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## Inhomogeneity and Aging of Ballpoint Pen Inks Inside of Pen Cartridges

**ABSTRACT:** Inhomogeneity and aging of ballpoint pen inks inside of cartridges, particularly near the tip of a pen, were studied by HPLC (high pressure liquid chromatography). No indication of aging in terms of changes in dye composition inside of a regularly used pen was observed. Ink entries on paper were, however, found inhomogeneous concerning concentration of phenoxyethanol, a volatile compound commonly present in ballpoint inks. Detectable and sometimes considerable aging of inks near the tip of cartridges not used for writing for many years was observed. Both evaporation of phenoxyethanol and aging of cationic dye mixture were detected at the start when writing with such pens. The consequence of this finding for ink examination, both ink comparison and ink aging, is discussed.

**KEYWORDS:** forensic science, questioned documents, ink dating, ink aging, HPLC, ballpoint ink

In the examination of questioned documents it is a common task to investigate if two or more documents have been written with the same type of ink. In ink dating, it is important to ascertain if two or more ink entries were written on the same occasion. The most common type of ink in these investigations is ballpoint pen ink. For both types of investigations, it is important that inks inside pen cartridges are homogeneous. Additionally, eventual aging of the ink inside a pen cartridge has been assumed negligible in comparison to aging of the ink entry on paper.

In a recent study, laser decomposition mass spectrometry was used to examine ink-on-paper samples from new and old pens (1,2). Crystal Violet and its degradation products were studied. In most cases no degradation was observed. In some pens, however, substantial degradation inside the cartridge appears to have occurred at a rate higher than what would occur if the dye were on paper. This conclusion was based on the assumption that the only dye in inks provided by a manufacturer is Crystal Violet and that Methyl Violet and Tetramethyl Para Rosaniline are formed by demethylation processes inside an ink after its manufacture. If this were the case, serious problems would arise in relative dating of inks. Two or more ink entries written by the same pen at widely different times might be classified as if they were written at the same time. Eventually, the fresher ink entry could exhibit more aging than the older one.

It is more probable that ink aging appears near the tip of a pen, particularly if the pen has not been used for writing for years. In this study aging and inhomogeneities of inks at the tip of various pen cartridges were studied. HPLC (high pressure liquid chromatography) has been employed for ink analyses. In our previous work, HPLC was used to measure quantitative changes in ink dye composition for inks exposed to light (3) and also aging of ballpoint pen inks in darkness (4). Recently, an application of HPLC for relative dating of ballpoint pen inks in casework was reported (5). This

technique is particularly suitable for measuring very small changes in the quantitative composition of inks, both the composition of dyes (such as Crystal Violet, Methyl Violet, Victoria Blue etc.) and solvents (phenoxyethanol). The composition of ink dyes and the concentration of the most common solvent—phenoxyethanol (PE) were measured in a single analytical step. High-sensitivity detection of PE was achieved using a fluorescence detector in connection with the diode array detector.

### Materials and Methods

#### *Extraction of Inks*

Ink entries in form of asterisks on ordinary white copy paper (Reference, 80 g, A4, made in Sweden) were produced using various ballpoint pens. Each asterisk corresponds to an ink line approximately 1 cm in length. Single asterisks chosen for analysis were cut out from paper and placed inside 2 mL glass vials equipped with 0.3 mL conical glass inserts (Scantec Lab, 0.3-CVK). The asterisks were put in the bottom of the insert and 30  $\mu$ L of methanol (HPLC grade) were added. The vial was closed using a removable plastic snap cap. The extraction time was kept to 1 hour. After that time the asterisk was removed from the glass insert using a needle and the vial closed by a crimp cap. During the whole procedure, the ink and the extract were protected from exposure to intense light. Aliquots of 20  $\mu$ L were taken for analysis. This procedure showed better reproducibility in the quantitative HPLC analysis of dye and solvent composition of inks than the procedure we used in our previous studies (3,4).

#### *HPLC Analysis*

Ink analyses were run on a Hewlett-Packard HP 1090 series II Liquid Chromatograph connected to the HP's HPLC<sup>3D</sup> ChemStation. The instrument was equipped with an auto-sampler, an auto-injector and a diode array detector from Hewlett-Packard. A Perkin Elmer fluorescence detector (LC 240) operating with the excitation wavelength of 270 nm and the emission wavelength of 310 nm was connected in series with the diode array detector. This

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instrumental setting was the most sensitive for fluorescence detection of phenoxyethanol. The detection limit was estimated to be approximately 0.05 ng PE injected onto the column. In some experiments the amount of PE detected in ink samples was rather high and the detector response was out of scale. The emission wavelength was in such cases changed to 330 nm, with the response approximately 3.5 times lower compared to that at 310 nm.

HPLC separations were performed using a 25 cm 5  $\mu$ m Zorbax<sup>®</sup> SB-C18 (4.6 mm ID, Scantec Lab AB) stainless steel column, if not otherwise stated. The mobile phase consisted of two solvents. Solvent A was a mixture of 20% acetonitrile and 80% water containing 10 mM KClO<sub>4</sub>, pH adjusted to approximately 3 with hydrochloric acid. Solvent B was 100% acetonitrile. The gradient was linear from 70% solvent A and 30% solvent B to solvent B in 14 min, followed by 8 min isocratic elution by Solvent B. After each gradient, the system was returned to starting conditions in 8 minutes. The flow rate was 1.0 mL/min at room temperature. The diode array detector was programmed to record chromatograms at 540  $\pm$  60 nm, 254  $\pm$  20 nm, 300  $\pm$  20 nm, 355  $\pm$  10 nm, 220  $\pm$  5 nm, 440  $\pm$  20 nm, 270  $\pm$  10 nm and 580  $\pm$  20 nm. Full spectra were acquired on all significant peaks from 190 nm to 600 nm. The analytical results in terms of the concentration of visible dyes were obtained from peak areas recorded at 540  $\pm$  60 nm if not otherwise stated. The signal from the fluorescence detector was recorded with the Omega Data system from Perkin Elmer.

## Results and Discussion

### *Ink From the Same Pen Analyzed at Different Occasions*

In our previous work (3,4) we followed the aging of ink entries on paper using ternary diagrams constructed for dyes generally present in blue-colored inks—Crystal Violet (CV), Methyl Violet (MV) and Tetramethyl Para Rosaniline (TPR). On aging, these cationic dyes decompose. This decomposition seems to imply a successive loss of methyl groups, which are substituted by hydrogen atoms. CV thus decomposes into MV, which subsequently decomposes to TPR and other, structurally similar compounds by successive loss of methyl groups. On exposure to light this decomposition process is enhanced and may be quite rapid (2,3,6,7).

The best evidence for eventual ink aging inside of pen cartridges would be provided by repeated analyses of ink from the same ballpoint pen on different occasions, separated by many years in time. If some aging inside the pen cartridge occurs, gradual changes in the composition of dyes would follow curves obtained previously (4) in ternary diagrams constructed for the system CV-MV-TPR. The ink entries must, however, be analyzed a short time after the ink is dispensed onto paper; otherwise, aging of the ink on paper will influence the results.

In our collection of ballpoint pens we found four different inks from 3 different manufacturers that were analyzed when fresh (within a month after writing onto paper) on widely separated occasions. Only one of these pens was analyzed several times and at occasions separated by more than 6 years, the three others were only analyzed twice within 3–4 years. Table 1 shows the results of these various HPLC analyses. The relative concentrations of TPR, MV and CV are calculated to give a total of 100%, regardless of the presence of other dyes in the chromatograms. The HPLC instrument and wavelength settings were the same in these analyses. The repeatability of the quantitative analysis of the dyes is normally good, with the relative standard deviation less than 1% for CV and MV. However, the aim of these analyses was not to compare the quantitative results with each other after several years. Thus, the

TABLE 1—Composition of ink entries written by four different ballpoint pens at occasions widely separated in time. The inks were analyzed shortly after the writing.

Ink Sample	Date of Writing*	Peak 5/ $\Sigma$ Dyes	% TPR	% MV	% CV
A	12–1997	0.57%	6.3	44.2	49.45
A	12–1999	0.40%	5.9	44.5	49.55
A	07–2001	0.43%	5.8	44.15	50.1
A	02–2002	0.34%	5.9	43.95	49.85
A	03–2003	0.46%	6.2	45.15	48.6
A	03–2004	0.45%	6.3	44.45	49.25
B	10–2000	1.28%	8.65	40.55	50.8
B	03–2004	1.47%	8.45	40.55	51.0
C	12–1999	3.08%	11.8	41.4	46.85
C	02–2004	2.96%	11.25	41.85	46.9
D	12–1999	1.90%	15.05	54.55	30.4
D	04–2003	1.74%	15.55	54.45	30.0

\* Month and year of the writing.

columns used are not the same, nor is the HPLC gradient employed always the same. The reproducibility of such analyses is not as good as the repeatability mentioned above. Nevertheless, no correlation between the composition of the cationic dyes and the relative age of ink in the cartridges can be observed. On aging, the concentration of CV should decrease and that of TPR increase (4). An additional decomposition peak, designated as “peak 5” (one of the small decomposition peaks mentioned in our previous study) eluting shortly before TPR (3,4) was measured. On aging, the concentration of this compound is expected to increase in relation to the other dyes. No such increase was noted.

It should also be mentioned here that the relative concentration of some other dyes observed in chromatograms obtained at 540 nm for inks in Table 1 was the same within the experimental error, unaffected by the time difference.

### *Drying of Ink and Aging of Dyes at the Tip of a Pen*

All the pens presented in Table 1 were regularly used for writing, at least once a month. In a real case a pen that has not been used for a considerable time may be encountered. It happens that such a pen does not write anymore or needs several attempts to start writing again. It may be expected that the composition of the ink close to the tip of such a pen is different from that well inside of the cartridge.

In our collection of ballpoint pens we have many pens with the time of manufacture known. The manufacturer of Ballograf ballpoint pens supplied us with the information about the code system engraved on their cartridges (year and month). Our collection contains Ballograf pens manufactured over a period of more than 30 years. The information does not say when the actual ink was manufactured, only when the cartridge was filled with ink.

We have carried out several experiments using these Ballograf pens. As some of these pens were known to not be in use for a long period of time—more than 10 years—such pens were considered for examination of ink evaporation and aging inside of the cartridge at the tip. The newer pens were purchased by our laboratory and, to our knowledge, never used for writing.

A number of pens was chosen and used to write 100 or more asterisks (each asterisk corresponds to a line of about 1 cm) on ordinary white paper for photocopy machines. The written asterisks were stored in darkness. After 1–2 days of storage in darkness, selected asterisks were extracted by methanol and the extract analyzed by HPLC. Table 2 summarises the results of one of the experiments.

TABLE 2—Composition of asterisks written by ballpoint pens manufactured in different years by Ballograf. The pens were either not used for writing at all (the pen from 2003) or not for many years.

Year of Manufacture	Asterisk No.	% Small Peaks	% TPR	% MV	% CV
2003	1	2.16	9.35	40.0	50.65
2003	50	2.05	9.35	39.85	50.8
2003	100	2.12	9.0	40.05	50.9
1997	1	3.06	8.0	39.1	52.9
1997	50	3.19	7.8	38.75	53.4
1997	100	3.13	7.75	38.45	53.8
1994	1	1.82	9.6	39.6	50.75
1994	50	1.91	9.55	39.7	50.75
1994	100	2.06	9.55	39.65	50.75
1991	1	1.03	5.7	36.95	57.35
1991	50	1.16	5.55	36.9	57.55
1991	100	1.18	5.45	36.8	57.75
1988	1	1.70	7.0	52.8	40.2
1988	50	1.48	6.45	52.85	40.7
1988	100	1.41	6.1	52.95	40.95
1984	1	1.26	7.85	38.4	53.75
1984	50	1.27	7.3	38.0	54.65
1984	100	1.28	7.45	38.0	54.55
1981	1	4.17	17.65	46.3	36.05
1981	50	3.68	16.4	46.1	37.5
1981	100	3.49	16.1	46.15	37.75
1977	1	3.10	13.1	42.6	44.35
1977	50	3.07	12.5	42.3	45.2
1977	100	3.02	12.35	42.2	45.5

Ballograf pens were used directly for writing; it was not necessary to scribble on another piece of paper to start writing. Asterisks numbers 1, 50 and 100 were chosen for the analysis. The relative percentage of the cationic dyes CV, MV and TPR were calculated to monitor aging of inks in the ternary system CV-MV-TPR. The sum of “small peaks”, meaning the sum of peak areas for additional decomposition peaks eluted prior to TPR (3,4) was also calculated. Table 2 can be used both for comparison between the different asterisks written by the same pen as well as between inks from the same manufacturer, produced at widely separated occasions.

Assuming that significant aging of ink inside of pen cartridges occurs, the relative percentage of CV should gradually decrease and that of TPR increase with the age of the cartridge. Additionally, the sum of small peaks would increase with the age of the cartridge. There is no such correlation observable in the table. The relative concentration of CV is actually higher in the cartridge manufactured in 1984 compared with that manufactured in 2003. Also the sum of small peaks observed for the cartridge manufactured in 1984 is one of the lowest obtained. The different values of the relative concentrations in the CV-MV-TPR system represent rather the various original compositions of the dyes employed in the manufacturing process. When an analysis of pure Methyl Violet purchased by our laboratory was performed, a mixture of MV, CV and TPR was detected. In pure Crystal Violet a small amount of MV was detected. The composition of technical dyes may be expected to vary a great deal.

The effect of aging of ink at the tip of pen cartridges can, however, be seen on many samples presented in Table 2. The differences in composition of the CV-MV-TPR systems are observed between the first asterisk and asterisk no. 50. The composition of asterisks 50 and 100 are, within the experimental error, the same. The question arises as to how large a portion of the ink close to the tip exhibits aged composition compared to the bulk sample. Therefore new samples

TABLE 3—Composition of inks in asterisks from ballpoint pens manufactured by Ballograf. The pens were either not used for writing at all (the pens from 2003 and 1999) or not for at least ten years. The composition of dyes and small peaks was calculated from chromatograms detected at 540 nm, the concentration of phenoxyethanol (PE) was monitored by fluorescence detector at 270/310 nm. The sum of dyes means the sum of peak areas for CV, MV and TPR.

Year of Manufacture	Asterisk No.	% Small Peaks	% TPR	% MV	% CV	PE/Σ Dyes
2003	1	3.12	11.08	41.27	47.65	0.63
2003	2	3.07	10.62	40.92	48.46	0.675
2003	3	2.86	10.62	40.92	48.45	0.73
2003	100	2.87	10.69	40.83	48.48	0.85
1999	1	3.11	6.825	38.40	54.77	0.81
1999	2	3.18	6.80	38.34	54.86	0.83
1999	3	3.07	6.68	38.24	55.09	0.875
1999	100	3.17	6.67	38.02	55.31	0.87
1993	1	2.16	10.42	40.46	49.12	0.583
1993	2	2.13	10.44	40.27	49.29	0.625
1993	3	2.22	10.48	40.30	49.22	0.66
1993	100	2.12	10.35	40.27	49.38	0.736
1988	1	3.04	11.23	53.23	35.54	0.415
1988	2	2.55	9.70	53.47	36.82	0.43
1988	3	2.56	9.30	53.49	37.21	0.39
1988	100	2.05	8.06	53.65	38.28	0.426
1982	1	3.015	15.10	44.54	40.36	0.62
1982	2	2.80	14.18	43.96	41.85	0.70
1982	3	2.49	13.54	43.86	42.60	0.74
1982	100	2.20	12.72	43.37	43.91	0.805
1973	1	6.40	21.35	46.08	32.58	0.40
1973	2	6.06	20.45	45.97	33.58	0.435
1973	3	5.70	19.80	45.87	34.33	0.478
1973	100	4.70	17.47	45.62	36.91	0.52

of Ballograf pens were taken and asterisks nos. 1, 2, 3 and 100 were analyzed. As in the previous experiment, the pens have either never been used for writing (pens from 2003 and 1999) or have not been used to our knowledge for at least ten years. Additionally, the effect of evaporation of ink at the tip was monitored as a ratio between PE and the sum of all dyes detected in the same ink sample. PE was detected by fluorescence, which was found more sensitive and free from overlapping with other compounds in comparison with UV-detection. The results are presented in Table 3.

This table reveals a significantly lower concentration of PE observed for the first asterisks written, in other words in the ink closest to the pen tip. The only exception is the pen from 1988. This phenomenon can be observed even for the pen from 2003, a pen that was used for writing for the first time after its manufacture. It seems that the process of evaporation of volatile and semivolatile compounds from cartridge tips can be quite rapid. Inhomogeneity of inks in terms of PE content may affect the results but a general increase of the concentration of PE with continuous writing is apparent.

The effect of aging of ink at the tip is also obvious. The concentration of CV increases and that of TPR decreases with continuous writing. A general decrease in the percentage of small decomposition peaks with writing can also be noted. This aging is particularly pronounced for older pens. While only the first asterisk written by the 2003 pen was different from the others, the concentration of CV increased continuously with writing for the three oldest pens (1988, 1982 and 1973). The difference in relative concentration of CV between asterisks no. 1 and 100 was more than 4% for the pen manufactured in 1973. This can be compared with the aging of ink entries on paper in darkness for about 2 years.

The results in Tables 2 and 3 represent extreme situations—pens not used for writing for a very long time, in some cases probably for

up to 20 years. Nevertheless the phenomenon is important to know, as are the problems encountered because of that in ink comparison and ink dating. If, for example, inks in two signatures are to be compared, letters and signs at the beginning of the signatures should not be taken for analysis. Microscopic examination may also be helpful for finding ink entries produced by “dried” pen tips. The photomicrograph presented in Fig. 1 illustrates the phenomenon. The text starting with the letter K was produced by a dried tip. The letter K is most probably different in composition from the following text.

Most of the analyses presented in this study were performed on Ballograf pens, because of our big collection of these pens and the knowledge about the year and the month of their manufacture. The design and the construction material of various ballpoint pens are different. Therefore, the extent and the rate of ink aging and evaporation at the tip may vary with the manufacturer. An additional extreme case was selected for analysis: a BIC pen of unknown age but not used for a considerable period of time, probably for more than 20 years. It is a cheaper pen with the cartridge made of plastic, while that of Ballograf is of metal. The pen was almost dry and some effort was necessary to make it work again. Table 4 shows results obtained for this pen and for a Ballograf pen manufactured in 1972, not used for writing for at least 10 years. Three hundred asterisks were written by each pen and a detailed analysis of successive

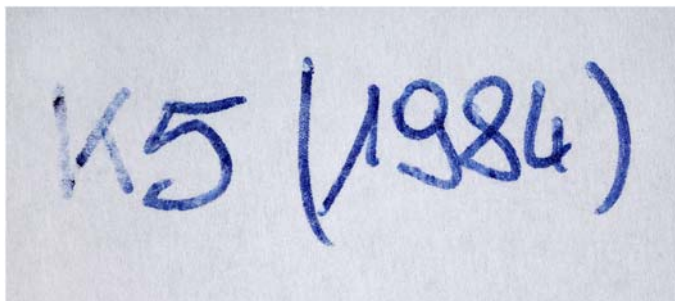


FIG. 1—The photomicrograph of text produced by a dried pen tip. The text starts with the letter K that clearly differ in the evenness of distribution and the amount of the ink from the following text. The letter K will most probably differ in composition from that of the following text.

TABLE 4—Detailed study of the changes in dye and solvent composition in writings from a more than 30-year-old Ballograf pen and an old BIC pen. More explanation in Table 3.

Manufacturer	Asterisk No.	$\Sigma$ Small Peaks, %	% TPR	% MV	% CV	PE/ $\Sigma$ Dyes
Ballograf 1972	1	4.68	17.75	45.90	36.35	0.253
	2	4.40	16.90	45.80	37.3	0.32
	3	4.00	16.55	45.75	37.7	0.34
	5	4.09	16.25	45.80	37.95	0.377
	10	4.27	16.15	45.80	38.0	0.35
	50	4.24	16.10	45.65	38.25	0.40
	100	3.97	16.15	45.65	38.2	0.435
	200	4.00	15.95	45.75	38.3	0.40
	300	4.11	16.00	45.85	38.15	0.411
	BIC unknown year	1	7.9	26.0	45.9	28.1
2		8.05	25.9	45.65	28.45	0.217
3		7.15	25.25	45.75	29.0	0.221
5		7.0	24.8	45.7	29.5	0.270
10		6.7	24.45	45.5	30.05	0.321
50		6.4	24.15	45.3	30.55	0.412
100		6.55	23.6	45.35	31.05	0.433
200		6.15	23.2	45.45	31.35	0.477
300		6.1	22.95	45.4	31.65	0.480

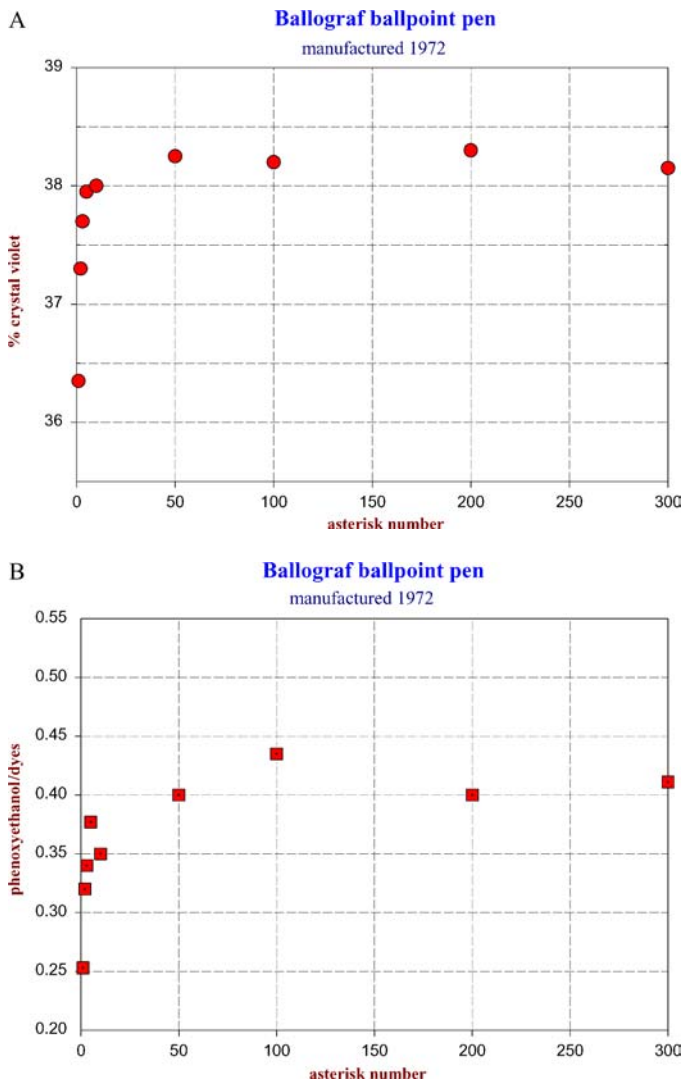


FIG. 2—Aging and evaporation of ink near the tip of a Ballograf pen manufactured in 1972. The figure shows changes in the concentration of Crystal Violet (CV) and the content of phenoxyethanol in asterisks written continuously one after the other with this pen. The pen was not used for writing for at least 10 years.

writing was performed. Three hundred asterisks correspond to a line of approximately 3 meters length but the way of writing is more similar to that of normal writing.

To illustrate the effect of evaporation and aging of dyes, the results in Table 4 were plotted in Figs. 2 and 3. The figures consist of two plots. The first plot shows the relative percentage of CV in the CV-MV-TPR system as a function of asterisk number. The ratio of PE to the sum of dyes against asterisk number is shown in the second plot. In both figures the plots for PE and CV seem to follow a similar pattern. For the 1972 Ballograf pen the aging and evaporation was only observed for the first three asterisks. Asterisk no. 5 and higher showed constant bulk concentration with some inhomogeneities in the PE content. Possibly the evaporation process penetrates somewhat deeper into the cartridge. This is in agreement with the other experiments performed using Ballograf pens and presented in Tables 2 and 3. The BIC pen also showed similarities in both plots. However, the phenomenon of aging inside of the cartridge was much more pronounced. The concentration of CV and PE increased very rapidly in the first 10 asterisks, but it continued to increase even after the asterisk 50 and 100. It might

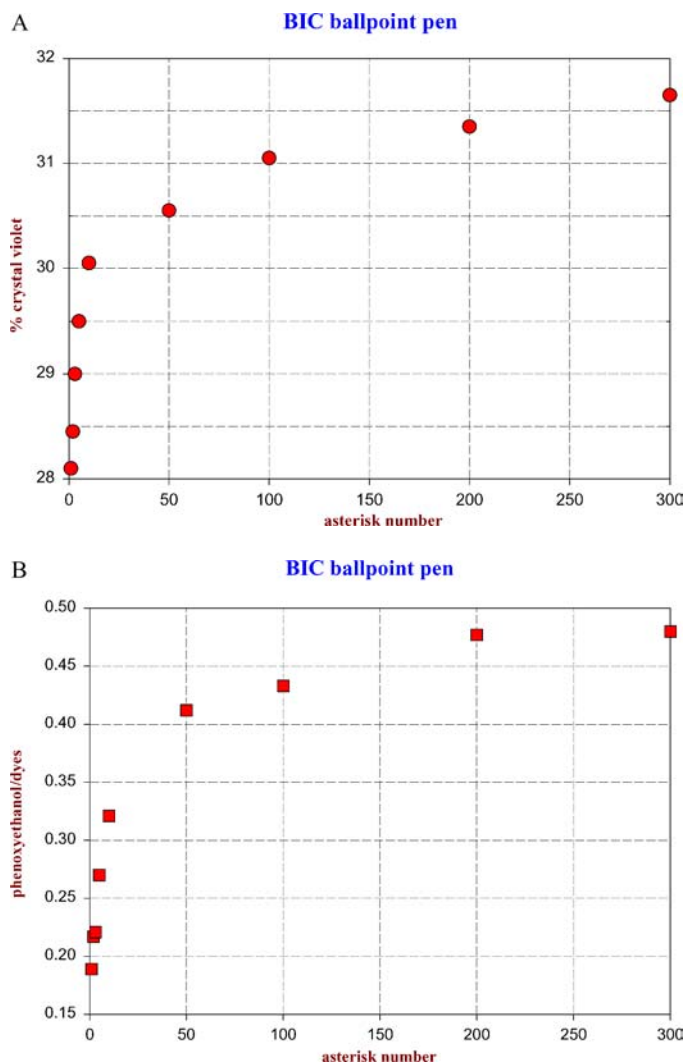


FIG. 3—Aging and evaporation of ink near the tip of a BIC pen, the year of manufacture unknown. The figure shows changes in the concentration of Crystal Violet (CV) and the content of phenoxyethanol in asterisks written continuously one after the other with this pen. The pen was very old and probably not used for more than 20 years.

cause serious problems if a pen in such condition is encountered in casework—either for ink comparison or for determination of the relative age of ink.

#### Inhomogeneities of Inks from Regularly Used Pens

Three ballpoint pens from different manufacturers were investigated. The pens were regularly used for writing, at least once a month. One hundred asterisks were written by each of the pens. Asterisks nos. 1, 25, 50, 75 and 100 were chosen for HPLC analysis. The chromatograms obtained at 540 nm were evaluated for dye composition of ink entries. Phenoxyethanol was detected by fluorescence and related to the concentration of dyes. The results are summarised in Table 5. The composition of dyes was found indistinguishable among the various asterisks analyzed. Therefore, this table only shows the ratio between PE and CV detected in the respective ink. Unlike the composition of dyes, this ratio is not exactly the same for each of the inks. Although the number of inks examined here was limited, the results indicate that ink entries are not homogeneous concerning the concentration of PE. Whether

TABLE 5—Variations in phenoxyethanol concentration in ink entries produced by different pens, regularly used for writing. The concentration of PE is related to that of Crystal Violet (CV).

Pen Manufacturer	Asterisk Number	PE/CV
BIC	1	0.98
	25	1.58
	50	1.67
	75	1.70
	100	1.81
SOLSTAR	1	0.320
	25	0.314
	50	0.317
	75	0.305
	100	0.378
UNKNOWN*	1	3.46
	25	3.69
	50	2.95
	75	3.31
	100	3.51

\* “SP-SBA” engraved on the cartridge.

these inhomogeneities are inside pen cartridges or the result of different rate of evaporation from the ink entries on paper (e.g., due to variations in line thickness) is not answered by this experiment. But the result is important to be aware of when studying the evaporation of PE from ink entries suggested for dating of inks.

#### Conclusions

The aim of this study was to find eventual inhomogeneities and aging of ink inside pen cartridges. No aging of dyes in the ink bulk material was discovered when the results of analyses of fresh ink entries produced by the same pen at widely separated occasions (more than 6 years apart) were compared. Inhomogeneities in terms of the ratio between volatile solvents, such as phenoxyethanol, and dyes were observed in many of the pens examined. Inhomogeneities in terms of the composition of the dye mixture were not observed in pens frequently used for writing. When pen cartridges not used for a considerable period of time (in many cases for more than 10 years) were investigated, aging of ink at the tip of the cartridge was detected. Two processes were investigated—the evaporation of PE from ink and changes in the composition of cationic dyes. When starting the writing with these pens, the concentration of PE and CV was sometimes considerably lower than that in bulk material. For almost all the pens investigated this aging and evaporation process was only observed for a few (about three) first written asterisks. One of the pens (manufactured by BIC) showed aging and evaporation from a much larger volume at the tip. The process was still noticed after writing 50 asterisks (corresponding to an ink line of approximately 50 cm in total). Although the condition of the pen cartridges chosen for this study was extreme, care should be taken when comparing inks in, e.g., two signatures. Taking samples from the beginning of the writing should be avoided and/or several ink entries from different positions should be analyzed. This is also important for relative ink dating, when two ink entries, written actually simultaneously, might be found different in the way normally caused by aging.

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