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Characterization of ballpoint pen ink by using non-destructive methods

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Abstract

Ink examination is an important forensic task conducted by question document examiner. It is interesting to know that the composition of different brands of ink are confidential but it is possible to examine the handwriting written by different brands of ink by using destructive and non-destructive methods. This study is mainly focused on the applicability of non-destructive methods to differentiate ball point pen ink made by different manufacturer in India. We have used only non-destructive methods in this study. In experimental work, we used VSC and FTIR both are the most attractive techniques as they maintain the integrity of document. Sample ink was applied on a blank paper and observation was made at different parameters. Most of the brands can be discriminated by VSC filtered light examination. IR analysis revealed that each brand is possible to differentiate by looking their spectra. At the end of the work we are able to differentiate among most of the brands by using non-destructive methods.

Keywords: Forensic documentation, question document, video spectral comparator, non-destructive, Fourier transform infrared spectroscopy.

Introduction

In India, document forgery is very common as the literacy rate increases. Ballpoint pens are easily available as well as cheaper than any other and also provide a good writing. It is the most evident question for document examiners to compare between two brands of inks. Ink analysis involves both chemical and physical examinations. Non-destructive methods are primarily used method before any chemical analysis. VSC was used to observe the optical property of inks. Forensic science deals with the applications of all the sciences to solve the problems related to crimes[1,2]. Anyone engaged in general questioned document examination has frequent need to try to discriminate between visually similar but possibly different writing materials[3]. Two types of ink analysis are being used in laboratories mainly destructive and non-destructive methods. However, non-destructive method is preferred most of the times by forensic document examiner. Based on the different chemical composition of various brand of inks FTIR spectroscopic examination is possible to make identification and differentiation[4]. A successful examination was made by using video spectral comparator instrument selecting the spectra of infrared (IR) absorption and luminescence for black pen ink[5,6]. In IR spectroscopy different brands shows absorption at different wavelength[7]. Although non-destructive methods did not provide any content information related to any brand.

Materials and methods

Brands that are easily available in India are studied at different wavelength by using VSC-6000 and made a standard data for ballpoint pen inks. Ten samples of blue and black ballpoint pens were purchased randomly at different shops in Lucknow. Experimental work was conducted by using white (A4 75 GSM) paper. By using VSC-6000 at different wavelengths samples were analyzed. Similarly, black ball point pens were also analyzed.

FTIR instrument was used to obtain the fingerprint spectra of ink of different brands. Infrared absorption of different brands of inks was characteristic and able to differentiate different inks on the basis of peak peaking value by different functional groups in the ink composition. All spectra compared to each other with their absorption wavelength range. In FTIR a standard obtained by using same blank page on which ink application was performed. Absorbance spectra obtained for both standard and samples. Ten blue and seven black ball point pens spectra obtained by using FTIR on a blank page size 18x12 cm, about 5mm diameter spot drawn on page. Observation was made by VSC.6000 (foster + freeman) instrument by putting sample spot applied directly on a paper. All blue brands on a single page and all black brands on a next page.

First observation was made by ordinary light, then sample was observed using spot filter at 400–640nm wavelength at 60 brightness. Next observation was made at IR absorption at 783nm wavelength.

Results and discussion

VSC 6000 H/S: First observation was made by ordinary light for blue and black pen inks Figure-1 1A and 1B at

magnification 1.50, integration 45ms, iris 49%, brightness 60 and gamma off. No any characteristic observation was made. Next observation was under spot filter at 400–640nm wavelength at 60 brightness. Blue Pen number 8 and 9 became indistinguishable, while pen number 7 gave maximum brightness (Figure-1 2A). All Black pen show similar pattern of disappearance, except 7 number pen (BK 427Bolly pen) (Figure-1 2B). Next observation was made by IR absorption at 783nm wavelength. All set of blue pen was difficult to identify. No any specific clear observation was made (Figure-1 3A, 3B). All set of black pen showed similar pattern of disappearance except set number 7 (Figure-1 4A, 4B). No any characteristic observation was made under UV radiation.

Similarly, all brands of black pens were observed. Firstly, examined under ordinary light and then under spot filter 400-640nm wavelength after this under IR absorption 783nm range.

Results of FTIR technique: Infrared absorption spectra observed for each and every brand of blue and black pens in the range of 3500–1000cm^{-1} wave-number versus absorbance ranges from 0.00 to 0.05.

First spectra obtained on a blank page. That reveals two spectral peaks one at about 785.80cm^{-1}, i.e. possibly indicate the presence of alkenes (CH_2=CH_2) is – trans stretching. Next at about 1542cm^{-1}, i.e. possibly indicate the presence of (C=C) str. for aromatic hydrocarbon.

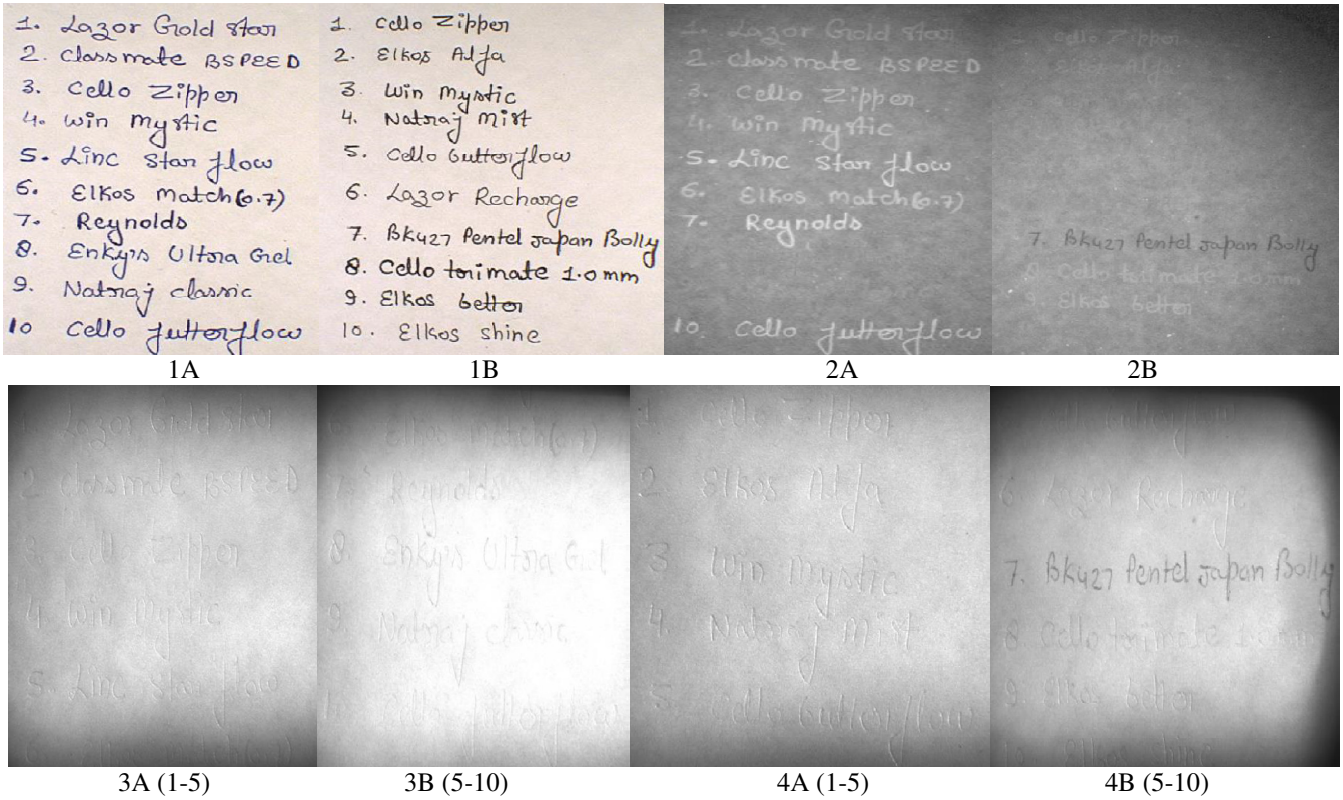
All spectra obtained from blue ball point pen showed more spectral peaks as compared to black ball point pen inks. i. Spectra of all blue ball point pen are limited most commonly from 611-3852cm^{-1}. ii. Spectra of all black ball point pen are limited commonly from 619-1543cm^{-1}. iii. Only Elko's Alfa and Nat raj black showed absorption at 3736-3828cm^{-1}.

At the end of the work we find out that it is difficult to make a clear differentiation among all set of blue and black ball point pen ink. But most of blue pen inks are easy to analyze as compared to black ball point pen ink. Only black BK 427 i.e. a Japanese product shows different features about all the parameters.

Results shows that optical examination of documents by V.S.C is the best tool and cannot replace by any other tool[7]. IR spectra interpretation revealed that each brand have different peak absorption that may help in two brand differentiation during the examination[8]. While in short FTIR gives a fingerprint spectra for each brand of blue and black pen. It is a better way to make identification of pen inks.

Less error chances, it is easy, convenient and eco-friendly in operation. The way to possibly differentiate these samples is to make a database for ink samples in FTIR.

After careful examination of all spectra revealed that the most informative region is from 2000-675cm^{-1}. A common characteristic peak with different absorbance is observed in all spectra approximately at 1584 and 1360cm^{-19}.



1A 1B 2A 2B

3A (1-5) 3B (5-10) 4A (1-5) 4B (5-10)

Figure-1: Results of video spectral comparator.

Table-1: Classification of samples for study.

Type of pen	Type of light	Name	Parameter	Value
Blue	Ordinary light	1(A)	Light	Flood
			Magnification	1.50
			Integration	45ms
			Iris	49%
			Brightness	60
			Gamma	Off
Black	Ordinary light	1(B)	Light	Flood
			Magnification	1.50
			Brightness	60
			Integration	43ms
			Gamma	Off
Blue	Spot filter	2(A)	Light	Spot 400-640
			Magnification	1.50
			Integration	125ms
			Brightness	60
			Gamma	On
Black	Spot filter	2(B)	Light	Spot 400-600
			Magnification	1.50
			Iris	69%
			Brightness	60
			Gamma	On
Blue (1-5)	Infrared	3A (1-5)	Light	Absorption 783nm
			Magnification	3.82
			Integration	22ms
			Iris	71%
			Brightness	60
			Gamma	Off
Blue (5-10)	Infrared	3B (5-10)	Light	Absorption 782nm
			Magnification	3.20
			Integration	17ms
			Iris	79 %
			Brightness	60
			Gamma	Off
Black (1-5)	Infrared	4A (1-5)	Light	Absorption 783nm
			Magnification	3.82
			Integration	22ms
			Iris	70%
			Brightness	60
			Gamma	Off
Black (5-10)	Infrared	4B (5-10)	Light	Absorption 782nm
			Magnification	3.82
			Integration	22
			Iris	71%
			Brightness	60
			Gamma	Off

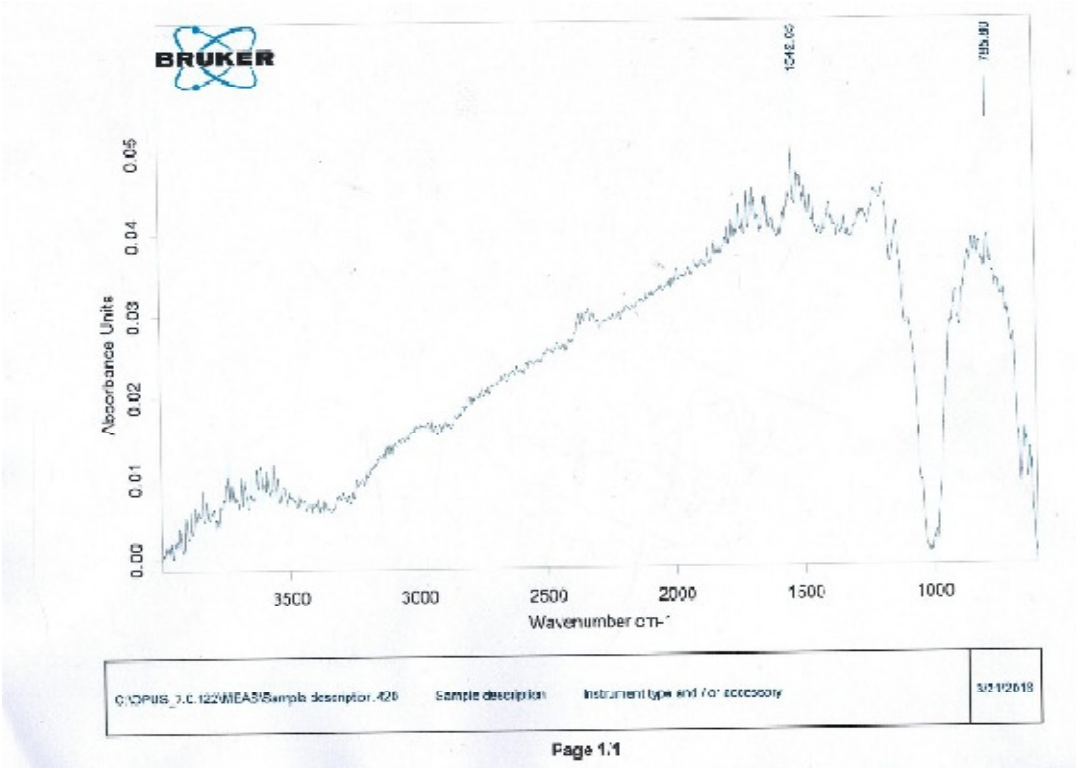


Figure-2: FTIR spectra of blank page.

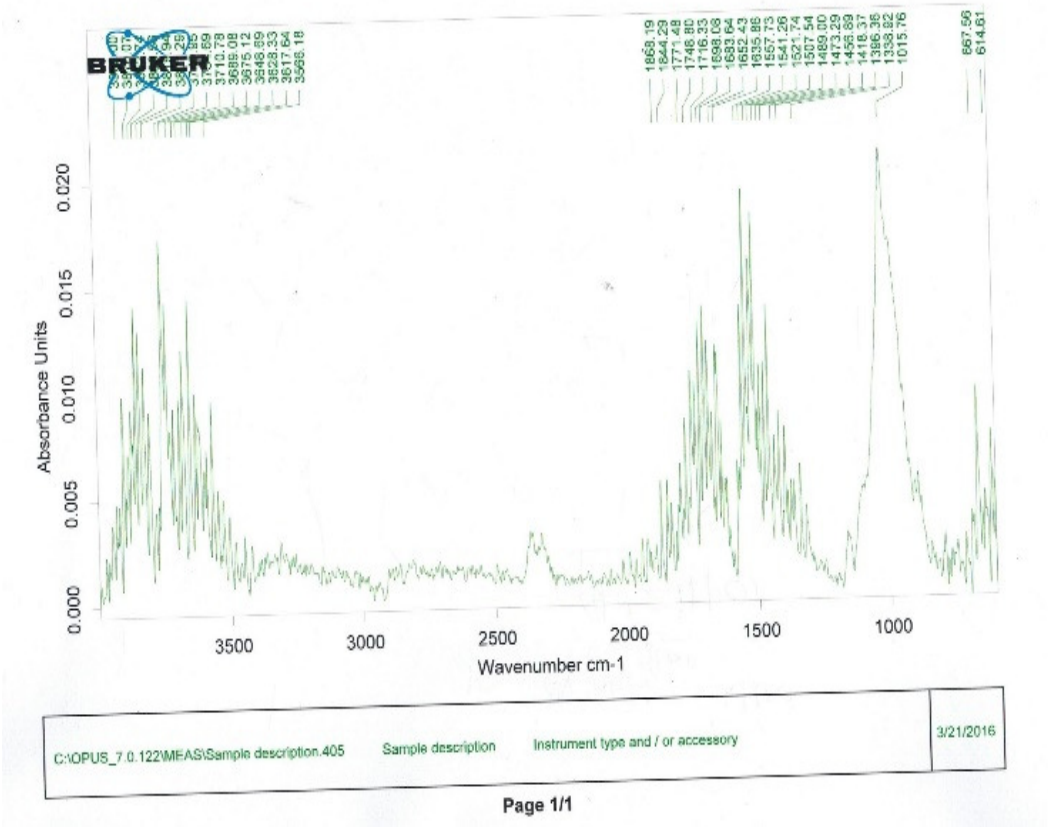


Figure-3: FTIR spectra of blue pen.

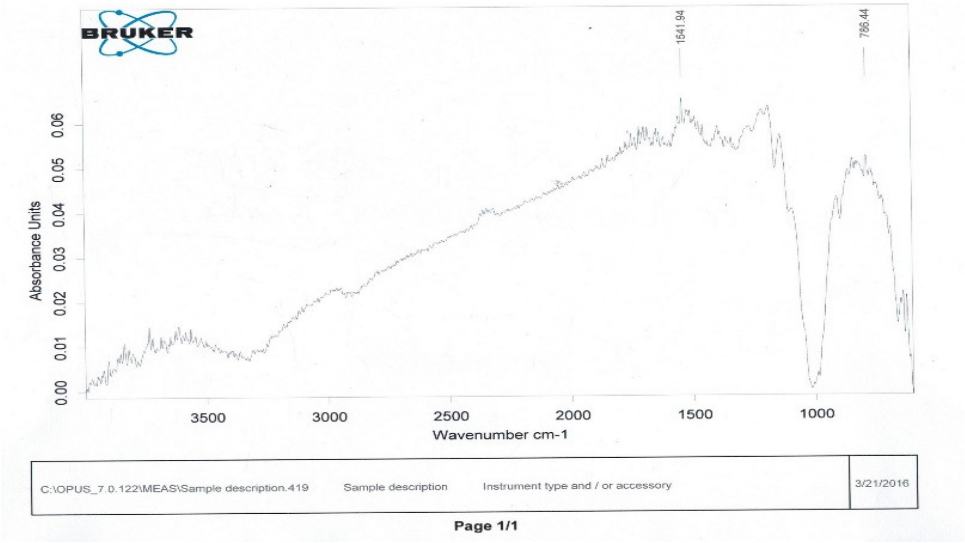


Figure-4: FTIR spectra of black pen.

Conclusion

It is not possible to make a clear distinguish between all brands of pen inks. Out of ten two blue set of pen are clearly differentiated by spot filter. One set of black pen become visual at the given parameter. With respect to differences between the inks under IR Absorption conditions, the greatest variations within the blue pen group was observed between 400-500nm and 700-900nm. All Inks absorbed strongly between 500-700nm and fully reflected above 900nm[10]. The maximum light absorption is found in the region 550-600nm and complete light transmission at 780nm[11].

In IR spectra peak absorption at 3200-3600cm^{-1} region is specific for the associated OH group in the spectra[12]. Another peak at the region 1380cm^{-1} shows the evidence of N-O group in the chemical composition. The CH_3 and CH_2 stretching bond vibrations are observed at the region of 2857-2900cm^{-1} [10].

The presence of the NH_2 group in the ink shows absorption at 3000-3600cm^{-1} region[8]. Most of the spectra shows an intense peak of carbonyl (C=O) from 1720-1725cm^{-1}, A characteristic ban for symmetrical and asymmetrical C-O-C vibrations at 940cm^{-1} and 1170cm^{-1} respectively[10].

Black pen ink comprises lesser number of absorption peaks as compared to blue pen inks. Spectra of all blue ball point pen are limited most commonly from 611-3852cm^{-1} Spectra of all black ball point pen are limited commonly from 619-1543cm^{-1}. Only Elko's Alfa and Nat raj black shows absorption at 3736-3828cm^{-1}.

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