Journal of the American Society of Questioned Document Examiners, Inc.
Volume 21, Number 1, June 2018

Classification and Ink-Dating of Inkjet Printed Documents with TDS-GC-MS

V. von der Kall*, J. Schram*, T. Rottes, D. Bogedain****

* University of Applied Science, FB 01 Chemistry, Frankenring 20, 47798 Krefeld, Germany

** Landeskriminalamt NRW, Völklinger Str. 49, 40221 Düsseldorf, Germany

In document examination casework, the need for a method to differentiate pigmented black inkjet inks and determining their age increases. More and more documents are produced using the inkjet print technique. Commonly this raises questions for the examiner concerning the machines used to produce the documents and the age of the prints.

The first part of this preliminary study aims to distinguish different inkjet inks (printed on paper) by analyzing their main volatile components and assigning them according to their composition. In the second step of the research, it will be assessed whether it is possible to date these inks by measuring the decrease of volatile ink components (e.g. 2-Pyrrolidone, TEGBE) as a function of time.

Introduction

Presently, being able to analyze an inkjet printing is one of the principal tasks for a forensic document examiner. However, with the beginning of the 90's dye-based inks have been replaced by pigmented inks more and more. These cannot be analyzed by the established methods for classification/differentiation of dye-based inks (e.g. High Performance Thin Layer Chromatography (HPTLC)). So far there are very limited possibilities available for examination. Colored pigments can be analyzed and classified by using Raman-Spectroscopy. But, there is no decent discriminative method for pigmented black inks as these are based on carbon black for coloration. Therefore, an examination of other ink ingredients, especially the volatile components, was considered.

In addition, the examination of volatile ink ingredients offered the option to explore the possibility of potential ink dating. After the introduction of valid age determination methods for ballpoint pen inks the need for a technique to determine the age of inkjet printed documents increased. Therefore, this study included the examination of the decrease of the volatile ink components as a function of time [1–4].

Instruments and Materials

Five different black pigmented inks were selected to conduct this study. In general, inkjet inks consist of solvents, pigments, wetting agents (e.g. Glycerin) and depending on the producer other additives, e.g. biocides, pH-regulators.

In the following table, the composition of the selected printer/ink types concerning their main components is shown (information yielded by material safety data sheets of the particular producer).

This paper is based upon a master's thesis utilizing gas chromatography coupled with mass spectrometry as a basis to develop a suitable analytical method.

© 2018 The American Society of Questioned Document Examiners, Inc.

Table 1. Composition of the selected Printer/ink types concerning their main components.

Printer	Brother	Epson	Canon	Canon	HP
Type	MFC-465CN	Stylus SX218	Pixma MP-450	Pixma MG-7550	Photosmart 6520
Ink	LC-1000BK	T0711 BK	PG-40	Refill of PGI-550PG BK	HP-364
Technology	Piezoelectric	Piezoelectric	Thermal	Thermal	Thermal
Main components according to MSDS:					
Water	65-75	<80	60-80	Unknown	70-80
Lactam/2-pyrrolidone	-	-	5-10	Unknown	<7,5
Glycerin	20-30	10-15	5-10	Unknown	-
Diethylene glycol	-	-	2-6	Unknown	-
1,5-Pentanediol	-	-	-	Unknown	<7,5
TEGBE	-	1-5	-	Unknown	-
Carbon black	5-10	-	-	Unknown	<5
other organ. materials	-	10-15	-	Unknown	-
1,2-benzisothiazol-3(2H)-one	<0,05	-	-	Unknown	contains benziso-thiazolon

In this study, the following machine arrangement was used to conduct the analysis:

- Gerstel Autosampler TDS A2
- Gerstel Thermic-Desorption System TDS 3
- Gerstel Pneumatic for in-situ derivatization
- Gerstel CIS
- Agilent Gas phase Chromatograph 6890 N
- Agilent Mass Spectrometer 5975 B
- Column: Agilent J&W HP-5MS UI (Length: 30 m, Diam. 0,250 mm, Film: 0,25 µm)

As reference substances for identification and external calibration, the following chemicals (synthesis quality) were used:

- 2-Pyrrolidone
- TEGBE 2-(2-(2-butoxyethoxy)ethoxy) ethanol
- Glycerin
- Diethylene glycol
- 1,5-Pentanediol

Prints were made on one type of paper from the same package:

- paper brand: real
- paper class: 80 g/m^2

Experimental

Print-outs were made weekly with the five above listed printers and the selected standard white paper. The word "und" ("and" in German) was chosen for test printing as it is very common. The words were arranged in blocks with several lines as well as single lines with several centimeters distance. The test documents were stored within ring binders between two sheets of paper under normal ambient conditions.

The analysis samples were prepared by cutting out printed letters using a scalpel with appropriate optical enlargement using a stereomicroscope. Samples consisted of the word "und" at the beginning of the study but were reduced to the letter "u" later, due to the large amount of volatile components in samples less than 1 month old.

For age determination, samples from one document of each printer were cut out weekly for a time period of four months and placed in a freezer at −18 °C using small plastic sample bags.

The cut-out samples were placed in thermal desorption tubes and inserted into the analysis system via autosampler (splitless injection-solvent vent mode).

For classification of the volatile ink components, the samples were extracted thermally for 4 minutes at 220 °C with following cryofocusing (Temperature CIS, start: −100 °C, after cryofocusing: 280°C (rate: 12.00 °C/s)). The optimized temperature program of the gas chromatograph (GC) oven starts at 45 °C with a hold time of 1 min, followed by heating to 270 °C with a (heating) rate of 30 °C/min. The GC was operated in constant flow mode, using helium at a flow rate of 1.2 ml/min.

For the identification of compounds, the NIST library and the known reference chemicals were used. A result from the NIST database was confirmed only if it corresponded with our knowledge of ink formulations.

For ink dating, derivatization of the volatile components was necessary, as the resolution and peak separation of the chromatograms were not suitable for quantification. The derivatization agent (N,O)-bis-trimethylsilyl-trifluoroacetamide was chosen. By substitution of active hydrogen groups (from −OH, −NH, −SH, −COOH) with trimethylsilyl, the derivatized ink components became less polar and suited better for the used column. This led to the introduction of the following discrete method for ink-dating: The samples were desorbed thermally at 240 °C for 5 minutes with added N,O-Bis-(trimethylsilyl)-trifluoracetamid (BSTFA) in the gas stream and subsequently cryofocused (Temperature CIS, start: −100 °C, after cryofocusing: 280°C (rate: 12.00 °C/s)). After insertion in the GC, the oven was set at 45 °C for 1 min and next the following ramps were applied: 1) heating to 100 °C with 30 °C/min, 2) 190 °C with 12 °C/min and 3) heating up to 270 °C with 50 °C/min. The GC was operated in constant flow mode using helium at a flow rate of 1.2 ml/min

For quantification, the Selected-Ion-Monitoring mode was used and a calibration with external standard solutions was conducted.

The published method for ink-dating of ballpoint pen inks [1] formed the outset for both described inkjet ink analysis procedures.

Results

Classification

After studying 120 material safety data sheets of black inkjet inks by printer manufacturers Brother, Canon, Epson and HP (82 thermal systems: Canon and HP, 38 piezoelectric systems: Epson and Brother) the following conclusions were drawn. In all MSDS of the pigmented based thermal printers 2-Pyrrolidone (Lactam) was listed, while in 31 of the 38 piezoelectric printers TEGBE/DEGBE was documented. It appeared that these components were not present together in one ink. Furthermore, it became obvious that Glycerin as humectant was very common since it was present in more than half (66) of the viewed MSDS.

The analysis of documents less than 1 month old, which were produced using the five different inkjet printers, showed that all prints could be differentiated by the presence of their volatile components. The following chromatogram displays the characteristic peaks for the ink cartridge Canon PG-40.

For all ink cartridges, the respective volatile components listed in the MSDS could be detected

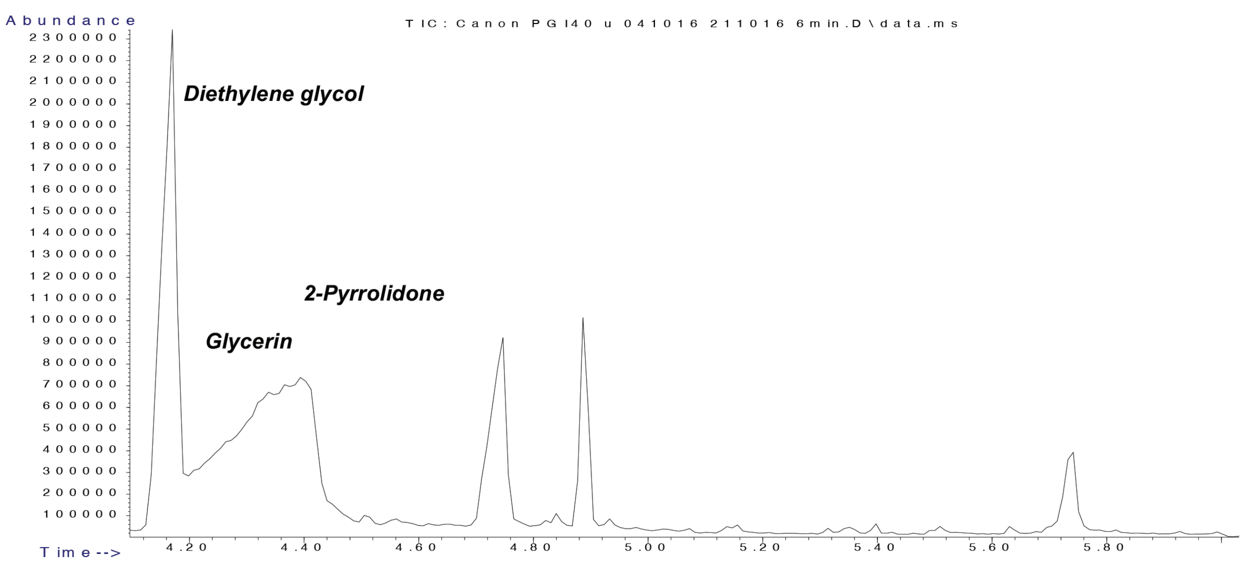

Figure 1. Canon Pixma MP-450 (Ink Cartridge PG-40).

except 1,2-benzisothiazol-3(2H)-one. However, the amount of this biocide in the ink was known to be very low so it could possibly be under the detection limit of the system.

In contrast, the analysis result of the Brother and Epson ink showed further components (Brother: DEGBE and Epson: 1,2-Hexanediol) that were not listed in the MSDS as being present in the ink formulation. Especially the finding of DEGBE in ink LC-1000bk supports the assumption that inks for piezoelectric systems regularly contain DEGBE/TEGBE.

In this regard, it was assumed that the refill ink for Canon PGI-550PG BK would include 2-Pyrrolidone as ingredient. Yet, the analysis of the refill ink showed no presence of the solvent. A comparison with the MSDS by the original ink manufacturer revealed that the refill deviates from the original ink formulation, which contains 2-Pyrrolidone.

The following table displays a summary of the analysis result.

Ink Dating/Age Determination

Before measuring the aging behavior, it was necessary to test if the sampling position on the paper influences the quantitative amount of volatile components in the same letter. Hence, a test sheet of printer Canon Pixma MP-450 was selected and the word "und" was cut out from the middle of a text block as well as from the beginning, middle and end of a single text line. The analysis of the four samples showed equivalent results.

For the subsequent recording of aging curves, the samples were prepared as follows: One fresh document of each printer was selected (approximately 1 week old). Every week one sample was cut out of these particular documents and was frozen at -18 °C in a small plastic sample bag. During the 4 month sampling time, the document was stored in a folder. Analysis followed defrosting the samples within the evidence bags (about 30 min). For each printer, an aging curve was measured at least 2 times using the aging method with BSTFA derivatization.

All five printers contained at least one volatile component that showed a significant decrease during the measured time period. However, some analytes displayed a high variation of the measurement values and were therefore excluded from evaluation. Further testing would need to be conducted for these printer samples. The statistical Neumann-Trend-Test [5], as well as visual evaluation of the reliable measurement data, led to aging curves for four out of five printers. Depending on the ink ingredients more than one component was affected by aging. The aging time appeared to vary depending on the overall composition and quantitative analyte amount. Except for Glycerin in ink *Canon PG-40* the aging of the different components appeared to have ended after 60 to at least 100 days.

Table 2. Summary of the results for Classification (XXX: component was present, only qualitative assignment).

Printer	**Brother**	**Epson**	**Canon**	**Canon**	**HP**
Type	MFC 465CN	Stylus SX218	Pixma MP-450	Pixma MG-7550	Photosmart 6520
Ink	LC-1000BK	T0711 BK	PG-40	<u>Refill</u> for PGI-550PG BK	HP-364
Technology	Piezoelectric	Piezoelectric	Thermal	Thermal	Thermal
Detected components:					
Lactam/2-Pyrrolidone	-	-	XXX	-	XXX
Glycerin	XXX	XXX	XXX	XXX	-
Diethylene glycol	-	-	XXX	XXX	-
1,5-Pentanediol	-	-	-	-	XXX
TEGBE	-	XXX	-	-	-
DEGBE	XXX	-	-	-	-
1,2-Hexanediol	-	XXX	-	-	-

Table 3. Summary of the results for Ink-Dating.

Printer	Substance	Decrease [%]	Aging-Time [Days]	Conclusion
Brother MFC-465CN	Glycerin	no decrease	-	No Aging detectable
	TEGBE	80	90	Aging detectable
Epson Stylus SX218	Glycerin	60, but strong fluctuation	70	No Evaluation
	TEGBE	80	70	Aging detectable
Canon MP-450	Glycerin	70	120	Aging detectable
	Diethylene glycol	70	80	Aging detectable
	2-Pyrrolidone	80	60	Aging detectable
Canon MG 7550	Glycerin	75	100	Aging detectable
	Diethylene glycol	80	80	Aging detectable
HP Photosmart 6520	1,5-Pentanediol	85, but strong fluctuation	80	No Evaluation
	2-Pyrrolidone	no decrease	-	No Aging detectable

The following Table 3 demonstrates the summary of the results of the aging behavior of the different inks and their main components.

In the following Figures 2 and 3 positive aging curves of two different inks, *Canon PG-40* and *Brother LC-1000BK*, are demonstrated. The curves show the mean of three measurements including the standard deviation:

However, as mentioned above not all inks gave reliable results in regard to the decrease of

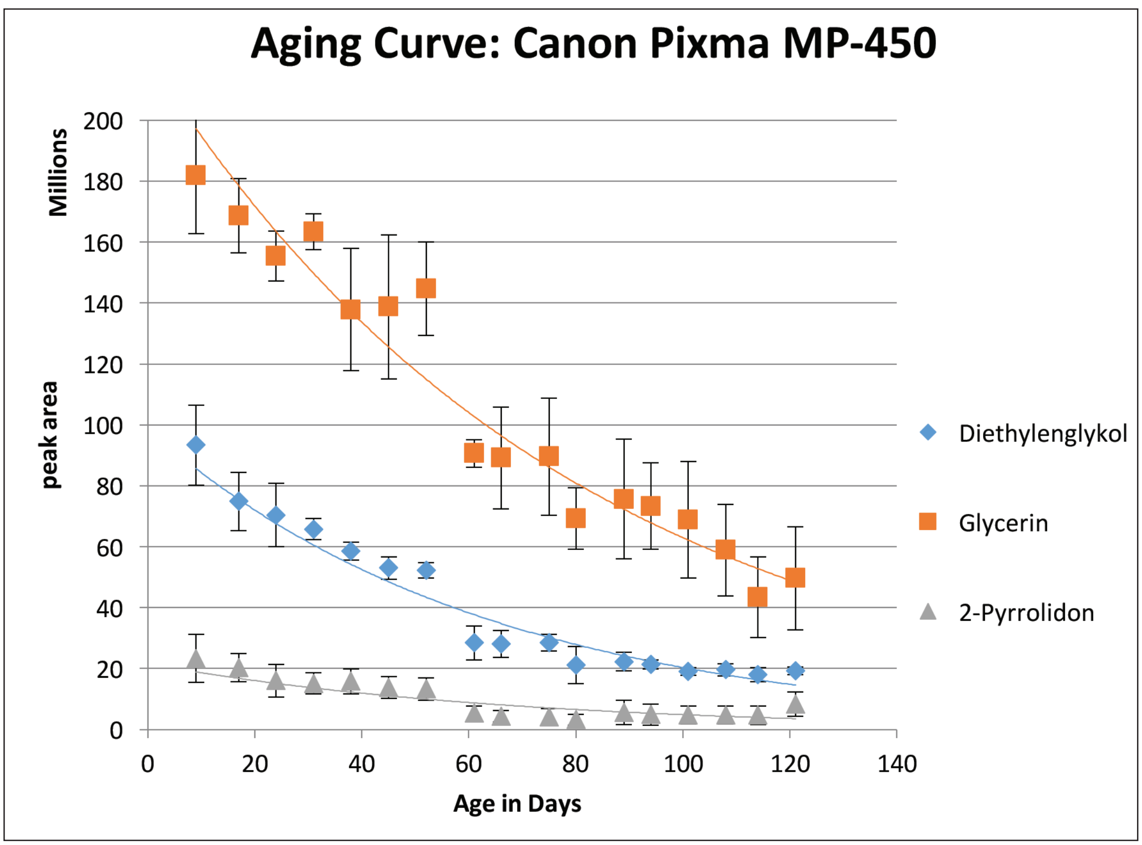

Figure 2. Aging curves of Canon Pixma MP-450 using Canon PG-40 ink.

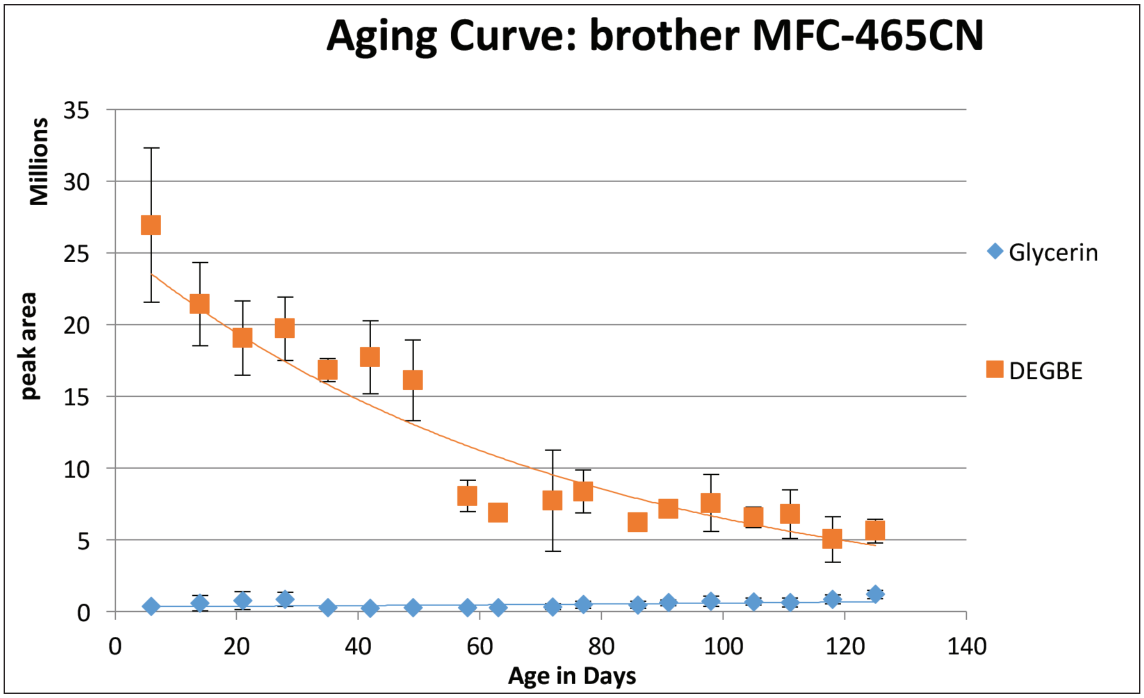

Figure 3. Aging Curve for brother MFC-465CN using Brother LC-1000BK ink.

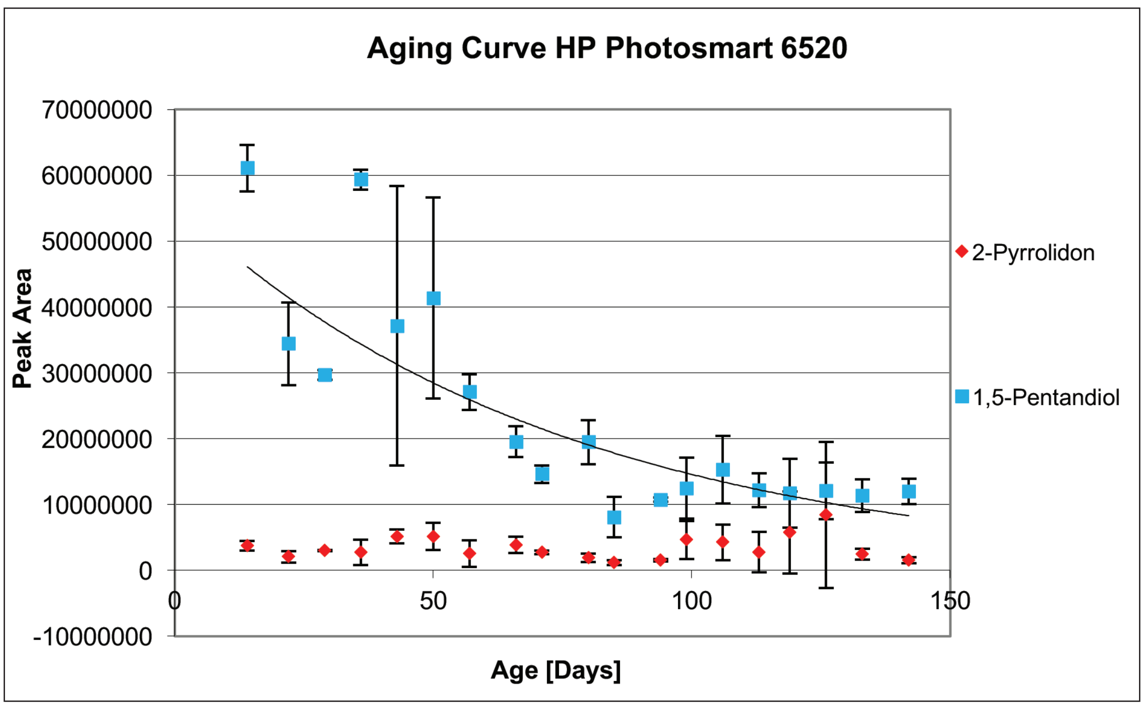

Figure 4. Aging Curve for HP Photosmart 6520 using HP-364 ink. (The curves show the mean of two measurements including the standard deviation).

solvents in relation to time. A low reproducibility for compounds in the inks *HP-364* and *Epson T-0711* did not allow an evaluation. An example for unreliable aging behavior is presented in the following Figure 4.

Contamination

Glycerin is used frequently in inkjet inks and appears to be an important component regarding age determination. As this humectant is contained in many daily used items as well, it was necessary to investigate the influence of different types of contaminations. Hence, known test print samples were deliberately contaminated with fingerprints, cigarette and e-cigarette smoke as well as hand lotion (containing Glycerin). By analyzing the prepared test samples with the standard classification method, it was possible to identify the contamination of the ink samples. Especially by observing and comparing blank values with samples peaks in the chromatogram, the influence of the test materials became apparent. Anyway, neither the fingerprints nor the cigarette/e-cigarette smoke influenced the measured amount of Glycerin on the sample. Solely, the hand lotion that was known to contain Glycerin affected the quantitative amount of analyte measured in the contaminated sample. Again, the comparison of the blank paper and the ink sample showed the same significant Glycerin contamination.

Furthermore, a short migration test of the volatile components between the printed documents and the blank white paper was conducted. Therefore, a one-month-old test sample as well as two blank paper samples were stored with direct contact to each other (one blank paper above, one blank paper below the printed document) and were analyzed after two weeks. The examination revealed that migration of the analytes can happen to a certain degree depending on the position (blank paper on top slightly higher contamination than on bottom) and the present volatile ink components. Further testing is necessary to evaluate migration effects.

Discussion and Conclusion

The developed methods for classification of different inks and age determination worked well and showed promising results in this preliminary study.

Inkjet inks can be distinguished by their individual chromatograms and most of the main components can be assigned in accordance to the respective manufacturer's material safety data sheet.

It is assumed that different solvents are contained in the inks depending on the respective printing system. An indicator for piezoelectric systems appears to be TEGBE/DEGBE, while 2-Pyrrolidone seems to be used for thermal inkjet exclusively. However, further examination of more ink samples is necessary for verification.

Four out of five printers contained at least one volatile component, which showed a significant aging behavior within the studied period of 4 months. While the decrease of volatile analytes seemed to end mostly after 60 to 100 days, the aging of one sample (*Canon Ink PG-40*) appeared to be still ongoing after 120 days. However, for some analytes, a high error rate was detected and therefore these data were excluded from evaluation. So far, it is not clear if the fluctuation of the measurement data was caused by possible differences in the printed document or if storing conditions could have influenced the outcome. Further examination of extended aging curves up to one year and investigation of cross contamination due to storing conditions should be conducted.

References

1. J. H. Bügler, H. Buchner, A. Dallmayer: "Age Determination of Ballpoint Ink by Thermal Desorption and Gas Chromatography-Mass Spectrometry"; Institute of Forensic Sciences, Bavarian State Bureau of Investigation, Munich

2. Aginsky, V.N. Ink Aging Testing – Do Preceding Indentation Examinations Affect Ink Aging Parameters? *Journal of the American Society of Questioned Document Examiners*, Vol. 17, No. 2, 2014, pp. 49-63.

3. A. Koenig, D.Kirsch, F.Koehler, C. Weyermann: "Reproduction and Evaluation of the TDS-GC/MS for ink dating purpose in Bundeskriminalamt, Wiesbaden", Universität Lausanne

4. F. Partouche, B. Espanet, C.Villena, C. Murie: "Forensic Analysis of Inkjet Printings by Pyrolysis GC/MS"; Forensic Documents Department, IRGCN; Rosny-Sous-Bois, France

5. J. Neumann, R. Kent, H. Bellison, B. Hart, Annals of Mathematical Statistics 12 (2) (1941) pages153–162