Forensic Analysis of Inkjet Printings by Pyrolysis GC/MS

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Abstract

There is a great number of forensic applications in which it is useful to compare black inks of inkjet printings, for example anonymous letters. Usually, forensic document examiners study dyes of inkjet printings using Raman spectrometry, Thin Layer Chromatography or High Performance Liquid Chromatography. These methods are ineffective when the examiner must study a pigmented ink. Most of black pigmented inkjet inks are based on carbon black.

Using our protocol, PY/GC/MS allows to study the solvents of an inkjet printing. For different inks, we find different solvents in different proportions. Thus, we have found 2-pyrrolidinone, glycerin… For this study, we have used 16 printings coming from 16 different inkjet cartridges (11 inks based on pigment, 5 inks based on dyes) and we have finally identified 13 different groups.

Introduction

At the present time, being able to analyse an inkjet printing is one of the principal need of a forensic document examiner. Last years, new protocols have been developped. They use Raman spectrometry, Thin Layer Chromatography ou High Performance Liquid Chromatography. These techniques allow dyes characterizing and are ineffective to analyse inks based on pigments. Few years ago, most of inks were based on dyes, these methods were discriminating enough. Nowadays, most of new inks are based on pigments and precisely carbon black, because of their properties of lightfastness for example. Thus, a forensic document examiner must develop new techniques to analyse documents printing by an ink based on pigments.

Inkjet inks are made of a colorant (2 to 8%), solvents like water, alcohol or MEK (35 to 80%), solubilizer of colorant for example 1-methyl pyrrolidinone, surfactant, humectant like glycol, penetrant for example isopropylic alcohol, dispersant, fixative, buffering agent, biocides, UV-blocker, anti-cockling additives, anti-oxydants.[1,2] During a printing, the paper can absorb inks elements by capillarity. The aim of this study is to find techniques to analyse these absorbed elements. The extraction of volatile compounds during an ink analysis has already been studied.[3]

This article proposes a new method which needs no preparation. In this case, the pyrolysis is not used to degrade polymers but as a heating mean to evaporate volatile compounds which are present in the paper sheet. In this article, we describe the results we can obtain with PY/GC/MS. Firstly, material and methodology used to analyse inkjet printings are described. Secondly, results for sixteen inkjet ink cartridges are described (eleven cartridges contain inks based on pigments; five contain inks based on dyes).

Experimental

Methodology

Printings are made on a single type of paper (Neusiedler office paper, 80 g/m^2) with different inkjet printers. These printings are kept in our office. This office has no specificity of temperature, light or humidity.

Two different analysis are realised : the first, one week after the printing, the second two months later. The making up of samples is done by cutting up the sheet of paper. Each sample has a surface of 4 mm^2 (dimension of one letter). After, the analysis is done by PY/GC/MS.

Tests are made on these 16 cartridges : Canon BC 10 (1), Canon BCI-24 (2), Canon BCI 3eBK (3), Epson T019 (4), Epson T040 (5), Epson T0321 (6), Epson T018 (7), Epson T007 (8), Epson T0548 (9), Epson T0481 (10), HP 15 (11), HP 56 (12), HP 51645a (13), Lexmark 16 (14), Lexmark 70 (15), Lexmark 48 (16). In the following parts, printings are codified by the number between brackets.

Materials

The pyrolysis is a well-known method to analyse different polymers like paints, fibers, toners, pneumatic tyres.[4,5]

Analytical pyrolysis was performed using a CDS Analytical Pyroprobe 2000 and 2500 pyrolysis autosampler. Samples measuring around 4 mm^2 were placed on quartz roads and into a sampling tube. Samples were pyrolysed for 15 s at 375°C. The pyrolysis interface temperature was set at 250°C. The pyroprobe autosampler was interfaced to a ThermoFinnigan Trace GC equipped with a Varian Factor Four VF-35ms (35% phenyl-65% methyl polysiloxane, 30m, 0.25 mm, 0.25 µm film thickness) and a ThermoFinnigan Trace DSQ mass detector. The column oven program started at 50°C and ramped at 5°C/mn to 180°C in order to detect volatile compounds. A second ramp at 10°C/mn to a final temperature of 280°C (held for 20 mn) followed. The GC was operated in constant flow mode using helium at a flow rate of 1 mL/mn. Pyrolysates were transferred to the GC inlet using a 10:1 split ratio. Mass acquisition began after 3.5 mn and was performed in two steps : from 33 to 300 amu during 26 mn, from 40 to 500 amu after. The length of the column was only 25 m after several operations of maintenance.

For the identification of compounds, the NIST library has been used. A result from this database was confirmed only if it corresponded with our knowledge of ink's formulation.

Results

After analysis, for these temperatures, we observe that the sample of paper sheet has not been burnt. The choice of temperatures is critical. If the temperature is increased, the paper is burnt and the intensity of these bands hides the information coming from the evaporation of volatile compounds.

These results are illustrated by four different pyrograms. By comparison with pyrolysis of nonprinted paper sheet, we deduct ink's compounds.

Figure 1 shows the printing 12 contains four different compounds. These compounds are 1,2 hexanediol (11,05), benzyl alcohol (11,87), 2 pyrrolidinone (14,69), and an unknown compound (15,41).

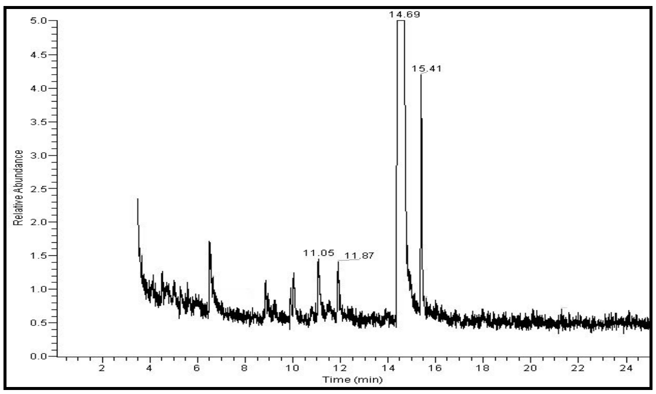

Figure 1. Pyrogram of a sample printed (12) by a HP 56 cartridge (Hewlett-Packard).

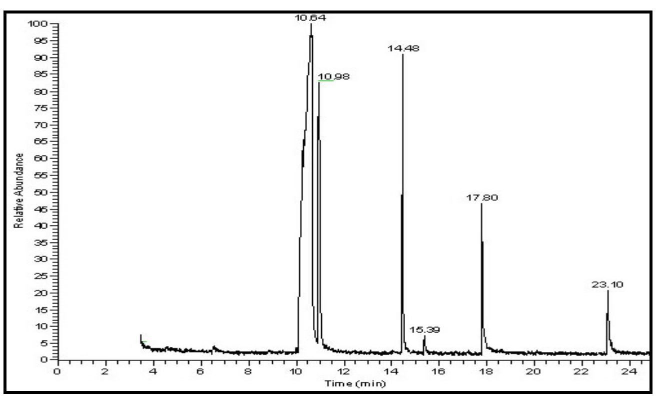

Figure 2. Pyrogram of a sample printed (9) by a T0548 cartridge (Epson).

On figure 2, six relevant peaks are observed. After identification, this printed sample encloses glycerin (10,64), 1,2 hexanediol (10,98), 2-pyrrolidinone (14,48), an unknown compound (15,39), triethylenglycol (17,8) and ethanol,2-(2(2-butoxyethoxy(ethoxy)) (23,10) (figure 2).

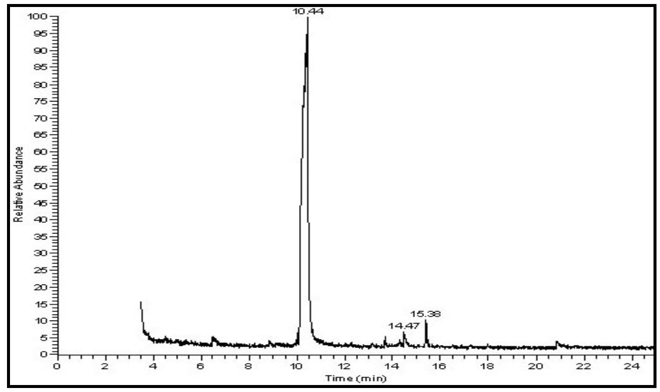

Figure 3. Pyrogram of a sample printed (3) by a BCI-3eBK cartridge (Canon).

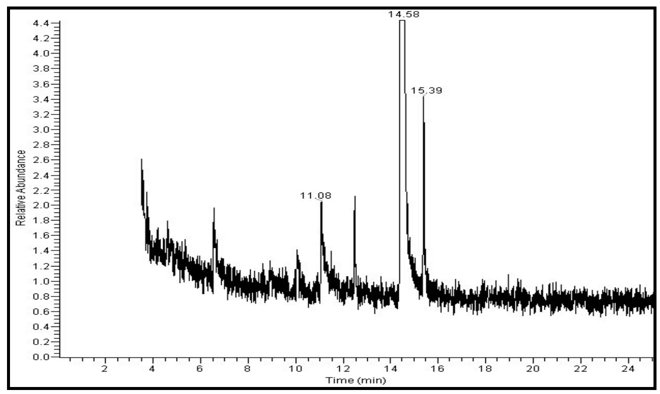

Figure 4. Pyrogram of a sample (16) printed by a 48 cartridge (Lexmark).

On figure 3, three peaks are observed. These peaks correspond to glycerin (10,44), 2-pyrrolidinone (14,47) and an unknown compound (15,39).

The figure 4 shows three relevant peaks. So, this printed sample contains 1,2 hexanediol (11,08), 2-pyrrolidinon (14,47) and an unknown compound (15,38).

In table 1, inks based on pigment are underlined. If two inks are exactly based on the same compounds, they are classified in the same group. Then, after analysis of table 1, 14 different groups are identified. Inks based on the same volatile compounds (cartridges 4 and 8, 14 and 15) could be discriminate by a semi-quantitative analysis.

In a second part, printings, two months old, has been analysed. These tests are illustrated by two pyrograms.

The figure 5 shows five peaks. This sample is still based on glycerin (9,11), 1,2 hexanediol (9,97), 2-pyrrolidinone (13,19), an unknown compound (14,09), triethylenglycol (16,57), but ethanol,2-(2(2-butoxyethoxy(ethoxy)) can no more be detected. (These times are different from the first analysis because the length of the column has been modified).

Table 1: Summary Table of all Results

RT	9,70	10,26	11,08	11,87	13,11	14,47	15,24	15,39	16,24	17,8	20,66	23,10
Compounds (CAS number)	iethylene glycol (111-46-6)	lycerin (56-81-5)	,2 hexanediol (6920-22-5)	enzyl Alcohol (100-51-6)	-Methylpyrrolidinone (872-50-4)	-pyrrolidinone (616-45-5)	-2Butoxyethoxy ethanol 4446-78-5)	nknown	enzoic Acid (65-85-0)	riethylene glycol (112-27-6)	exane 1,6 diisocyanate (822-06-0)	thanol,2(2(2butoxyethoxy(ethoxy)) 43-22-6)
1		x						x				
2		x						x	x			
3		x				x		x				
4						x	x					
5		x				x	x				x	
6		x				x		x				
7		x				x	x					
8						x	x					
9		x	x			x		x		x		x
10			x									
11						x		x				
12			x	x		x		x				
13	x				x	x						
14						x						
15						x						
16			x			x		x				

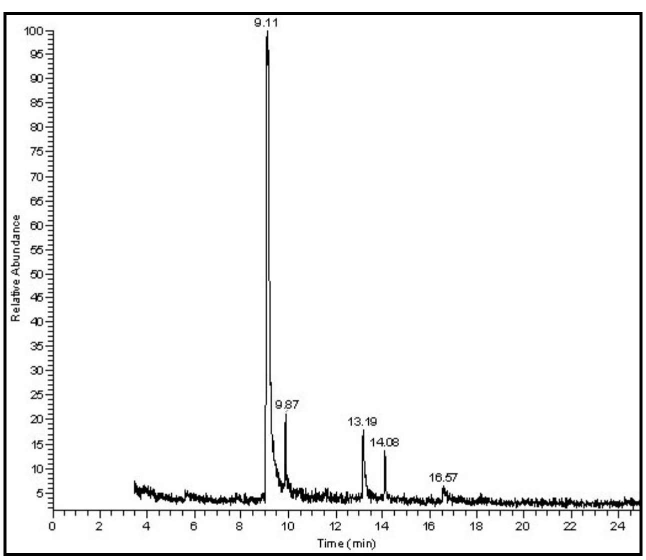

Figure 5. Pyrogram of a two months old sample (9) printed by a T0548 cartridge (Epson).

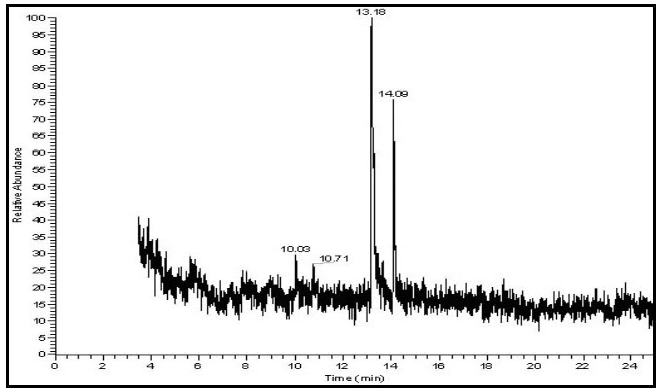

Figure 6. Pyrogram of a two months old sample (12) printed by a HP 56 cartridge (Hewlett-Packard).

The figure 6 shows four peaks. This sample is still based on 1,2 hexanediol (10,03), benzyl alcohol(10,71), 2 pyrolidinon (14,09), and an unknown compound (14,09). We have the same results as for a one week old printing. The results' quality is poor, but they are still informative. Figures 5 and 6 show that for a sheet of paper printed two months ago, the PY/GC/MS allows to detect most of the volatile compounds.

If the aim of a case is to determine if two printings can have been made with the same printer, the interpretation of differences should be done carefully. Indeed, we have observed that one compound can not be detected two months after printing with the T0548 cartridge (Epson).

Discussion

The analysis of elements separated by chromatography allows to detect solvents or semi-volatile compounds. Other types of products can not be detected by this pyrolysis.

On one hand, compounds like glycerin, 2-pyrrolidinon are common in an ink's formulation. On the other hand, diethyleneglycol and benzoic acid are more specific, and can be found in few analyses.

Sixteen cartridges have been studied. After identification of compounds detected by PY/GC/MS, thirteen different groups have been found. For twelve inks based on pigment, ten different groups are determined. If we perform analysis using usual methods like TLC or Raman, any discrimination is impossible. For a printing aged of more than two months, it is possible that one compound could no more be detected by PY/GC/MS. Thus, the disappearance of a compound has been studied.

The figure 7 illustrates that sixty days after printing, the quantity of pyrrolidinone detected by PY/GC/MS is stable.

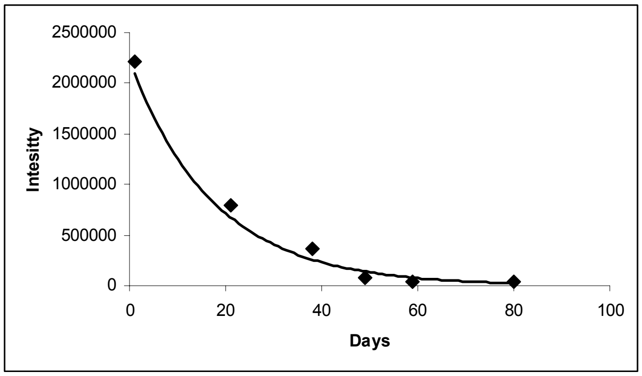

Figure 7. Evolution of the pyrrolidinone peak's intensity detected by PY/GC/MS for an HP cartridge (12).

Conclusion

1 – The analysis by pyrolysis GC/MS gives qualitative information on inkjet printings. To compare pigmented inks, this method allows to determine relevant chemical elements and is discriminative, compared to Raman, HPLC or HPTLC. But, because of the disappearance of compounds with time, difference should be analysed carefully.

2 – Since the identification of chemical elements is allowed by this method, the creation of a database should be possible. But, in this case, the formulation used by inkjet ink's maker has to be permanent. To valid the chemical identification of compound, it should be interesting to develop contacts with ink's makers.

3 – Now, the influence of type of paper should be studied. In this article, we have used a classic paper. For example, if a quality photo paper is used, the results should be different.

4 – Actually, we study the discrimination of inkjet inks using semi-quantitative characteristics of a pyrogram.

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Author Biography

Franck Partouche studied chemistry at the University of Marseille (France). In 2001, he joined IRCGN (Rosny-sous-bois, France) in the Vehicle department and carried out research on polymer characterization. Since September 2003, he is member of the Documents department in IRCGN. His main researches focus on the characterization of inkjet inks in the field of forensic examination. He has contributed to develop new protocols using FTIR and PY/GC/MS.