (also mass independent) described in this paper are less dependent on these appearance factors.

the same entry. However, that method cannot be applied to ballpoint inks containing solvents which boil higher than phenoxyethanol. For fast quantitative transmission of such solvents into vapor state ink samples removed from a questioned document have to be heated at the temperature higher than 200°C: in that case the resulting chromatogram profile would be distorted drastically by the paper's thermodecomposition products.

The technique proposed in this paper accumulates the advantages of the above mentioned methods [9,16] and does not depend on the nature of vehicles and dyes contained in dried ballpoint inks. It is based on measuring the amount of all available volatile components and of any colored one of dried ink, on determining all relevant vehicle-to-vehicle ratios (as it is suggested in [9]) and ratios of every vehicle and the colored component chosen, and on comparing the calculated ratios' values with those obtained for known ink of the same formula.

Experimental Procedure

Ink Samples—Lines of a violet ballpoint ink (made in Italy) have been placed on a white paper for notes during a year.

Sampling Devices—A safety razor and a syringe needle, 1 mm I.D., with a plunger to remove bored out samples.

Extracting Vessels—Camag (Switzerland) micro vials (N-11 polypropilene) with cone shaped interiors, a 10 µL Hamilton (USA) syringe.

Instruments—A Hewlett-Packard (USA) Model 5890 gas chromatograph equipped with a flame ionization detector (FID) and HP split/splitless injection system; a Carl Zeiss Jena (Germany) Model M-40 UV-VIS spectrophotometer.

GC Conditions—Column: SCOT, SP-1000 (polyethylene glycol 20M terminated with nitro-terephtalic acid; Supelco, Inc., USA), 25 m × 0.5 mm I.D. Carrier: Nitrogen, 4 psi, 40 mL/min. Oven: 50°C (0.5 min) + 10°C/min = 220°C (6 min). Injection: 2 µL, splitless, $T = 250$°C. Detector: FID, $T = 250$°C.

Procedure—The first step of the procedure includes the identification of a questioned ink formulation using methods of TLC and GC (or gas chromatography—mass spectrometry for unknown volatile components identification) and formulation information obtained from the ink's manufacturers. Then samples of the Q entry and entries written by the chosen ink of the same formula (with known ages) are removed by a micro-pellet technique [14] or cut out with a sharp razor blade (entries of about 2 cm in length[4]) and analyzed by using GC and spectrophotometric methods as follows.

Every sample is extracted in a vial with a solution of an appropriate substance used as an internal standard. At the end of the extraction process about 2 µL aliquot for every sample is removed and analyzed by GC. The mass (m) of any volatile components detected in the ink samples analyzed is calculated by means of the internal standard method.

The same samples are extracted in a strong solvent like dimethylformamide or pyridine, and the absorption spectra of the colored extracts obtained are recorded. The absorbance (A) measured at the absorption maximum of a dye presented in the ink analyzed is read for every sample, and the ratio of "m/A" is calculated.

If the chromatogram of an ink analyzed has at least two peaks corresponding to appropriate volatile components, X and Y, then three aging parameters can be estimated: the value (Ratio 1) directly proportional to the masses' ratio of those components that

[4]Samples of 1 cm in length of ink line can be used if the methods of microanalysis mentioned at the end of section on Ballpoint Ink Age Determination by Volatile Components Comparison are applied for quantitative determination of ink dyes.

is determined by ratioing one peak area to the other (as it was proposed in the work [9]):

$$\text{Ratio } 1 = (\text{Peakarea}_X)/(\text{Peakarea}_Y) \tag{1}$$

and, besides, the two following vehicle-to-dye ratios:

$$\text{Ratio } 2 = m_X/A \tag{2}$$

$$\text{Ratio } 3 = m_Y/A \tag{3}$$

Finally, "aging curves" (like curves 1 to 3 in Fig. 5) for the known ink can be obtained from those three sets of Ratios plotted versus actual age, and using these aging curves, the age of the Q entry can be evaluated as a mean value of the three results obtained for this entry by means of the vehicle-to-vehicle [9] and vehicle-to-dye ratio techniques (like it is shown in Fig. 5).

The following example illustrates this procedure.

Example—Entries known to have been written by the violet ballpoint ink (made in Italy) were examined. The ages of these entries were 4, 13, 26, 40, 48, 57, 67, and 78 days, and 6.5, 10, and 11 months.

Every sample (2 cm slivers) was extracted in a vial with 15 μL of carbon tetrachloride containing methylstearate (25 mg/mL) as an internal standard). The extraction time was 60 minutes.

About 2 μL aliquot for every sample was removed and analyzed by GC. In each sample two volatile components of the ink—phenoxyethanol (component X) and phenoxy-ethoxyethanol (component Y)—were detected, and their masses (m_X and m_Y) were calculated. The value of Ratio 1 was also calculated for each sample.

The samples were removed from the extracting solutions and dried. Then they were extracted with 1.2 mL of dimethylformamide and the absorption spectra of the colored extracts obtained were recorded. For every sample the absorbance (A) measured at $\lambda = 595$ nm (the absorption maximum of methyl violet—the main color ingredient of the ink analyzed) was read and the values of Ratio 2 and Ratio 3 were calculated.

The obtained three sets of Ratios were plotted versus actual age of the known ink entries (see curves 1 to 3 in Fig. 5).

After that the 29-day-old entry written by the same ink was analyzed (as a Q entry) in the same way as the known entries. The values of Ratio 1 (Q1), Ratio 2 (Q2), and Ratio 3 (Q3) were obtained for the Q entry, and using the previously plotted aging curves, the age of this entry (approximately 30 days) was determined as the arithmetic mean of 38 (Q1), 28 (Q2), and 23 (Q3) (see Fig. 5).

Results and Discussion

Figure 5 shows three "aging curves" obtained for a violet ballpoint ink (made in Italy) by using vehicle-to-vehicle (curve 1) and vehicle-to-dye (curves 2 and 3) ratio techniques and the way to use these curves to determine the age of Q entries.

The example described illustrates a case when two volatile components of the ink analyzed were determined.[5] In similar cases the use of three "aging curves" like those depicted in Fig. 5 can enhance the reliability of the results of dating inks. Moreover, the

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[5]Since sensitivity of the detector to one of the volatile component (phenoxyethanol) was a little bit more than that to the other (phenoxyethoxyethanol), the values of Ratio 1 were some more than corresponding values of Ratio 2/Ratio 3 (see Fig. 5).

use of the combination of these techniques can help to diminish possible misinterpretations of the results of dating ink, especially in cases when, as the author's own practice showed, bad correlation is observed between the ages of writings and corresponding values of vehicle-to-vehicle ratios obtained.

And of course, contrary to the vehicle-to-vehicle ratio technique [9], the proposed vehicle-to-dye ratio technique is applicable in frequently encountered cases when only one volatile component can be determined in an aging ink.

The obvious shortcoming of the described vehicle-to-dye ratio technique is the necessity to remove about 2 cm of inks from questioned documents (in order to obtain correctly measurable absorptivity values of dyes in the inks' extracts).

To overcome this shortcoming some other analytical methods for quantitation of dyes in ink extracts can be applied, such as microspectrophotometry, densitometic TLC, or spectrophotometry combined with beam condensing systems and micro cuvettes. With help of these methods samples of 1-cm of ink lines are quite enough to be examined by using the proposed vehicle-to-dye ratio technique.

Ballpoint Ink Age Determination by Volatile Components Comparison.
Sequential Solvent Extraction Approach

The method of sequential solvent extraction of the colored (nonvolatile) components of aging inks has been developed by Cantu [3,4] and then comprehensively described by Cantu and Prough in the work [5].

A new ballpoint ink age determination technique described in this Section is based on the principles of the above mentioned method [5] and deals with ink's volatile components.

The technique includes the sequential extraction procedure in which one solvent ("weak") extracts volatile components of an aging ink with the extent of extraction depending on the ink age, while another solvent ("strong") extracts these volatile components practically completely from both, fresh and old, entries written by ballpoint inks of the same formula.

Experimental Procedure

Ink Samples—Up to 15-years old entries written by Soyuz blue-violet ballpoint inks of the same formula.

Tools, GC Equipment and Chromatographic Conditions—were the same as those described in the previous section.

Procedure—Approximately 10 micro discs (1 mm diameter) or about a 1-cm sliver of ink on paper are removed using a boring device or a safety razor, respectively, and placed in a micro vial with cone shaped interior. 10 μL of a "slowly extracting weak" solvent containing a certain substance as an internal standard is added and the vial is capped.

In a certain period of time (usually not more than 60 min) about 2 μL of the extract is taken for GC analysis.

The sample is removed from the extracting solution, dried and placed into another micro vial. The second extraction is carried out with 10 μL of a "fast extracting strong" solvent also containing an internal standard (the same or, preferably, another one). About 2 μL of the extract is removed and analyzed by GC.

Then the masses of a vehicle component determined in each of the two extracts analyzed (*M*1 and *M*2 for the first and second extractions, respectively) are calculated by means of the internal standard method, and "percent extraction" (see [5]), that in the present work means the percent of the mass of the ink vehicle component (%M) extracted in

the "weak" solvent (relative to its total amount contained in the sample analyzed), is calculated as follows:

$$\%M = M1/(M1 + M2) \times 100 \tag{4}$$

The values of %M obtained for all samples analyzed are plotted versus the age of these samples (as it is shown in Fig. 6). Using such a percent extraction aging curve the age of the Q entry analyzed by the described way, can be determined (see Fig. 6).

Example—Entries known to have been written by Soyuz blue-violet ballpoint inks of the same formula were examined. The ages of these entries were 2, 10, and 27 days, 2, 3, 4, and 5 months, 6, 12, and 15 years.

Every sample (1 cm slivers) was placed into a Camag micro vial with cone shaped interior and extracted for 60 min with 10 μL of carbon tetrachloride ("slowly extracting weak" solvent) containing methylstearate (25 mg/mL) as an internal standard. About 2 μL of every extract was taken for GC analysis.

The samples were removed from the extracting solutions, dried and placed into other micro vials. The second extraction was carried out for 2 min with 10 μL of chloroform ("fast extracting strong" solvent) also containing methylstearate in the same concentration. About 2 μL of every extract was removed and analyzed by GC.

Then the masses of phenoxyethanol (the only volatile component reliably detected in all ink samples analyzed) contained in each of the two extracts obtained for every sample analyzed were calculated, and the "percent extraction" of phenoxyethanol (%M) was determined by using Eq (4).
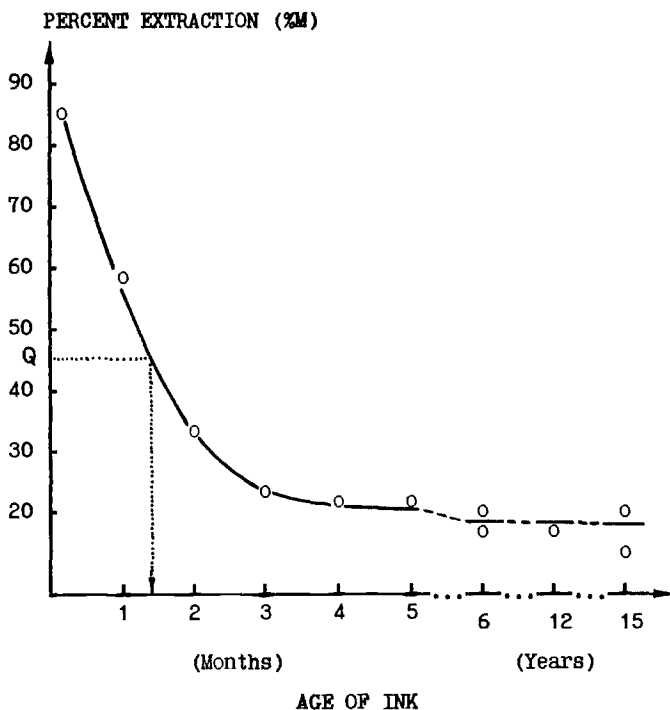

FIG. 6—*Aging curve obtained for Soyuz blue-violet ballpoint inks of the same formula using the sequantial extraction procedure.*

The values of %M obtained for all samples analyzed were plotted versus the age of these samples (see Fig. 6).

Results and Discussion

Figure 6 represents the aging curve obtained for Soyuz blue-violet ballpoint inks of the same formula. The curve shows significant aging taking place over a period of about 3 months. After this period until the age of 15 years the extent of the extraction of the volatile component (phenoxyethanol) from the ink entries has been kept at a level of about 20%.

This experimental result characterizing the mechanism of evaporating volatile components (like phenoxyethanol, phenoxyethoxyethanol and so on high boiling vehicles frequently used as the ingredients of ballpoint inks) from aging inks can be interpreted as follows. The process of such evaporation is carried out from the surface of ink line placed on a paper. To reach the ink line surface a vehicle must diffuse from the inner layers of the line. However, resins and other viscous ballpoint ink ingredients limit a diffusion process (to some extent, of course). In addition, as soon as the reaction of cross-linking or polymerization of these ingredients has started, those diffusion processes are getting more and more slow, and at a certain stage of ink aging they stop completely "keeping" the remained micro drops of the ink volatile components inside the aging ink line for a practically infinite period of time (or until extracting by a solvent or heating[6] "frees" them).

So when using a strong solvent capable to dissolve hardened ink resins (like chloroform used in the example discussed), those vehicle remainders can be easily detected even in very old ballpoint ink writings (Fig. 6 demonstrates it for 12- and 15-year-old entries written by Soyuz blue-violet ballpoint inks of the same formula). Hence, by this way it can be possible to obtain additional information about formulations of old questioned inks or to try solving other forensic tasks, for example, like that mentioned in footnote 6.

A different situation takes place when a "weak" (with regard to hardened ink resins) solvent is used. It cannot penetrate into an old ink line, so it extracts ink volatile components only from outside layers of the ink line. But the newer the ink, the more outside ink layers (up to the whole ink material for fresh inks) become available for the weak solvent, and hence, the more quantity of volatile components is extracted.

Returning to Fig. 6 one can see that the above considered tendency, indeed, characterizes the behavior of a weak solvent: the extracting efficiency of carbon tetrachloride decreased from about 90% (fresh writings) to about 20% (old writings).

The proposed method has shown good efficiency for dating ballpoint inks which contain comparatively high boiling vehicles (those that boil higher than 200°C). At the same time, when using this technique one should remember that samples of approximately equal thickness (depth) of ink line are to be taken from questioned and known ink entries. It seems quite obvious because thicker lines "store" more ink volatile components than thinner ones.

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[6]The present author has found that high boiling vehicles cannot be completely removed from ballpoint inks by their heating (without damage of the paper on which the inks have been placed). Besides, it has been noted that heating (accelerated aging) of the inks often leads to much more extent of evaporation of their high boiling volatile components (approximately 10 to 100 times greater) than it takes place at the result of long natural aging of these inks. In this connection, a procedure has been developed that can enable discrimination between naturally and artificially aged inks of the same formula. The procedure (it will be described in the next publication) was successfully used in the author's expert practice to establish a fraudulent nature of questioned documents (those that had been artificially aged).

Determining Age Changes of Nonvolatile Colorless Components of Ballpoint Inks

As a rule, synthetic resins and polymers are mixtures of oligomers and other compounds of different stability. So it can be supposed that detectable changes in relative content of these components or even in their qualitative composition may occur when ink ages. This suggestion was confirmed in the present work by studying an aging process of several ballpoint inks of different formulations.

The proposed procedure is based on a TLC separation of colorless nonvolatile ingredients of ballpoint inks of known and Q ages and the assessment of the resulting chromatograms under UV illumination. (The procedure of densitometric evaluation of the resulting chromatograms is also being developed. The procedure includes the modified peak ratioing technique described partly in [17] that is less mass dependent and so more correct than the well-known peak signal-to-peak signal ratio technique [7,18]).

Experimental Procedure

Ink Samples—Lines of a Parker blue ballpoint ink and Soyuz blue-violet ballpoint ink have been placed on a white paper for notes for a period of six years.

TLC Materials—High-performance (HP) TLC silica gel 60-F_{254} (10 × 10 cm) precoated glass plates (Merck, Germany) and also thin-layer plates of 10 × 10 cm cut out from precoated Merck TLC silica gel 60-F_{254} aluminum backed 20 × 20 cm plates.

Procedure—Samples (4-cm slivers[7]) of the known ink having the same formula with the Q ink are placed into cone shaped micro vials and extracted with chloroform, carbon tetrachloride, or some other suitable solvent. The extracts obtained are applied onto a precoated TLC or HPTLC plate with fluorescent indicator. The plate is developed in an eluent capable, on the one hand, to separate colorless components of the ink examined and, on the other hand, to prevent overlapping of the zones of these components and of those extracted from a paper.[8]

The resulting chromatogram is observed under UV illumination (254 and 366 nm) to detect the location of the zones of colorless non-volatile components of the ink analyzed.

If not less than two such zones have been detected (within a chromatographic track corresponding to a sample of the ink entry of a certain age), then possible correlations between relative proportion of any two of these colorless components and the age of the analyzed ink entry is determined by means of visual "semiquantitative" assessment [18] or by evaluating the relative proportion of the two chosen components of the known and Q inks with the aid of scanning densitometry (some limitations of this technique are considered below).

After a correlation "relative content of two components—age of ink" has been established the second stage of the procedure is carried out. It includes the same operations described above but now samples (2 cm slivers, for HPTLC, or 4 cm slivers, for TLC) are taken from the ink entries of known and Q age.

Finally, the age of the Q entry is determined by comparing the corresponding data obtained for the Q and known entries.

The capabilities of this approach are illustrated by the following examples.

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[7]Sample sizes can be sufficiently diminished if HPTLC plates are used instead of TLC plates and if a procedure for sensible visualization of separated zones of ink colorless components is applied.

[8]For several ballpoint inks from the collection of the author the mobile phases consisting of acetone and low boiling saturated carbohydrates, with or without low boiling alcohols, showed good efficiency and selectivity (see *Example*). But in general, the composition of an eluent depends on the nature of colorless components of the ballpoint ink analyzed.

Example—Entries of known ages (up to six-year-old) written by a Parker blue ballpoint ink and Soyuz blue-violet ballpoint ink were examined.

Every sample (4 cm slivers) were placed into a micro vial with cone shaped interior and extracted for 2 min with 20 μL of chloroform (extraction in carbon tetrachloride during about 60 min also gave good results). The obtained colored extracts (as chloroform dissolved the dyes of the ballpoint ink analyzed) were applied with the help of glass capillaries onto 10 × 10 cm TLC plates cut out from a precoated Merck TLC silica gel 60-F_{254} aluminum backed 20 × 20 cm plate.

The samples taken from the Soyuz blue-violet ballpoint ink entries were eluted in a solvent system of acetone—hexane (1:4, v/v), and the ones taken from Parker blue ballpoint ink entries were chromatographed in a mixture of acetone—hexane—ethanol (5:20:1, v/v).

The resulting chromatograms as viewed under UV light at 254 nm are depicted in Figs. 7 and 8.

Results and Discussion

Figures 7 and 8 demonstrate the view under UV illumination of thin-layer chromatograms of samples taken from the entries of known ages written by a Parker blue ballpoint and Soyuz blue-violet ballpoint ink, respectively. A to D point out separated colorless components of the inks analyzed. The other spots in the chromatograms correspond mainly to the substances extracted from the paper on which the analyzed inks had been placed.

For the Parker ink (Fig. 7) the link between the relative proportion of substances A (R_f value was about 0.4 in this development) and B (R_f value was about 0.25) and the age of the ink writings examined is quite obvious even by means of a visual assessment: ratio "substance A/substance B" gradually increases as the ink ages (it is minimum for the fresh, one-day old entry—the first track in Fig. 7, and maximum for the six-year old entry—the fifth track in Fig. 7).

This example shows that the eluting solvent applied is selective enough for the given "ink–paper" system.
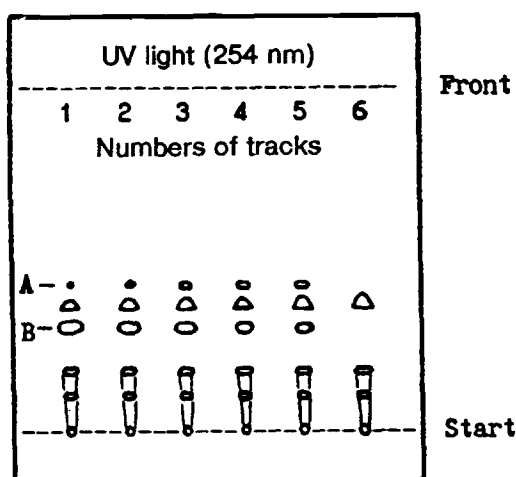

FIG. 7—*Thin-layer chromatogram obtained for the extracts from the Parker blue ballpoint ink entries of different ages (under UV 254 nm): 1—one day; 2—one month; 3—one year; 4—three years; 5—six years; 6—paper.*
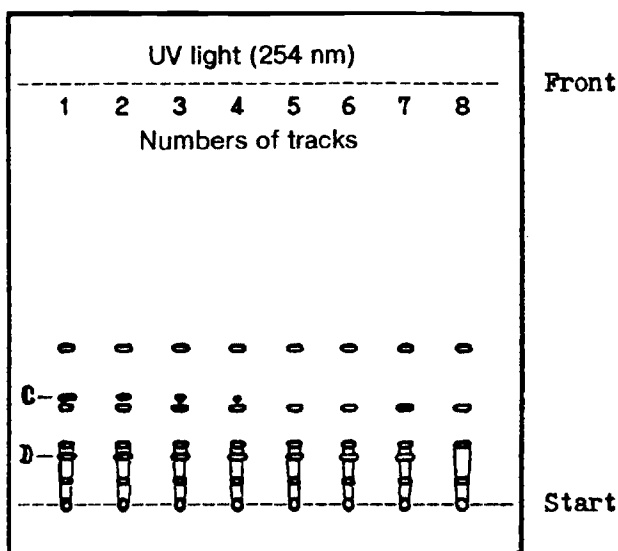
FIG. 8—*Thin-layer chromatogram obtained for the extracts from the Soyus blue-violet ballpoint ink entries of different ages (under UV 254 nm): 1—one day; 2—one month; 3—five months; 4—one year; 5—one-and-a-half year; 6—two years; 7—six years; 8—paper.*

The next example (Fig. 8) illustrates another situation. There are two colorless components, C and D, on the chromatogram which are the fractions of phenoloformaldehyde resin of the Soyuz ink analyzed. It is seen that the relative proportions of these components change as the ink ages leveling off after about a year and a half since the ink has been placed on paper. The problem is that only component C (R_f value was about 0.2 in this development) is located in a "pure" part of a chromatographic track, whereas a zone of component D (R_f value was about 0.1) is overlapped by the zones of the paper's ingredients.

In this particular case such overlapping is not too critical because the D zone dominates over less UV light absorbing tailed spots of the paper's extracted ingredients (furthermore, in this particular case the component D can be converted into a strongly light absorbing derivative by a reaction with diazotized amines). But, of course, in general such a situation is not desirable, especially in connection with the necessity of applying the densitometric evaluation of chromatograms for calculating relative contents of analyzed ink colorless components and subsequent obtaining corresponding aging curves (by plotting the ratios determined for each known dated ink sample versus age).

So the last example illustrates difficulties that may occur when using this technique and shows that preliminary studying of chromatographic behavior of the known inks' colorless components in the presence of substances extracted from the paper on which the ink had been placed, should be considered as a necessary and important part of this approach.

Another important thing should be mentioned in connection with using of densitometric thin-layer chromatography for evaluating the relative proportions of the ingredients of samples analyzed. The matter is that the widespread peak signal-to-peak signal ratio technique, though it sometimes seems quite applicable (see, for example, the works [7,18]), often produces statistically bad results [17–19].

In fact, using this technique an analyst must be confident that in his or her case of comparing separated samples the obtaining relationship between signal output (peak

height or peak area) and the content of a separated zone is well approximated either by the function

$$\text{Signal} = \text{empirical constant} \times \text{content} \tag{5}$$

that is a form of Beer's law [20], or by the function

$$\text{Signal} = \text{empirical constant/content} \tag{6}$$

because only in such cases the signal-to-signal ratio technique is, in fact, mass invariant.

However, in many works (see, for example [19,21] devoted to studying "signal-content" relationships in TLC it has been shown that this is not so and it was demonstrated that other functions like different polynomials or the Michaelis-Menten function gave much better results.

In connection to this an attempt of improving the signal-to-signal ratio technique has been made in the work [17].[9] Basing on the result of this work, a TLC method including an "improved" signal-to-signal ratio technique with the corresponding software is now being developed by the author and will be described in the next publication.

The procedure considered in this Section uses ink samples of more than 1 cm length of ballpoint ink line. Therefore, the work on improving the analysis' procedure is being carried out with the aim to increase the sensitivity of the detection of ballpoint inks' colorless non-volatile ingredients, for example by chemical reaction on the plate.

Conclusion

The four techniques considered in this paper can be used effectively for determining the relative age of entries written by ballpoint inks on the same piece of paper. In some cases (when the conditions of ink aging are known) these methods can also be applied to determining the absolute age of ink.

Of course, these techniques can be applied only to the ink entries aging in darkness and within the known temperature interval. Knowledge of aging conditions is extremely important and allows to avoid gross mistakes when interpreting the results of the examination of ink dating.

Further work is necessary for testing the application capabilities of the described techniques on a wide range of ballpoint inks that are in the market. Besides, some other works on ink aging problem which include a study of degradation of ink colored components as the ink ages and developing the above mentioned "improved signal-to-signal ratio technique" are now in preparation.

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