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Analysis of Bic Cristal Medium Ballpoint Pen Inks

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This work studies the ink composition of 26 BIC Cristal Medium ballpoint pens, 13 blue and 13 black, purchased from various countries around the world in 2008. The volatile components of these inks were studied by gas chromatography/mass spectrometry (GC/MS) preceded by a liquid-solid extraction, with the use of retention time locking (RTL) for the 1st time in the forensic field. The RTL tool assures reproducible retention times, and the realignment of the chromatograms assures rescaling of the time axis of the chromatogram. In order to determine the qualitative composition of dyes present in each ink, thin-layer chromatography (TLC) was used, followed by the identification of those colorants by liquid chromatography tandem mass spectrometry (LC/MS-MS). The study revealed that at least 2 different blue-ink formulations were used around the world in this period of time but that the formulation of the black inks was identical for all the studied pens. The differences found in the blue-ink formulations regard not only volatile components but also dyes. The great differences found in the concentration of the volatile component phenoxyethanol (PE) present in the 2 blue-ink formulations lead to important differences in the natural aging process of these 2 blue formulations as measured by the loss of the amount of PE against the time. The amount of PE varied depending on the BIC ink formulation between 221.9 µg and 84.7 µg per lineal centimeter of ink stroke 1 day after the ink was deposited on the paper.

Introduction

The study of an ink and its aging, as well as matching an ink with another, is an important goal in the forensic examination of questioned documents. The association of a given ink with a pen and a model could also be a very interesting point to a forensic document examiner.

Writing inks are complex mixtures of 1 or several colorants, a carrier or vehicle with 1 or several solvents, and resins. Ballpoint pen inks are viscous and insoluble, or only slightly soluble, in water.

In this work the study of the ink composition of some ballpoint pens of the same brand and model (BIC Cristal Medium) was carried out. Two groups of inks were studied, 13 black and 13 blue, all of them bought in different countries around the world. Considering the common brand and model of the pens, the same colorants were expected, with possibly some small differences in volatile components.

TLC is a well known and widely used separation technique for discriminating inks (Capello and others 1983). From 1971, when Sen and Ghosh developed a method with this technique for iron-based inks, until the year 2007, when Weyermann and others reported the differentiation of blue ballpoint pens by laser desorption ionization mass spectrometry and high-performance TLC, authors such as Cantu and Brunelle (1980), Cantu and Prough (1987), Brunelle and Lee (1989), Lyter III (1993), Aginsky (1993, 1994, 2006), Tsutsumi and Ohga (1998), and Jasuja et al. (2005) described extensively the use of this technique, both to discriminate and to date inks. The ASTM Standard Guide (2005) for Test Methods for Forensic

Writing Ink Comparison E1422-05 included this technique to reach conclusions on the similar or different origins of 2 samples of ink. The solvent system n-butanol, ethanol, and water (50:10:15) is 1 of the developing solvents (solvent system II) proposed in that guide.

Although TLC can be used to discriminate between inks that have a different dye composition, it does not characterize these dyes. Similar dyes having the same color and TLC properties might have different molecular structures. In this work, LC-MS/MS has been applied for the identification of these dyes in BIC inks after the development of the TLC plates.

Liquid-solid extraction followed by a GC-MS analysis allows the volatile ink components to be differentiated. This methodology, reported by Aginsky (1993, 1994) as well as by Gaudreau and Brazeau (2002) and Weyermann (2005), is used both to determine the volatile components present in an ink (especially phenoxyethanol, or PE) and to measure their loss due to evaporation after an ink is deposited on the paper.

In the present work, a method of GC-MS has been developed for the separation, further determination, and quantifying the ink volatile components. Full scan mode is used to identify the ink volatile components and selected ion mode (SIM) for detection of specific analytes. In SIM mode, the MS gathers data for the masses of interest rather than looking for all the masses over a wide range. In this way the components could be quantitatively evaluated with increased sensitivity compared (by a factor of 10 to 100 times) to full scan mode. GC-MS in scan mode has been used to evaluate the ink volatile components, and the SIM mode was used for quantifying phenoxyethanol (PE), applying in both cases retention time locking (RTL) method.

Variations in GC of system components (column type, carrier gas, detector type…) and of instrumental parameters (pressure, temperature program, etc.) imply modifications of peak elution; thus, developing an analytical method requires external standards for elution time correction.

As an alternative, Hewlett-Packard Company has created a software which allows applying "method translation" when system components or instrumental parameters are modified. Method translation is based on rescaling the time axis of a chromatogram without changing peak elution pattern. The most useful applications of method translation found are the following:

- Apply the same method using different column or the same method employing different gas carrier.
- Optimize a method on the same column with variations in gas flow rate and temperature program.
- Adapt a method to different detectors operating at different conditions (e.g., outlet pressure).
- Retention time locking.

The "retention time locking" (RTL) tool is an operating mode that allows evaluating the instrumental variables of the chromatographic system such as the nominal pressure, the length of the column, the flow rate, and the oven temperature ramp, minimizing their influence over the retention times.

Retention time is a key parameter in a chromatographic separation, since most of the peak identifications are based on their retention times. While carrying out a calibration using the equipment software, keeping the retention times constant is of the greatest importance for the validation of the method.

There are many routine equipment maintenance actions that alter retention times, such as the cutting of the column. Even in multidisciplinary laboratories, it is not possible to get exactly the same retention times when a method is transferred from 1 instrument to another, even if the conditions in which the method runs are identical. This necessitates a different calibration for each instrument and precludes comparing chromatograms obtained from different instruments. The RTL allows obtaining virtually the same time from 1 system to another, saving analysis time. The advantages of its use are:

- It is not necessary to update the calibration curve when installing or cutting a column or when performing routine maintenance.
- The results can be compared between different instruments and/or laboratories.
- Provides the ability to lock a peak and reproduce exactly a method developed in another laboratory or a published method.
- Provides the capability to differentiate between closely eluting peaks.

This is the 1st time the RTL approach has been applied to ink volatile components determination. It is a promising tool to develop a fast and efficient GC method which will facilitate the identification of compounds in complex mixtures like inks.

Methods and Materials

Chemical and Reagents

Ethylene glycol (99,8%), propylene glycol (purity grade ≥99,5%), hexylene glycol (99%), phenol (≥99%), aniline (≥99,5%), ethoxy ethoxyethanol (99%), 2-ethylhexanol (≥99,6%), benzyl alcohol (≥99%), phenylethanol, phenoxypropanol (≥93%), methoxy methylethoxy propanol (99%), dimethoxy propane (98%), 2-aminotiluene (99%), diethylaniline (99%), diphenoxyethane (99%), dipropilene glycol (99%), crystal violet, methyl violet2B certified 80%, and Victoria blue B were purchased from Sigma Aldrich (Steinheim, Germany); and 2-phenoxyethanol was obtained from Fluka (Steinheim, Germany). Acetonitrile gradient grade was supplied by Teknokroma (Barcelona, Spain).

Ink Samples

Lines of BIC blue and black ballpoint inks were placed on an 80 g multipurpose white paper. The BIC ballpoint pens used in this work were purchased in the year 2008 around the world: USA, Portugal, Spain, Argentina, Brazil, England, Germany, France, Belgium, Israel, and Holland.

Standard solutions of 50 mg/l of each analyte were prepared in acetonitrile.

Sampling

Harris Uni-core (Shunderson Communications, Inc., Canada) 1.20 mm-sized hole punches were used to remove 10 plugs of each ink-on-paper sample (equivalent to ca. 1.2 cm). The sampling was carried out at different time intervals, beginning with the 1st sample taken an hour after having written with the ballpoint pen. Three different samples of each ballpoint ink were taken and analyzed.

Extracting Vessels

Agilent 1.5 ml vials with 0.1 ml micro inserts, 28×6 mm with spring bottom (polymer) PK100 were purchased from Supelco.

TLC Materials and Procedures

The inks sampled from paper (10 plugs) were extracted with 100 µl of n-butanol:ethanol:water (50:10:15) mixture, and the coloured extracts were applied on high performance (HP) TLC silica gel 60- (20×20 cm) precoated glass plates (Merck, Germany). The plates were developed in n-butanol:ethanol:water (50:10:15).

GCMS

The inks sampled from paper (10 plugs), as well as paper blanks, were extracted in acetonitrile (70 µl) for 2 minutes in a rotary mixer before GC analysis. Two different sampling protocols were used for validating the RTL method and for evaluating the PE amount.

The RTL method was evaluated by analyzing 3 different samples (a,b,c) of each pen at time intervals. Two samplings were done, 1 at 1 hour after writing and the 2nd at 1 day after the ink was deposited on the paper.

For evaluating the amount of PE, the sampling was carried out at different time intervals. The 1st sample was taken 1 day after having written with each ballpoint pen. One sample was taken each day for the next 6 days; and after that, 9 samples were arbitrarily taken during the following 13 weeks.

The extracts were analyzed using an Agilent 6890N gas chromatograph interfaced with an Agilent 5973 inert mass selective detector and equipped with a split/splitless injection system. The column used was a DB-17MS (30 m×0.25 mm i.d. × 0.25 µm film thickness – 50%-Phenyl - methylpolysiloxane).

GC Conditions and MS Parameters

The injection volume was 1 µL, and was achieved in splitless mode. Helium was employed as carrier gas, with a column flow rate of 1,2 mL/minutes. Initial oven temperature was 60º C, then ramped at 10º C/minutes to 149º C, and finally raised at 30º C/minutes to 250º C, remaining at this temperature for 2 minutes.

The injector and ion source was set at 250º C, transfer temperature was set at 260º C, and the detection voltage at 1588. Quantification of peaks was made in time scheduled selected ion monitoring (SIM mode), choosing the following ions: m/z 94/138/77.

LC-MS/MS

The inks sampled from paper (10 plugs) were extracted in n-butanol:ethanol:water (50:10:15) mixture (200 µl) for 2 minutes in a rotary mixer before HPLC analysis. The extracts were analyzed using an Alliance 2695 coupled to a model 2996 DAD (Waters, Milford, USA). A reversed-phase Luna C18 column (150 x 2.0 mm i.d., particle size 3 µm; Phenomenex, Torrance USA) with a Phenomenex C18 guard column (4 x 2.0 mm i.d) was used. The eluents were water/acetic acid (99.5:0.5, v/v) (phase A) and methanol (phase B). An isocratic program was employed for the analysis: 1-solvent A 100% for 20 minutes, 2-solvent B 100% for 5 minutes, and 3-solvent A 100% during 7 minutes.

Pen	Source	Rf Value			
		Component A Violet	Component B Violet	Component C Violet	Component D Blue
Bic1	USA	0.39	0.45	0.48	0.55
Bic2	Portugal	0.39	0.45	0.48	
Bic3	Spain	0.39	0.45	0.48	
Bic4	Argentina	0.39	0.45	0.48	
Bic5	Brazil	0.39	0.45	0.48	0.55
Bic6	Oxford - England	0.39	0.45	0.48	
Bic7	Germany	0.39	0.45	0.48	
Bic8	France	0.39	0.45	0.48	
Bic9*	Pocket Spain	0.39	0.45	0.48	
Bic10	Belgium	0.39	0.45	0.48	
Bic11	Glasgow - Scotland	0.39	0.45	0.48	
Bic12	Tel Aviv - Israel	0.39	0.45	0.48	0.55
Bic13	Holland	0.39	0.45	0.48	

Table 1. List of blue BICs used and Rf values of the different components separated with TLC of the 13 blue ballpoint pens BIC Medium examined in this work. *Bic9 is a BIC pocket.

Pen	Source	Rf Value		
		Component E Violet	Component F Violet	Component G Yellow
BicN1	USA	0.39	0.44	0.81
BicN2	Portugal	0.39	0.44	0.81
BicN3	Spain	0.39	0.44	0.81
BicN4	Argentina	0.39	0.44	0.81
BicN5	Brazil	0.39	0.44	0.81
BicN6	Oxford - England	0.39	0.44	0.81
BicN7	Germany	0.39	0.44	0.81
BicN8	France	0.39	0.44	0.81
BicN9*	Orange Spain	0.39	0.44	0.81
BicN10	Belgium	0.39	0.44	0.81
BicN11	Glasgow - Scotland	0.39	0.44	0.81
BicN12	Tel Aviv - Israel	0.39	0.44	0.81
BicN13	Holland	0.39	0.44	0.81

Table 2. List of black BICs used and Rf values of the different components separated with TLC of the 13 black ballpoint pen BIC Medium examined in this work. *Bic N9 is an orange BIC.

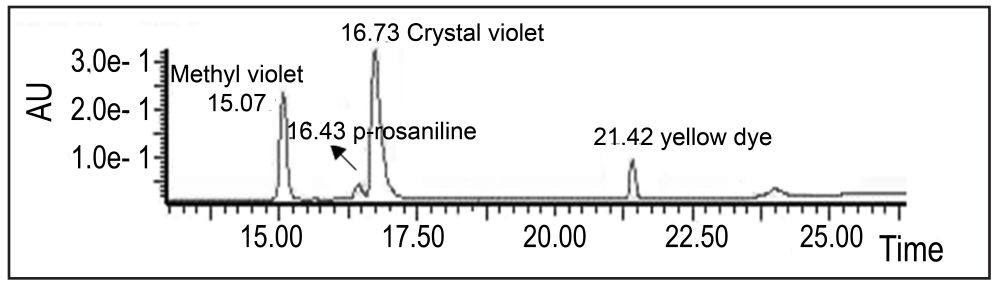


Figure 1. Chromatogram of the dyes present in a black ink (BICN 1) detected at 280 nm with diode array detector.

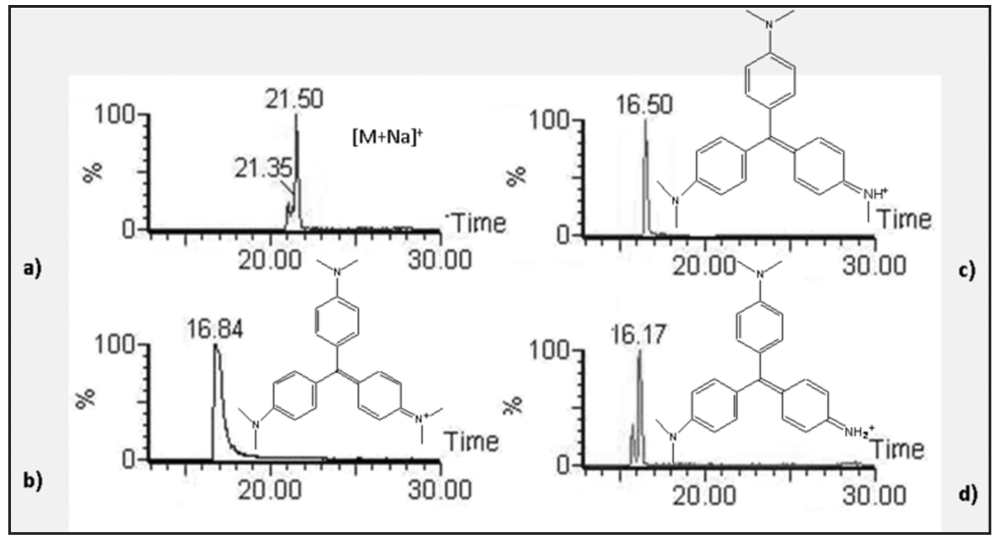


Figure 2. ESI-MS spectra in positive mode (voltage cone 45 V) of a) yellow dye, b) crystal violet, c) methyl violet and d) p-rosaniline.

The flow rate and column temperature were set to 0.250 mL/minute and 30º C, respectively.

The injection volume was 10 µL; complete spectral data was accumulated in the range 190-800 nm each second.

Results and Discussion

TLC Analysis of Dyes

One widely accepted methodology for separating the various dyes present in inks is thin-layer chromatography. Following the guidelines given in the ASTM E 1422-05, 13 blue and 13 black inks were developed in 2 separate plates. The solvent system employed was n-butanol-ethanol-water, 50:10:15; this is the system II of the mentioned guide.

The results of TLC examinations were documented by indicating the ink examined and the Rf of the spots visible under white light.

The same composition of colorants was expected for all the blue inks as well as for the black inks. However, based on the Rf values of (Table 1), at least 2 different mixtures of dyes could be clearly distinguished for the blue inks analyzed. All the black inks presented the same chromatogram (Table 2), showing the same composition with regard to colorants.

From the results shown in Tables 1 and 2, it was obvious that the Rf for the 1st dye in both cases was 0.39. The 2 other dyes were separated for the blue inks but not in the case of the black ones. In this case, the difference in the Rf value could be due to the co-elution of the 2 dyes.

LC-MS/MS Analysis

The 4 blue-ink components were analyzed with the LC-MS/MS technique with the aim of

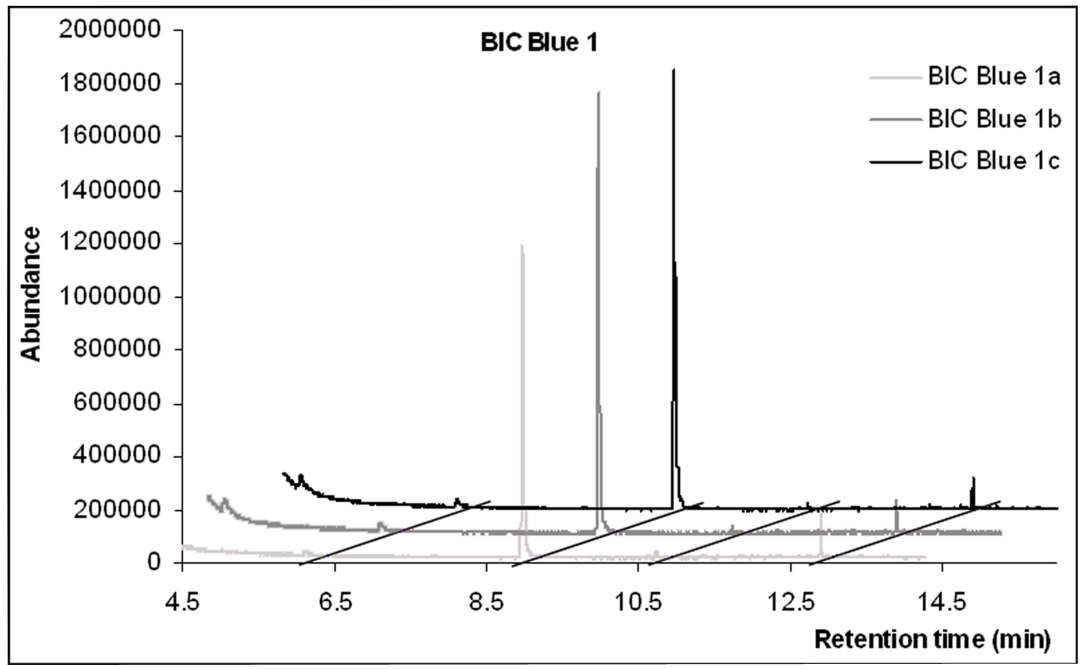


Figure 3. GC-RTL chromatograms of 3 samples (a, b, c) from the same BIC1 and collected at the same time interval, blue ink, in scan mode.

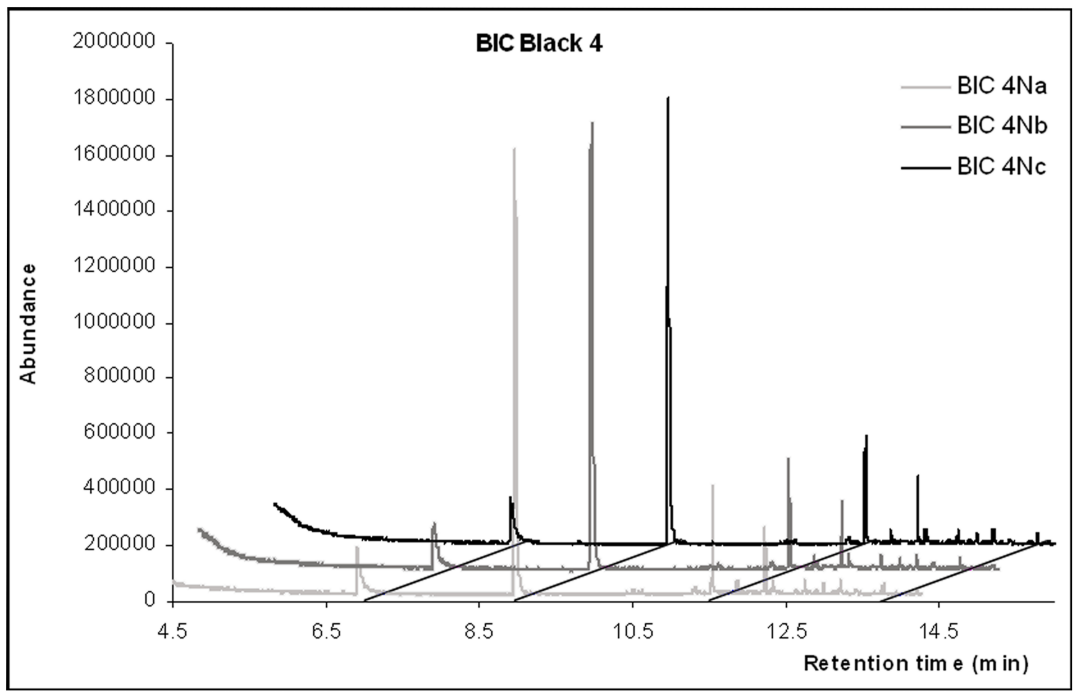


Figure 4. GC-RTL chromatograms of 3 samples (a, b, c) from the same BICN4 and collected at the same time interval, black ink, in scan mode.

determining the molecular composition of these dyes. There were expected to be the 3 dyes of the crystal violet family, and Victoria blue dye as the 4th.

LC-MS/MS is a powerful technique which has very high sensitivity and specificity and allows the detection and identification of chemicals in a complex mixture through their unique fragmentation spectra. Following the routine procedure, the results obtained with LC-MS/MS confirmed the a priori hypothesis of the dyes being triarylmethane dyes and specifically: tetramethyl pararosanilin (TPR – Component A), methyl violet (MV – Component B), crystal violet (CV – Component C), and Victoria blue (VB – Component D).

The same process was followed with the black inks. From the TLC results, 2 pararosanilines and a dye absorbing in the yellow region were expected. In this case, the LC-MS/MS allowed the detection of an additional violet dye. Three violet dyes, characterized as TPR, MV, and CV, and a peak with absorbance at about 590 nm (in the yellow region) were detected, as can be seen in Figure 1 and Figure 2.

The yellow dye found had a molecular ion of 453.1, had at least 1 methyl group, and formed adduct with sodium. At this moment, we have not managed to characterize the molecular structure of this dye.

GC-MS

Retention Time Locking

Since gas chromatographic elution shows significant run-to-run variations due to fluctuations in temperature, pressure, column degradation, or matrix effects, different approaches have been developed to minimize those variations. One of these is the so-called "Retention time locking" (RTL) (Blumberg and Klee 1998).

To lock a given method, one should calibrate the retention time against the head pressure. The procedure to develop a RTL method can be summarized as follows:

- Select an analyte from the matrix which is included in the calibration standards, easily identifiable and eluting in the most critical part of the chromatogram (neither too soon nor too late). In our case, the analyte was PE.
- Run 5 calibrations at 5 different head pressures: Pn –20%, Pn –10%, Pn , Pn + 10%, Pn + 20%, taking the head pressure of the nominal method (Pn) as the reference.
- The retention time of the target analyte (PE) is determined for each calibration run and the corresponding set of retention times and head pressures are fitted with a polynomial of degree 2. Once the fit is accepted, the calibration is stored and becomes part of the GC method.
- Fix the desired retention time of the target analyte (PE, Rt 9.0 min); so thus, the retention time will become locked and the GC method updated.

Once following the RTL method, retention time for PE was fixed at 9.0 minutes; and subsequently, all the other volatile components retention times were also fixed.

To evaluate the RTL method, each ink was sampled 3 times. After sample preparation, the 3 samples were injected in the GC system in RTL mode. Only a peak corresponding to a volatile component was considered; the quantity of the component was not evaluated.

The resulting chromatograms are shown in Figures 3 and 4. As can be seen, the 3 chromatograms for the same ink can be perfectly overlapped; that indicates a good stability of the retention time for the volatile components of the inks applying RTL method.

Despite being a very useful tool in the GC/MS technique, the RTL method is not very well known and is rarely employed in analytical laboratories.

Volatile Components

Once the RTL method was optimized, the 26 inks were analyzed by GC-RTL in scan mode with the aim of comparing the volatile components used in the manufacturing of the inks purchased in different countries.

Little differences between amounts of the volatile components were expected among the inks of each group, the blue one and the black one.

Two completely different behaviors were achieved; while all the black inks maintained the same chromatographic profile, at least 2 completely different ink formulations were detected for the inks in the blue group.

Three chromatograms in scan mode, arbitrarily chosen, BICN1, BICN4 and BICN7, have been overlapped showing the same volatile compound composition in the 3 inks, Figure 5.

The variations in the spectra after 12 minutes might be due to batch variations in the inks from different countries.

Scan chromatograms of the blue inks, samples BIC5 and BIC6, each representative of a different formulation, have been overlapped. As shown in

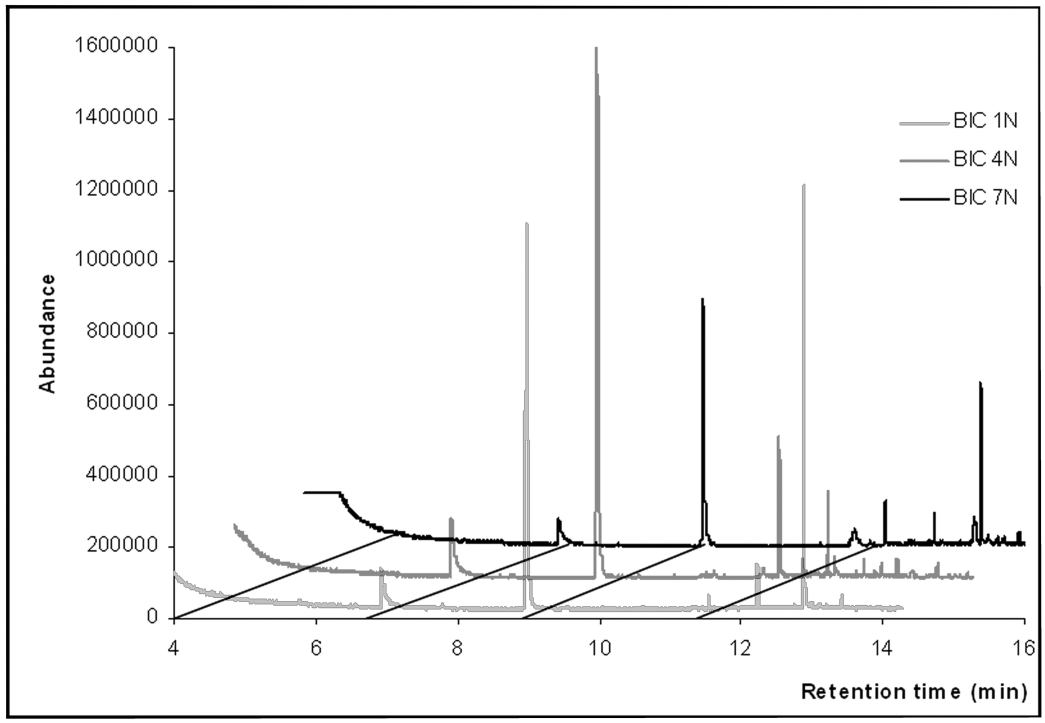


Figure 5. GC-RTL chromatograms of samples BICN 1, BICN 4, and BICN 7 in scan mode.

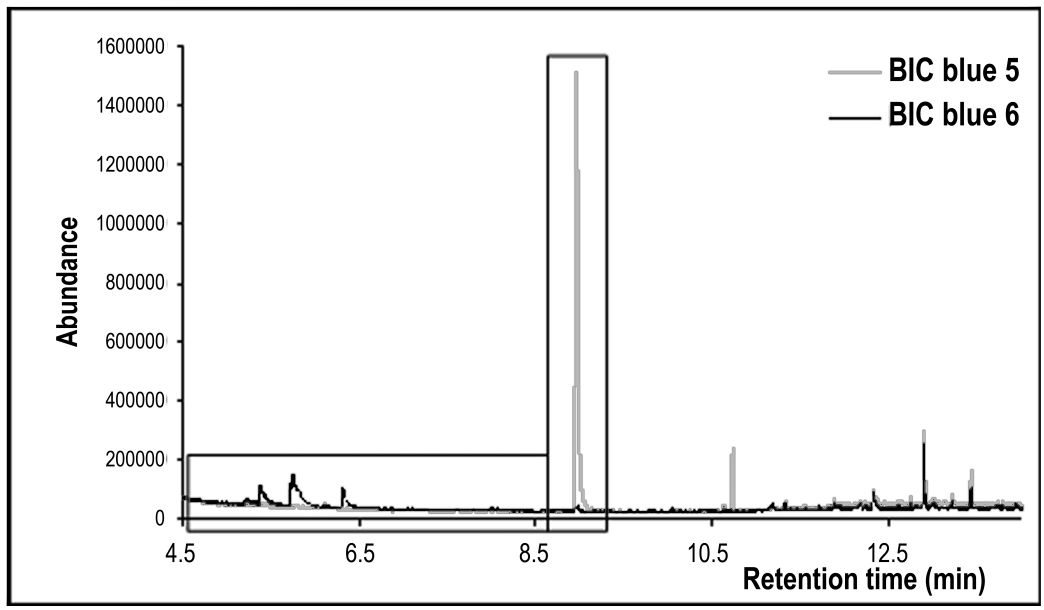
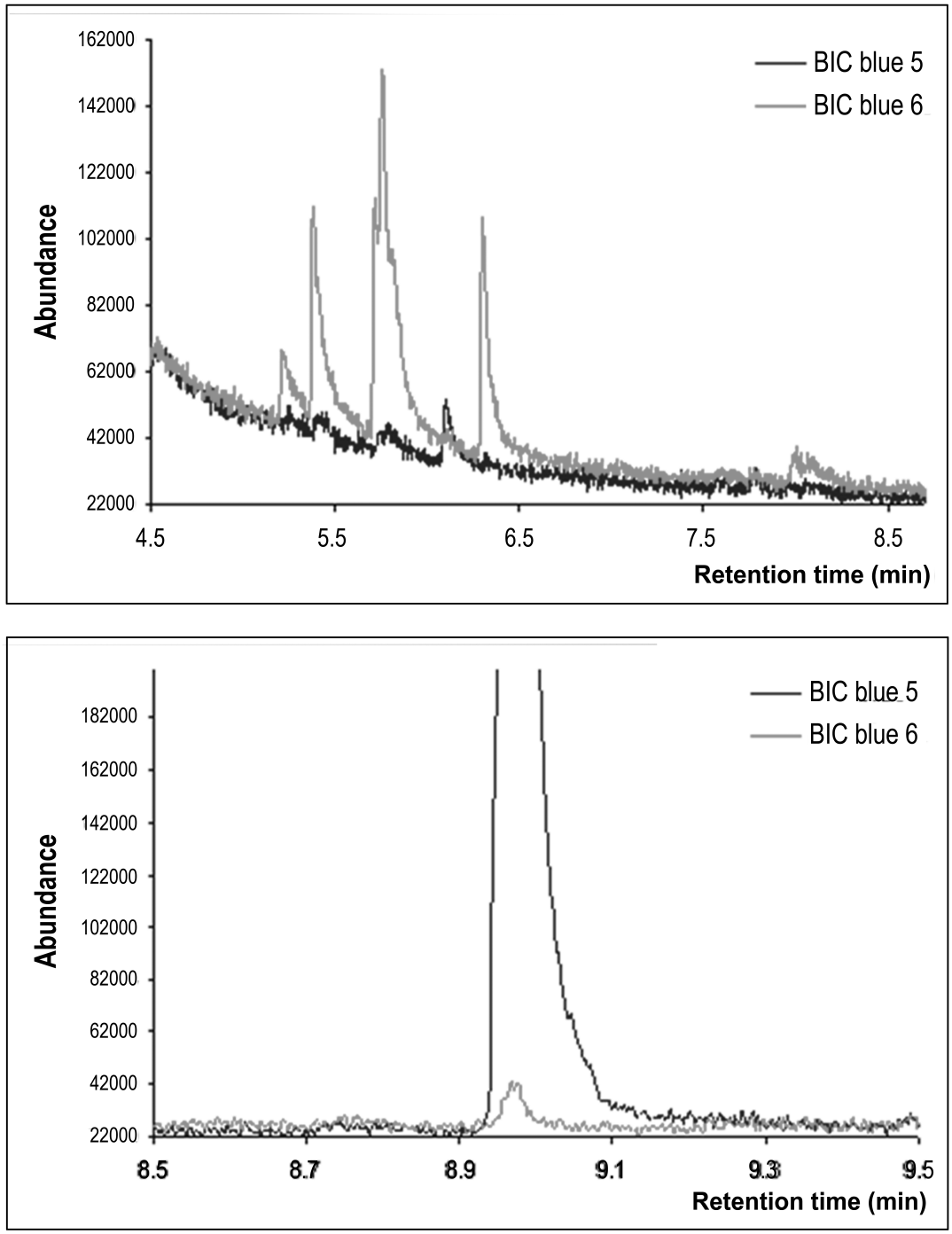


Figure 6. GC-RTL chromatograms of BIC5 and BIC6 in scan mode.



Figures 7a (above) and 7b (below). GC/MS-RTL chromatograms amplified from Figure 4 of BIC5 and BIC6 in scan mode.

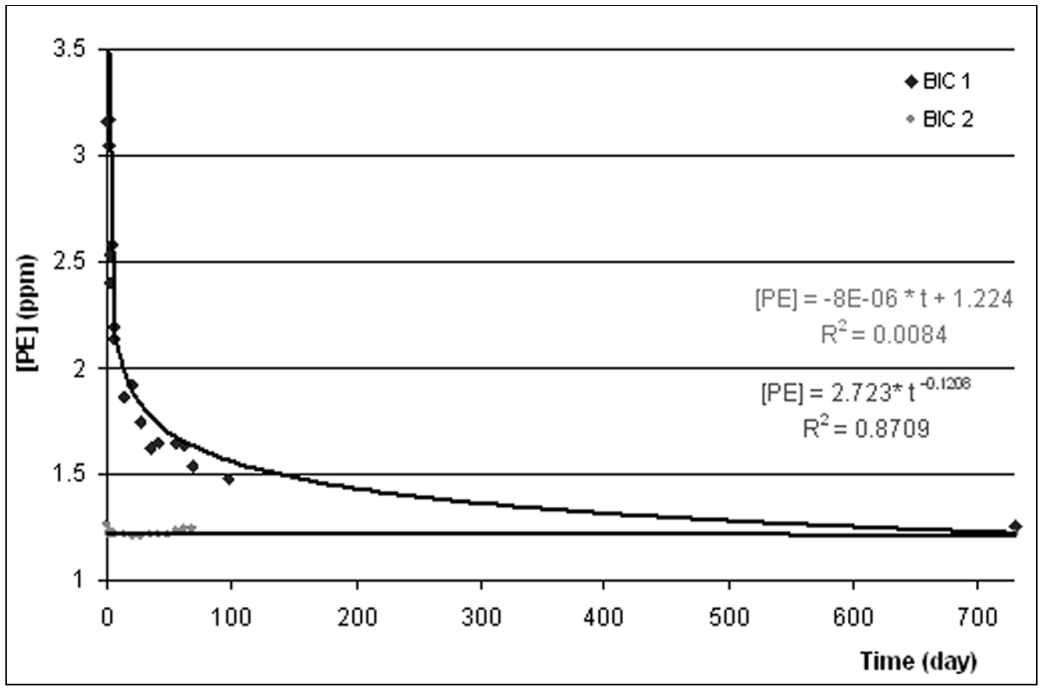


Figure 8. Aging curves of BIC1 and BIC2.

Figure 6, there is no peak coincidence; thus, the 2 inks have different compositions. In Figure 7, a close-up detail of the overlapped chromatograms shows the differences between the detected peaks

One of the most remarkable differences between the 2 blue-ink compositions was in the amount of PE detected. Although the peak of PE appeared in the chromatograms of all the 13 blue inks, the concentration of this substance was completely different from 1 blue ink formula to another, as can be seen by the differences in the heights of the peaks (Figure 7b).

Since determination of the loss of PE is 1 of the methods of choice for dating an ink, the substantial difference in these concentrations should be studied to assess the possible implications on the dating method.

In the inks with a lesser concentration of PE, peaks corresponding to other volatile components appeared in the chromatograms (between retention times 4.75 and 6.5 minutes) (Figure 7a). A further study is warranted to follow their behavior.

Loss of Phenoxyethanol

BIC1 and BIC2 samples have been selected as representative of the 2 different blue-ink formulations. BIC1 ink formulation contained 3 times more concentration of PE than BIC2 ink after 1 day deposited on the paper.

PE has been quantified by GC/MS in SIM mode for monitoring its decrease in concentration versus time. Contrary to what would be expected, the 2 formulations showed different behaviors relating to the loss of PE. While the amount of PE in BIC1 ink had a fast decreasing profile in merely the 1st week, in the BIC2 ink, the amount of PE was relatively constant, at around 1.20 mg/L, (Figure 8).

According to Aginsky (1993, 1994), the volatile compounds of ballpoint inks leveled off between 2 and 3 years. Heating an ink at 70º C for 2 hours just to the stabilization level would be equivalent to approximately 2 years of a natural aging at 20º C. Therefore, if a questioned ink is fresher, there will be differences between the measurement of the volatile compounds of the non-heated ink and the measurements of the heated ink. If, on the contrary, the ink was older than 2 or 3 years, there would be no difference in the measurements of the volatile compounds of both inks (heated or unheated) because of the stabilization of the ink volatile compounds.

In this case, TLC formulations were aged artificially by heating at 70º C during 2 hours just to the stabilization level. Their final concentrations

of PE were measured, and the amounts were approximately 1.20 mg/L in both cases. Taking into account the PE aging concentration profile obtained for BIC1 and BIC2, we could conclude that this ink-age predicting method would not be applicable to BIC2 type pens since its PE concentration remained constant at 1.20 mg/L despite heating.

Detecting a difference in the amount of PE may only be useful in estimating the age of a blue ink of the BIC1 formula but not blue inks of the BIC2 formula. This would mean that unless we know ahead of time the type of ink we are dealing with (BIC1 or BIC2 type), detecting the same PE concentration in an ink, before and after heating of the samples, could not lead to conclusive results for dating the inks of this type of pens.

Furthermore, if a questioned sample showed an initial concentration of approximately 1.20 mg/L, nothing could be concluded regarding its age. The results obtained (no change in the PE concentration) could be due to the ink being effectively old (if BIC type 1) or not (if BIC type 2). Giving a conclusion in the previous situation could lead to error unless the inks were previously identified.

Conclusion

The 1st conclusion of this work is that even if 2 pens are from the same trademark and model, specifically BIC Medium, they can contain completely different ink formulations.

At least 2 different ink formulations (regarding both the dyes and the volatile components) were found among the 13 inks of the blue group. The 1st cluster included the pens purchased in Brazil, Israel, and USA; the 2nd included the BIC Medium blue from Argentina, Belgium, England, France, Germany, Holland, Portugal, Scotland, and Spain.

In contrast, the 13 black inks appeared to have the same composition of dyes and volatile components.

Regarding the dye compositions, the blue inks in the 1st group had 1 more dye, Victoria blue, than those in the 2nd group.

Regarding the volatile components, 1 of the most important differences between the blue inks was that 1 of the formulations had 3 times more PE than the other.

Studying the loss of the PE once the ink was deposited on the paper disclosed 2 completely different behaviors. The inks of the 1st group showed a gradual loss of PE over time, while the concentration of PE in the inks in the 2nd group remained almost constant with time.

This result has important implications in the assessment of the time an ink remains deposited on paper in terms of the loss of the volatile component PE. When 2 samples of the same ink formula, 1 heated and another unheated, show the same amount of PE, one cannot conclude anything about the age of the ink on the paper. If any conclusion is made, an error can result.

A further investigation is necessary in this case identifying and following other volatile components against time.

RTL is a little-known and underused tool patented in 1998. Results of this work make it a highly promising tool in forensic sciences.

Acknowledgments

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