

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.

1. 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 (negligible portion) of the sample from an unimportant area of the document with the permission of the court.

2. Materials and Method

2.1. 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.

2.2. 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'.

2.3. 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 for 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.

2.4. Preparing Pellet for Scanning

2ml 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.

2.5. 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}

3. Results and Discussions

3.1. 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].

Table 1.

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

Pure ink		Extracted ink		Functional group (Assignment)
%Transmittance	Peaks(cm^{-1})	%Transmittance	Peaks(cm^{-1})	
61.095	655			C-H "Opp"
85.866	996			N-H Wag
		82.466	1000	=CH
81.86	1045	73.079	1048	C-O Asymmetric stretching
85.674	1082	82.572	1127	C-O Symmetric stretching
86.898	1141			C-O-C Symmetric stretching
85.236	1182			C-O-C Symmetric stretching
85.709	1302			C-N Stretch
86.038	1346	84.958	1346	C-N Stretch
85.42	1395			C-N Stretch
86.155	1469	83.545	1473	C-H Bend
87.33	1495			C-H Bend
		60.252	1659	C=N stretching
96.097	2121	96.228	2125	-C≡C- stretch
45.102	3268	44.163	3268	N-H stretch

Table 2.

Peaks of FTIR absorption, % transmittance and functional group assignments for pure and extracted cyan ink of Brand A.

Pure ink		Extracted ink		Functional group (Assignment)
%Transmittance	Peaks(cm^{-1})	%Transmittance	Peaks(cm^{-1})	
83.85	992	84.061	996	N-H Wag
75.687	1045	76.584	1045	C-O Asymmetric Stretching
83.989	1115	84.706	1119	-C-H Wag
82.871	1220	85.183	1220	Aromatic Ether (Ar-O) vibration
84.918	1465			C-H Bend
		84.924	1473	C-H Stretch
63.847	1640	61.929	1644	C=C Stretch
96.1	2106	96.081	2121	-C≡C- Stretch
42.638	3305	43.452	3268	O-H Stretch (Carboxylic Acid)

Table 3.

Peaks of FTIR absorption, % transmittance and functional group assignments for pure and extracted black ink of Brand A.

Pure Ink		Extracted ink		Functional group (Assignment)
%Transmittance	Peaks(cm^{-1})	%Transmittance	Peaks (cm^{-1})	
19.426	1026	19.5	1026	C-O stretch
87.309	1119	87.229	1119	-C-H Wag
83.434	1424	83.368	1424	C-H (In ring) stretch
82.222	1454	82.169	1454	C-H Bend
96.735	1663	96.524	1663	C=N stretching
		100.373	2005	-C≡C- stretch
100.295	2125	100.286	2125	-C≡C- stretch
77.091	2836	76.977	2836	C-H stretch
76.663	2944	75.654	2944	-C-H stretch

Table 4.

Peaks of FTIR absorption, % transmittance and functional group assignments for pure and extracted yellow ink of Brand A.

Pure ink		Extracted ink		Functional group (Assignment)
%Transmittance	Peaks(cm^{-1})	%Transmittance	Peaks(cm^{-1})	
		77.2	762	C-H "Opp"(Aromatic)
23.14	1026	18.751	1026	C-O stretch
86.668	1119	87.487	1119	-C-H Wag
83.228	1413	83.431	1424	C-C(In ring)stretch

Pure ink		Extracted ink		Functional group (Assignment)
%Transmittance	Peaks(cm ⁻¹)	%Transmittance	Peaks(cm ⁻¹)	
82.534	1454	82.211	1454	C-H bend
92.968	1659	97.472	1711	C=N stretching
99.832	2125			-C≡C- stretch
78.061	2836	76.956	2836	C-H stretch
76.21	2948	75.61	2944	-C-H stretch

There are indications of the presence of triarylmethane dyes, epoxy resin, alkyd resin, and solvents in the inks as there were peaks assigned to the vibration of aromatic ether (Ar - O), asymmetrical and symmetrical stretch vibration of aliphatic ether (C - O), asymmetrical and symmetrical stretch vibration of the C - O - C bonds.

Table 5.

Peaks of FTIR absorption, % transmittance and functional group assignments for extracted yellow ink of Brand B.

Extracted ink		Functional group (Assignment)
%Transmittance	Peaks(cm ⁻¹)	
18.191	1026	C-O stretch
87.838	1119	-C-H Wag
83.92	1421	C-H (In ring) stretch
82.621	1454	C-H Bend
100.403	2125	-C≡C- stretch
77.248	2832	C-H stretch
76.515	2944	-C-H stretch
68.872	3320	O-H stretch (Carboxylic acid)

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)	
23.463	1026	C-O Stretch
87.876	1119	-C-H wag
85.066	1413	C-H (In ring) stretch
83.096	1454	C-H bend
100.205	2125	-C≡C- stretch
77.499	2832	C-H stretch
77.443	2944	-C-H stretch
69.655	3324	O-H stretch (Carboxylic)

Table 7.

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

Extracted ink		Functional group (Assignment)
%Transmittance	Peaks(cm ⁻¹)	
20.197	1026	C-O stretch
86.38	1119	-C-H wag
83.319	1413	C-H (In ring) stretch
82.322	1454	C-H bend
94.587	1674	C=N stretching
99.959	2125	-C≡C- stretch
77.649	2836	C-H stretch
76.22	2948	-C-H stretch

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.

Table 8.

Peaks of FTIR absorption, % transmittance and functional group assignments for extracted magenta ink of Brand B.

Extracted ink		Functional group (Assignment)
%Transmittance	Peaks(cm ⁻¹)	
18.093	1026	C-O stretch
87.258	1119	-C-H wag
83.647	1424	C-H (In ring) stretch
82.335	1454	C-H Bend
100.31	2113	-C≡C- stretch
77.172	2832	C-H stretch
76.102	2944	-C-H stretch

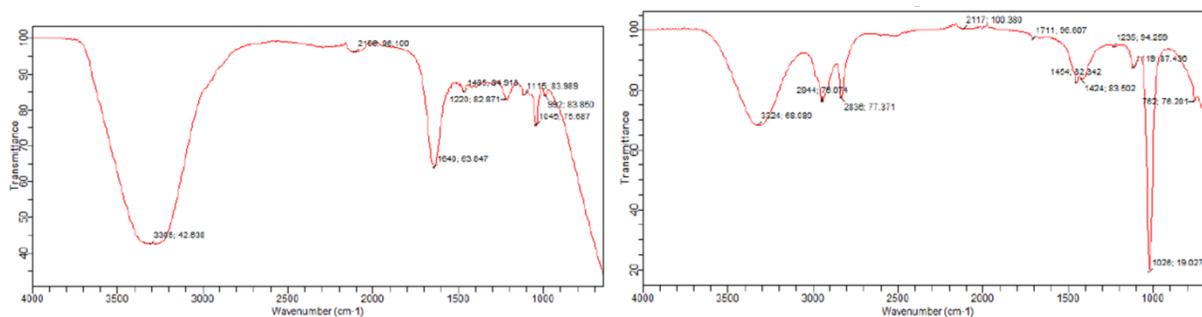


Figure 1.
FTIR spectra of (A) pure (B) extracted magenta ink of Brand.

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.

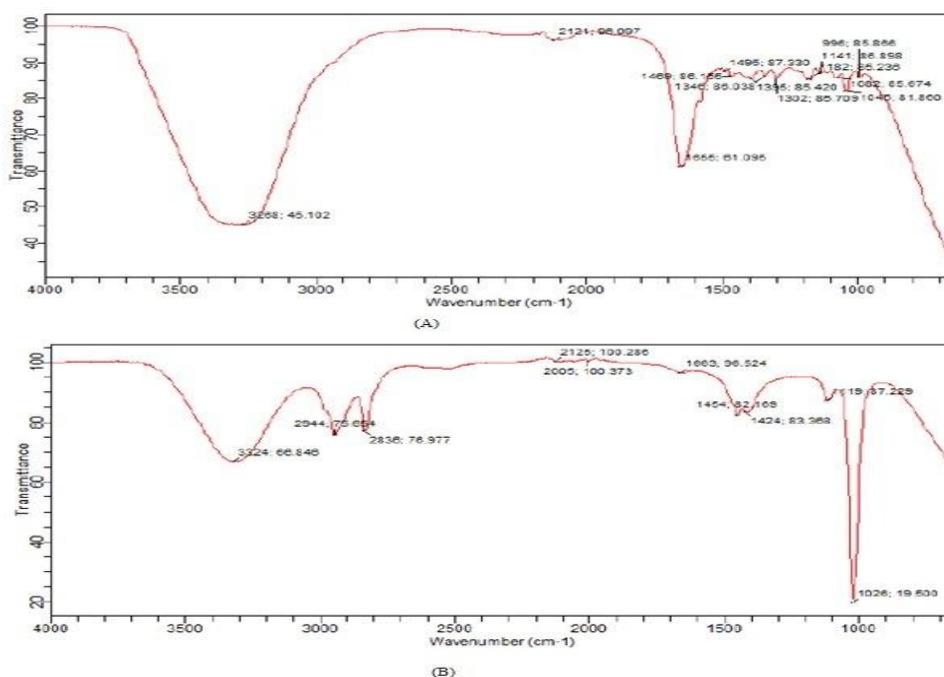


Figure 2.
FTIR spectra of (A) pure and (B) extracted cyan of Brand A.

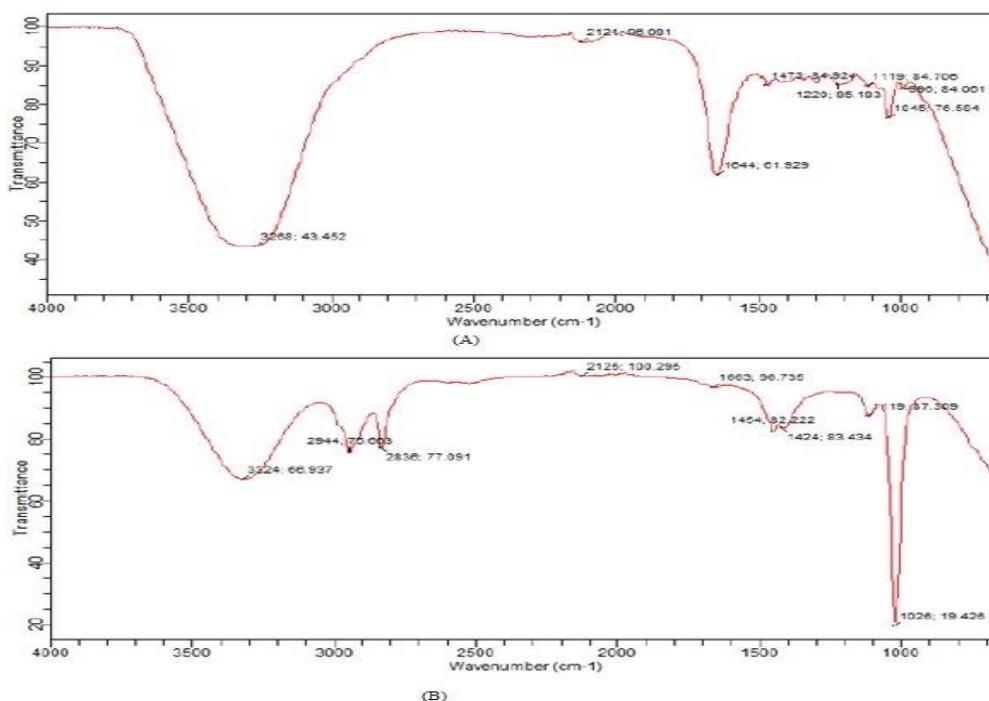


Figure 3.
FTIR spectra of (A) pure and (B) extracted yellow ink of Brand A.

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.

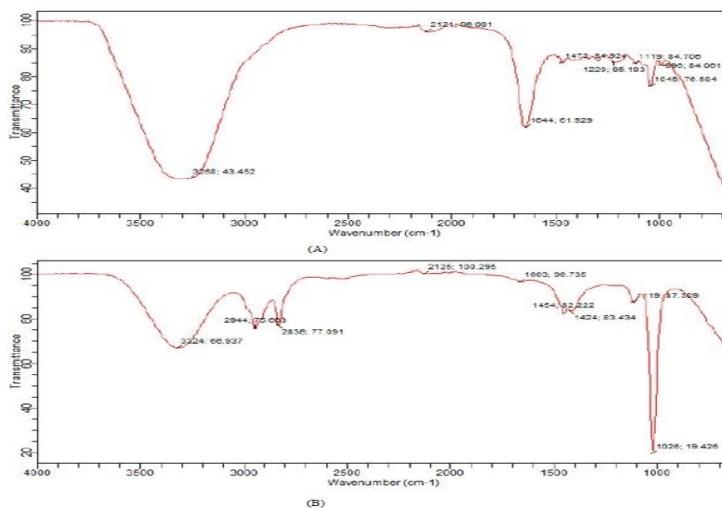


Figure 4. FTIR spectra of (A) pure and (B) extracted black ink of Brand A.

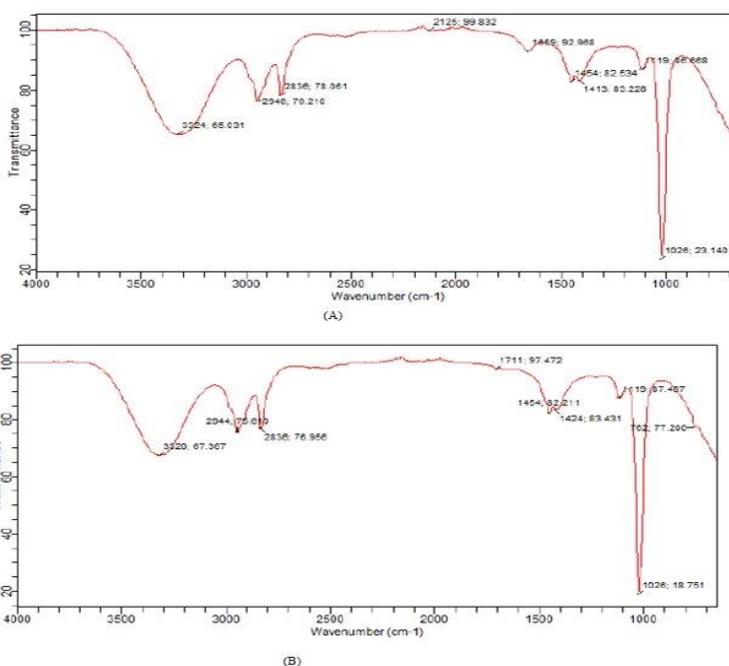


Figure 5. FTIR spectra of (A) methanol (B) methanol and paper extract.

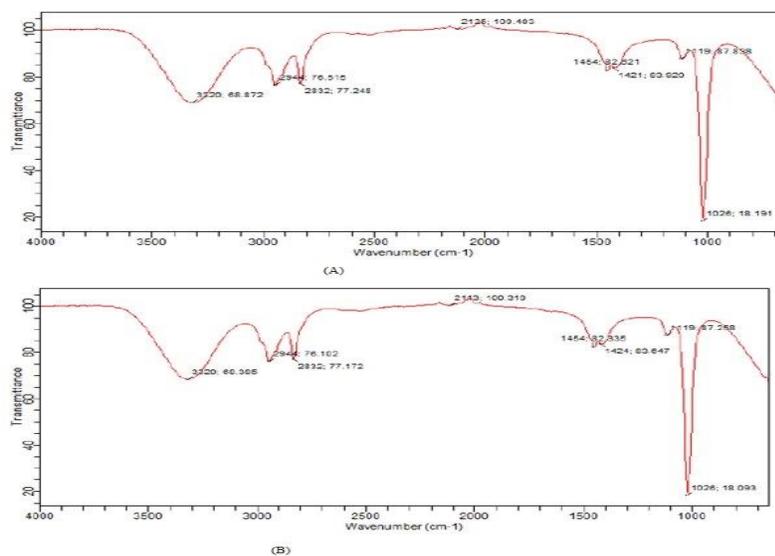


Figure 6. FTIR spectra of extracted (A) black ink of brand B and (B) magenta of Brand B.

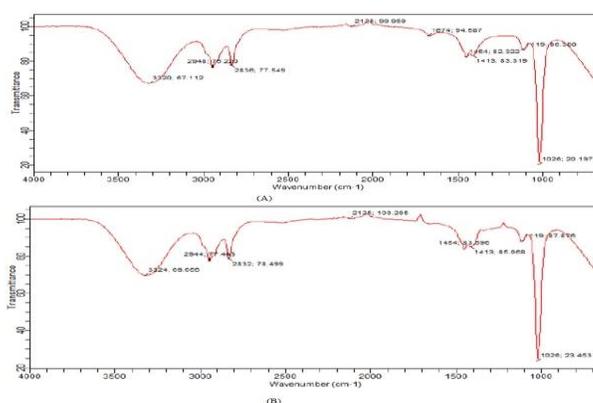


Figure 7.
FTIR spectra of extracted (A) yellow ink of brand B and (B) cyan of Brand B.

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 $\text{--C}\equiv\text{C--}$ 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 $\equiv\text{CH}$ 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 $\text{Lmol}^{-1}\text{cm}^{-1}$) according to the following equation [13],

$$A = \epsilon d C \quad (1)$$

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 (I_a):

$$I_a = I_0 - I_t \quad (4)$$

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 (I_a). 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

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

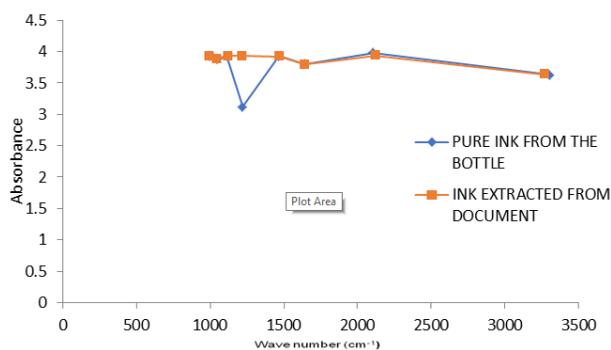


Figure 8.
Variation of absorbance with wave number of FTIR absorption by pure and extracted magenta ink of Brand A.

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.

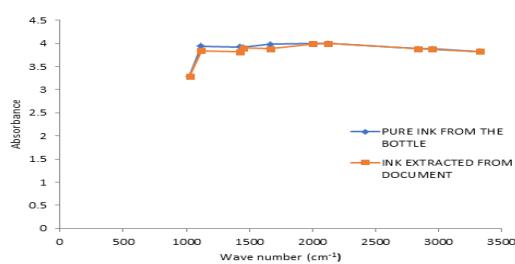


Figure 9.
Variation of absorbance with wave number of FTIR absorption by pure and extracted black ink of Brand A.

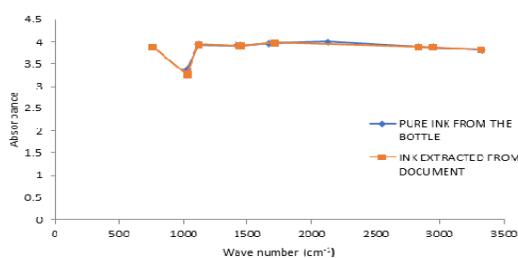


Figure 10.
Variation of absorbance with wave number of FTIR absorption by pure and extracted cyan ink of Brand A.

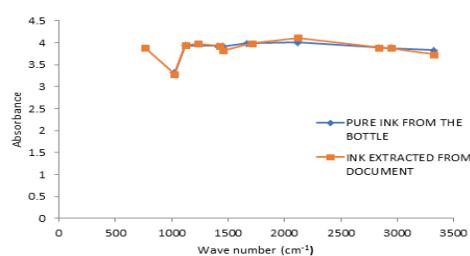


Figure 11.
Variation of absorbance with wave number of FTIR absorption by pure and extracted yellow ink of Brand A.

From the plot, it can be seen that both pure and extracted inks of the same brand exhibited maximum absorption at the same wave number and also show similarity or closeness to similarity in each other wave number. This shows that the extracted ink has some compatibility factors with the pure ink of brand A.

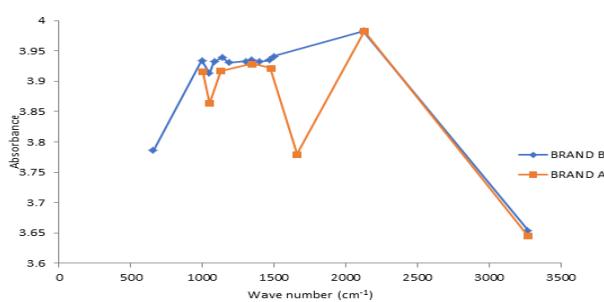


Figure 12.
Variation of absorbance with wave number of FTIR absorption by yellow ink extracted from printed documents of Brand A and B inks.

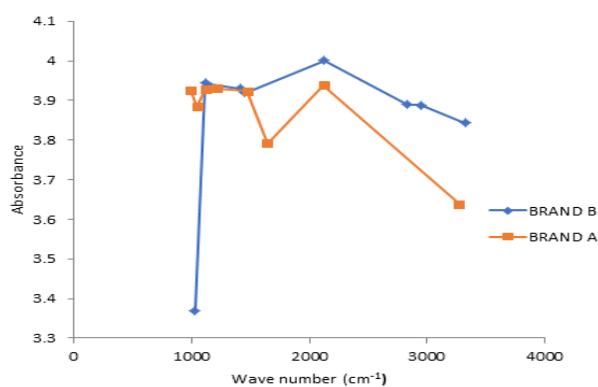


Figure 13.
Variation of absorbance with wave number of FTIR absorption by black ink extracted from printed documents of Brand A and B inks.

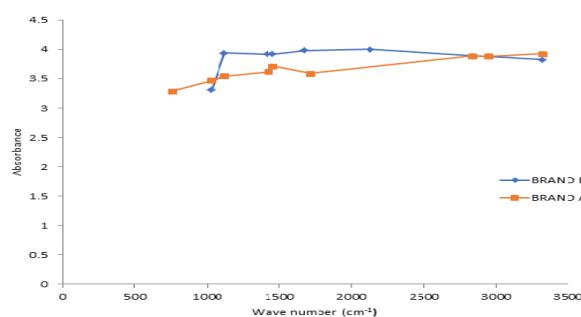


Figure 14. Variation of absorbance with wave number of FTIR absorption by cyan ink extracted from printed documents of Brand A and B inks.

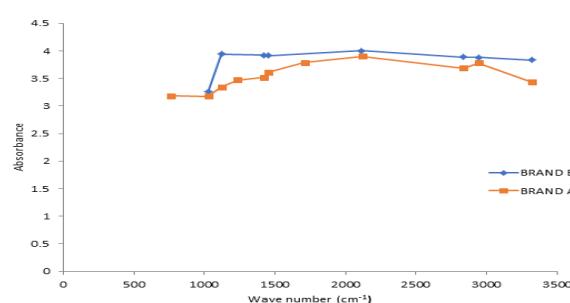


Figure 15. Variation of absorbance with wave number of FTIR absorption by magenta ink extracted from printed documents of Brand A and B inks.

4. Conclusion

Based on the obtained results the following conclusion can be drawn. Fourier Transform Infrared Spectroscopy, though strictly not nondestructive could be used for examination of inks on documents taking extremely small (Negligible portion) of the sample from an unimportant area of the document with the permission of the court.

Fourier Transform Infrared Spectroscopy is a simple, direct and reproducible method of comparing computer printing inks. Inks when extracted from printed documents will exhibit similar absorption spectra while those from different brands will give marked differences in their absorption bands.

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