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Analysis of laser printer and photocopier toners by spectral properties and chemometrics

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ABSTRACT

The use of printers to generate falsified documents has become a common practice in today's world. The examination and identification of the printed matter in the suspected documents (civil or criminal cases) may provide important information about the authenticity of the document. In the present study, a total number of 100 black toner samples both from laser printers and photocopiers were examined using diffuse reflectance UV–Vis Spectroscopy. The present research is divided into two parts; visual discrimination and discrimination by using multivariate analysis. A comparison between qualitative and quantitative analysis showed that multivariate analysis (Principal component analysis) provides 99.59%pair-wise discriminating power for laser printer toners while 99.84% pair-wise discriminating power for photocopier toners. The overall results obtained confirm the applicability of UV–Vis spectroscopy and chemometrics, in the nondestructive analysis of toner printed documents while enhancing their evidential value for forensic applications.

1. Introduction

Ink analysis has always been a crucial part of forensic questioned document examination, with the aim of determining the authenticity of the document. In the present era of technology, the increased use of computers, printers, photocopiers, scanners, and multifunction systems have reduced the number of the handwritten document to a large extent [1]. In recent past, toner-based digital printing has become one of the most common ways to not only generate office or personal documents, but also the fraudulent documents. For instance, numerous cases involving false medical records, clone cheques, illegitimate property documents, false contracts, and counterfeit currency, travel and identity documents are frequently received in forensic laboratories for comparison and identification [2].

Forensic document examiners (FDE) are generally asked to ascertain i) if the document is original or build up, ii) find the mode of preparation of the document, iii) look for alterations, deletions, obliterations, if any and iv) link the suspected document to its source. However, with the availability of wide variety of pen inks, printer inks, and toners, having only minute differences in their chemical composition, the identification of fraudulent documents was never an easy task for FDEs [3]. In addition to the similar constituents of inks and toners, the technological advances in the mode of preparation of documents (printers, photocopier, and multifunction devices) have furthermore complicated the investigation processes [4].

1.1. Printing Process and Chemical Composition of Toners

Toners are complex mixtures with a particle size of approximately 8–12 μm. The basic components of toners are polymers, resins, pigments or dyes, iron oxide, amorphous silica, charge control agents, paraffin wax, surfactants and other inorganic/organic additives. The actual makeup of these toners differs from manufacturer to manufacturer and is kept a secret with the purpose of bringing uniqueness to its properties.

However, certain polymers like polyester, polystyrene or polyacrylate are commonly found in most of the toners. These polymers allow efficient particle manufacturing and lower melting point to enable rapid thermal fusing [5]. Dyes and pigments are added to impart a specific color to the toners. Some of the pigments which are likely to be present are azopigments, acetamides, methyl violet, nigrosine, victoria blue, phthalocyanines, carbon black, and quinacridones. Charge control agents such as iron oxide enable the charge characteristics of the toner. The tribo-charging characteristics, transparency and flow characteristics of each toner particle are maintained with the help of surface additives like silica, titanium oxides, organo-metallic salts. Certain other components, for instance; surfactants, paraffin wax, enhance the adherence of toner particles to the surface of the paper while preventing them from sticking to the heated fuser rollers [5–7].

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Although the composition of toner and the design of printing devices vary among most of the manufacturers, the process of electrophotography remains the same [8].

1.2. Literature and the Aim of Current Research

A variety of analytical techniques have been utilized to study different features of powder toners necessary for their discrimination. For decades, chromatographic and spectroscopic methods were used in the discrimination of toner samples. Methods like thin layer chromatography [9–11], Pyrolysis gas chromatography and/or mass spectrometry [12,13] and Fourier transform infrared spectroscopy [14,15] have proved their utility in the destructive analysis of toners. Infrared spectroscopy with microscopic reflection–absorption [16,17] and elemental analysis of toners with scanning electron microscopy (SEM EDX) [18,19] were also studied for their potential to ascertain various constituents in the powder toners.

Alternative methods like Raman spectrophotometry [20,21], X-ray fluorescence spectrophotometry [20], DART–MS [22], and desorption/ionization mass spectrometry (LDI–MS, MALDI–MS, DESI–MS) [21,23–25] have also gained interests in the fields of forensic discrimination of printed inks. More recently, studies utilizing laser-induced breakdown spectroscopy (LIBS) [26–35] and laser ablation inductively coupled plasma time of flight mass spectrometry (LA–ICP–TOF–MS) [36–42] have been used for the examination of exhibits for forensic significance. Even after a considerable research in this field, none of the aforementioned technique has reached the forensic science laboratories as a routine method of analysis for suspected documents.

It has been shown by many researchers that the composition of the toners depends on manufacturer's practices and in such cases, even the slight variations in composition can bring about vast differences in the instrumental response. Therefore, the resulting data obtained is supposed to be dependent on multiple variables. In such scenarios, multivariate analysis helps in extracting structural information from the spectral data [43,44] without losing the relevant information. Therefore, multivariate analysis has been proven to be useful in fields of experimental chemistry [45,46] environmental studies [47,48] agricultural food products [49–51], along with forensic discrimination of paint analysis [52], fire debris [53], medicine counterfeits [54], psychoactive substances [55,56] soil characterization [57], and questioned documents [58–62], and were established to be adequate, prompt and more powerful aid [52]. However, there are limited studies dealing with the use of multivariate analysis for discrimination of toner samples. These studies showed discrimination and characterization of printer toners using LA-ICP-MS [5], SEM-EDX [19], and LIBS [7,29].

The results obtained were handled according to the PCA and other multivariate analysis, but these techniques come up with their own disadvantages. For example, laser ablation methods use lasers to remover certain amount of toner from the surface of the paper, causing damage to the sample [5,19,29]. Such practices are not favored in forensic science laboratories as the forensic examiner has to return the original documents to the court, without causing any damage to either the printed/written text or to the document as a whole. Examiners are even not allowed to staple or fold the documents (exhibits). Moreover, not all forensic laboratories are equipped with such sophisticated instruments. The author's in one of the studies [5] have also compared the analysis of printed toner samples with that of powder samples obtained from the storage bins of the same printer's which is otherwise not possible in real forensic cases. In the present research, the authors have conducted the analysis in completely nondestructive manner while the methodology provides the best discrimination in less time with high sample throughput.

Therefore, the present work aims at establishing the methodology, by combining diffuse reflectance UV–Vis spectrophotometry with multivariate analysis, to gain insight into characteristics of black toner samples, obtained from various manufacturers. The first approach focuses on examination, analysis and visual comparison of the samples. The second approach utilizes the applicability of principal component analysis on the same set of samples in order to achieve effective discrimination based on their optical properties. Hence, this research proposes a fast, efficient and reliable method of discrimination of printed toner samples, to be put into the routine analysis of suspected documents in forensic science laboratories. It shall be noted that this is the first information on nondestructive analysis of toners to the best of the author's knowledge and this methodology may be extended to other forensic disciplines as well. Moreover, the analysis of toners obtained using this methodology may further help the forensic document examiner to answer the main query about suspected printed documents that whether the whole of the document is prepared from the same source at the same time, depicting if it is original or forged.

Table 1
The different laser printers and photocopier machines with model number included in the study.

Sample no.	Sample type Laser printer model no.	Sample no.	Sample type Photocopier model no.
LI	HP 100MFPM 126nw	P1	Ricoh Aficio MP 2000 L
L2	HPPro MFP M 128 Fn	P2	Sharp AR 5620 N
L3	HP 1022 w	P3	Canon 7105
L4	HP M 1005 MFP	P4	Xerox 7228 PSCL
L5	HPPro M1136 MFP	P5	Canon 5020
L6	HPPro MFP M128 FW	P6	Canon IR 5055 N
L7	HPPro MFP M 435nw	P7	Canon IR 6000
L8	HPP 2035	P8	Canon 5050
L9	HP1320n	P9	Konica Minolta Bizhub 36
L10	HPM1319f MFP	P10	Konica Minolta B C224e
L11	HP 1020	P11	Work Centre Xerox 5755
L12	HP1015	P12	Xerox 440DC
L13	HPPro P 1108	P13	Canon IR 2525
L14	HPM 1213 nf MFP	P14	Canon7500
L15	HPP 1007	P15	Toshiba 2320
L16	HPP 1566	P16	Canon 6055
L17	HP 1505	P17	Canon 3010
L18	HP 1008	P18	Xerox 7328
L19	HP 1020 PLUS	P19	Xerox 3117
L20	HP 132 a	P20	Canon 3245
L21	Samsung 267*287 series	P21	Xerox Work Centre 5700
L22	HP 2251	P22	Canon 3570
L23	HP 202N5	P23	Konica Minolta 164
L24	Brother 1574	P24	Ricoh PCL 6
L25	Canon 2900 LBP	P25	Ricoh CS 200
L26	Brother 2321	P26	Xerox Copy Centre 128
L27	Samsung 4021	P27	Xerox 7335
L28	HP MFP 427	P28	Ricoh SP-1
L29	Samsung 2071	P29	Canon Image Runner 2870
L30	Canon MF 4750	P30	Kyocera 180
L31	HP 551 M	P31	Canon 2300
L32	HP P 1006	P32	Sharp 5618
L33	Brother 1211	P33	Sharp 5020
L34	HP 1525 N	P34	Konica Minolta 215
L35	HP 1606 dn	P35	Xerox 5790
L36	Canon 2420	P36	Canon 3300
L37	Samsung Express 2876	P37	Konica Minolta 165e
L38	Canon 3108 B	P38	Canon 3225
L39	Samsung 2161	P39	Canon 5075
L40	Canon 3700	P40	Kyocera 1035
L41	Canon LBP 2900	P41	Kyocera 2035
L42	Brother 1601 DCP	P42	Konica Minolta 1100
L43	HP 1522 nF	P43	Canon 7000
L44	Samsung SCX 3401	P44	Konica Bizhub C-454
L45	HP 226 dn	P45	Canon Image Runner 2270
L46	HP 450 M	P46	Canon 3235
L47	Panasonic KX	P47	Canon 4150
L48	Samsung SC 4300	P48	Canon 2200
L49	Brother 2701 D	P49	Canon 2800
L50	Lexmark CS 720 de	P50	Canon 2318 L