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Changes in Composition of Ballpoint Pen Inks on Aging in Darkness

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ABSTRACT: A method for comparison of the relative age of ink entries written by the same ballpoint pen on documents stored in darkness is presented. Inks were extracted from the document and analyzed by HPLC (high performance liquid chromatography). On aging, changes in the chemical composition of the inks were noted. These changes were similar to those observed when inks were exposed to light or heat. The aging was followed by using ternary diagrams constructed for dyes generally present in blue-colored inks—Crystal Violet, Methyl Violet, and Tetramethyl Para Rosaniline. The procedure is applicable for relative dating of ink entries in diaries, notebooks, etc., where often several ink entries are written by the same ink. However, a prolonged exposure of the document to daylight and/or artificial light (light from fluorescent tubes) as well as to extensive heat will render the whole procedure inapplicable. An example of the use of the proposed method in casework is given.

KEYWORDS: forensic science, inks, HPLC, ternary diagrams, aging of inks, relative age determination, document examination

In forensic examinations of documents the dating of ink entries is often of considerable importance. There are two approaches for dating inks on documents—relative and absolute dating. Many efforts have been made to solve this problem—see, for example, Ref 1. For the determination of the relative age of inks it is important to ascertain the order in which ink entries were made.

This study has a major limitation. It has been devoted to solving only one type of relative age determination. Questioned documents encountered in our casework include diaries and calendars, when the question to be answered is if the ink entries were made chronologically, according to the date written, or if they were made later (e.g., at one and the same occasion). It is not unusual for the same ballpoint pen to be used repeatedly for a considerable time period. It is also important that inks in such documents are not often exposed to light or heat. The effect of light on the composition of blue ballpoint pen inks was examined in our previous study (2). The light exposure would influence the composition of the ink considerably and in a manner similar to normal aging. Also accelerated aging of ink by heating and by exposure to high humidity will change the ink composition in a similar way.

Materials and Methods

Examined inks

As part of the ink-dating project, which has been carried on in our laboratory for some time, ink-entries in the form of asterisks have been produced repeatedly (once a month for about two years) on different types of paper and stored in various places and conditions. One of the documents involved in this project was an ordinary notebook containing lined paper. Blue colored ballpoint pen inks from several different ink manufacturers were used for writing asterisks in this notebook. Each asterisk corresponded to about 1 cm ink in length. The notebook was kept at room temperature and closed all the time.

Extraction of Inks

Single asterisks were cut out from the paper in the notebook and placed inside 2 mL glass vials. Approximately 0.2 mL methanol (HPLC grade) was added and the ink material extracted for 30 min at room temperature, followed by heating the vial contents up to boiling point for 1–2 min. The methanol extract was then transferred to a 200 μL conical glass inset and evaporated to dryness by a stream of nitrogen. The dry residue was dissolved in 20 μL methanol. During the whole extraction procedure, the ink and the extract were protected from exposure to intense light. Aliquots of 20 μL were taken for analysis. It means that the whole sample was taken for one analysis.

HPLC analysis

Ink analyses were run on a Hewlett-Packard series II Liquid Chromatograph connected to the HP's HPLC^{3D} ChemStation. The instrument was equipped with auto sampler, auto-injector and diode array detector from Hewlett-Packard. HPLC separations were performed using a 25 cm 5 μm TSKgel ODS-120T (4.6 mm ID, Tosohaas Bioseparation Specialists) stainless steel column. The mobile phase consisted of two solvents. Solvent A was a mixture of 20% acetonitrile and 80% water containing 10mM $KClO_4$, pH adjusted to approximately 3 with hydrochloric acid. Solvent B was 100% acetonitrile. The gradient was linear from solvent A to solvent B for 20 min, followed by 5 min isocratic elution by Solvent B. The flow rate was 1.0 mL/min at room temperature. The diode array detector was programmed to record chromatograms at 540 ± 60 nm, 254 ± 10 nm, 300 ± 20 nm, 355 ± 10 nm, 220 ± 10 nm and 440 ± 20 nm. Full spectra were acquired on all significant peaks from 190 nm to 600 nm.

Results and Discussion

Decomposition of Basic Dyes on Aging

Basic dyes, such as Crystal Violet, Methyl Violet, Victoria Blue, and Tetramethyl Para Rosaniline, are often found in ballpoint pen inks. In our experiments, a combination of Crystal Violet (CV) and Methyl Violet (MV) and Tetramethyl Para Rosaniline (TPR) was

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found in every blue-colored ball pen ink. Commercial Methyl Violet consists in reality of all these three different components and is presumably the compound added by ink manufacturer.

The lightfastness of these cationic dyes is rather poor. On exposure to daylight, both CV and MV decompose. This decomposition seems to imply a successive loss of methyl groups, which are substituted by hydrogen atoms. Crystal Violet thus decomposes into Methyl Violet, which subsequently decomposes into TPR and further into other, structurally similar compounds, by successive loss of methyl groups.

We have observed similar decomposition of the basic dyes in blue ballpoint pen inks on aging in darkness. Compared with compositional changes on exposure to light, the changes due to aging are much slower. Figure. 1 shows HPLC chromatograms obtained for one of the inks examined in this study. The four chromatograms were recorded for the ink stored in darkness at room temperature (20–23°C) for: (a) 1 day, (b) 9 months, (c) 13 months and (d) 22 months, respectively. The ink stored for 1 day is designated as fresh ink in this figure. Figure. 2 shows the analysis of another ink stored at the same conditions. It can be seen in these figures that the relative concentration of CV decreases and that of TPR increases on aging.

In our previous work (2), we evaluated the quantitative changes in ink composition on exposure to light using ternary diagrams. The diagrams were constructed for the CV-MV-TPR system. We have used ternary diagrams and the same system also for illustration of changes in ink composition on aging in darkness.

The ternary diagram for four of the blue inks studied in this work is shown in Fig. 3. Arrows mark the initial compositions of the inks examined (i.e., those of fresh inks). The samples of inks were taken at about 4-month intervals. The changes in ink composition follow similar curves as those obtained on exposure to light—starting from the left, going upwards and to the right. The distance in the diagram between the subsequent measurements for the same ink is not exactly the same; it depends on experimental errors as well as such factors as the different thickness of various ink entries. The

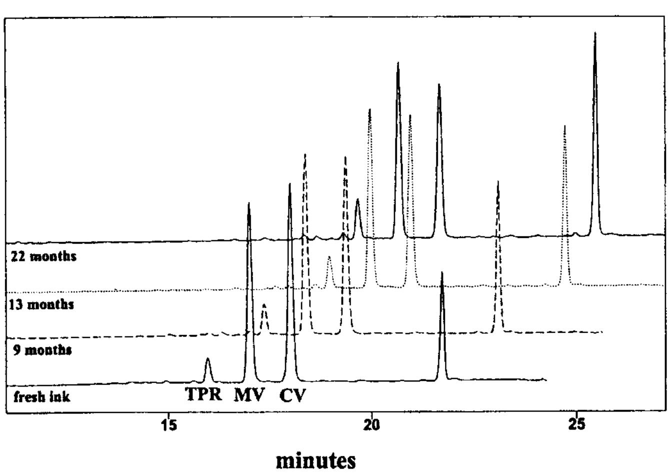

FIG. 1—*Effect of aging on the composition of a blue ball pen ink. HPLC chromatograms were obtained at the detection wavelength of 540 nm, using a diode array detector. Ink samples were extracted by methanol from text written inside a notebook, stored in darkness. The traces represent the chromatograms for the same ink as fresh, respectively nine months, 13 months and 22 months old. The measurable changes in the ink composition were observed when the age difference was about three to four months. The upper chromatograms are shifted along the time axis to make the comparison easier.*

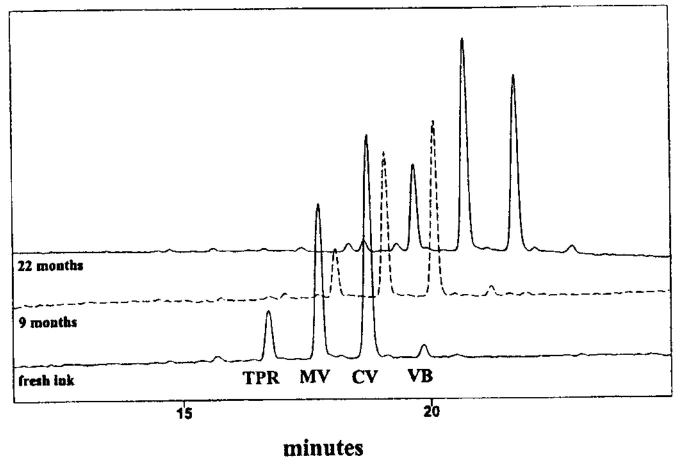

FIG. 2–*HPLC chromatograms recorded at 540 nm for another sample of blue ballpoint pen ink stored in darkness. The traces represent chromatograms obtained for fresh ink, nine months old and 22 months old ink, respectively. The upper chromatograms are shifted along the time axis in the manner similar to that used in Fig. 1. The peak designated VB has been identified as Victoria Blue.*

changes caused by exposure to daylight for 1 day correspond to those achieved by aging for at least 1 month in darkness. The kind of ink, the thickness of ink layer on paper, and the kind of paper are all parameters that can influence the rate of compositional changes. In our experiments, for ink entries inside a notebook, differences in the composition of the same ink were detectable for ink entries separated at least 3–4 months in time (Fig. 3).

The loss of methyl groups from CV and MV does not end with the formation of TPR. The process of losing methyl groups continues and additional decomposition compounds are produced. These compounds are eluted prior to the TPR peak. Also, this observation is in agreement with the results of exposure of inks to light. The decomposition peaks detected at 540 nm with the retention times shorter than that of TPR were designated as peaks 1–5 in our previous work (2). The plot of the sum of peak areas of peaks 1–5 against age of ink entries is shown in Fig. 4. Peak areas are expressed in relative units, so that the sum of peak areas of peaks 1–5 together with those of TPR, MV and CV is 100. For inks investigated in this study, stored in darkness and with age range from fresh to about 2 years old, the amount of the decomposition products represented by peaks 1–5 seems to increase linearly with the age of ink. The straight lines in Fig. 4 are parallel with similar slopes. The lines do not pass through the origin of coordinates. The reason for these features is that inks contain various amounts of the decomposition products presumably already from production. Fig. 4 gives an additional dimension to the ternary diagram in Fig. 3. The changes in the ink composition on aging as manifested by the ternary diagram for the system CV-MV-TPR should be accompanied by similar changes in the amount of the decomposition peaks 1–5 if the investigation concerns the same ink.

Use of the Proposed Diagrams in Casework

The consequence of the results presented in Figs. 3 and 4 is that the composition of ink stored at darkness will slowly change with time. The difference in age of two ink entries for about 4 months or more should cause measurable differences in the composition in a predictable way. Thus two or more documents written using the

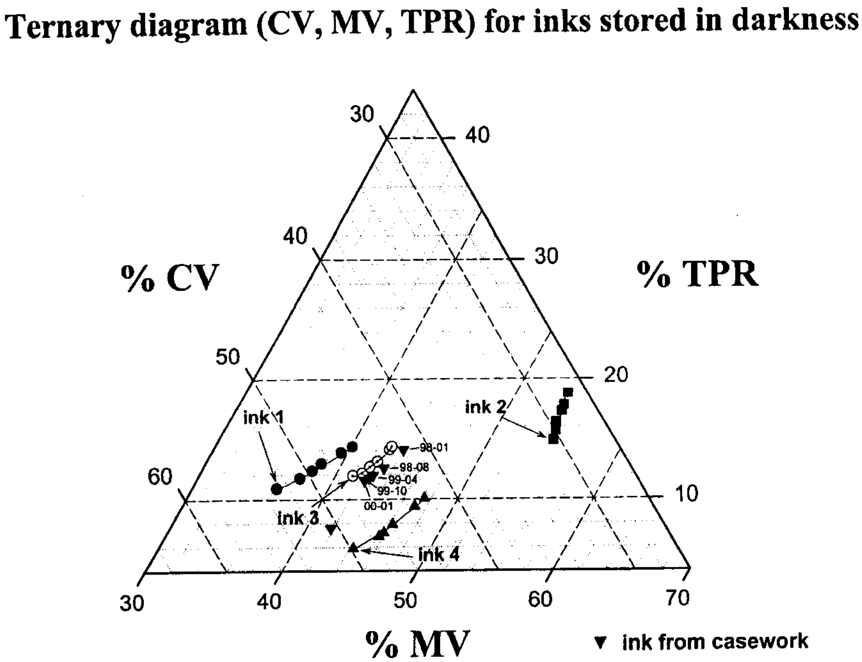

FIG. 3–*Ternary diagram constructed for the system CV-MV-TPR. Four different blue colored inks from different manufacturers have been used in these experiments. Arrows mark the initial composition of fresh inks. On aging, the composition of the inks changes in the direction upward and to the right in the diagram. The spacing in time between the subsequent measurements on the same ink is about four months. The difference in age between the fresh ink entries and the oldest ones is thus about two years.*

The upside-down triangles are from casework and represent the compositions of inks from dated notes in a diary—more information in the text.

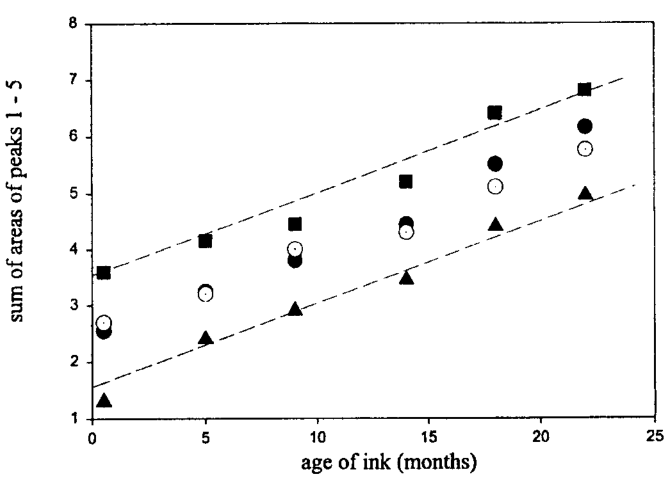

FIG. 4—*A plot of the sum of peak areas of the decomposition peaks 1–5 as a function of the age of the inks. This diagram is a complement to the ternary diagram in Fig. 3. The symbols used for the different ink samples studied are the same in this figure. The concentration of peaks 1–5 seems to increase approximately linearly with the ink age. The dashed lines are intended to lead the eye in the diagram.*

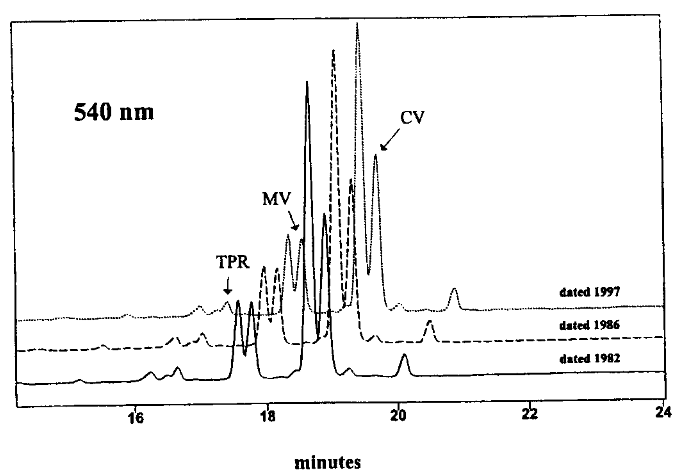

FIG. 5—*HPLC chromatograms obtained for methanol extracts from ink entries on three different documents, dated 1982, 1986, and 1997. The detection wavelength is 540 nm. The peaks representing CV, MV, and TPR are marked. Note the absence of differences in the composition of the ink samples despite the large differences in the date stated. This finding indicates that the text written on all these three documents is of the same date or from occasions not very far from each other in time.*

same ink at the same occasion or very close to each other in time will be found indistinguishable by this method. If these documents are dated back to essentially different dates, the forgery will be revealed.

We have met several examples of such forgeries in our casework. Figure 5 illustrates one of these cases. Three documents, dated at three widely different occasions, were submitted for examination. The HPLC chromatograms detected at 540 nm for methanol extracts of the three ink entries are indistinguishable (Fig. 5). Although this study was not applied to ink entries separated more than two years in time (for lack of such samples), the composition of ink entries separated ten years in time should not be exactly the same.

A kind of document recurrently encountered in the forensic science laboratory are diaries or calendars with notes written with ballpoint pen inks. Every note in such documents is dated; however, the suspicion is that some of these notes have been made at the same time at a later occasion, for example, to prove an alibi. If all the ink entries in a diary are written by different inks, the case can not be solved in this way. Nevertheless, people often use the same pen for making daily notes. If the same kind of ink is used for longer than about four months, the diagrams proposed in this study may be applied to investigate whether the date of these notes is correct.

Upside-down triangles in Fig. 3 (the ternary system CV-MV-TPR) represent analyses of ink entries in a diary, subjected to investigation in our laboratory. There were frequently notes written in the diary, starting with the year 1998 and continuing until beginning of 2000. The document was sent to our laboratory for examination in September 2000. The optical inspection of the ink notes found several types and shades of ballpoint pen inks, used only for shorter time periods. One of the inks, however, seemed to be used repeatedly for a period of almost two years. Six samples of this ink shade were taken from notes separated at least 3–4 months in time from each other, extracted and analyzed. Five of the six upside-down triangles in Fig. 3 are labeled by year and month from the diary. All these five ink entries have compositions consistent with those for ink entries for the same ink but of different age. The older the ink entry, the more upwards and to the right in the diagram its composition is compared to the fresher ink entries. The sixth triangle corresponds to ink extracted from the note dated in the middle of 1999. Obviously, the composition of this ink is not at all in correspondence with the other five. The simple conclusion is that this ink is of different kind, only similar in color shade to the first one.

The conclusion we have drawn from our results was that the various notes represented by the five upside-down triangles in Fig. 3 were not written at the same time, but chronologically according to the date in the diary. It is of course impossible to claim that the dates are correct.

Unfortunately, there is a drawback to this method. If the various notes on the documents to be dated have been exposed to various amounts of light in extent sufficient to change the composition of ink noticeably, changes in composition due to pure aging will be overshadowed by the effect of light. At this moment we cannot distinguish between the decomposition of CV on aging in darkness and on exposure to light. So it is possible to alter the apparent age of ink entries deliberately by an adequate exposure to light. But this implies sufficient knowledge about the effect of light on the composition of ballpoint pen inks.

Also the exposure to heat (and in combination with high humidity) will change the composition of inks in the manner undistinguishable from that of pure aging. Our experiments revealed that for most of the inks investigated the exposure to 100°C for 4 h resulted in changes in ink composition corresponding to normal aging for about four months.

Conclusions

The method of relative dating of two or more ink entries written by the same ballpoint pen ink has been proposed in this study. Ternary diagrams for the system CV-MV-TPR have been used to illustrate changes in the ink composition due to aging in darkness. The method is applicable to ink samples stored in darkness for example on the pages of a book or pad of paper. An extensive exposure to light (2) or heat will change the composition of ink samples considerably and overshadows the effect of normal aging.

As a consequence, the proposed method should be applied mainly for ink entries in diaries and similar documents, where more than two ink samples may be found in chronological order. The compositional changes should follow the curves predicted by the ternary diagrams for most of the samples and not in a random manner, which is the case when some of the samples are exposed to different amount of intensive light or heat.

References

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