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CASE REPORT

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Dating of Ballpoint Pen Ink

ABSTRACT: In this paper we describe a case in which a cash book, dated of the year 2000, was sent to the Forensic Science Division, Document Laboratory, Zurich Canton Police in March 2003. The questioned document was a list of 29 pages containing a consecutive handwritten numbering and dated entries (payments) made of blue ballpoint pen ink. By definition, a cash book has to be written by hand and the entries have to be made daily. The questioned document was suspected to have been written within a short period (e.g., a few hours) and backdated. The document lab was asked to determine the date of the entries of the questioned list. On one hand, we were asked, if the cash book had been kept on account consecutively during the period of one year, and on the other hand, the judges were interested in knowing, if the document could have been written in 2003 and back dated to 2000. To answer these questions, the document was examined for latent elements by electrostatic detection device (ESDA). The relative dating of the entries was performed by the quantification of the ballpoint pen ink dyes and their degradation products using HPLC. Results show that it is possible to determine the relative age of entries written by ballpoint pen within a relatively short time scale, if storage and supporting material of the different samples are the same or at least similar.

KEYWORDS: forensic science, forensic document examination, ballpoint pen ink analysis, ink dating, HPLC, ESDA, dye decomposition

Document labs are often confronted with the question, if the content of a document such as a receipt, legal agreement, will, etc. has been changed by adding a part to it, if parts have been erased, or if some important entries have been overwritten. But one of the most challenging investigations is the dating of entries. If a questioned document is written by means of mechanical devices (typewriter, inkjet printer, laser printer, copy machines, etc.) a maximum age may be determined from the market introduction of the applied technique or the type of ink. In case of handwritten entries, this method is only valid for very old documents. However, a maximum age determination is in general not adequate to answer the question concerning a forgery by backdating. Because the signature, produced with ballpoint pen, is often the only handwritten trace in a questioned document, it represents the most important element for document dating analysis.

In the past years, different research has been undertaken to study the degradation process of ballpoint pen ink dyes (1–5). Applied ink dating analyses have recently been collected in a valuable and useful paper by V. N. Aginsky (5). Much effort has been put to ink dating in the past but not all of the published methods are reliable and some of them were wildly criticized (6).

Regarding dating of documents in general, *absolute* and *relative* dating have to be distinguished: With absolute dating, the analytical dates lead to the determination of a time frame, in which a questioned entry must have been produced. With relative dating, samples of two or more questioned areas (or different sheets) are analyzed and compared to determine which sample is older/younger than the other(s).

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Reference collections of standard ink lines on paper that have been stored in controlled conditions for natural aging are often used for the calculation of aging curves. Absolute dating of questioned document samples, which are known to have been stored in similar conditions leads to reliable results. Nevertheless, one has to be careful with the interpretation of the results because questioned documents usually reach the lab after passing through the police office and/or lawyer's office, where especially exposure to light is an unknown parameter during this period of time. Thus, this may provoke artificial aging of a document resulting in a sample looking older than it actually is.

Another problem is the ink composition at the time of the writing process. Ink composition ratios within different ballpoint pen types may vary on a large scale even if their dye ingredients are the same. One of the most frequent dye components in ballpoint pen inks is crystal violet (hexamethyl-pararosanilin) which is always present with its decomposition product methyl violet (mixture of penta-, tetra- and trimethyl-pararosanilin). Hexamethyl-pararosanilin (HP) is an unstable compound, therefore it can be used for dating studies. Unfortunately, the HP/methyl violet ratio varies, as mentioned above, from pen to pen.

The unknown storage conditions (temperature, influence of light, ozone from e.g., copy machines installed near to the storage place of the questioned document, etc.), the unknown composition of the ink at the moment of the writing process as well as differences in supporting material (e.g., different paper types) are the reason, why a comparison of lab standard inks and inks from questioned entries have to be undertaken with extreme care.

However, a relative dating may be performed in several cases (but always with some restrictions): electrostatic detection (ESDA) for visualization of indented impressions may provide information that are in contradiction with entries on a questioned document. Therefore, ESDA should be executed in all cases of document dating because it is a non-destructive and rapid method.

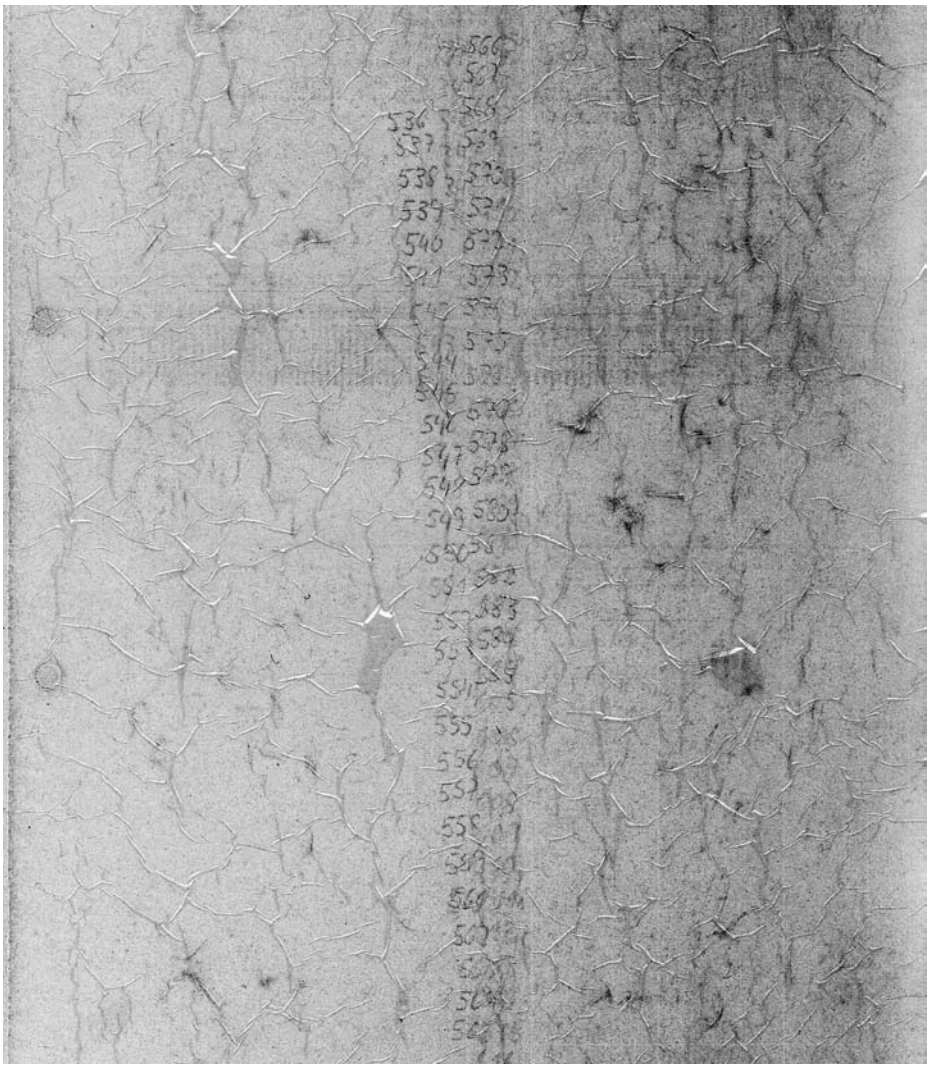

FIG. 1—*ESDA of page 18. The indented impression from the expense voucher column on page 16 (starting from No. 536) is in a clean alignment and clearly shifted to the left of the corresponding columns on page 17 (starting from No. 566) and page 18. This marks prove, that at least, the expense voucher column on page 16 was written in one writing process and not one by one on the corresponding date.*

If the questioned document contains an intersection between two or more lines, it can be important which of the lines has been produced first and, as a consequence, is older than the other(s). Intersecting lines may be examined by different methods (Personal Communication: European Document Experts Working Group, 2004).

Analysis of ink dyes is recommended, especially if the questioned document contains parts of entries on the same page (additions) that are suspicious. In this case, storage conditions and supporting material are most likely to be identical for both the disputed and undisputed entries.

Material and Methods

The evidence examined was a cash book of 29 pages. All consecutively pre-numbered pages were of the same material (yellow colored paper sheets). The handwritten entries had been performed with pencil(s) (expense voucher number column) and ballpoint pen(s) (date, text, and amount lines).

Electrostatic Detection Apparatus investigation (ESDA) was performed (prior to destructive ink analysis) on each page by preconditioning of the document at 65% relative humidity for about 30 min.

Samples of ballpoint pen ink were taken by cutting lines of 5×1 mm ($l \times w$) out of the document. The samples were chosen in such a manner as to build up a chronological database. Each sample was placed in a small polypropylene capped tube. The ballpoint pen ink was extracted with 40 μL of methanol. The tubes were sealed, shortly vortexed and left for 15 min at room temperature. The extracts were transferred into HPLC micro-vials via micropipette filters. Then, the vials were capped and HPLC was performed (apparatus: HP 1090, stationary phase: RP-18 CC 150/4.6 Nucleosil 100–5 column, mobile phase: potassium perchloride buffer pH 3.0/methanol). Ink dye components were identified and quantified using Agilet ChemStation software.

Results and Discussion

ESDA has shown relevant indented impressions on pages 17, 18, and 28: The expense voucher numbers 536 to 565 from page 16 become visible on pages 17 and 18. This is not unusual because the pre-numbered sheets may have lain in a sequential stack during the writing process onto page 16. But the whole indented impression column is in a clean alignment and clearly shifted to the left of the corresponding columns of page 17 and 18 (Fig. 1). This proves,

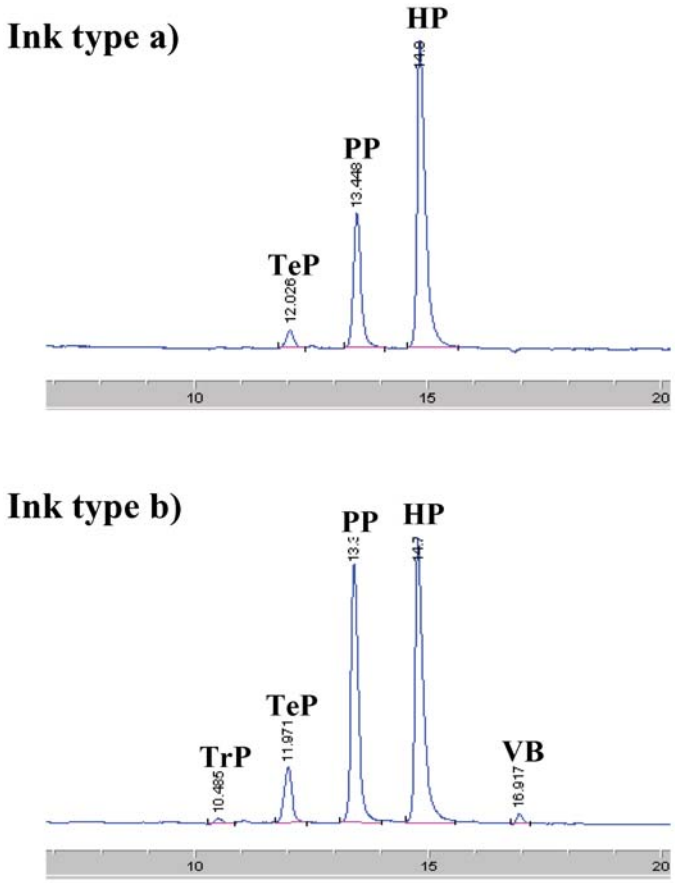

FIG. 2—*HPLC chromatogram of ballpoint pen ink types a) and b) from January to August and September to December, respectively. The ink types are distinguishable by the different concentration ratios of crystal violet (HP, at 14.8 min) and its degradation products (methyl violet: PP, at 13.4; TeP, at 12.0; and TrP, at 10.5 min) as well as by the ingredient Victoria blue (VB, at 16.9 min) that is only present in ink type b).*

that at least, the expense voucher column of page 16 was written in one writing process and not one by one on the corresponding date.

Indented impressions from one entry line on page 21 have been visualized on page 28. Thus, page no. 28 was lying under page no. 21 at the moment the mentioned line was written. No drastic anachronism (multiple entries indicating a delay of weeks or months) was detected within the entire document. Therefore ESDA-results were not sufficiently important for the court to prove a dramatic falsification of the document. Nevertheless, the method has shown to be adequate and useful for relative dating.

With HPLC analysis, two different types of ballpoint pen ink could be differentiated: Type a), entries on pages 1 to 19 (January to August 2000), and Type b), entries on pages 20 to 29 (September to December 2000). Both ink types a) and b) consisted of crystal violet (= hexamethyl-pararosanilin, HP) and its decomposition products pentamethyl-pararosanilin (PP), tetramethyl-pararosanilin (TeP) and trimethyl-pararosanilin (TrP). However, their dye component ratios was different. Another difference between the ink types was an additional dye component in ink type b), namely Victoria blue (VB) (Fig. 2).

As long as an ink is stored inside a pen cartridge, dye components are preserved from degradation and, as a consequence, the dye-to-dye ratio is stable (7). In an aging tests series of three years with ten different blue ink ballpoint pens in our lab, no day degradation could be detected within the pen cartridges. Aging processes start at the moment of ink application onto the substrate (e.g., paper) due to contact with oxygen, light, ozone, etc. Both crystal violet (HP) and Victoria blue (VB) decompose with time.

HP is transformed to its decomposition product PP by desmethylation. PP is transformed to TeP and latter to TrP. While HP concentration always decreases with time, the change of PP concentration depends on the HP/PP ratio at the beginning of the process: high HP concentration with low PP concentration at the beginning would result in an increase of PP amount with time since more PP is produced than decomposed. In a graph with the HP/PP ratio as a function of the writing date (older entries on the left of the X-axes), this results in an increasing dating curve. Low HP concentration with high PP concentration at the beginning would result in a decrease of PP amount with time and correspondingly with a decreasing dating curve. The calculation of the HP/PP or HP/VB quotient has the advantage that the amount of extracted ink does not influence the result.

In both ink types of the presented questioned document, the initial HP/PP ratio was such that the calculated HP/PP quotients of each sample would decrease with increasing ink age resulting in an increasing dating curve.

The results are summarized in a graph as a function of the corresponding date (Fig. 3). It is self-evident that the resulting dating curves from the two ink types can not be correlated to each other.

The amount of VB was too small to be taken into account for dating analyses in ink type b) and not even present in ink type a).

After this first analysis, the questioned document was stored for another 50 days in controlled conditions (room temperature, environmental humidity, and in darkness) similar to usual office conditions. After that additional controlled aging, samples were taken from the same lines as in the first series. Subsequently, they were analyzed for dye quantification using the mentioned HPLC method. The data interpretation is represented as a function of the writing date plus 50 days and superimposed on data of the first series (Fig. 4). For better comparison of the curve shapes, the "date of entry" has been shifted 50 days for the second series samples.

At the beginning of the degradation, the process is logarithmic and becomes almost linear with time. As a consequence the shape of the degradation curve should flatten with time. The superimposition of the two series should give an impression of the writing period of the questioned document: if the document has been written within a few weeks in e.g., 2003, an additional aging of 50 days would result in a flatter dating curve. But if the document has really been written in 2000, an additional aging of 50 days would not have a significant influence on the dating curve.

Summary

In a questioned cash book, dated the year 2000, the age of the entries was contested. An ink analysis was performed and an aging curve of the ink dyes data were interpreted. Two different ballpoint pen ink types were detected (one type for the entries dated from Jan. to Aug. 2000 and another one for the entries dated from Sep. to Dec. 2000). After the first series of ink analyses, the document was stored in controlled ambient conditions for 50 days and ink analyses were repeated on a second series of samples. The dating curve was then calculated for this second series as well. The two curves of the first eight months were superimposed for comparison. The curve shapes showed no dramatic irregularity: the similarity of the slopes of both dating curves was in agreement with a writing period that could not

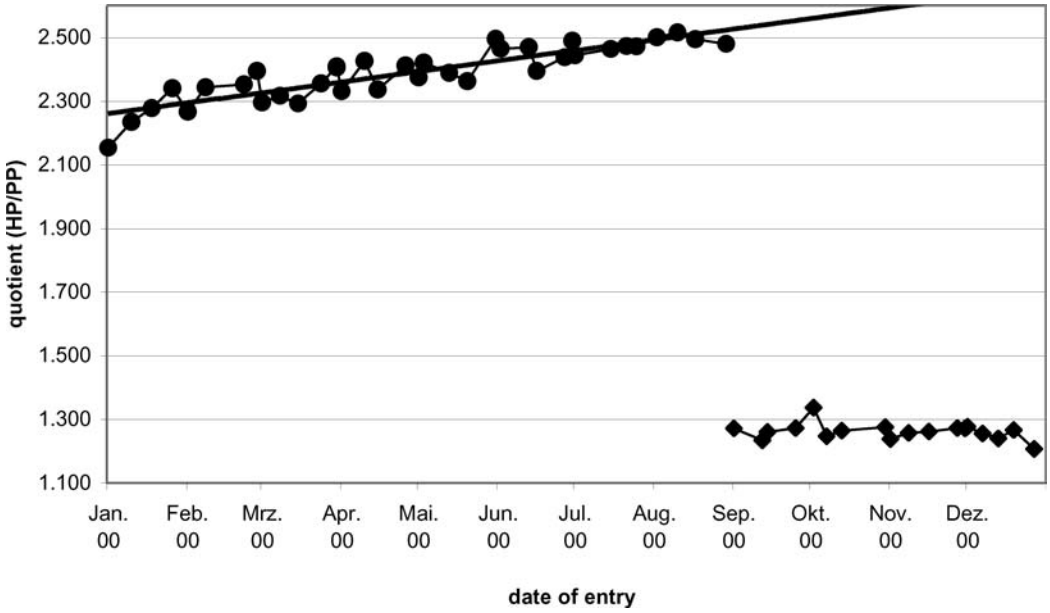

FIG. 3—*Data interpretation of HPLC-analysis of the samples that were taken from the questioned document: the quotient of hexamethyl-pararosanilin/pentamethyl-pararosanilin (HP/PP) is represented in a diagram as a function of the writing date. A trend-line has been calculated for ink type a) [●] showing the degradation of crystal violet. For ink type b) [◆] such a trend was not visible and was not calculated for that reason.*

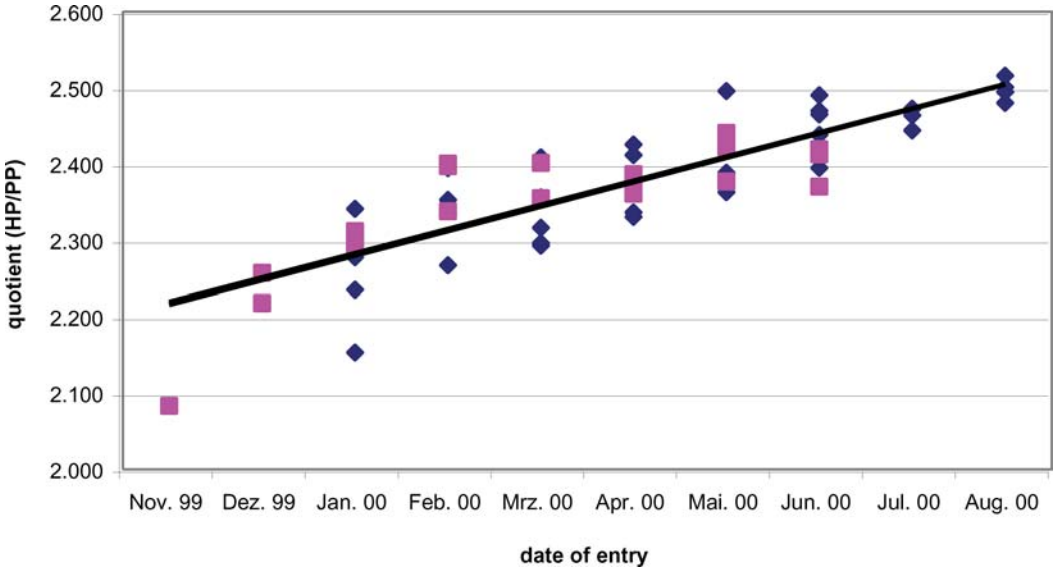

FIG. 4—*Data interpretation of HPLC-analysis of the samples that were taken from the questioned document when it was received as well as after an additional storing time: superimposition of ink analysis series 1 (■) with the repeated analysis of samples after an additional natural aging of 50 days (◆). Backdating of 50 days of the second series has been made for better comparison.*

be too young. Thus, no deliberate misrepresentation was concluded. The last four months were interpreted as "non-conclusive." Prior to ink analyses, small dating irregularities could be detected by ESDA.

Conclusion

It has been shown that HPLC analysis of ballpoint pen inks is a good and valid method to perform a relative dating of documents. If there are enough samples and enough time space between the samples, a reliable statement can be given. For some inks (depending on the composition), it is even possible to give a very rough estimation of the absolute age.

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