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Infrared Spectroscopic Technique for the Forensic Discrimination of Marker Pen Inks

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ABSTRACT: Commercial permanent and non-permanent blue, red, green and black marker ink pens from three different brands were studied to determine their distinguishable properties in terms of Infrared (IR) spectrum. The study was intended for use in forensic investigation of crime scenes involving writing on hard non porous surfaces using marker ink pens. The method of sample collection was by swab method using cotton buds while the IR spectrum was recorded using the Attenuated Transmitted Reflectance (ATR) spectroscopic technique. The inks showed some selective distinguishable properties in terms of IR spectral patterns. Comparison of IR spectra showed that non-permanent inks have weak amine bands at 823-850 cm^{-1}, with emphasized dissimilarity between permanent and non permanent ink at 2345 and 2361 cm^{-1} attributed to the C≡C vibrations, 1736 and 1737 cm^{-1} corresponding to the C=O stretching and 1204 cm^{-1} attributed to the C-O bending. It can be concluded that marker ink pens left at a crime scene can be swabbed using cotton bud and further analyzed in the laboratory for discrimination using IR technique.

Keywords: Spectroscopic technique, marker pen, infrared spectroscopy, cotton swab

Introduction

Ink analysis is an important forensic procedure that can reveal useful information about questioned documents [1]. Investigations are most often aimed at authenticating the document or at determining its age or origin. It also can help to verify other document such as historical and archeological document that are claimed to be original document but may have been altered or invented recently [2]. The simplest description of inks is that ink is a liquid, semi-liquid or solid preparation which can used to draw graphics sign on a support [3]. Inks designed for use in different writing instruments or printing methods have quite dissimilar components. Recipes for formulations of inks have been modified over the years. Chinese were the first to use ink, usually mixing lake colours and black pulverized stone, but the birth of real ink occurred in the third century B.C [4]. Modern inks contain many substances aiming to improve ink characteristics [5]. Although it is difficult to determine whether an individual marker pen was used to criminal cases, it is feasible to identify the brand of marker pen. This requires some kind of classification or discrimination between the different brands of inks.

Spectroscopic methods such as Fourier transform infrared spectroscopy (FTIR) [6-8] and chromatographic technique [9-13] has been successfully applied to the analysis of inks. The advantage of FTIR method is that it is a non-destructive method. On the other hand, FTIR analysis provides minimal sample preparation and cost-effectiveness.

Analysis of inks from questioned documents has been identified based on writing pens and the extraction of inks from inked lines written on papers. Most often sample plugs obtained by poking inked lines with a blunt needle are employed. However, writings on walls or solid permanent matrices such as whiteboards are difficult to analyze as ink are difficult to obtain in a sufficient amount for forensic analysis. Additionally, the analyses of marker pen inks have not been widely reported.

This study was undertaken to analyze marker inks from writing made on solid matrices especially whiteboard of non-porous surface and to distinguish between the permanent and non-permanent marker pen inks using spectroscopic analysis.

Experimental

Preparation of Sample

Three brands of permanent and non-permanent marker pens (Faber Castell, Artline and Faster) consisting of four different colours which were blue, black, red and green from each brand were used in this study. All marker ink samples were allocated specific reference codes. Control standard ink samples, were easily collected by using a direct dry swab method from marker pen nibs. Simulated cases written marker ink were prepared by writing threat sentence on whiteboard surface after which the inks were swabbed using cotton swabs moistened with ethanol.

Infrared Spectroscopy

FTIR spectra using a micro-ATR attachment in the mid-infrared spectral range were recorded in the reflectance mode on an infrared spectrophotometry (Nicolet Avatar, USA). Spectra were recorded in the range of 400 cm^{-1} to 4000 cm^{-1}.

Germanium cells with the ATR objective were used in this analysis on swabbed ink samples. Small amount of ink samples were removed from cotton swabs using forceps. It was then placed on the germanium cell and pressed together between two germanium cells. IR spectra of the ink were recorded and compared in terms of major peaks similarities, differences and intensities.

Results and Discussion

The study focused on the analysis of small amounts of inks without prior pre-concentration. The results will be discussed in terms of the ability of the analysis to be used to discriminate between samples or to trace and confirm the use of a particular ink in a crime scene associated with writing on a white board.

Comparison between Bulk and Swab Ink Samples

Depending on the ink samples, different absorptions were detected in the IR spectra. IR analysis of blank cotton swab did not produce any peak that could interface with absorption peak of ink samples.

Spectral bands at 2883 to 2929 cm^{-1} in many bulk and swab samples for permanent inks allowed for the identification of aromatic ring bands in ink compositions. **Fig. 1** shows the spectra containing absorptions corresponding to the aromatic ring in an ink composition. The top spectrum represents the swab ink sample while the bottom spectrum represents the bulk ink samples for permanent blue Faber Castell marker ink.

The presence of aromatic ring is consistent with the formulation of a typical permanent marker ink that contains aromatic ring as one of its compositions.

Spectral bands at 1587 to 1507 cm^{-1} can be seen in some bulk and swab ink samples except for black non-permanent Artline and Faber Castell ink samples. Intensity ratios of these bands are different. All the spectra that showed these bands correspond to the CH_2 vibration on linear aliphatic chain. **Fig. 2** shows the spectra with the CH_2 vibrations for both the top and bulk non-permanent Faster green ink.

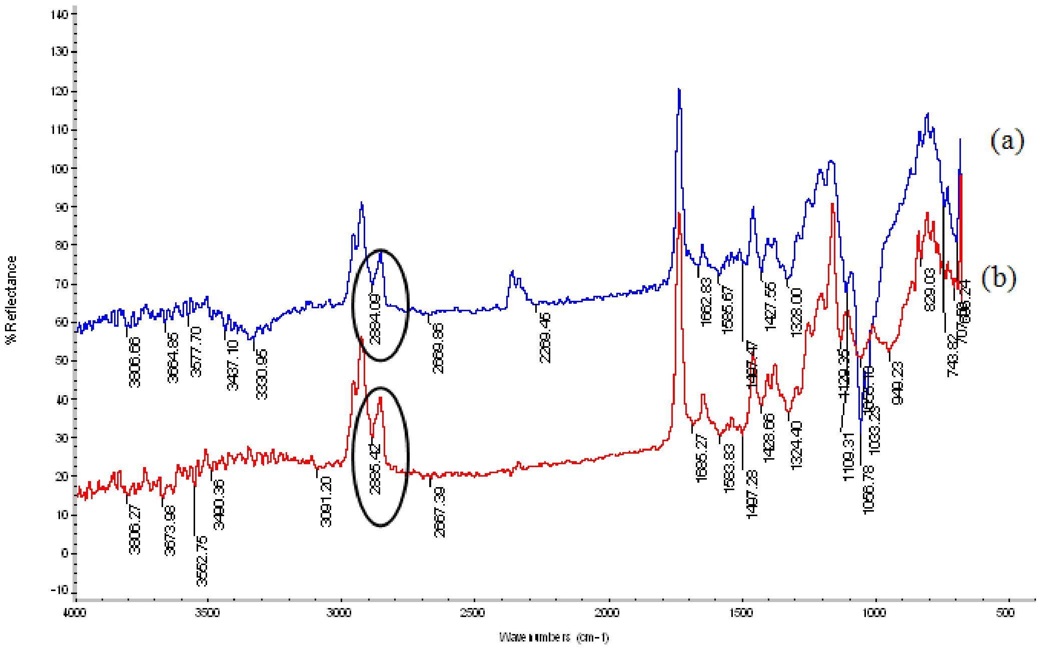

Fig. 1: IR spectra of blue Faber Castell marker ink sample containing aromatic ring for (a) swab and (b) bulk

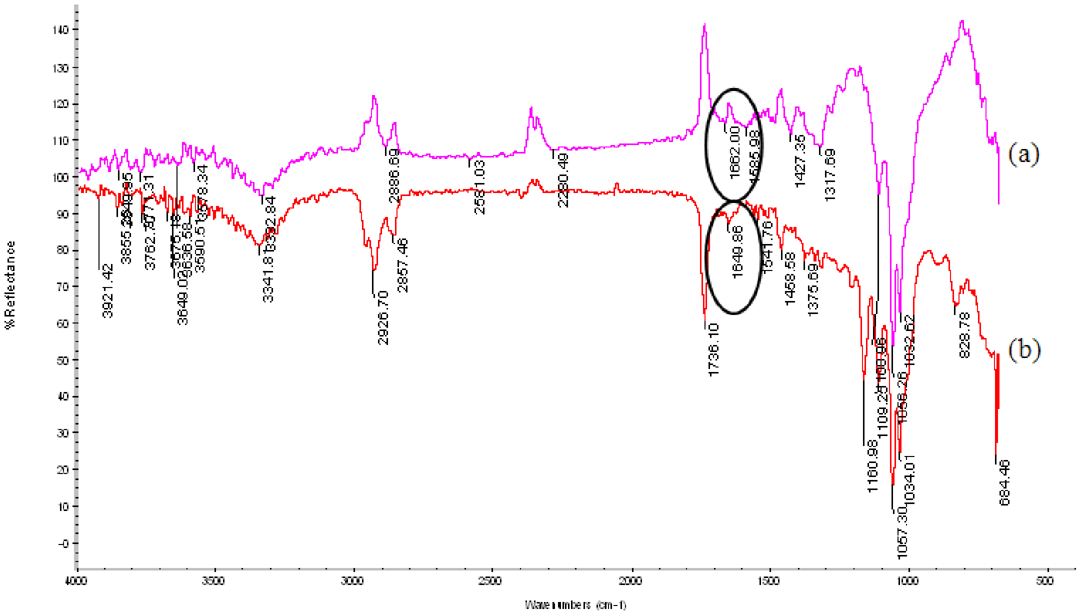

Fig. 2: Spectra of the non-permanent Faster green ink samples showing bands attributed to CH_2 vibrations for (a) swab and (b) bulk

Other representative bands that can be observed in nearly all the ink samples are those corresponding to alkene bands at 1683 to 1662 cm^{-1}. This can be clearly seen in many bulk and swab ink samples for permanent and non-permanent marker ink. **Fig. 3** shows some spectra of bulk and swab samples in the amide band region.

Comparison between bulk and swab samples of all samples showed good similarities and revealed sufficient class characteristics based on the functional groups present. Thus, the swab ink samples used were adequate in reproducing the bulk ink sample used.

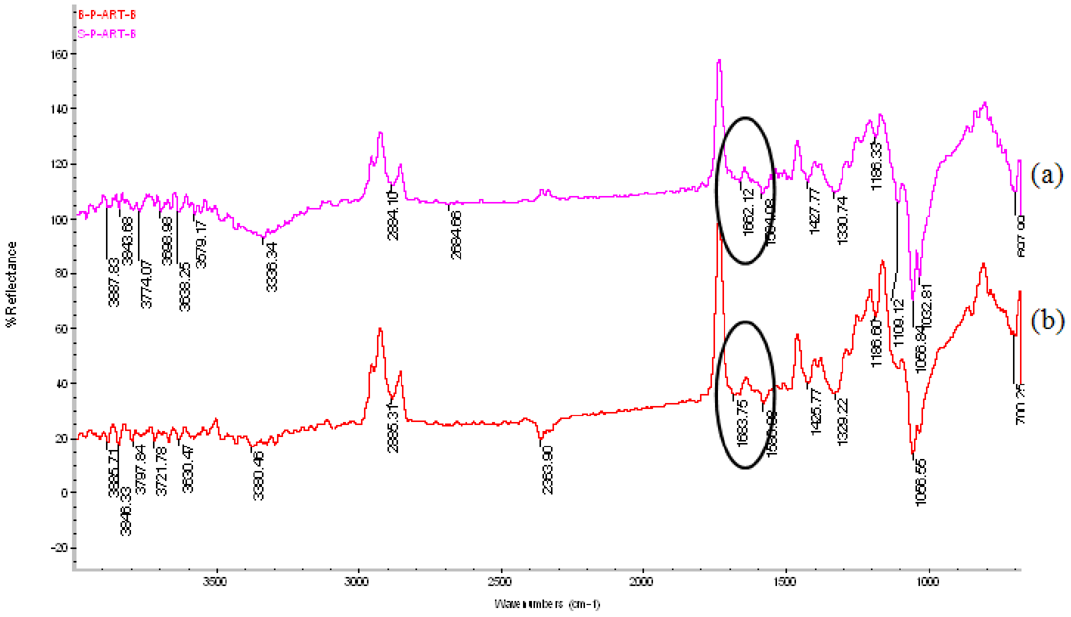

Fig. 3: IR spectra profile of (a) swab and (b) bulk permanent blue Artline sample which indicate the presence of amide bands

Comparison between Permanent and Non-permanent Inks

The entire non-permanent ink sample except the black Artline ink and the permanent ink samples showed a weak absorption at 823-850 cm^{-1}. These bands are very close to the 848 cm^{-1} amine bands. **Fig. 4** shows a spectrum of non-permanent ink containing weak absorption of amines vibrations that are not present in the permanent ink formulation of the same brand.

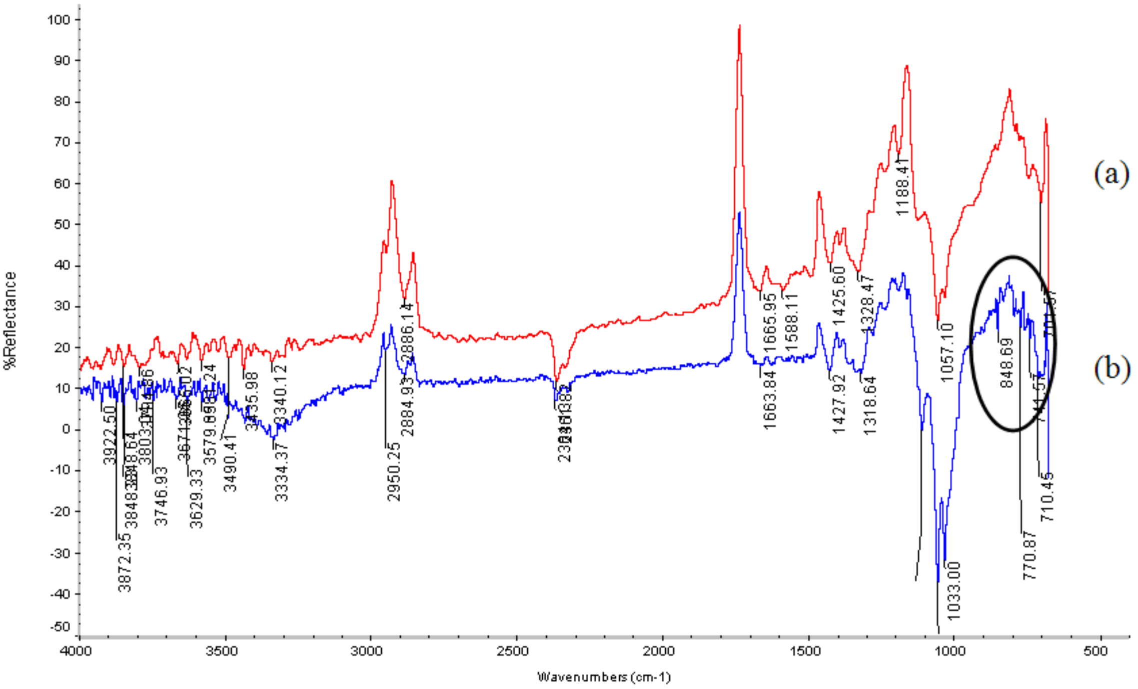

Fig. 4: IR spectrum of (a) permanent and (b) non permanent green Artline marker ink bulk samples

Other bands which discriminate between permanent and non permanent ink samples were the sharp IR band at 2927, 1735 and 837 cm^{-1} that can be seen clearly in non-permanent Faber Castell spectrum and Faster. Those bands refer to the alkanes stretching striations, ketone vibrations and amines bands respectively. Two bands at around 1579 and 1184 cm^{-1} were attributed to the alkenes stretching vibrations and C-O vibrations bands can be observed in all permanent ink samples except permanent Artline red. **Fig. 5** shows the spectral differences between the permanent and non-permanent blue Faster ink sample.

Spectral differences between inks of different manufacturers

The same differentiations in spectral profile of marker pen inks from inks colour were also examined in order to further differentiate between the different brands of inks analysed.

Black Permanent Ink Samples

Fig. 6 shows the IR spectra of black permanent ink from different brand. Both of the permanent Artline and permanent Faber Castell spectra showed absorption of C≡C stretching at 2361 and 2366 cm^{-1}. Other diagnostic bands that could differentiate between inks by manufacturers were the presence of amine bands at 829 cm^{-1} for permanent black Faster ink.

Black Non-permanent Marker Ink Samples

The presence of bands at 2345 and 2361 cm^{-1} were attributed to the C≡C vibrations for Artline and Faster ink samples. The strong bands only occur for non-permanent Faber Castell and Faster at 1736 and 1737 cm^{-1} which corresponded to the C=O stretching. Bands at 1204 cm^{-1} vibration bands which were observed clearly for Faber Castell and Faster but not for Artline were attributed to the C-O bending. **Fig. 7** shows the differences of absorbance intensities between non-permanent black ink samples from various brands.

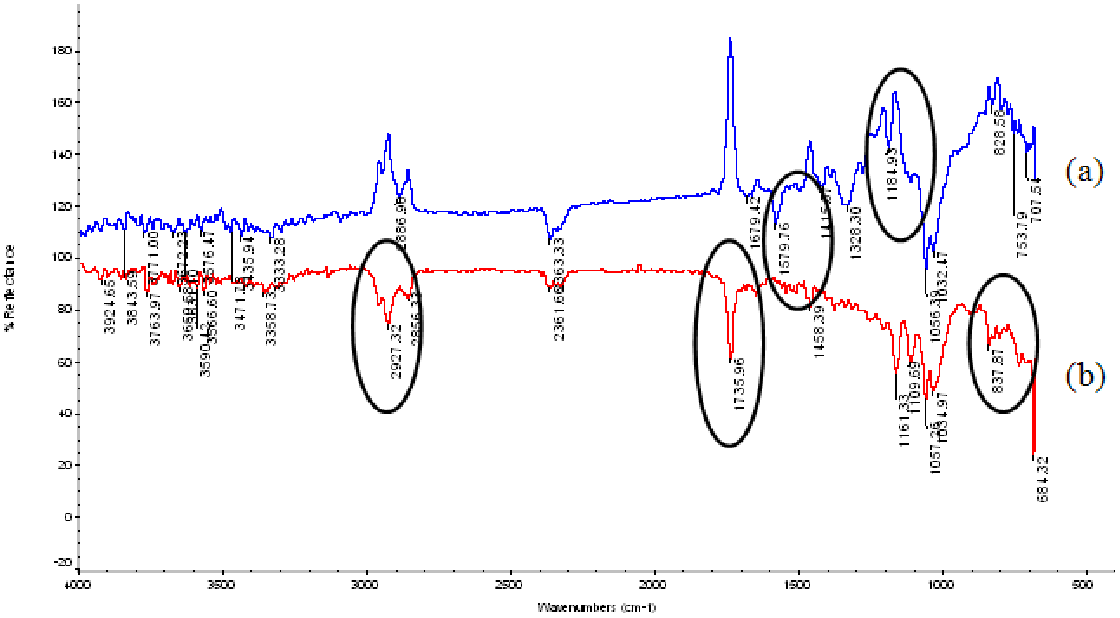

Fig. 5: Comparison of spectra for (a) permanent and (b) non-permanent Faster blue ink samples

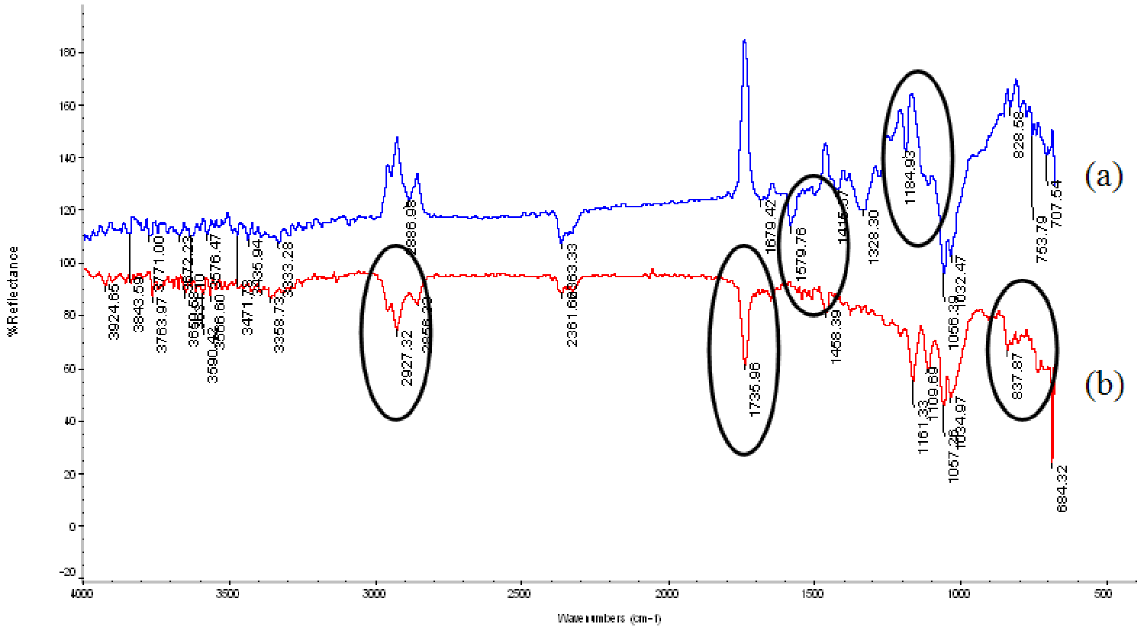

Fig. 6: Reflectance FTIR spectra of bulk permanent black ink samples from different brand (a) Artline and (b) Faber Castell

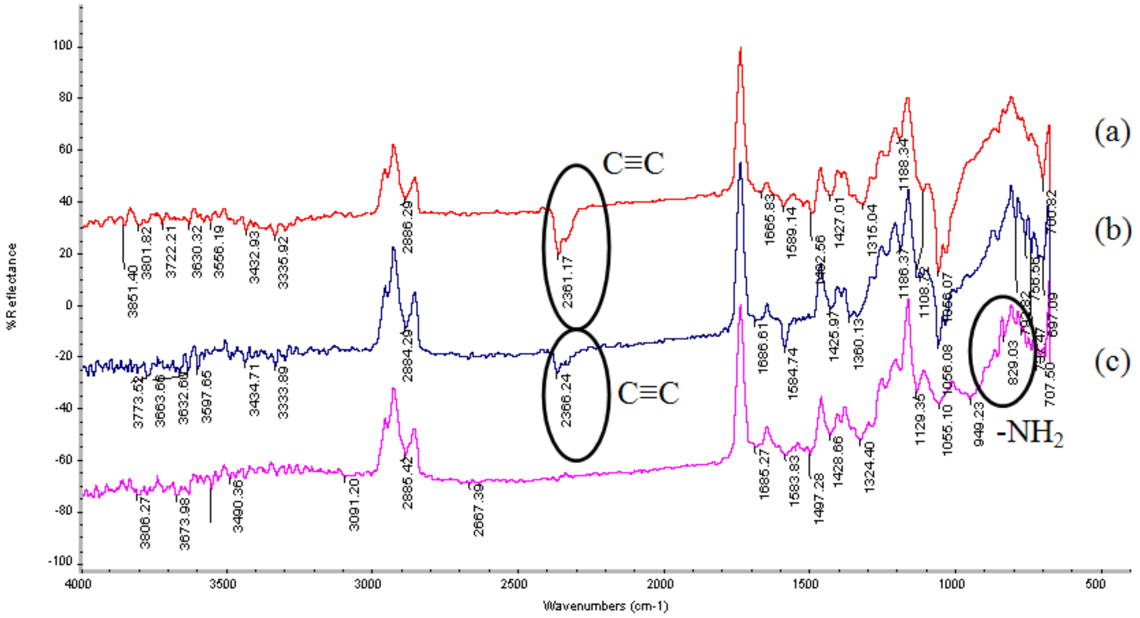

Fig. 7: FTIR spectra of non-permanent black ink samples from different brand (a) Artline (b) Faber Castell and (c) Faster

Conclusion

The present study demonstrated that commercial permanent and non-permanent blue, red, green and black marker ink pens can be swabbed off a whiteboard using cotton wool and analyzed in the laboratory. The inks showed some selective distinguishable properties in IR spectral patterns.

Comparison of IR spectrum peaks (bands) showed that non-permanent inks have weak amines bands at 823-850 cm^{-1}. Other bands that emphasized the dissimilarity between permanent and non permanent ink samples were 2345 and 2361 cm^{-1} which were attributed to the C≡C vibrations, 1736 and 1737 cm^{-1} which corresponding to the C=O stretching and bands at 1204 cm^{-1} vibration which attributed to the C-O bending. The present of the diagnostic peaks in the IR spectra can be used to discriminate between inks analyzed in this study.

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