International Journal for Pharmaceutical Research Scholars (IJPRS)

V-3, I-2, 2014 ISSN No: 2277 - 7873

RESEARCH ARTICLE

Analysis of Black Ballpoint Pen Inks

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Manuscript No: IJPRS/V3/I2/00247, Received On: 30/04/2014, Accepted On: 10/05/2014

ABSTRACT

The present study was designed to perform the analysis of black ballpoint pen inks. The ballpoint pen inks components were separated by TLC and then separated components were analyzed by means of Ultraviolet visible (UV-Vis), infrared (IR) and NMR spectroscopy. UV-Vis analysis was successful in characterizing black ballpoint pen inks of different brands. IR analysis revealed that each brands could be characterized and then differentiated by looking the pattern of each spectra. NMR spectroscopy has been useful for the comparison of ink brands. The present findings indicate that by the above used analytical techniques the forgery of documents can be caught.

KEYWORDS

Black Ballpoint Pen, TLC, UV-VIS, IR, NMR Spectroscopy

INTRODUCTION

Ink analysis does focus on a new chemical and analytical methods or techniques. It is a step to increase the discriminating power of ink analysis.[1] Ink analysis involved the examination of documents using the naked eye, oblique lighting conditions and using special optical filters. It can be performed using optical, spectroscopic and chromatographic methods.[2] This study is necessary since the usage of ballpoints pens are extensively used in documents. Ball point pen inks contain one or more dyes. Characterization and identification of dyes of ball point pen inks is very important in forensic document examination. Some problems may arise because mixtures of dyes give complex instrumental responses especially when dyes are not pure substances.

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It is true that rhodamine 6G shows three different color bands on a thin layer chromatographic (TLC) plate after separation over the past 40 years, document examiners have strived on the scientific examination and identification of writing inks. Government agencies at all levels and lawyers in the private sector are using the examination of inks as a mean of establishing the authenticity or fraudulent nature of questioned documents. Ball point pen inks contain one or more dyes. Characterization and identification of dyes of ball point pen inks is very important in forensic document examination. Some problems may arise because mixtures of dyes give complex instrumental responses especially when dyes are not pure substances. A number of methods of ink analyses have been applied to the field of forensic documents examination.[3] With the advent of electronic communication, electronic signatures and a whole way of electronic business transactions, the paper based documents remains an over preset problem and

is still of great interest in forensic sciences. There are occasions when documents used in criminal activities or in the course of civilization either all udder created specifically for the purpose of deception. Many cases of this kind have been reported in the world of document examination. This allows the determination of whether entries have been added or altered. Different types of ink have slightly different chemical composition so can be readily distinguished by comparative microscopy or chromatographic methods. The dating of documents and writing is another issue in the evaluation of authenticity. To solve this problem it is necessary to utilize some techniques chartering the document creation and history. The challenge faced by document examiners in such cases is to search for any clues that suggest that a particular ink entry was placed on the document some time other than indicated. There are two approaches- either physically or chemically determine the date of age of inks on documents.[4] One determines and compared the static i.e. compositional characteristics of questioned inks with those of a collection of an ink, each having a known production date the other determines the dynamic (aging) characteristics of inks. The static approach deals with inks analytical profiles that do not changes with age when using this approach the examiner tries to detect and identify tags (optical brighteners or other unique components) specially added by the manufacture. If a tag has been detected in the ink analyzed, the manufactures files are consulted to determine the initial production date of the ink. This may allow one to establish that the questioned ink was not available at the time the document was allegedly prepared. This approach has limitation that only a few ink formulation usually contain the tags, unless the same tags has been detected both ion a questioned ink and an ink of similar composition in the slandered ink reference library (collection) the identification of the questioned ink formulation with hundred percent certainly is hardly possible. This is because ink formulas are not unique and no matter how comprehensive the collection of reference samples is, it will never be complete. The dynamic approach measures the characteristics of an aging ink that change with time. In the frame work of this approach several ink dating methods are currently applied to cases.[5-9] The dynamic approach measurements may be non-destructive or destructive. Ideally nondestructive, comparative techniques are used to distinguish between different inks on a document. Although inks may appear very similar to the human eye, they can be very different when viewed in the infra-red region of the spectrum or when illuminated by high energy light at specific wavelength which excite fluorescence the degree of variation relates to the chemical composition of the ink. These nondestructive techniques include infrared spectroscopy, visible and infrared luminescence, filtered light examination and micro-spectrophotometry. However, these techniques are limited and suffer from insufficient discriminating power to allow the differentiation between similar inks (e.g. from the same manufacturer). This problem is becoming more challenging as sophisticated writing and printing technologies are evolving. Hence, further destructive techniques are now frequently necessary to provide a more rigorous comparison. These techniques can be carried out on a relatively things amounts of ink, taken grow the pen line of a single character; therefore, extraction methods are used for identification of inks. Thin layer chromatography is a well-established technique for the comparison of inks. Thin layer chromatography procedures are rapid and have been optimized by document examiners and ink chemists. It is still plays a very important role in the routine examination of inks, although a great deal of research and development work is underway involving the eval. The comparison of writing inks has been made possible by the introduction of chromatographic methods which impact on the detection of fraudulent documents. Subtle alterations to documents such as insurance claims, wills and tax returns can have significant financial implications and a prime concern of document examiners and ink chemists have become to assess when the document entries were made and to detect the

alterations or additions to a document. Two inks can be compared by both chemical and physical examinations by using different techniques such paper and thin-layer chromatography[10] and other modern methods. Being rapid and relatively simple to use, thin-layer chromatography is the most successful method used for the separation and subsequent comparison of ink components.[11]

MATERIALS AND METHODS

Materials

Black ballpoint pen ink of two different Indian brands was used to analyze in this study. The sample codes for the black ballpoint pen ink used are as listed in table 1.

Table 1: Sample of black ballpoint pen inks of different brands

S. No.	Ink Brand	Code
1.	Reynold Black	X1
2.	Cello Black	X2

Methods

Thin Layer Chromatography

The separation of ink components will be carried out by TLC which includes preparation of silica gel glass plates in distilled water. All of the spots were approximately 0.5-0.8mm in diameter and the amounts of the ink applied were about 1.0-1.5µg. the origin were at1.0 cm from the bases of the plate. The developing solvents used were ethyl acetate/ethanol/water (70:35:30). Different colors of dye component will be eluted from plate and collected for further analysis. The retardation factor, R_f (the ratio of distance traveled by the compound to the distance traveled by the solvent) and color tones of the separated bands were recorded.

Spectroscopic Analysis

UV: Ink extract were used for UV–Vis analysis with ethanol used as a blank solvent. Absorbance spectrum was recorded in the wavelength range 200-800 nm. From the absorbance, the maximum absorbance from each sample was obtained. The spectra with regards to the maximum wave length and relative height of the components peak were compared for each sample.

IR: 10µL of ink sample were added to 100 mg of KBr powder. The sample extract were then grinded with KBr powder using mortar and pestle. The sample was totally dried and then pressed into KBr disc. Five tone pressures were applied to the sample to form a transparent disc. Infrared spectrum for each sample was recorded in the range of 450cm^{-1} to 4000cm^{-1}.

NMR: Ink extracts were used for NMR analysis by making NMR tubes. In NMR tubes, 4 drops of sample extract was mixed with approximately 4.0 ml solvent (chloroform) and finally closed tightly.

RESULTS AND DISCUSSION

Table 2 shows the color bands and the R_f values of black inks developed by solvent system used as such serially obtained on silica plate under normal incident daylight. From developed chromatogram ink samples of different brands X1 and X2 showed four separated bands with R_f values given in table 2. The separated bands were analyzed using UV, IR and NMR spectroscopy.

Table 2- Separate color bands of different black fountain pen inks and their R_f values

Reynold black (X1)			Cello black (X2)		
Color band	**Code**	**R_f**	**Color band**	**Code**	**R_f**
Pink	X14	0.35	Black	X34	0.47
Purple	X13	0.50	Gray	X33	0.50
Light black	X12	0.62	Purple	X32	0.67
Black	X11	0.72	Pink	X31	0.72

The inks of the two brands from ballpoint pen were examined by UV-Vis spectrophotometer in the wavelength range from 200-800 nm. Fig 1 shows the absorbance spectra from three brands of black ballpoint pen samples.

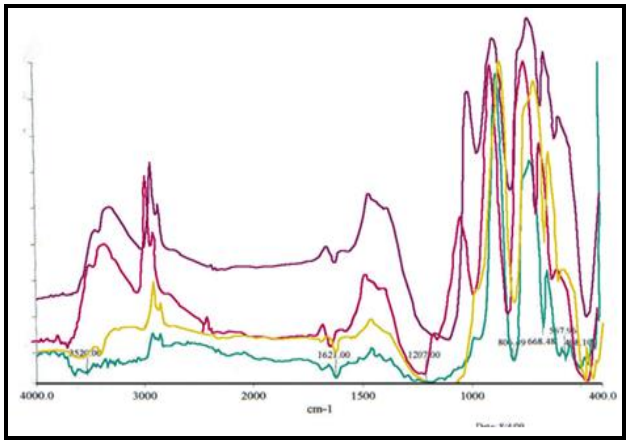

Figure 1: FTIR of dye stuff obtained from inks. X1 & X2 black ballpoint inks

All of the ink samples showed one maximum absorbance peak in the wavelength range 260-290nm. X2 ink samples showed the highest absorbance at wavelength 260 nm, X1 at 250nm as shown in fig 2.

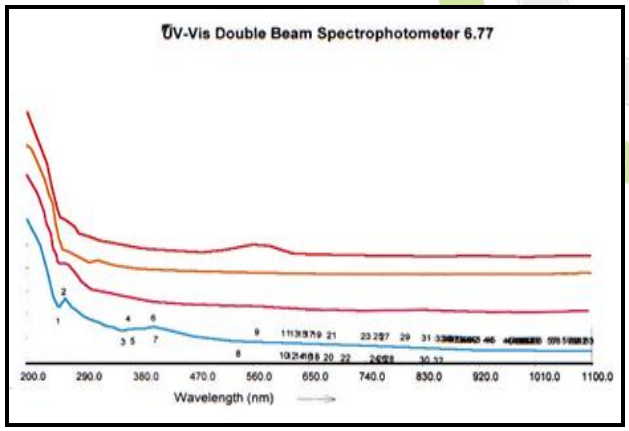

Figure 2: UV ofdye stuff obtained from X1 & X2 black ballpoint pen inks

The IR spectra for each brand generally showed a broad peak at 3000cm^{-1} to 3600cm^{-1}. This indicates the presence of the NH_2 group in the ink formulations. That was expected since ballpoint pen ink contained amine group. Three brands of the pens were analyzed in the region of 450cm^{-1} to 4000cm^{-1}. The discrimination of these inks by IR spectra is due to the presence or absence of a particular absorbance peak as well as the intensity of the peak. Based on graph the spectra of black ballpoint ink from different brand X1 and X2 were quite similar. All spectra possessed a broad peak in the range 3000cm^{-1} to 3600cm^{-1} indicating the presence of CH_2NH_2 group in these inks and the presence of peaks in the range 1600cm^{-1} indicate the presence of aromatic compound or C=C or C=N group and peak in the range of 1100cm^{-1} indicate the presence of C-O-C bond. These spectra showed a broad peak in the range 3000cm^{-1} to 3600cm^{-1} indicating the presence of CH_2NH_2 group in these inks and the presence of peaks in the range 1600cm^{-1} indicate the presence of aromatic compound or C=C or C=N group and peak in the range of 1100cm-1 indicate the presence of C-O-C bond. Ballpoint pen ink of two brands showed peak in the range from 1000cm^{-1} to700cm^{-1}. The NMR spectra presented in fig. 3 for each brand generally showed a peak at 7.0-7.5ppm. This indicates the presence of aromatic or CHX_3 and peak at 2.3-2.6ppm, it shows the presence of $(CH_3)_3N$ and 3.7ppm indicate the presence of CH_2X_2.

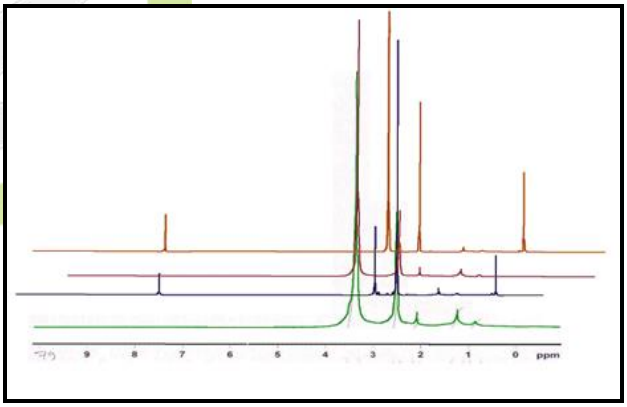

Figure 3: NMR of dye stuff obtained from X1 & X2 black ballpoint pen inks

CONCLUSION

UV-Vis analysis showed that black fountain pen ink samples that are X1 and X2 displayed only one peak at the wavelength in the range of 210 to 280nm. For IR/NMR analysis is not easy to discriminate these inks since all the samples have the same formulation. However the difference can be seen by looking at the intensity of main peak as well as the pattern of each spectrum.

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