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TECHNICAL NOTE

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Comparison of Natural and Artificial Aging of Ballpoint Inks

ABSTRACT: Solvent evaporation caused by aging from ballpoint inks was measured by gas chromatography/mass spectroscopy (GC/MS). The sample preparation was carried out with two different thermal desorption systems. The results are compared. Thirteen inks were classified with regard to their solvents, polymers, and additives. The variation of the aforementioned compounds caused by aging was monitored for naturally and artificially aged samples. In this paper, the results are compared and discussed with respect to forensic casework.

KEYWORDS: forensic science, age determination, artificial aging, ink, gas chromatography/mass spectroscopy, thermal desorption

In the last years the direct method of dating ink entries based on the analyses of the solvent evaporation from the writing has been a subject for several forensic investigations (1–6).

Recently Bügler et al. (6) published a method for age determinations of ballpoint inks by gas chromatography/mass spectroscopy (GC/MS) based on sample extraction by thermal desorption in two steps. It is postulated that the amount of phenoxyethanol (PE) in fresh pen strokes evaporates at a moderate temperature whereas the amount of PE which is included in the polymer matrix in older pen strokes needs a higher extraction temperature. The method is applicable if PE does not evaporate from the writing too fast.

The following paper describes a variation of the method.

Material and Methods

Equipment

For thermal desorption of the ink samples on paper two different thermal desorption units were used:

- Atas Desorption System Optic III with Linex Injector and cold trap, equipped with a CombiPAL autosampler, connected to a Thermoelectron GC/MS-system Trace GC/DSQ.
- Markes Desorption System Unity/Ultra TD with cold trap, connected to an Agilent 6890N GC/MS system.

In the Atas system the sample is placed directly into the liner where thermal desorption takes place. The gas is frozen out in a part of the column which is led through the cold trap cooled by liquid nitrogen. In the Markes system thermal desorption is carried out in glass tubes. The gas is gathered in a cold trap which is cooled by a peltier element.

The preconditioning of the glass tubes is performed by heating the tubes at 300°C for 30 min.

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For the monitoring of the instrument performance 1 μL of a solution of PE (Merck, purity >99%), 2-decanone, 2,3-dimethylnaphtalin and n-pentadecan in acetone (Merck, purity >99.8%) on paper was analyzed using the same conditions under which the analyses of ballpoint inks were carried out.

Desorption of Ink Samples

Desorption Method—A piece of pen stroke on paper (length: 0.7–1.0 cm) was cut out and placed into the liner (Atas) or the thermal desorption tube (Markes). The sample was heated in three steps at 100°C (15 min), 140°C (15 min), and 200°C (10 min) and the desorption gas was collected in the cold trap at −80°C (Atas) or −15°C (Markes). After every thermodesorption step the sample was removed from the heating system. By heating the cold trap (300°C/min: Atas; 100°C/min: Markes) the desorption gas was given onto the column for analysis at the following conditions:

Column: ZB5ms Guardian
Carrier Gas: He, 1.2 mL/min
Oven program: 100°C, 3 min; 100–200°C, 15°C/min; 200–320°C, 25°C/min; 320°C, 6 min

Integration of the signals was performed on chromatograms of the single ion mode.

Screening of Contents—In order to find criteria to differentiate between the inks, screenings of the volatile compounds were performed.

For the screening of the volatile contents of the ballpoint inks, ink samples on paper were put on glass pins which were placed into the glass tubes and heated at 240°C. The collection of the gas and the GC/MS-analyses followed the aforementioned conditions.

Accelerated Aging

For accelerated aging of ballpoint inks, samples were cut out (0.7–1.0 cm of the pen strokes) and put into an oven at 45°C.

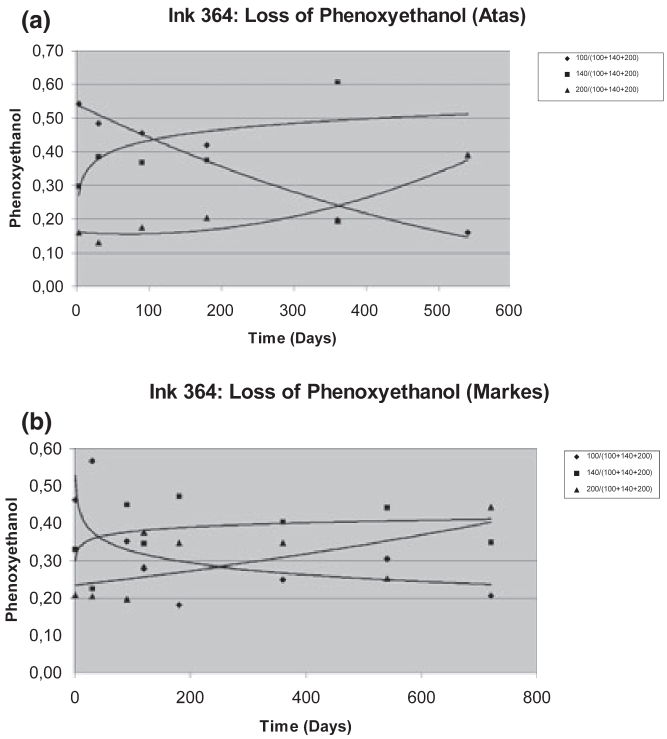

FIG. 1—*(a) Validation of the two systems (Atas). (b) Validation of the two systems (Markes).*

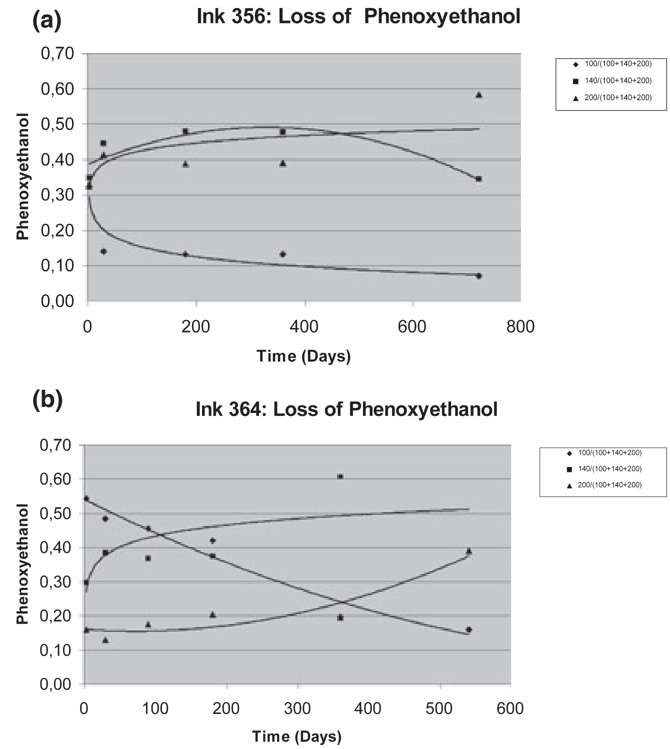

FIG. 2—*(a) Fast aging ballpoint ink. (b) Slowly aging ballpoint ink (see also Fig. 1a).*

In a time range from 2 to 33 1/3 days the loss of the solvents and the variation of polymer compounds and plasticiziers was measured.

Results

Validation of the Systems

Naturally aged samples of the same ink were analyzed on the Atas and the Markes system. In all cases only single measurements were made.

The standard deviation was measured by analyzing samples of an ink standard with a natural age of 18–21 days once a week. The standard deviation of 10 measurements was 0.06–0.07.

The graphs for the variation of PE, measured at the three temperatures shows a very good correspondence for the two systems. So it is possible to control the reliability of the results of one system by the other (Fig. 1).

Natural Aging

The main compound which gives information about the aging of a ballpoint ink is PE which is used as a solvent in nearly all inks. The loss of PE was monitored for natural and artificial aging of inks in three thermal desorption steps at 100, 140, and 200°C. The amounts of outgassing PE at each temperature was brought into relation ratio to the total amount of PE measured in the three steps. These mass-independent results corresponded to those which were reported by Bügler et al. (6) for fast aging and slowly aging inks. The fast aging inks show a loss of PE within the first month while the slowly aging products lose the solvent during a time of 3 months or more (Figs. 2*a* and 2*b*).

Accelerated Aging

The results obtained by analyses at the three temperatures for the samples from accelerated aging (Fig. 3) correspond to those of the naturally aged inks (Fig. 2*b*).

The loss of PE caused by accelerated aging of ink samples of defined natural ages is shown in Figs. 4*a* and 4*b*. Accelerating aging in three steps was carried out with ink samples with a natural age of 3 months (storage at 45°C for 3, 6, and 17 days) and 1 year (storage at 45°C for 3, 6, and 9 days). For writings of unknown age the amount of PE of the original sample and the variation of this amount by three steps of heating allow estimations of the original age of the writing.

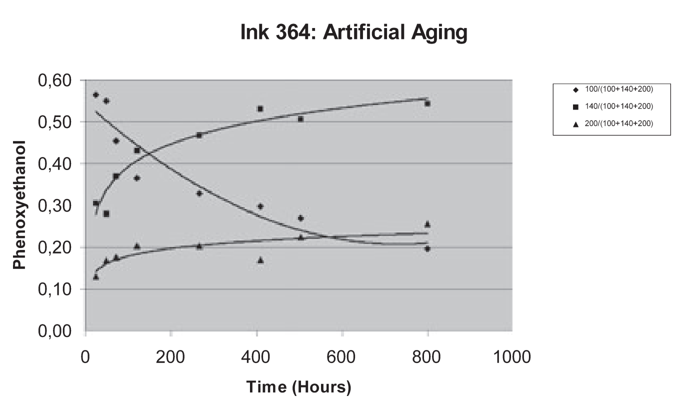

FIG. 3—*Artificial aging of ink 364 at 45°C.*

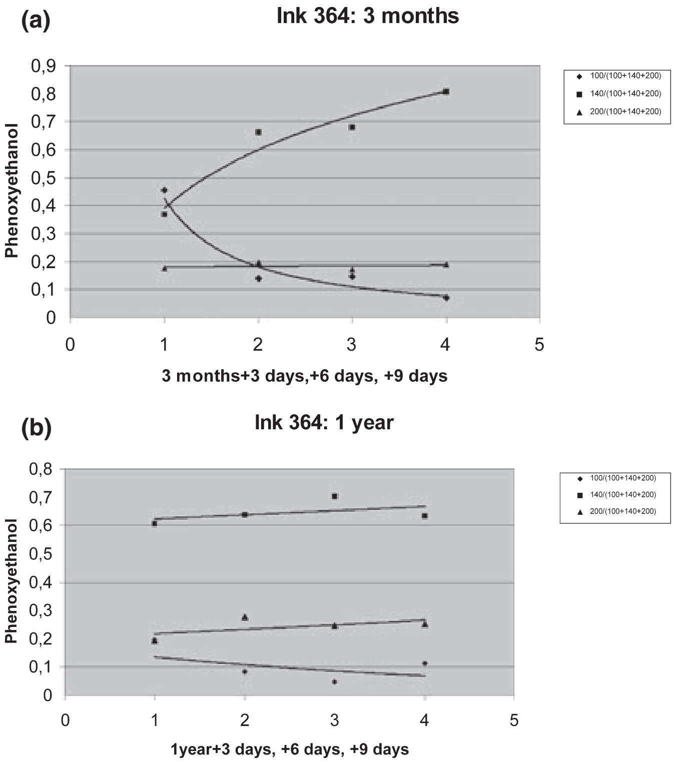

FIG. 4—*(a) Artificial aging of a 3-month-old ink sample. (b) Artificial aging of a 1-year-old ink sample.*

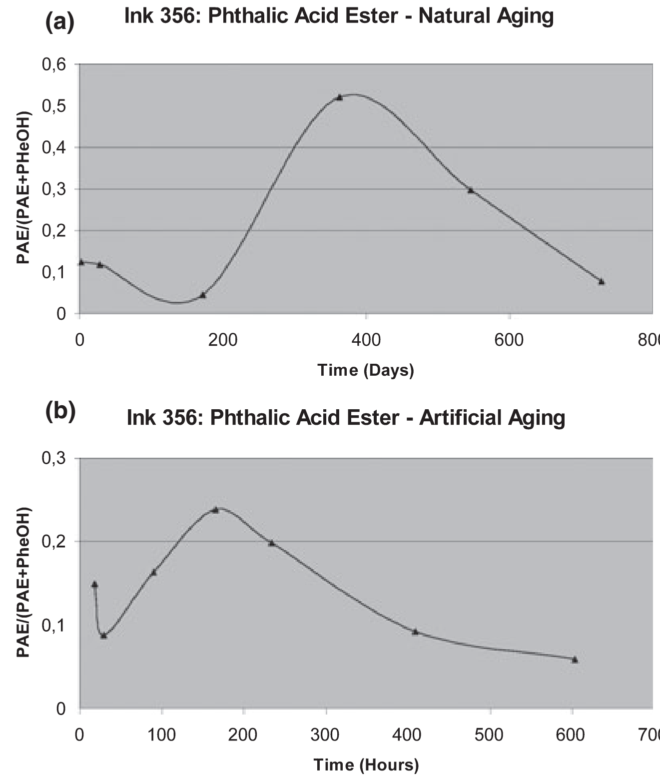

FIG. 5—*(a) Fast aging ink 356—Natural aging: phthalic acid ester/phthalic acid ester + PE. (b) Fast aging ink 356—Artificial aging: phthalic acid ester/phthalic acid ester + PE.*

Estimations on the Age of Writings Based on other Compounds in Addition to Phenoxyethanol

For fast aging inks which contain large amounts of phenoxyethoxyethanol, phtalic acid esters, or phtalic anhydride, estimations about the age of questioned writings are possible based on the variation of these compounds by aging of the writing.

Seven of the ballpoint inks analyzed show characteristic graphs for the variation of phthalic anhydride or phthalic acid esters by aging of the pen strokes. This result, which is obtained for the naturally aged inks, corresponds to that of the artificially aged samples of the same inks (Figs. 5*a* and 5*b*).

For five inks which contain a huge amount of phenoxyethoxyethanol the decrease of this solvent at 140°C referred to the amount of PE allowed estimations on the age of the pen strokes (Fig. 6).

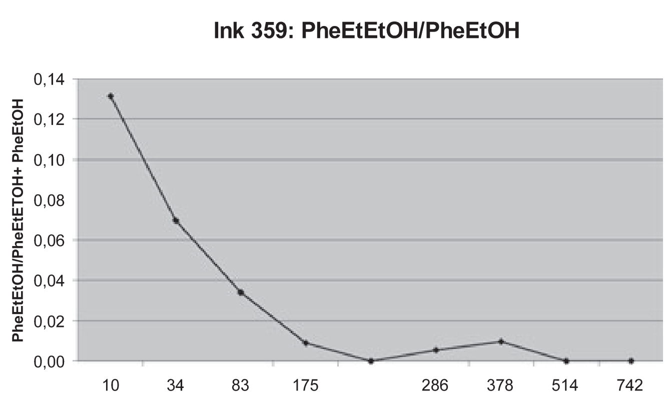

FIG. 6—*Ink 356—Decrease of phenoxyethoxyethanol.*

Discussion

As reported by several authors in the past (1–6), the loss of PE can be used as a reference to the age of a writing produced with ballpoint ink.

It is possible to differentiate between inks which lose most of the solvent very quickly (within 1 month) and inks which lose the biggest amount of the solvent within 3 months or more.

In our laboratory, these results could be verified by using thermodesorption GC/MS-chromatography with two GC/MS-systems with different thermal desorption systems. The sample preparation and the conditions of the analyses were the same, and the results obtained from the two systems, i.e., the amounts of PE detected at the three temperatures in relation to the whole amount of PE, showed a good correspondence.

If either of the thermodesorption GC-MS methods is applied to forensic casework, the results may not give the necessary information to estimate the age of a questioned ink. This is possible if samples of the same ink are measured three or four times within a larger range of time (1–3 months). The storage time can be shortened by accelerated aging at 45°C (3–33 1/3 days). For this purpose, tests of accelerated aging at 45°C of fresh and naturally aged older samples were performed.

It was shown that the decrease of PE in slowly aging inks of artificially aged samples corresponds well to that of natural aging and allows conclusions on the original age of the questioned writing.

The results concerning the outgassing of PE cause some limitations to forensic case work if the samples delivered for analysis are of the fast aging type.

In that case the variation of other contents of the ink caused by aging can give more information. For seven inks which contained small amounts of plasticizers or phthalic anhydride as polymer a variation of these compounds was obvious which allowed further estimations on the age of the writing. Further studies will be carried out to support this result.

If the loss of phenoxyethoxyethanol in relation to the decrease of PE in inks which contain a huge amount of phenoxyethoxyethanol is monitored, a variation of phenoxyethoxyethanol can be noticed which gives additional information concerning the age of the ink.

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