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## Age Determination of Ballpoint Pen Ink by Thermal Desorption and Gas Chromatography–Mass Spectrometry\*

**ABSTRACT:** Two main approaches can be used for determining the age of an ink: indirect dating and direct dating. Indirect dating is based on the chemical analysis of an ink followed by comparison with known samples in a reference collection. The collection should contain information about the inks including the market introduction dates. This approach may allow for an anachronism to be detected. The second concept is based on measuring ink components that change with age. The analysis of solvents in ballpoint inks may be a useful parameter for determining the age of ink on paper. In a previous study, the authors demonstrated that thermal desorption of ink directly from paper, followed by chemical analysis using gas chromatography–mass spectrometry (GC–MS), is a promising procedure for characterizing ink-binder resins and solvents. Preliminary tests showed that monitoring the evaporation of ink solvent from ink on paper is not a suitable method for ink dating. Thermal analysis of ink on paper in two steps revealed that fresh ink releases a relative amount of solvent at a certain low temperature in a defined period of time, which decreases as the ink ages. As a consequence, this relative amount of solvent released at a certain low temperature, and its decrease with time, can be used to estimate ink age. This age-dependent parameter was studied in 85 different inks ranging in age from 1 week to 1.5 years. It was found that some inks showed a significant decrease of this parameter up to an age of several months, and that the aging process can be monitored within this period. For other inks, however, the age-dependent parameter decreases relatively fast, e.g., within a few days, to a constant level, which can be too fast for casework. Based on these results, a general procedure for assessing the age of ballpoint pen inks on paper was developed.

**KEYWORDS:** forensic science, questioned documents, ink dating, age determination, ink, resin, gas chromatography–mass spectrometry, thermal desorption, volatiles, document examination

Dating writing ink can be a challenge in the field of forensic document examination. Several methods are available in order to estimate the age of a written entry on a questioned document. A dating method is referred to as relative if the age of two or more entries is compared to each other. Absolute dating is performed if no reference in a questioned document is available for comparison. In both cases, chemical methods can be used to obtain information about the age of a document by measuring age-dependent parameters of ink.

The first widely used age-dependent parameter was the extent of chloride migration, mainly from fountain pen inks, into the surrounding paper (1). A prerequisite for this method is that the ink must contain a sufficient content of chloride salts. The extractability of dyes from ballpoint inks on paper is another approach that has been used for ink dating (2,3). The method has been discussed in the literature, but there remains some controversy about the technique (4). Volatile solvents in ballpoint inks are also used to assess the age of ink on paper. Solvent evaporation from ink on paper can be divided into an initial fast process, and after a few hours to days, the evaporation slows down and reaches a low, steady rate (5). A major problem concerning measurements of solvent content in samples of ink on paper is the unknown sample size, i.e., the unknown amount of ink in the sample. To overcome this problem, Stewart (6) proposed to relate the content of a solvent with

relatively low boiling point to the content of a solvent with relatively high boiling point in the same sample. He showed in an example that this ratio may change with time. Locicero et al. (7) examined ink on paper by analyzing the liquid extract with gas chromatography–mass spectrometry (GC–MS). They determined the solvent content in the sample and related it to the amount of an unidentified ink compound, which was observed to be stable in time. They concluded that, after a few hours, ink dating is impossible using this approach, as the decrease in solvent content was smaller than the error of quantification. Aginsky (8) developed an approach using GC–MS to measure the amount of solvent from ballpoint ink on paper for ink dating. The described methods are based on the analysis of two samples of ink, one of which is treated thermally at a moderate temperature between 60 and 80°C. This thermal treatment is called “artificial aging” (9). Aginsky developed two liquid-extraction methods for the analysis of solvent content in the heated and the unheated sample of ink on paper. Both methods lead to an age-dependent parameter that changes as the ink ages. The method was found to be applicable to ballpoint ink with an age of up to 2 years at the most. Gaudreau and Brazeau (10) used Aginsky's approach and slightly modified the sample handling. Also in this modified version, two samples are used, one of which is heated at a moderate temperature before analysis.

The observed age-dependent effects are thought to be based on the aging of ink resins caused by oxidation and cross-linking of the binder polymer in the course of the heating procedure (artificial aging) (8). These processes may then result in a different extraction efficiency for the ink solvent from the polymer in fresh and old ink samples, respectively. However, no direct proof for this theory has been demonstrated.

In the methods mentioned above, two ink samples are needed in order to generate one value to indicate the ink age. As a result,

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sample size variation and variation of ink amount, which can be large when taking samples from handwriting entries, may contribute significantly to error rates. As well, sample preparation, like solvent extraction steps, may introduce contamination. Currently, no published method is available for avoiding errors introduced by sample size and by sample preparation. No extensive studies have been published in the literature with respect to the applicability of dating methods on different ballpoint ink compositions.

In a recent paper, the authors introduced a technique whereby thermal desorption was followed by GC–MS analysis for the characterization of solvents, binder resins, and additives from ink without sample treatment (11). The usefulness of the method was shown by analyzing a series of over 300 different ballpoint inks chosen randomly from a reference collection at the Forensic Science Institute of the Bavarian State Bureau of Investigation and grouping them into solvent and binder resin classes. In this paper, the authors describe the application for dating ballpoint pen inks. This research will introduce a general procedure for ink dating that is used at the Forensic Science Institute of the Bavarian State Bureau of Investigation. The results demonstrate that heating ballpoint ink on paper influences the chemical composition, suggesting a reason for the observed age-dependent behavior. The application range of the proposed procedure was studied by analyzing 85 different types of ballpoint pen inks over a period of 1.5 years.

## Methods and Materials

### Instrumentation

Thermal desorption of ink samples on paper was performed in a TDS2 thermal desorption unit equipped with an autosampler (Gerstel, Mülheim, Germany). The unit was connected to a KAS2 injector (Gerstel) coupled with a liquid nitrogen cooling unit. The injector is part of a gas chromatograph–mass spectrometer (Agilent 6840N/5973N, Agilent Technologies, Santa Clara, CA). Samples were placed in preconditioned silanized glass thermal desorption tubes (Gerstel). The tube and glass wool conditioning was performed by purging with argon (100 mL/min) in a tube conditioner (Gerstel) at 250°C for 30 min.

### Evolved Gas Analysis

A sample of ballpoint pen ink on paper was removed (length: 30 mm; width: 1 mm) and placed in a thermal desorption tube. The tube was heated in the TDS2 from 50 to 100°C with a temperature gradient of 2°C/min (minimum gradient of the thermal desorption unit). Simultaneously, the vaporized compounds were transported by a helium (He) carrier gas flow (5 mL/min) via a heated transfer line (silanized retention gap: 0.3 m, 280°C) directly into the mass spectrometer. The amount of 2-phenoxyethanol (PE) was monitored by scanning the ion signal  $m/z = 138$  in selected ion-monitoring mode.

### Thermal Desorption of Ink on Paper

A sample of ballpoint pen ink on paper was removed (length: 5–30 mm; width: 1–2 mm) and placed in a thermal desorption tube. The tube was heated in the TDS2 up to the desired temperature (at 12°C/min). Unless stated otherwise, analytes were collected for 5 min at a temperature of 200°C by a flow of He (40 mL/min) and trapped in the cooled injector at –100°C. Subsequently, the injector was heated (280°C, 60°C/min), the compounds were transferred onto the column, and analyzed in the gas chromatograph–mass spectrometer. GC–MS conditions were as follows: (i) inlet: solvent vent with a

vent flow of 40 mL/min, purge time was 1 min; (ii) column: HP5MS (Agilent Technologies), 30 m × 0.25 mm × 0.25 μm; (iii) carrier gas: He, constant flow of 1.2 mL/min; (iv) oven program: 45°C hold 1 min, 45–100°C at 30°C/min, 100–190°C at 12°C/min, 190–270°C at 50°C/min, and 270°C hold 3 min; (v) MS acquisition: solvent delay was 1 min, total ion current was scanned in the range of  $m/z = 35$ –550 with a sampling rate of 3 scans/sec, and MS transfer line temperature was 280°C. Integration of the phenoxyethanol signal was performed by manually integrating peak area in the extracted ion chromatogram ( $m/z = 138.10$ ). The identification of chemical compounds in the obtained spectra was achieved by comparison of the mass spectra with a standard mass spectral library (Mass spectral libraries NIST Rev. D.04.00, Agilent Technologies). Instrument performance was monitored at the beginning of each batch of samples by analysis of a 1 μL standard solution of 10 ng/μL phenoxyethanol (Merck [Darmstadt, Germany], reagent grade, purity >99%) and 10 ng/μL *n*-hexadecane (Fluka [Seelze, Germany], standard for GC, purity >99.8%) in acetone (Merck, analytical grade, purity >99.8%) on preconditioned silanized glass wool (Supelco [Munich, Germany], pesticide grade) in a thermal desorption tube using the aforementioned analytical conditions. Values obtained for the standard sample indicate a decrease in system performance if a relative deviation of more than 10% from the expected values is observed. The limit of quantification (LOQ = mean of blank measurement + 10 × standard deviation of blank measurement) for the thermal desorption/GC–MS of phenoxyethanol with standard office paper as sample matrix was determined to be 1 ng, and the limit of detection (LOD = mean of blank measurement + 3 × standard deviation of blank measurement) is 0.4 ng.

### Sample Preparation

Samples of ink on paper were prepared with ballpoint inks chosen from the ink library at the Forensic Science Institute of the Bavarian State Bureau of Investigation from the following manufacturers/suppliers: Germanstar Ink (Kreuzlingen, Switzerland), Formulabs Iberica (Badalona, Spain), Staedtler (Nürnberg, Germany), Bic (Shelton, CT), Sanford (Oak Brook, IL), Tratto (Milan, Italy), Zebra (Edison, NJ), Micro (Seoul, South Korea), Schmidt (Sankt Georgen, Germany), Sakura (Osaka, Japan), Waterman (Hamburg, Germany), Cri (Kolkata, India), Stanger (Espelkamp, Germany), Ampro (Terheijden, The Netherlands), Fma (Turin, Italy), Styb (Albacete, Spain), and Lamy (Heidelberg, Germany). All pens used were of medium point size. Unless stated otherwise, samples were applied onto standard office paper (80 g/cm<sup>2</sup>) with a writing force of *c.* 1 Newton (N) using commercially available pen cartridges. The strokes were made with a commercially available plotter (model Hewlett-Packard 7475A), equipped with a fixture to hold a pen cartridge. The fixture was made of metal and had a total weight of 100 g, which is equivalent to a vertical writing force of *c.* 1 N. The pen cartridge was moved using the manual control buttons of the plotter in the slow mode. For lower or higher writing forces, different fixtures were used, each having a weight equivalent to the desired vertical writing force. Pen strokes were placed onto the sheets at least 15 mm apart. Sheets were stored in folders with blank sheets in between under general room conditions (darkness, 25°C, *c.* 50% relative humidity).

## Results and Discussion

### Preliminary Study of Aging Effects of Ballpoint Ink

PE is a very polar component, so its detection and quantification are strongly dependent on instrument performance. Quality control

utilizing external and/or internal standards is absolutely necessary to make accurate measurements for the procedures described.

The analysis of ink components using the aforementioned thermal desorption method revealed that more than 95% of all ballpoint inks contain PE as a major solvent (11). Similar results were obtained by LaPorte et al. (12). Other solvents include benzyl alcohol, 2-ethylhexanol, *N*-methylpyrrolidone, alkylglycols and alkylethers, organophosphates, and phthalates. In order to determine the evaporation rate of these compounds, the content of volatiles in ballpoint pen strokes with ages up to several months was monitored. It was found that thermal desorption using the parameters developed in a previous study (11), i.e., a desorption temperature of 200°C for a period of 5 min, yielded a recovery rate of at least 95% for the solvent phenoxyethanol. This was regarded as adequate for all further experiments. Figure 1 depicts the decrease of phenoxyethanol in a single ink entry that has been aged 45 weeks.

Figure 1 demonstrates that more than 95% of the PE evaporates within the first period of a few days after applying the ink onto paper. The remaining amount of PE evaporates slowly in a second period leaving a residue that may be detectable after years. These results are in agreement with the results obtained by liquid extraction and GC-MS analysis (5,7). Other common constituents of ballpoint inks were found not to be as useful as PE for ink dating. For example, diethylene glycol evaporates quickly, labile compounds such as benzyl alcohol are subject to oxidation, and phthalic acid esters are too ubiquitous in the matrix and surrounding environment.

Initially, the authors attempted to determine whether the analysis of the absolute concentration of PE in a pen stroke by thermal desorption and GC-MS is a suitable technique for ink dating. To evaluate the usefulness of this approach, it was necessary to estimate the error that would be introduced by sampling as well as the variance of the amount of solvent contained in different ballpoint inks available on the market. Therefore, ink strokes of the same formulation of ballpoint ink were generated with a pen by applying different writing force ( $f$ ), starting with  $f = 0.3$  N up to a maximum of  $f = 8$  N. Samples were analyzed immediately by thermal desorption at 200°C for 5 min. This temperature and period were found to be best suited for the analysis of volatile ingredients in ink on paper matrix (11). The analysis of solvent content revealed a maximum difference of 800% between the strokes written with minimum and maximum force. The assessment of the variance of different inks with respect to their solvent content was performed on 25 different pen types with standard strokes ( $f = 1$  N) of an age

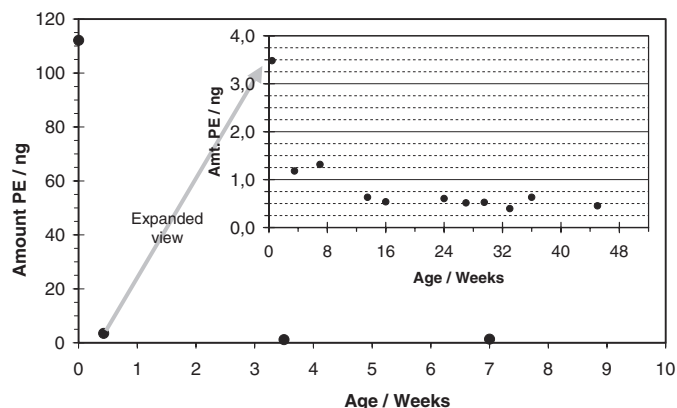


FIG. 1—Decrease of 2-phenoxyethanol in an ink entry on paper. Sample amount was each 5 mm. The inset represents an expanded view, covering an extended time frame while the y-axis is enlarged.

of 1 week up to 22 weeks. It was found that the solvent content of these ballpoint inks range from 0.3 up to 25 ng/mm for the ink samples with an age of 1 week, and from 0.1 up to 15 ng/mm for the samples with an age of 22 weeks. Therefore, there is a significant variance in the solvent content for inks with the same age but having different formulations. One proposal to overcome the problems associated with this variance might be to determine the possible formulation of the ink under investigation and to obtain knowledge about its composition and its aging behavior. However, even if the chemical composition is attributable to a sample from a reference collection, variation may exist when analyzing the questioned ink due to insufficient information regarding the initial solvent content and the aging behavior. Due to the aforementioned uncertainties and the possibility of variation, it does not appear to be practical to derive definitive conclusions based on the absolute solvent content of PE. This finding is in agreement with the results obtained by other groups using liquid extraction and GC-MS as analytical techniques (7). As a conclusion from these experiments, the solvent content in a pen stroke can only be used for ink dating if a value can be generated. This will be independent of the sample amount and the formulation of the ballpoint ink under investigation.

#### Thermal Analysis/Evolved Gas Analysis

Further studies were performed using an ink dating procedure that involves “artificial aging” (i.e., heating of an ink stroke at moderate temperatures), as it is used in the dating methods published by Aginsky (8) and Gaudreau and Brazeau (10). It is expected that heating of an ink sample causes solvent evaporation, as well as oxidation and cross-linking of binder resins. In order to get more insight into the effects caused by heating, evolved gas analysis was performed. The experiments were conducted on samples of pen strokes of four different types of ballpoint inks between the ages of 3 and 12 months. The strokes were heated slowly from 50 to 100°C in the thermal desorption unit, while the evaporating amount of PE was monitored. In Fig. 2, a set of curves for one of the four inks is depicted. The curves show that the strokes of this ink with an age of 3 months start to release PE at 50°C, whereas the strokes with an age of 9 months do not release the solvent until 65°C (Fig. 2).

As a result, the onset temperature of detectable solvent evaporation was below 50°C for ink with an age of 3 months. For older ink samples the temperature was higher. For instance, samples of

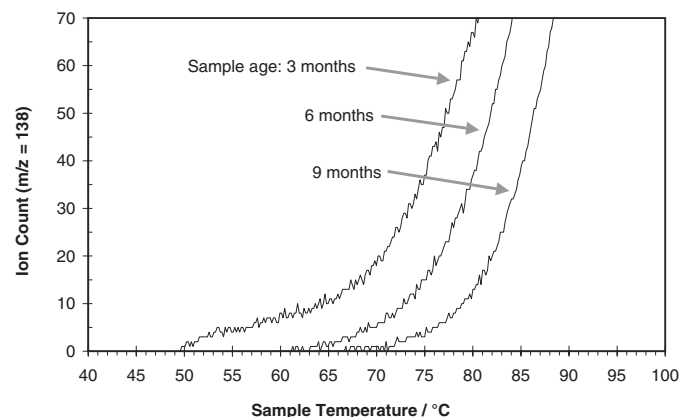


FIG. 2—Set of curves representing the amount of 2-phenoxyethanol (molecular ion  $m/z = 138.10$ ) that evaporated while heating samples of ballpoint ink on paper slowly in the thermal desorption unit (evolved gas analysis). Sample size was 30 mm.

the four inks with an age of 9 months showed each an onset temperature of higher than 70°C. From these observations it was concluded that the amount ( $M_1$ ) of solvent released from the tested ballpoint inks on paper at a certain low temperature in a certain time interval depends on ink age.

The method using evolved gas analysis to determine the onset temperature of detectable solvent evaporation is not practical for some types of casework because the required sample size of a 30-mm pen stroke is rather large. It was expected that a quantitative determination of the solvent amount desorbed at low temperatures in a certain time interval would yield a value that is equivalent to the onset temperature of detectable solvent evaporation. Less sample would be needed for this analysis. The value  $T_1 = 70^\circ\text{C}$  was selected as the low temperature for further experiments. This desorption temperature seemed to be best suited to differentiate between fresh and old ink entries. Herein, "fresh" means less than 3 month, and "old" means more than 6 months. For  $T_1 = 70^\circ\text{C}$ , a desorption period of 20 min was chosen in order to collect sufficient solvent for GC-MS analysis. As mentioned before, the parameters  $T_2 = 200^\circ\text{C}$  and  $t_2 = 5$  min were found to result in a value that represents the total PE content in the sample. Figure 3 shows two total ion chromatograms obtained after desorption of a sample of ink at 70 and 200°C.

In order to eliminate the unknown variable of sample amount in the quantitative measurement, the amount  $M_1$  has to be divided by the total amount of ink present in the sample. As mentioned above, the total amount of ink solvent in the second, long-lasting period of slow solvent evaporation is almost constant. Consequently, the total amount of ink in the sample was approximated by the total amount of ink solvent in the sample. To demonstrate this argumentation, Table 1 lists the data for the amount of PE extracted thermally at 70°C ( $M_1$ ), together with the amount obtained from the same sample at 200°C ( $M_2$ ). The table lists data for six samples with different age.

This experiment shows that the total amount of ink solvent, which is represented by the value determined at a desorption temperature of 200°C ( $M_2$ ), is more or less constant. The variations in  $M_2$ , for example the increase in  $M_2$  for samples with an age of 8.5

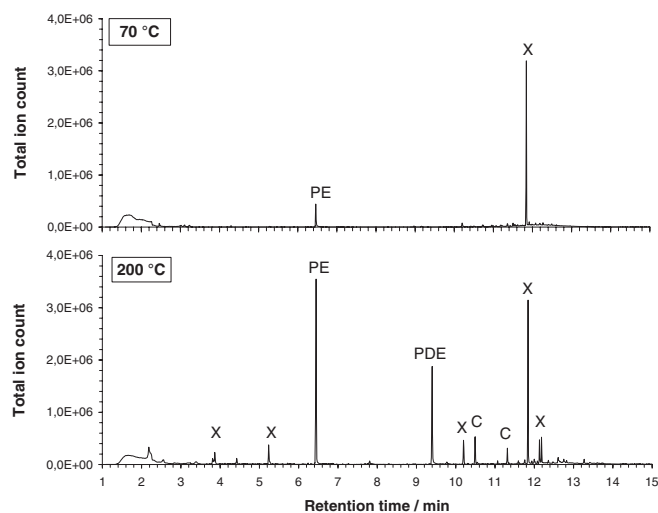


FIG. 3—Total ion chromatograms obtained after thermal desorption of a sample of ink on paper in two steps. Sample size was 5 mm. Chromatogram (70°C): desorption temperature = 70°C. Chromatogram (200°C): desorption temperature = 200°C. Compounds: PE, 2-phenoxyethanol; PDE, phenoxyethoxyethanol; C, ink colorant fragments; X, compounds from paper matrix.

TABLE 1—Amount of 2-phenoxyethanol obtained in a two-step desorption at different temperatures (70°C and 200°C) from samples of a ballpoint pen ink on paper.

Sample Age/ month	Desorption at 70°C		Desorption at 200°C		Ratio $V = M_1/(M_1 + M_2)$ $\times 100\%$
	Int./1000	$M_1/\text{ng}$	Int./1000	$M_2/\text{ng}$	
0.8	3630	27.88	22,040	169.3	14.1
2.9	2692	20.68	22,840	175.4	10.5
8.5	2346	18.02	28,460	218.6	7.6
10.2	2296	17.63	28,580	219.5	7.4
13.3	971	7.46	23,710	182.1	3.9
19.4	363	2.79	17,190	132.0	2.1

Sample amount: 20 mm. Int., area integration of extracted ion chromatogram  $m/z = 138.10$ .

and 10.2 months, reflect the variation in ink amount caused by sampling and poor homogeneity of ink lines on paper. In contrast, the amount of solvent recovered at 70°C ( $M_1$ ) decreases strongly with ink age. Obviously, the total amount of solvent in an ink sample on paper may be divided into two different fractions: a relatively low temperature is sufficient for effective thermal extraction of a first fraction, whereas a higher temperature is needed for the remaining fraction, and the relative amount of the first fraction decreases with ink age. Table 1 also lists a value  $V$  representing the fraction of  $M_1$  with respect to the sum of desorbed solvent  $M_1 + M_2$ . The decrease of the values  $V$  indicates that problems caused by sample-size variation are eliminated in this way.

These considerations led to the following procedure for ink dating:

- 1 A sample of ink on paper is heated at a temperature  $T_1 = 70^\circ\text{C}$  for a period  $t_1 = 20$  min. The evaporated solvent PE is collected, and the amount  $M_1$  is quantified.
- 2 The same sample is heated at a temperature  $T_2 = 200^\circ\text{C}$  for a period  $t_2 = 5$  min. The evaporated amount  $M_2$  is quantified.
- 3 The ratio,  $V = M_1/(M_1 + M_2) \times 100\%$ , is calculated.

A test on samples of the same pen with the same age, but different sample size, proved that the method is mass independent and yields the same value,  $V$ , for different sample sizes (Table 2). The influence of the paper on the ratio  $V$  was studied using different papers in combination with one ballpoint ink. Table 2 lists the results for this experiment. From the values  $V$ , it can be concluded that the proposed method depends on the type of paper, with standard office paper resulting in the highest values  $V$ . All further experiments were therefore performed using samples on standard office paper (80 g/m<sup>2</sup>).

TABLE 2—Results of experiments with writing samples of different length on different paper types.

Sample Length/cm	Paper Type	Ratio V/%
0.5	Standard office paper, 80 g/m <sup>2</sup>	25
1	Standard office paper, 80 g/m <sup>2</sup>	23
2	Standard office paper, 80 g/m <sup>2</sup>	24
3	Standard office paper, 80 g/m <sup>2</sup>	22
0.5	Recycling paper, writing pad, 80 g/m <sup>2</sup>	16
0.5	Paper for color toner copying machines, 100 g/m <sup>2</sup> , coated	14
0.5	Office paper with acidic sizing, 80 g/m <sup>2</sup>	10

The same ballpoint ink was used and all samples were the same age. Sample width was 1 mm.

## General Testing and Improved Procedure

To test the general applicability of the procedure, a selection of 60 ballpoint inks was used. Each ink contained PE as a major solvent, but otherwise had different chemical compositions, based on data in our reference database (obtained by HPTLC and GC-MS analyses). The selection included blue and black ballpoint inks collected between 1998 and 2002 from 20 manufacturers/suppliers. Sample ages ranged from fresh to *c.* 20 months. The test was performed using pen strokes that were applied onto the same office paper, with the same writing force ( $f = 1$  N), and the sheets were stored in a folder under general room conditions. In the folder, every sheet with sample strokes was separated from the following sample sheet by a blank sheet to avoid sample carryover from the front side of one page to the back side of the following. A distance of 15 mm was kept between sample strokes to avoid cross-contamination of different strokes next to each other, as it is possible that ink solvents migrate significantly from a pen stroke into the surrounding paper (11,13).

Twenty-three of the inks had no detectable amount of solvent PE evaporated at  $T_1 = 70^\circ\text{C}$  (sampling time:  $t_1 = 20$  min), independent of sample age. Fifteen inks were classified as "aging fast," with their  $V$  ratio decreasing below 10% within a period of 2 weeks, and staying on this level during the remaining test period of 20 months. One ink is depicted in Fig. 4 ("C," solid circles) as an example. This aging speed concerning the  $V$  ratio is too fast for most practical cases. The remaining 22 inks were classified as "aging slowly." As expected from the evolved gas analysis study described above, their  $V$  ratios are high for the fresh samples, but decrease within the test period to values below 10%. An example of this group is shown in Fig. 4 ("B," solid squares). The uppermost dots in Fig. 4 (solid triangles) represent the mean of all obtained values plus 3 standard deviation units. The range below these points covers all the possible values  $V$  for ballpoint inks of different age in our test series with a probability of more than 99%.

The results were generalized and used for forensic casework in a subsequent test phase. The decision criteria were as follows: (i) if a ratio  $V$  higher than 10% is detected for an ink sample, then the aforementioned uppermost dots were used to estimate a maximum age; and (ii) if a ratio of less than 10% is obtained, no conclusion

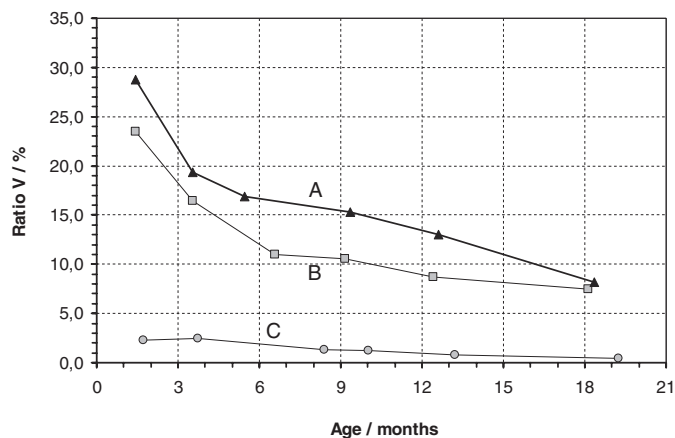


FIG. 4—Examples of ratios  $V$  obtained in the first test series using the preliminary dating procedure. Data were obtained for  $T_1 = 70^\circ\text{C}$ ,  $t_1 = 20$  min, and  $T_2 = 200^\circ\text{C}$ ,  $t_2 = 5$  min. A: Points represent average of all values obtained in the test series plus 3 standard deviation units; B: data for a "slowly aging ink"; C: data for a "fast aging" ink.

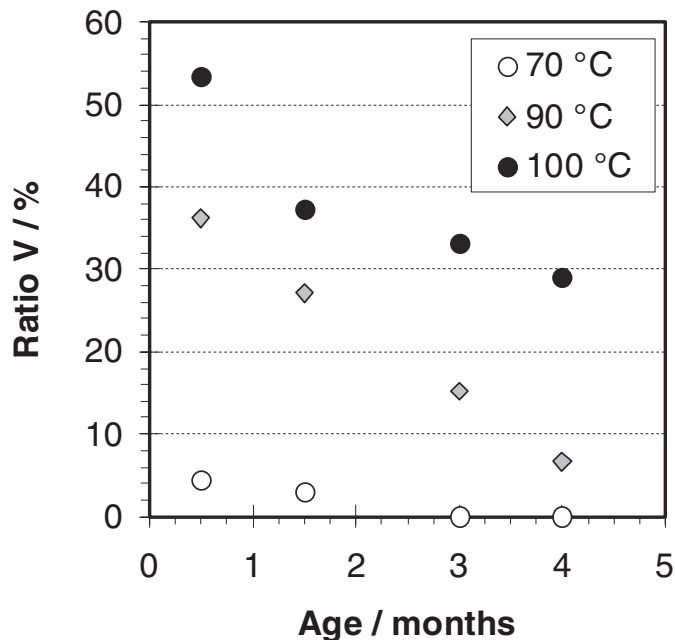


FIG. 5—Ratio  $V$  versus sample age determined at different temperatures  $T_1$ . All other parameters were constant in this experiment.

was drawn, as the ink may be old and "aging slow" or relatively fresh and "aging fast." For example, a ratio of  $V = 25\%$  leads to the conclusion that the ink is not older than 2 months (Fig. 4). The author's experience in the test phase revealed that a large number of the inks in casework samples are the "aging fast" type and release no or too little solvent at  $T_1 = 70^\circ\text{C}$ . No conclusion could be drawn regarding ink age.

To improve the general applicability of the method and to overcome the aforementioned problems, the influence of higher temperatures  $T_1$  on the resulting ratio  $V$  was studied. It was hypothesized that this might result in more solvent obtained at  $T_1$  and more accurate quantification for inks with low solvent content. Additionally, a method independent of instrumentation should not be based on absolute ratios  $V$  for assessing the age of a ballpoint ink. Figure 5 shows measurements of the ratio  $V$  for ink samples of different ages using different temperatures. These measurements were performed on four different ballpoint inks. The result was that each ink has an optimum temperature  $T_1$ , resulting in a high amount of solvent evaporating in the first desorption step. At the same time, it yields a high difference between the ratio  $V$  for a fresh and an old ink entry. This temperature was *c.*  $90^\circ\text{C}$ .

The observed effects resulted in the following improvements for the ink dating procedure: the parameters  $T_1 = 90^\circ\text{C}$  and  $t_1 = 5$  min are used in the first desorption step and the measurements of the ratio  $V$  are repeated four times in the same way within a time frame of 8 weeks. The overall decrease of the ratio  $V$  versus time can then be calculated. Figure 6 shows the values of a typical aging curve obtained with the improved procedure.

The measurement of the change in the ratio  $V$  within a certain time period results in a method that is independent of absolute values. In a second comprehensive study, the improved method was tested on 25 ballpoint pen inks, which were selected so that all main types of resins, solvent mixtures, and manufacturers of ballpoint inks were included. The selection consisted of blue and black ballpoint inks from 15 major manufacturers/suppliers collected between 1997 and 2005. Samples of the inks with ages between 1 and 22 weeks were analyzed. The result of the study was that a

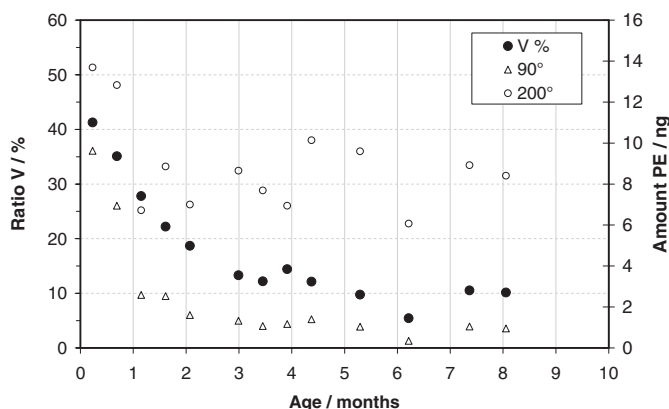


FIG. 6—Aging curve measured using the improved procedure with  $T_1 = 90^\circ\text{C}$ . Solid dots represent values for ratio  $V$ , empty triangles and circles are integration values (manual, extracted ion chromatogram for  $m/z = 138$ ) for the amount of solvent 2-phenoxyethanol obtained at  $T_1 = 90^\circ\text{C}$  and  $T_2 = 200^\circ\text{C}$ , respectively.

decrease of at least 5% in ratio  $V$  within a time period of 8 weeks shows that the ink was not older than 4 months. A higher decrease in  $V$  indicates a fresher ink. In Table 3, the tested inks are listed together with data about their chemical composition. The abbreviation “s” (“s” = “slowly aging ink”) denotes that the decrease of the ratio  $V$  for the ink can be monitored in a period of several months using the improved method described above. For the other half of the tested inks,  $V$  is decreasing to a constant value within 1–2 weeks (“f” = “fast aging ink”). As mentioned previously, an aging period of 2 weeks may be too short to be useful in most practical cases, as most documents are older than 2 weeks at the time they are brought to the laboratory.

It was observed that all the “slowly aging inks,” that are suited for dating using the described method contain the acetophenone–formaldehyde resin as a binder. Other ingredients do not appear to influence the aging speed. This finding indicates that the type of resin may be one of the main parameters that affects the aging behavior of some ballpoint inks.

## Conclusions

The analytical method using thermal desorption and GC–MS, which was previously developed for the direct analysis of solvents, additives, and resins in writing ink on paper, was successfully applied to ink dating. It was proven by evolved gas analysis that the extent of evaporation of solvent from an ink sample on paper at a certain low temperature is age dependent. This leads to the conclusion that the solvent content in an ink sample on paper can be divided into different fractions, which differ in the temperature needed for their effective evaporation. The proposed dating procedure is based on measurements of the change of a relative value within a certain time frame, and therefore is independent of sample amount and of the analytical instrumentation.

Two comprehensive test series on 85 ballpoint inks reveal that there are inks which age slowly, enabling the measurement of the age-dependent parameter  $V$  within a practicable timeframe of several months. But there are also ballpoint inks that do not show a decrease in the age-dependent parameter in the time frame between 2 weeks and 1.5 years. Practical casework confirmed that the dating procedure described herein can be applied to ink entries with a maximum age of several months. In combination with the information about the chemical composition of each of the tested inks, the results from this study indicate that the aging behavior of a ballpoint ink depends on the type of binder resin in the ink composition. However, the dependence of the absolute values of the

TABLE 3—Inks tested in the second test series with 25 different samples of ballpoint inks.

Manufacturer	Year of Introduction	Color and TLC Group	Resin Class	Solvents	Aging
1	1997	Black 4/19	AF	PE, PDE, <i>N</i> -methylpyrrolidone	s
2	2000	Blue 1/4	AF	PE, PDE	s
1	2000	Black 4/19	AF	PE	s
3	2000	Blue 3/29	AF	PE, PDE	s
3	2000	Black 4/34	CF	PE, PDE	f
4	2000	Black 4/19	AF	PE, PDE	s
5	2001	Blue 4/17	CF	PE, dipropylene glycol	f
5	1999	Black 4/19	AF	PE, PDE, ethyldiethyleneglycol	s
6	2002	Black 6/7	Alkyd	PE	f
7	2002	Black 4/40	Alkyd	PE, PDE, propylene glycol	f
8	2003	Blue 1/13	AF	PE, PDE, diisopropylene glycol	s
8	2003	Black 4/19	AF	PE, PDE, ethyldiglycol	s
9	2003	Blue 1/33	CF, Alkyd	PE, PDE, hexylene glycol	s
9	2003	Black 4/19	AF	PE, PDE, hexylene glycol	s
10	2003	Blue 4/1	Alkyd	PE, butylene glycol	f
11	2003	Blue 1/1	Alkyd	PE, PDE, benzyl alcohol	f
12	2003	Blue 1/37	AF	PE, PDE, butylene glycol	s
12	2003	Black 4/47	AF, Alkyd	PE, PDE, butylene glycol	s
13	2004	Blue 1/4	AF	PE, benzyl alcohol	f
13	2004	Black 4/42	Unknown	PE, benzyl alcohol	f
14	2005	Blue 8/17	Alkyd	PE, benzyl alcohol	f
14	2005	Black 4/19	Alkyd	PE, benzyl alcohol	f
15	2005	Blue 1/5	CF, Alkyd	PE, PDE	f
15	2005	Black 4/46	CF, Alkyd	PE, PDE	f
15	2005	Blue 1/13	CF	PE, PDE, triocetylphthalate	f

The inks were analyzed using the improved dating procedure.

AF, acetophenone–formaldehyde resin; CF, cyclohexanone–formaldehyde resin; PE, 2-phenoxyethanol; PDE, 2-(2-ethoxy)ethoxybenzene; s, “slowly aging ink”; f, “fast aging ink.”

measured parameter on the type of paper indicates that the paper composition also influences the aging of some inks.

Current efforts concentrate on further elucidation of the detailed aging mechanisms of ballpoint ink, especially with respect to the influence of paper type and ink resin composition. The development of an improved analytical GC-MS method that allows derivatization of the analytes evaporated by the thermal desorption unit is also a main objective. The strong dependence of the obtained values for PE on analytical system performance could be reduced, and the application range of the method might be extended.

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