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Fourier transform infrared spectroscopy and chemometrics for the characterization and discrimination of writing/photocopier paper types: Application in forensic document examinations

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ABSTRACT

The aim of the present work is to explore the non-destructive application of ATR-FTIR technique for characterization and discrimination of paper samples which could be helpful to give forensic aid in resolving legal cases. Twenty-four types of paper brands were purchased from local market in and around Chandigarh, India. All the paper samples were subjected to ATR-FTIR analysis from 400 to 4000 cm^{-1} wavenumber range. The qualitative feature and Chemometrics of the obtained spectral data are used for characterization and discrimination. Characterization is achieved by matching the peaks with standards of cellulose and inorganic fillers, a usual constituents of paper. Three different regions of IR, i.e. 400–2000 cm^{-1}, 2000–4000 cm^{-1} and 400–4000 cm^{-1} were selected for differentiation by Chemometrics analysis. The discrimination is achieved on the basis of three principal components, i.e. PC 1, PC 2 and PC 3. It is observed that maximum discrimination was procured in the wave number range of i.e. 2000–4000 cm^{-1}. Discriminating power was calculated on the basis of qualitative features as well, and it is found that the discrimination of paper samples was better achieved by Chemometrics analysis rather than qualitative features. The discriminating power by Chemometrics is 99.64% and which is larger as ever achieved by any group for present number of samples. The present result confirms that this study will be highly useful in forensic document examination work in the legal cases, where the authenticity of the document is challenged. The results are completely analytical and, therefore, overcome the problem encounter in traditional routine light/radiation scanning methods which are still in practice by various questioned document laboratories.

1. Introduction

Forensic science is closely associated with the judicial system and hence to the legal cases. Forensic science is continually evolving with new techniques/methods and hence helping the judicial system in legal cases where forensic examination is necessary. Therefore, the techniques being used in forensic casework must be reliable, objective, and analytical and must show repetitiveness. The National Academy of Sciences (USA) in their recent report on the current status of forensic science stressed upon the problems being faced by the experts and also the necessary remedies to overcome those problems [1]. To get better results from the analysis, the analytical techniques should be computable and correlated with statistical confidence, so that possibility of errors is minimized. Also, the automated and economic analysis would make it ideal to maximize its specificity and efficiency.

The field of questioned documents involves the analysis of paper documents (handwritten or typed/printed). The paper being produced from the fibers which are in water suspension, squeezed through the screen, hard-pressed and dehydrated, to obtain a mat that is built with linkage of randomly intermixed fibers.

The final sheet is chemically treated with different coatings like poly vinyl acetate (PVA) or starch for manufacturing various kinds of papers. The smoothening treatment of the paper surface is usually done with kaolin, $CaCO_3$, $CaSO_4$ and TiO_2. Due to these manufacturing processes/treatments, the paper composition varies depending on the manufacturer and its use as well.

Today, the production of most of the paper is meant only for short term uses. However, it has been more than two hundred decades since the discovery of paper; still it is the one which is used as a medium for data storage or information carriers. In spite of electronic period, the past decade has witnessed 35% increase in paper consumption for recording of data [2].

For examination of the paper and its related products, some government organizations like ASTM, TAPPI, and Bureau of Indian Standards (BIS), provide standard methods [3] but all these methods are

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Table 1
The minutiae of the paper sample used in the present study; the tick mark symbol (✓) represents the appearance of a peak at a particular wave number (cm^{-1}). Extra peaks are marked in the column under extra characteristic peaks.

Serial no.	Sample ID	664 ± 5	710 ± 5	869 ± 5	896 ± 5	1050 ± 5	1240 ± 5	2892 ± 5	3330 ± 5	3662 ± 5	Extra characteristic peaks
1	A				✓			✓			**612, 519, 428**
2	B	✓	✓	✓	✓		✓	✓	✓		
3	C	✓	✓	✓	✓		✓	✓	✓	✓	
4	D	✓	✓		✓		✓	✓	✓		
5	E	✓	✓	✓	✓	✓	✓				**440**
6	F	✓	✓		✓		✓		✓		**1652, 1455**
7	G	✓	✓		✓		✓	✓	✓		**1651, 440**
8	H	✓	✓		✓	✓	✓	✓			
9	I	✓	✓	✓		✓	✓				
10	J	✓	✓		✓	✓	✓	✓	✓	✓	**432**
11	K	✓	✓		✓	✓	✓				
12	L	✓	✓		✓	✓	✓	✓	✓	✓	
13	M	✓	✓		✓		✓	✓	✓		**1652, 1455**
14	N	✓	✓		✓	✓	✓	✓	✓	✓	**1652, 1560**
15	O	✓	✓		✓	✓	✓	✓	✓		
16	P	✓	✓	✓	✓	✓	✓	✓	✓		
17	Q	✓	✓		✓		✓	✓	✓		**438**
18	R	✓	✓		✓		✓	✓	✓		
19	S	✓	✓	✓	✓	✓	✓	✓	✓		**1652, 1455**
20	T	✓	✓	✓	✓	✓	✓	✓	✓		**1652, 1454**
21	U	✓	✓	✓	✓	✓	✓	✓	✓		**438**
22	V	✓	✓		✓	✓	✓	✓	✓		
23	W	✓	✓		✓	✓	✓	✓	✓		
24	X	✓	✓		✓	✓	✓	✓	✓	✓	

not practically possible in the forensic cases because most of them require standard environmental conditions and moreover most of them are destructive in nature. Therefore, the document experts require only such techniques which could be performed in normal laboratory conditions, less expensive, fast, and non-destructive in nature.

The physical properties, i.e. color, tearing strength, fiber content, thickness, fluorescence can be used to discriminate various types of paper, but the process of paper manufacturing is so much complex and also it makes the papers indistinguishable physically from their appearance. Moreover, these methods are destructive sometimes.

Analytical techniques such as mass spectrometry [4–9], X-rays coupled with different detectors [10–12], XRD [13] were used by the various groups to discriminate and characterize the paper samples. In these techniques most of them are destructive and others are having their own limitations in characterization as well as their low discrimination power.

In one of our previous work [14], we differentiated the 19 paper samples using diffuse reflectance UV–Vis spectroscopy (DP = 99.70%) but the same analytical method couldn't be used for characterization of paper.

Kher et al. [15] studied paper samples using ATR IR spectroscopy and DRIFT spectroscopy, however, they could discriminate these samples up to 67.86% discrimination, which is very, low as far as the forensic examination is concerned. Because in forensic cases the discrimination should be as high as near to 100%. Moreover, in their work, they didn't characterize the paper samples and the sample size was very limited (08 samples).

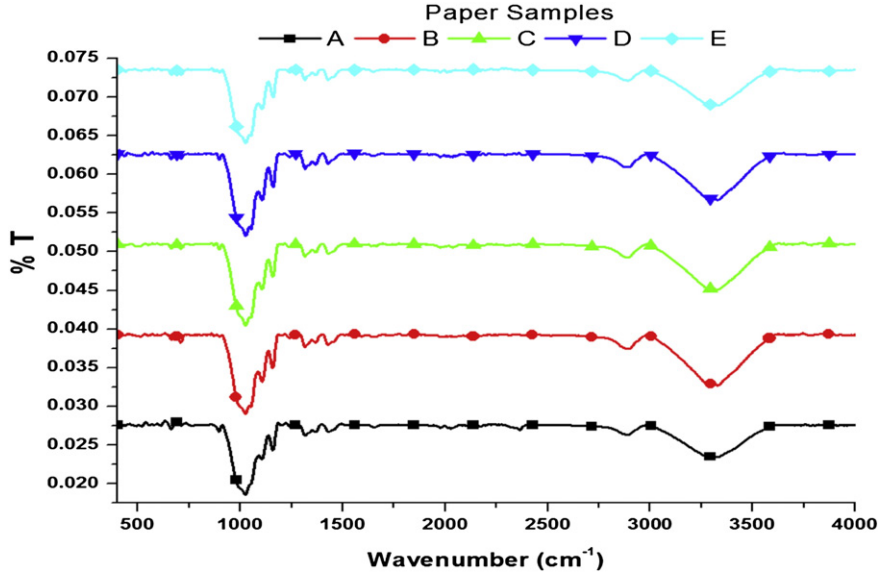

Fig. 1. FTIR spectra of paper samples A to E with wave number range 400–4000 cm^{-1}.