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Effectiveness and potential of SEM-EDX for analysis & differentiation of overlapped black pen inks

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Abstract
Digitalization and advancement in technology has made documents acquire new values and serve new purposes, it is plausible that they are turning into the medium of fraudulent manipulation or mere instruments of camouflaging the truth. This advancement has made ink analysis extremely challenging. Determination and utilization of best possible non-destructive technique for analysis of ink has become the need of the hour. In the past, Scanning Electron Microscope with Energy Dispersive X-ray (SEM-EDX) have been used successfully for analysis of various types of evidence in the field of forensic science but its use for pen ink examination is very limited. The present study demonstrates the effectiveness and potential of SEM-EDX for analysis and differentiation of black ball point, gel and fountain pen inks in handwritten documents. It proved to be highly effective and comprehensive partially destructive technique for analysis of handwritten documents having overlapping with two or more black inks. However, it did not prove its efficacy in deciphering obliteration. Nevertheless, it can efficaciously complement with the present workflow of questioned document examination to provide qualitative as well as quantitative data toforensic document examiners.
Keywords: Forensic documents examination; pen inks; alterations, overlapping of inks, SEM-EDX

Introduction

In modern-day situation the sphere of forensic document examination not only deals with examination of handwriting but also with the examination and evaluation of writing ink. In earlier times, forensic document examiners labored with the examination and identification of ink in documents. Ink analysis serves as a critical key in determining the authenticity of document under question. Examination of ink not only helps in determination of forgery but it also aids in determing the age of document[1]. The composition of ink serves to be an important criteria to determine the age of ink. In ancient times, people used oral language for communication but later the dire need to evolve and communicate effectively led to development of visible signs. The inclination towards communication among other humans led to development of different writing instruments[2].

In spite of digitalization, writing instruments are still used to write or sign any document. The type of writing instrument used, its model, composition of ink etc. all play important role in determining the authenticity of a document. The choice of writing instruments has also evolved with time. Modern writing instruments include chalk, graphite, pencils, crayons, different types of pens etc[3].The commonly used writing instrument consists of pens either with ball point, gel or fountain pen ink. Each type of ink is comprised of a colorant and a vehicle. The factors or dyes which impart color to the ink are known as colorants whereas the liquid or oil based medium used to dissolve the colorants is termed as vehicle. Along with these, certain other components are also added to the ink for enhance user experience. Lubricants, flow control agents, polymers, stablizersetc are frequently added to impart characteristic properties to the ink. The consistency, surface phenomenon and pressure required for writing varies with different type of inks. Ball point pen inks are oil based thereby they have thick consistency and required high pressure for writing. In contrast to this, gel pen and fountain pen inks are water based, thus are less thick and require less writing pressure[2,3,4].

In document examination, it sometimes become crucial to determine whether a particular pen was used to write certain material. In case of alterations in documents such as additions, obliteration or overwriting, it is important to establish whether the two inks are from the same source. Several

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techniques have been used for examination of ink on document. Writing can be seen on a paper or any other surface due to the phenomenon of adhesion or absorption. The penetration of liquid writing ink used is mainly due to absorption[4,5]. In order to extract absorbed ink from the document and analyse it, researchers have been using techniques like chromatography. Though, it is a one of the most successful technique used for examination of ink, it is the most destructive technique as well[6-11].Recent studies show increase in use of spectroscopic technique over chromatographic techniques as they are less or non destructive in nature[12,13,14]. Sharif et.al (2019) distinguished between blue, black, green and red fountain pen inks using UV-Vis spectroscopy, TLC, and FTIR spectroscopy[15]. Similarly, Kumar & Sharma (2017) analysed writing inks using destructive UV-Vis spectroscopy and non-destructive diffuse reflectance UV-Vis-NIR spectroscopy for analysis of ink but before analysis, the ink was dissolved in a solvent making it a destructive method of examination[16]. Since, majority of techniques used for analysis have been destructive in nature thereby it is important for a forensic document examiner to analyse the documents as well as ink using non-destructive techniques.

Scanning Electron microscope (SEM) or scanning electron microscope-energy dispersive X-ray (SEM-EDX) have majorly been used in studying the sequence of strokes. It has a high success rate for determining the sequence of red sealing ink and gel pens[17]. Previous researchers have established the efficacy of SEM in characterization of fraudulent documents including analysis of paper and ink, and demonstrates how their morphological and chemical profiles can be compared for authentication and establishment of source of the document[18]. The use of SEM-EDX for determination of manipulations in the document as well as composition of ink is very limited. Very less studies have been reported in which SEM-EDX has been used for analysis of pen ink. Therefore, the present study focuses on determination of efficacy and potential of SEM-EDX for differentiating between ball point, gel and fountain pen inks in case of alterations including additions, obliterations and overlapping of inks.

Materials and Methods

Preparation of Samples

180 samples were prepared for analysis with black ball point, gel and fountain pen ink. Two different brands of pen were used for each of the pen type. The brands chosen were flair and Reynolds for ball point pen, Rorito and Natraj for gel pen and cello and chelpak for fountain pen. All the pens were purchased in West Delhi area and were chosen on the basis of their popularity and public demand. The sample for analysis were prepared on Century Star White A4 sheets cut into strips of 75 mm by 25 mm. The samples having alterations such as additions, obliterations and overlapping of ink were prepared using different combination of inks as shown in table 1. After a 12-hour drying period, all the prepared samples were kept in plastic bags and stored in a closed container to protect them from light and prevent degradation of ink.

Table 1: Combination ofblack pen inks

S.No.	Combination of black inks	Ball point pen ink (Flair) (BB1)	Gel ink (Rorito) (BG1)	Fountain pen ink (Cello) (BF1)
1.	**Ball point ink (Reynolds)(BB2)**	BB1,BB2	BG1,BB2	BF1,BB2
2.	**Gel ink (Natraj) (BG2)**	BB1,BG2	BG1,BG2	BF1,BG2
3.	**Fountain pen ink (Chelpak) (BF2)**	BB1,BF2	BG1,BF2	BF1,BF2

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Instrument Used

The scanning electron microscope (SEM) is a microscope that utilizes electrons rather than light to obtain a magnified picture. These electron discharges are viewed on a monitor. The effectiveness of this instrument increases on being used with other instrumental detectors. SEM is made out of a few essential frameworks, all of which collaborate to magnify the image. Fundamentally, the electron segment can be thought of as an enormous vacuum tube with the cathode (electron gun) at the top providing electrons and the sample at the base going about as an anode or focus for the electrons. The path of the electron gun is constrained by a sequence of electromagnetic lens inside the body of the column. These lenses are responsible for shaping and positioning the electron beam. The intensity of the electron beam is constrained by the voltage and diameter of the beam which are regulated by the analyst. The electron beam causes various connections close to the surface of the sample. These interactions are detected by the detector present in the sample chamber. One of the detector used is electron dispersive X-ray (EDX) detector. It is a semi-conductor. Since light is made up of photons and separate energy level, X-rays are emitted when electron beam strikes any element. These X-rays are emitted at a particular energy level for every single element. These characteristic energy levels are studied and helps in identification of a particular element. Attaining data on SEM-EDX is quite straightforward. The alignment of the sample is important to start the imaging automatically. It is advised to set the electron gun as low as possible to attain the highest quality image[19,20].

The spot should also be placed as low as possible in order to prevent charging i.e. aggregation of electron on sample surface. Aggregation of electrons on the surface of the sample leads to reduction in the features of the sample. In case the sample to be observed is not conductive, it needs to be coated with a conductive material to prevent charging. Sputter coaters can be used to coat the sample with electrically-conducting material such as gold, palladium, graphite etc. It is also useful in improvising the contrast. The appropriate changes in the contrast and brightness will enhance the topographical features of the sample. After viewing the image on the monitor, further analysis can be carried out using EDX detector. Elemental composition of sample can be determined using this detector[19,20].

Procedure of Examination

Theprepared samples were analysed using ZEISS SEM-EDX EVO-18 accessed at Amity University, Noida, Uttar Pradesh, India. Before analysis on SEM-EDX, the samples were coated with gold particles using Quorum sputter coater. The sample was kept in the sputter coater for 45 mins and then was placed on the studs for analysis. The electron high tension was kept at 20kV for obtaining the elemental spectrum. The spectrum was first observed for blank paper on which the samples were prepared followed by analysis of individual and overlapped inks.

Results and Observations

The both ball point ink samples comprises of similar elemental composition, although with a few quantitative differences depending on the element selected has been shown in Table 2. In ball point pen inks, the most abundant elements, excluding carbon (C) and oxygen (O), are silicon (Si) and Magnesium (Mg). In spite of similar elemental composition, the weight percentage of these elements vary among BB1 and BB2 which helps us in distinguishing between two inks. The weight percent of these elements further vary in case of overlapped inks.

Comparably, the elemental composition of gel pen inks is also similar. The most abundant elements apart from carbon and oxygen are Magnesium and Silicon. In case of BG2, additional micro elements i.e. calcium, iron and palladium are also present which helps the examiner to differentiate between the two gel inks with a great extent of conformity. As far as overlapping of ink is concerned, the areas with overlapped gel pen inks depicted the presence of reduced quantity of calcium and palladium whereas iron was not present in the overlapped area. This might be possible due to formation of compound of iron with oxygen. A drop in weight percentage of oxygen can also be seen in it.

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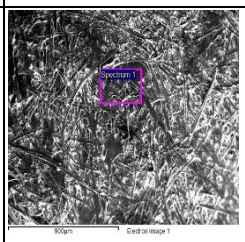
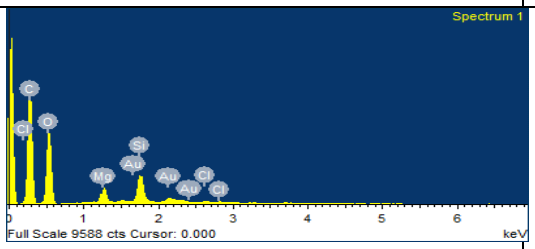
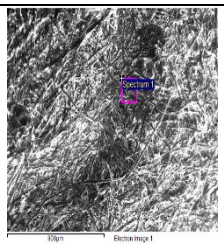
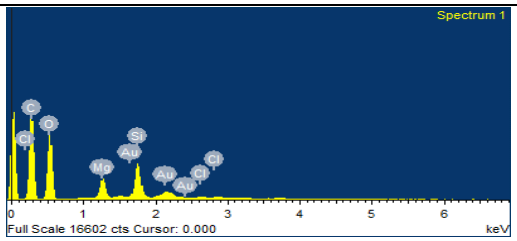
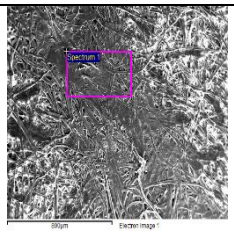
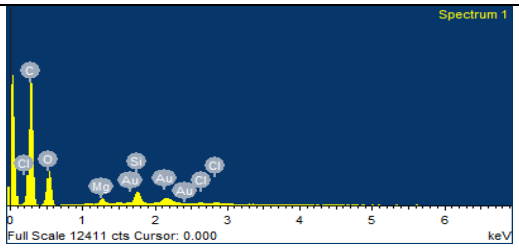
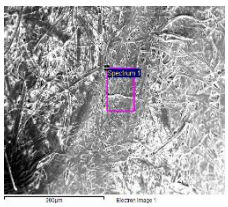
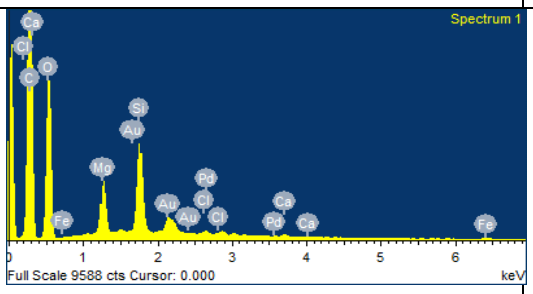
The basic composition of fountain pen inks is also similar to that of ball point and gel inks. The abundance of magnesium and silicon is second highest after carbon and oxygen in these inks as well. Among the two fountain pen inks, small quantity of sulphur and calcium can be observed in BF1 whereas instead of sulphur and calcium, aluminium and chlorine is present in BF2. Presence of extra micro elements and the different weight percentage of elements corroborates the facts that samples under examination consists of two different types of inks.

Table 2: Observations of Analysis of Black Ink with SEM-EDX

S.No.	Sample	Focused Site	Spectrograph	Elemental Composition		
11.	BB1			Element	Weight %	Atomic %
				C K	50.27	58.71
				O K	44.47	38.99
				Mg K	1.63	0.94
				Si K	2.45	1.22
				Cl K	0.15	0.06
				Au M	1.03	0.07
				Totals	100.00	
12.	BB2			Element	Weight %	Atomic%
				C K	48.13	57.36
				O K	43.89	39.27
				Mg K	2.33	1.37
				Si K	3.49	1.78
				Cl K	0.21	0.09
				Au M	1.96	0.14
				Totals	100.00	
13.	BG1			Element	Weight %	Atomic %
				C K	62.18	70.13
				O K	33.86	28.67
				Mg K	0.71	0.39
				Si K	1.24	0.60
				Cl K	0.21	0.08
				Au M	1.81	0.12
				Totals	100.00	
14.	BG2			Element	Weight %	Atomic %
				C K	44.87	54.91
				O K	44.30	40.70
				Mg K	2.86	1.73
				Si K	4.14	2.17
				Cl K	0.24	0.10
				Ca K	0.14	0.05
				Fe K	0.23	0.06
				Pd L	0.66	0.09
				Au M	2.56	0.19

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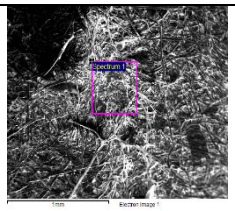
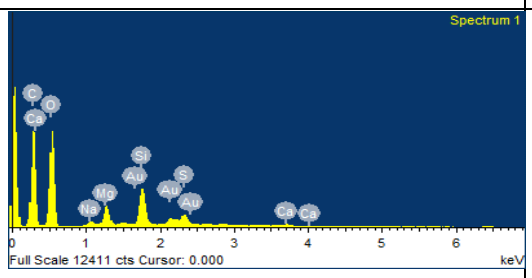
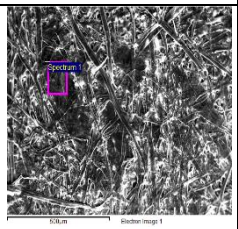
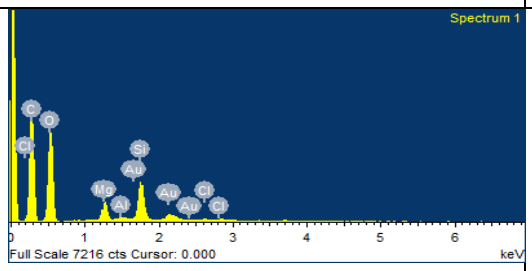
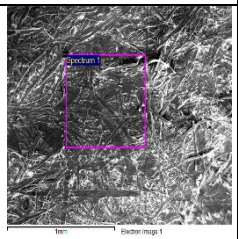
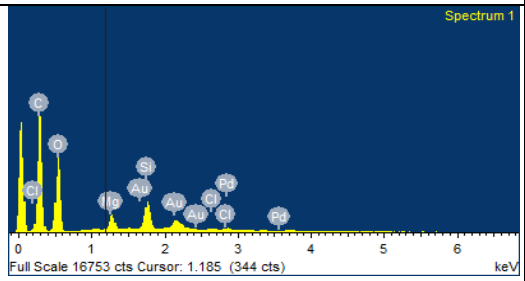
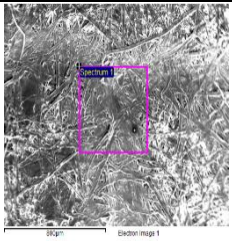
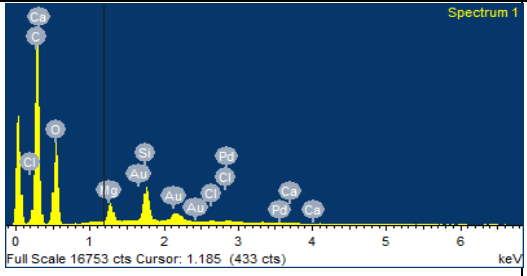
				Totals	100.00	
15.	BF1			Element	Weight%	Atomic%
				C K	44.25	53.47
				O K	47.41	43.01
				Na K	0.42	0.26
				Mg K	1.88	1.12
				Si K	2.81	1.45
				S K	1.04	0.47
				Ca K	0.17	0.06
				Au M	2.02	0.15
				Totals	100.00	
16.	BF2			Element	Weight %	Atomic %
				C K	46.45	55.34
				O K	46.74	41.81
				Mg K	1.78	1.05
				Al K	0.16	0.08
				Si K	3.01	1.53
				Cl K	0.16	0.06
				Au M	1.71	0.12
				Totals	100.00	
17.	BB1BB2			Element	Weight %	Atomic %
				C K	44.69	54.26
				O K	46.86	42.72
				Mg K	1.91	1.15
				Si K	2.89	1.50
				Cl K	0.16	0.07
				Pd L	0.76	0.10
				Au M	2.72	0.20
				Totals	100.00	
18.	BG1BG2			Element	Weight %	Atomic%
				C K	49.00	58.44
				O K	43.16	38.65
				Mg K	1.88	1.11
				Si K	2.81	1.43
				Cl K	0.19	0.08
				Ca K	0.15	0.05
				Pd L	0.52	0.07
				Au M	2.29	0.17

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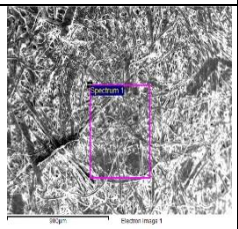
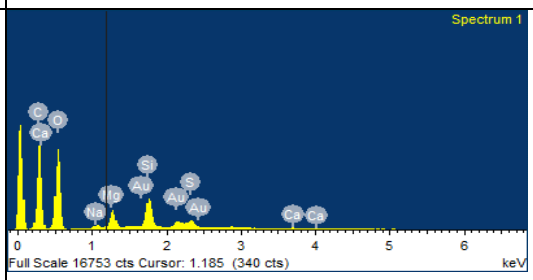
				Totals 100.00
19.	BF1B F2			Element / Weight % / Atomic % C K 44.74 53.96 O K 47.10 42.64 Na K 0.46 0.29 Mg K 1.88 1.12 Si K 2.71 1.40 S K 0.87 0.39 Ca K 0.11 0.04 Au M 2.14 0.16 Totals 100.00

Conclusion

From the current research the SEM-EDX has been illustrated to be a sophisticated tool for determining the elemental composition of similar appearing ball point, gel and fountain pen inks. It has proved to be successfully utilized for comparison of inks on handwritten documents. The techniques has proved to be successful in identification of presence of multiple blue inks in altered documents. Being a rapid, effective and partially-destructiveapproach SEM-EDX could be readily integrated into existing analysis workflow for analysis of ink. Though the technique is not successful in deciphering obliterations but the concrete and comprehensive results obtained from it about the composition of ink can successfully support the decision making capability of the forensic document examiners. Therefore, it can be concluded that SEM-EDX is a promising and efficient tool for differentiation of overlapped black inks and can serve as an important step towards corroborating and homogenizing ink identification methods in questioned document examination. It will also enable the examiner to select the most appropriate technique for ink examination. However, further study using chemometrics can be done to strongly validate the results. Along with chemometrics, future work might include how age of ink can affect the result.

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