Forensic Examination of Inks Extracted from Printed Documents using Fourier Transform Infrared Spectroscopy

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Abstract

Yellow, cyan, magenta and black inks were extracted from documents printed using two common brands of printing cartridge in Nigerian market and analyzed to identify/compare the functional groups present using Fourier Transform Infra-red Spectroscopy (FTIR). The FTIR spectra obtained were found to show highly characteristic absorption bands depending on the composition of the printer inks. Also, the results indicated the presence of triarylmethane dyes, epoxy resins, alkyd resin and esters in all the inks as they are peaks assigned to the vibration of aliphatic ester, asymmetrical and symmetrical stretching. The pure ink and its extract from the same band were also found to exhibit similar FTIR spectra while inks extract from different brands exhibits marked difference in absorption bands. This research can provide valuable information if an admitted sample is provided for comparing with the suspect printed document.

Keywords: Forensic science, ink analysis, Document examination, FTIR.

Introduction

Examination of inks on questioned documents has become common, and law enforcement agencies using this technique during their criminal investigations. Questioned documents can include diary entries, or whole diary, reconstructed files and false dated correspondence, prepared to show a particular sequence of events, occurred in the past or more simply a forged signature or an altered cheque [1,2]. Subtle alteration to documents, such as papers involving medical malpractice, tax returns, will scripts and insurance claims, divorce judgments, copyright certificates, agreements related to labour management disputes; employee problem settlements and a variety of contracts etc. can have significance financial implications.

These kinds of many cases have been submitted by a number of crime reporters or document investigators. Incidents of forgery have increased tremendously and to alter these documents printers, copiers (inkjet printer) are widely used. The detection of alterations or additions to a document and an assessment of when the document was written have become a prime concern of document examiners and ink chemists [3,4]. Document examiners have invented methods which have been successfully used for examining and identifying printing inks scientifically. These techniques include paper chromatography, paper electrophoresis, luminescence, micro spectrometry, diffuse reflectance Fourier transform infrared, luminescence photography, laser excitation and spectroscopy, thin-layer chromatography, high-performance liquid chromatography, and capillary electrophoresis [1-10]. There is little or no information regarding the application of a sequence of selected standard techniques to the Nigerian population of inks used in printing. Also, no report presenting result of characterization/comparison of inkjet printer inks collected from the market in Nigeria. There is a need to make effort in filling the gap in current analytical methodology of forensic questioned document examination in the country. Characterization of writing/printing instruments used to produce the document such as ink; paper etc. may be a leading step in the investigation of forgery in Nigeria.

The aim of this study therefore is to analyze, compare and contrast ink extracted from printed documents using two brands of printing cartridge in the Nigerian market. This will be achieved by subjecting the extracted inks to Fourier Transform Infrared Spectroscopy (FTIR) analysis. It is hoped that the results from this study will provide valuable information/data if an admitted sample is provided for comparison with the suspect printed document in Nigeria. Also, the proposed method in the study could be used for examination of ink on documents taking extremely small

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Materials and Method

Materials

All reagents used were analytical grade reagents obtained Sigma Aldrich Company U.S.A. Double distilled water was used throughout for the preparation of samples and dilution of the stock standard solutions. The glass wares used in the study were decontaminated by overnight soaking in 5 % HNO₃.

Sample collection

The method used in sample collection is that of Sharma et al. [11]. Five colored printouts each containing of cyan, magenta, yellow and black color were printed from inkjet printers of two leading ink printing manufacturers (Silver tosh and Hewlett Packard) in Nigerian Market. White paper of A4 size was used to take all samples. All four printed color i.e. cyan, magenta, yellow, and black from each printout were extracted, analyzed and interpreted. The two leading manufacturers were marked as A and B respectively and their different models were marked as 1, 2, 3 and so on. The samples were given marking as A1, A2, A3, A4, A5,.....A10 for different models of brand A and B1, B2, B3, B4,....; for different models of brand B.

Separation of ink from printed Document

The ink from the printed document was separated following the method of Sharma et al. [11]. A colored squared block of constant area was taken from the sample document and cut into small pieces. The pieces of paper were then transferred to 15 ml beaker and titrated with 5 ml of methanol. The sample was then allowed to be extracted at room temperature with intermittent shaking. The methanol extract was then transferred to 10 ml volumetric flasks after filtering through a filter paper. The extract was made up to 4 ml. The same procedure was followed for all samples of cyan, magenta, yellow and black. In order to avoid any interference and to record the response of matrix i.e. paper and the reagent i.e. methanol towards IR, the blank samples of matrix and reagent were also prepared following the same procedure.

Preparing Pellet for Scanning

2 ml of methanolic solution was taken in a china dish and evaporated at room temperature to dryness and heated for about 10 minutes in an oven. The residue was scratched from the walls of china dish and mixed intimately with dry KBr. After this process pellets were prepared by using a pellet maker. The same procedure was followed for all samples of Cyan, Magenta, Yellow and Black Color.

Scanning of Samples

The FTIR analyses of the samples were carried using a spectrometer from Agilent technology. The scanning was done through a wave range of 3500 to 400 wave number cm⁻¹

FTIR Study

Figures 1-5 shows the FTIR spectra of pure and extracted inks of Brand A while the spectra obtained for Brand B are presented in Figures 6, 7. Peaks obtained from the various spectra as well as assignments to the respective peaks are presented in Tables 1-5. The results presented show the various % transmittances corresponding to the respective wave length of absorption. It should be noticed that most of the absorption bands in the inks spectra are complex peaks, and exhibited band in different areas that are common to many organic compounds typically used in ink formulation. For instance, Peaks in the range from 2000 to 1700 cm⁻¹ were observed, which is the characteristic frequency of carbonyl (C=O) stretching vibration indicating that aliphatic acids or their esters are present in the ink colors studied [12].

| Pure Ink | Extracted ink |
|----------|---------------|
| % Transmittance | Peaks(cm⁻¹) | % Transmittance | Peaks(cm⁻¹) |
| 61.095 | 655 | 82.466 | 1000 |
| 85.866 | 996 | 73.079 | 1048 |
| 81.86 | 1045 | 82.572 | 1127 |
| 85.674 | 1082 | 86.898 | 1141 |
| 85.236 | 1182 | 85.709 | 1302 |
| 86.038 | 1346 | 84.958 | 1346 |
| 85.42 | 1395 | 83.545 | 1473 |
| 86.155 | 1469 | 87.33 | 1495 |
| 45.102 | 3268 | 60.252 | 1659 |
| 96.097 | 2121 | 96.228 | 2125 |
| 44.163 | 3268 | 61.095 | 1000 |

Table 1: Peaks of FTIR absorption, % transmittance and functional group assignments for pure and extracted magenta ink of Brand A.

Results and Discussions

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The FTIR spectra obtained were also found to show highly characteristic absorption bands depending upon the compositions of the printer inks as it could be seen that every printer ink batch exhibits characteristic IR spectra.

| Extracted ink | Functional Group (Assignment) | % Transmittance | Peaks(cm⁻¹) |
|---------------|--------------------------------|-----------------|-------------|
|               | C–O Stretch                    | 23.463          | 1026        |
|               | –C–H Wag                       | 87.876          | 1119        |
|               | C–H (In ring)Stretch           | 85.066          | 1413        |
|               | C–H Bend                       | 83.096          | 1454        |
|               | –C≡C– Stretch                  | 100. 205        | 2125        |
|               | C–H Stretch                    | 77.499          | 2832        |
|               | O–H Stretch (Carboxylic)       | 69.655          | 3324        |

Table 6: Peaks of FTIR absorption, % transmittance and functional group assignments for extracted black ink of Brand B.

| Extracted ink | Functional Group (Assignment) | % Transmittance | Peaks(cm⁻¹) |
|---------------|--------------------------------|-----------------|-------------|
|               | C–O Stretch                    | 20.197          | 1026        |
|               | –C–H Wag                       | 86.38           | 1119        |
|               | C–H (In ring)Stretch           | 83.319          | 1413        |
|               | C–H Bend                       | 82.322          | 1454        |
|               | C=N Stretching                 | 94.587          | 1674        |
|               | –C≡C– Stretch                  | 99.959          | 2125        |
|               | C–H Stretch                    | 77.649          | 2836        |
|               | –C–H Stretch                   | 76.22           | 2948        |

Table 7: Peaks of FTIR absorption, % transmittance and functional group assignments for extracted cyan ink of Brand B.

Different brands of ink cartridge also exhibited different characteristic IR spectra. Also, some common ingredients in different brands gave similar FTIR spectral bands for those components. It was also found that pure ink and its extract from the same brand exhibited similar FTIR spectra. For instance, similar peaks for O–H Stretch, C–O asymmetric were stretching for the same brand. However, ink extracts from different cartridges of different brands on the same paper exhibit marked differences.

| Extracted ink | Functional Group (Assignment) | % Transmittance | Peaks(cm⁻¹) |
|---------------|--------------------------------|-----------------|-------------|
|               | C–O Stretch                    | 18.093          | 1026        |
|               | –C–H Wag                       | 87. 258         | 1119        |
|               | C–H (In ring)Stretch           | 83.647          | 1424        |
|               | C–H Bend                       | 82.335          | 1454        |
|               | –C≡C– Stretch                  | 100.31          | 2113        |
|               | C–H Stretch                    | 77.172          | 2832        |
|               | –C–H Stretch                   | 76.102          | 2944        |

Table 8: Peaks of FTIR absorption, % transmittance and functional group assignments for extracted magenta ink of Brand B.
The difference between various samples of ink can be seen by observing at the intensity of main peak, the pattern of each spectrum and the absence or presence of some characteristic bands.

Figure 2: FTIR spectra of (A) pure and (B) extracted cyan of Brand A.

Figure 3: FTIR spectra of (A) pure and (B) extracted yellow ink of Brand A.

Figure 4: FTIR spectra of (A) pure and (B) extracted black ink of Brand A.

Figure 5: FTIR spectra of (A) methanol (B) methanol and paper extract.

Figure 6: FTIR spectra of extracted (A) black ink of brand B and (B) magenta of Brand B.

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For instance C–H “Opp” (Aromatic) peak which was observed at 762 in the yellow ink extracted of brand A was absent in brand B, the −C≡C− stretch peak at 2125 present in the black ink extract of brand A was absent in brand B, the N–H Wag at 996 in the extracted cyan ink sample of brand A was absent in brand B Cyan ink sample, the ≡CH peak at 1000 in the magenta ink sample extract of brand A was absent in brand B.

According to Beer-Lambert law, absorption is related to concentration (C in mole), path length (d in cm) and molar absorptivity (ε in Lmol⁻¹cm⁻¹) according to the following equation [13],

\[ A = εdC \quad (1) \]

If the incident radiation entering the sample cell is given by \( I_0 \) and the amount transmitted is \( I_t \). The transmittance of the solution is defined as the fraction of the incident radiation that is transmitted and can be written as,

\[ T = \frac{I_t}{I_0} \quad (2) \]

On the other hand, percentage transmittance is given in equation 3 while equation 4 gives

\[ T = \frac{I_t}{I_0} \times \frac{100}{1} \quad (3) \]

The amount of light that is absorbed (Iₐ):

\[ I_a = I_0 - I_t \quad (4) \]

From the logarithm of equation 4, equation 5 is obtained,

\[ \log I_a = \log I_0 - \log I_t = \log \left( \frac{I_0}{I_t} \right) \quad (5) \]

The left hand side of equation 5 corresponds to absorbance (Iₐ). Therefore, the relationship between absorbance and transmittance is given according to equation 6,

\[ A = \log \left( \frac{1}{T} \right) \quad (6) \]

Since % transmittance is equal to transmittance x 100, equation 5 can also be written as

\[ A = \log \left( \frac{100}{\%T} \right) = 2 - \log \left( \frac{1}{T} \right) \quad (7) \]

Using equation 6, values of absorbance were calculated and plotted with their corresponding wave numbers. These are presented in Figures 8-15. In Figures 8-11, plots showing the variation of absorbance with wave number of FTIR absorption by pure and extracted inks of Brand A are presented. Figures 12-15, show plots of the variation of absorbance with wave number of FTIR absorption by inks extracted from documents printed using the different studied brands (Brand A and B). From the plot, it can be seen that two brands exhibited marked differences in their absorbance.
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spectra while those from different brands will give marked differences in their absorption bands.

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