

COMPARATIVE STUDY BETWEEN ERASABLE AND DISAPPEARING INKS USED IN FORGING DOCUMENTS

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ABSTRACT

The aim of this work is to compare between erasable and disappearing inks and study their role in the forgery of different documents. The obtained results showed differences between erasable and disappearing inks that help the documents examiner to deal with them when submitted in cases. The disappearing ink which contains phenolphthalein loses its color by time faster than that contains thymolphthalein. While the color of erasable ink did not generally change by time at room temperature but changed on exposure to UV light. On the other hand, the disappearing ink is absorbed by paper while erasable ink remains on paper surface. The two types of ink are more stable on polycarbonate polymer sheets. The polymer component of erasable ink is chemically bonded with polycarbonate polymer leading to ink stability. The presence of Ti in the pigment of disappearing ink acts as tag in forgery examination due to its diffusion inside polycarbonate sheet.

Keywords: Erasable inks, disappearing inks, forgery, polycarbonate polymer sheet, pigment

1. INTRODUCTION

Forensic document examination is a branch of forensic science that studies all components of documents. Inks are one of the most important components in all documents. Ink analysis can be used to link a suspect to a crime or determine the authenticity of a questioned document which can be taken in consideration when analyzing ink for a questioned document. The slight chemical interactions that may occur between the paper and the ink can be taken in consideration when analyzing ink for questioned documents. [1].

The methods used in forensic ink analysis include microscopy, different light sources, thin layer Chromatography (TLC), liquid chromatography, capillary electrophoresis (CE), infrared and Raman spectroscopy. Although there are general ASTM standards for questioned document analysis, ASTM 1789-04 (standard guide for writing ink identification) and ASTM 1422-05 (standard guide for test methods for forensic writing ink comparison) were withdrawn in January 2013 and 2014,

respectively, with no replacement. However, ink analysis falls within the category of questioned document analysis, ASTM E 444 (standard guide for scope of work of forensic document examiners) [2].

In 2013 Braz *et. al.*, [3] published a review article on using of Raman spectroscopy for the analysis of inks on questioned documents, where this technique is very important for inks and paper analysis. Infrared spectroscopy is a common technique in the analysis of inks from questioned documents which can be useful to solve crimes. FT-IR spectrometer has been used in combination with Scanning Electron Microscopy/ Energy Dispersive X-Ray Spectroscopy (SEM-EDXS) mapping to successfully determine the sequence of intersecting lines of ink [4]. In all countries, Government and private sectors were using the ink examination as a method to ensure the authenticity or fake nature or forgery of the questioned document [5]. However, ink analysis has been used by forensic scientist to identify inks on questioned documents. Examination and dating of inks on questioned

documents has become common, and law enforcement agencies use this technique during their criminal investigations. Ink analysis involved the examination of documents using the naked eye, oblique lighting conditions with special optical filters. It can be performed using optical, spectroscopic and chromatographic methods [6]. Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) was utilized for the analysis of ink samples using KBr as a background [7]. This analysis was found to give discrimination between the ink spectra. Also Micro-Attenuated total reflection with infrared spectroscopy (Micro-ATR-IR) was found to be a simpler technique for acquiring and getting on the spectra of ink samples but it is more easy [8]. FTIR was used to analyze different historical writing ink samples and revealed the possibilities to identify the historical ink based on their chemical composition, and the nature of ingredients in different types of inks. However, only KBr pellet and ZnSe cell methods were successful [9]. On multivariate chemometrics for the forensic discrimination of inks based on their visible spectra showed that the results of Ultraviolet-visible spectra of ink were difficult to compare but, the used ink sample seized or confiscated was very important to overcome this problem [10]. Each of the spectra represents the average of the absorption from the same batch. Chemometrics application such as, discriminate analysis (DA), principal component analysis (PCA) and cluster analysis (CA) were successively used to calculate the discriminate model. UV-VIS examination may indicate that the document has been stained by chemicals or other materials that may affect the ink analysis [11]. In addition to the previous methods of the ink analysis on documents, the optical examinations of documents are considered superior at the first examination of the documents [12].

The aim of this study is to evaluate and characterize the different brands among the erasable and disappearing inks. In addition, comparing between them and using different methods to study the forgery of documents.

2. EXPERIMENTAL

2.1. Materials

2.1.1. pens

Different types of Ballpoint pens containing blue colored erasable inks with a small eraser incorporated within the pen, which are made in china and Japan as:

- Blue colored Erasable ball point pens ink with a small eraser incorporated within the pen which is typed as (XZB 0.8 mm), made in china (pen code E1).

- Blue colored erasable ball point pens ink with a small eraser incorporated within the pen which is typed as (SCM v1259, 0.5mm), made in china (Pen code E2).

- Blue colored erasable ball point pens ink with a small eraser incorporated within the pen which is typed as (the pilot "Frixion"), made in Japan (pen code E3).

1g ink from each pen was dissolved in 100 mL distilled water.

2.1.2. Chemicals

Solid colorless acid-base indicators, namely thymolphthalein and phenolphthalein were used. They were purchased from Alpha Chemica, Mumbai, India. Other reagents such as glycerol (Sigma-Aldrich), ethanol by (Sigma-Aldrich), by sodium hydroxide (Sigma-Aldrich), and Titanium dioxide (TiO₂) Euromedex-France were also used for preparation of disappearing ink formulations. Distilled water was used as a dissolving medium for all ink formulations

2.1.3. Documents

- Local writing-photocopy and printing paper (80g) which is made of 80% bleached bagasse kraft pulp, 15% bleached soft wood pulp and 5% calcium carbonate which is produced by the Egyptian Sugar and Integrated Industries Company, Quena, Egypt (Paper Code, P1) .

- Plastic documents, such as laboratory polycarbonate white sheets, these sheets were

produced by Polyee Plast Company, Cairo, Egypt (Plastics Code, P2).

2.1.4. Equipment

- Magnifying lenses (Zeiss) have magnification from 10X to 40X, ZEISS Group, Germany.

- Microscopes Leica have magnification from 10X to 500X, Leica Microsystems develops and manufactured by microscopes and scientific instruments, Germany.

- Video Spectral Comparator 6000 (VSC6000), Foster and Freeman, England.

- Ultraviolet lamp with wavelengths 254 nm and 365 nm (Vilber Lourmat, France).

- A Data Colour SF 600⁺ Relative colour, USA.

- Quanta FEG (field emission gun) 250-EDAX TEAM, Netherlands.

2.2. Methods

2.2.1. Preparation of disappearing ink

Disappearing ink formulations (100 ml) based on thymolphthalein (Pen code D1), and phenolphthalein (Pen code D2) were prepared according to E-Molla *et.al* [13]. Briefly, 1g of thymolphthalein or phenolphthalein was dissolved in 5 mL ethanol. The pH of the prepared solutions was adjusted at 9.5-10.5 using 1 N of NaOH solution, where the blue color in case of thymolphthalein and red color in case of phenolphthalein of the indicator appears in the alkaline media. Then, distilled water was added until total volume became 100 mL, then Glycerol was added dropwise as a rheology modifier to control the viscosity of the prepared ink solution.

2.2.2. Optical Tests

The optical examination of documents was carried out by video Spectral Comparator 6000 (VSC6000). These sets enable examiner to identify forgery in documents by using illumination restricted to selected parts of the infra-red, visible or ultra-violet portions of the light spectrum in which the hidden strokes

glow and the disappeared inks fluoresces under the influence of UV rays.

2.2.3. Printing

Papers were separately marked with both blue colored erasable ink and disappearing ink using IGT printer by spreading the ink uniformly on paper and plastic samples.

The papers were observed visually at different time intervals (after 2 and 5 hours then 1, 3 and 5 days) to see whether the ink disappeared or not.

2.3. Color measurements

Color measurements are used as evidence in the forensic field by examining the changing of inks color.

The color strength (K/S) was determined for erasable and disappearing ink on paper sheet samples by calculating the value K/S from the Kubelka- Munk equation [14].

$$K/S = (1-R)^2 / 2R$$

Where R is the average observed reflectance, K is the absorption coefficient, S is the scattering coefficient and K/S is the corresponding color strength.

- The corresponding K/S value was calculated for each ink sample using Data Colour SF 600⁺ Relative color.

3. RESULTS AND DISCUSSION

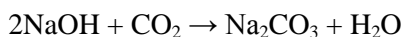
3.1. Disappearing ink

Disappearing inks are water-based, acid base indicators. They are used as scan of writing a check, only to have the ink disappears later. They consist of thymolphthalein or phenolphthalein solutions which are blue and pink or red, in basic solutions, respectively. When exposed to air, the solvent evaporates leaving the indicators in neutral state causing disappearance of their colors.

3.1.1. Mechanism of color disappear

Throckmorton [15] reported that disappearing ink becomes visible when treated with any alkaline solution. As the alcoholic

thymolphthalein react with sodium hydroxide present in the structure of ink it becomes colored (blue) in this alkaline solution and when sodium hydroxide reacts with carbonic acid (formed from the reaction of carbon dioxide with water vapor) in the atmosphere forming sodium carbonate; which is less basic than sodium hydroxide; according to the following reaction:



The pH of the ink decreases gradually causing fading of ink color because the pH transition range of thymolphthalein between 9.3 and 10.5 in which its color disappears below 9.4 and becomes blue above 10.6.

The disappearing ink could be removed spontaneously from the surface of the paper by exposing to air for a period.

3.1.2. Colour strength measurements

Fading time

Fading time of writing is defined as the time from writing to its color disappearance (complete fading). This means that when the fading time is short, the handwriting is unstable (short handwriting stability) and vice versa depending on the concentration of the components of the disappearing ink, especially concentration of the base and indicators, where the color of the writing was blue disappeared in case of thymolphthalein and red disappeared in case of phenolphthalein.

Fading of inks

Different brands of ink were spread on the surface of paper samples and allow drying at room temperature then measuring the reflectance from two hours up to three days and calculating the changes in value of the color strengths (K/S) using the Kubelka-Munk equation[14].

The color strength values of disappearing ink samples were calculated in Table (1) and graphically represented in Figure (1). The change in color strength values (K/S) give an

indication on fading of inks, Where each color is measured at 254nm [13].

The data in Table (1) reveals that the the colour of disappearing ink fades by time as results of lowering its pH due to sodium carbonate formation. Consequently, the values of K/S decrease. On the other hand, Phenolphthalein loses its color faster than Thymolphthalein.

3.2. An erasable inks

Erasable ink is a type of ink easily removed by certain rubbers incorporated in each pen. It has different colors likes blue, red, green and the black. This type of inks could be removed from the surface of paper mechanically by erasure or by effect of heat and reappear by cooling. It is a type of viscous ink that depends largely on the heat generated during erasure which affects the solvent of ink.

Fading of Inks

Different brands of blue erasable ink are disseminated on surface of one type of paper sheet samples and allow to dry at room temperature. Then, the fading of ink color is determined for each sample by measuring the reflectance of ink (R) at different time intervals, ranging from two hours to three days, either at room temperature between 20-25° (a) or by exposing to ultra violet light at 254 nm (b) .

The color strength values (K/S) of blue erasable ink stroke samples were calculated from the Kubelka- Munk equation. The data are compiled in Table (2) and graphically represented in Figurer (2).

Table (2) and Figurer (2) showed that the color of erasable ink did not generally change by time especially at room temperature, while at using UV light the colour changed very slightly, may be due to the produced heat from UV lamp .

The fading of this type of ink need an external heat factor whether friction by eraser or by direct raise of temperature.

Table 1: The disappearing inks decay at different time intervals

indicator	time	2hours	5hours	1 day	2 days	3 days
Phenolphthalein	K/S	2.5	1.5	1.1	1	0.5
Thymolphthalein	K/S	3	3	2.5	1.5	1.1

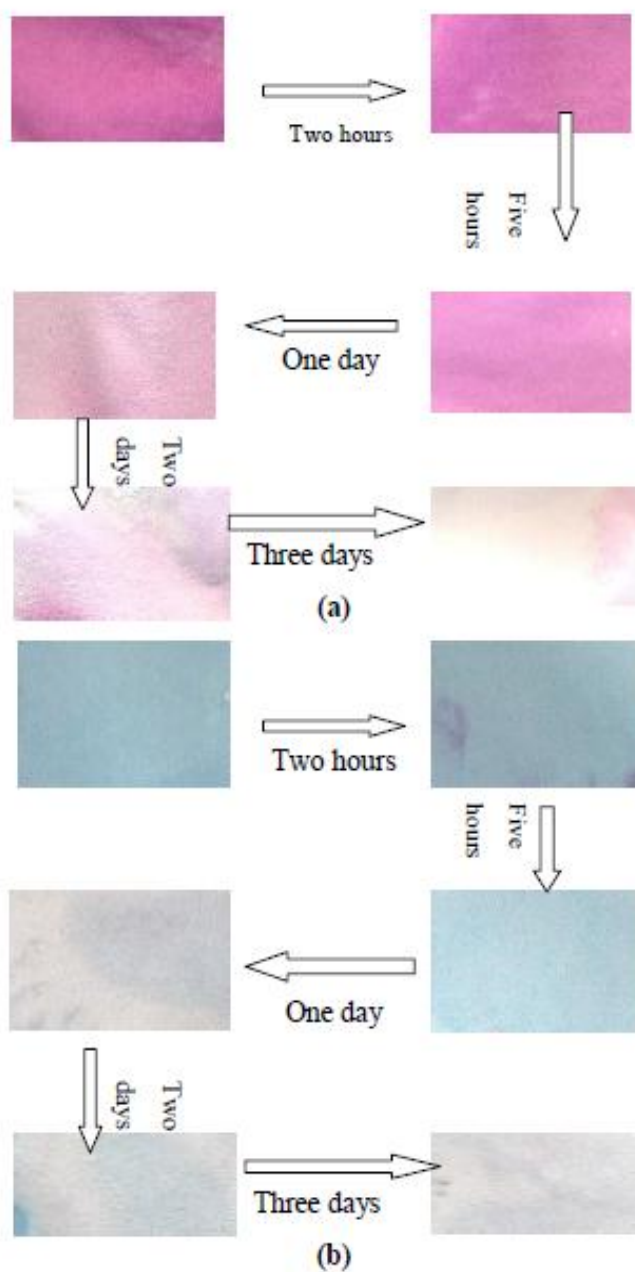
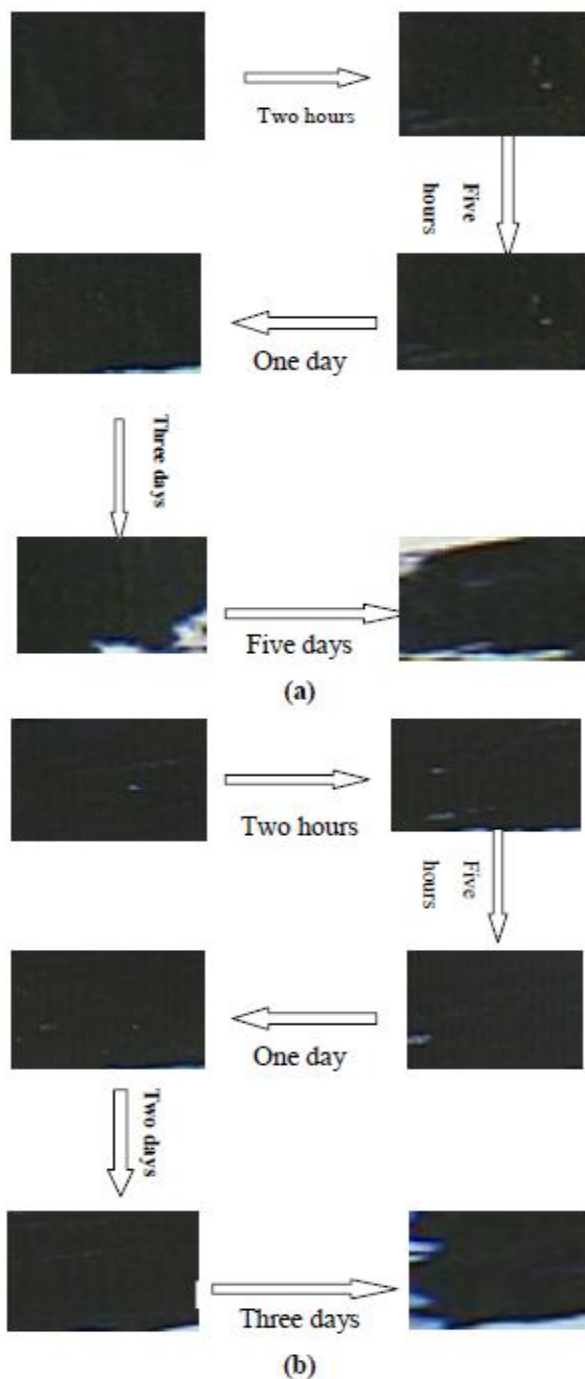


Figure 1: The disappearing inks decay at different time intervals containing (a) Phenolphthalein and (b) Thymolphthalein

Table 2: Effect of time on the erasable ink decay (a) at room temperature and (b) under ultra violet light

	time	2hours	5hours	1 day	2 days	3 days
a	K/S	5	5	5	5	5
b	K/S	5	5	4.5	4.5	4.5

**Figure 2: Effect of time on the erasable ink decay (a) at room temperature and (b) under ultra violet light.**

3.2.1. The specifications of strokes for the erasable inks

The erasable inks belong to the viscous inks so they have the same specification of writing viscous materials

A groove is strokes feature; it is defined by a vacuum inside it as a result of the dissemination of ink on the paper surface and is identified clearly via the incident light using a magnifying glass.

Striation is another strokes feature; it is defined by spaces without ink or relatively light line along the path of the stroke, which is due to the presence of impurities on tip of pens that prevents the spill or flowing of ink during execution of inks stroke.

3.3. Comparison between erasable and disappearing inks on paper sheet using scanning electron microscopy (SEM)

The disappearing inks belong to liquid inks family, so their components displacement inside the layers of the paper, and therefore ink

is absorbed [16] and [17] Figure (3), but in case of erasable inks the components of these inks are still on the surface of paper because this belongs to viscous inks family, Figure (4).

3.4. Effect of erasable and disappearing inks on polycarbonate sheet

The scanning electron microscope of polycarbonate cross section sheet with blue erasable ink reveals that the ink penetrates the polymer sheet Figures (5) and (6). So, blue erasable ink is more stable in case of polycarbonate sheet.

The scanning electron microscopy of polycarbonate sheet with disappearing ink reveals that the ink penetrates the polymer sheet, Figures (7) and (8).

The above results reveal that the blue disappearing ink is more stable in case of polycarbonate sheet and takes more time to disappear because the sheet does not absorb CO_2 easily from air; consequently, the acid medium is not formed easily.

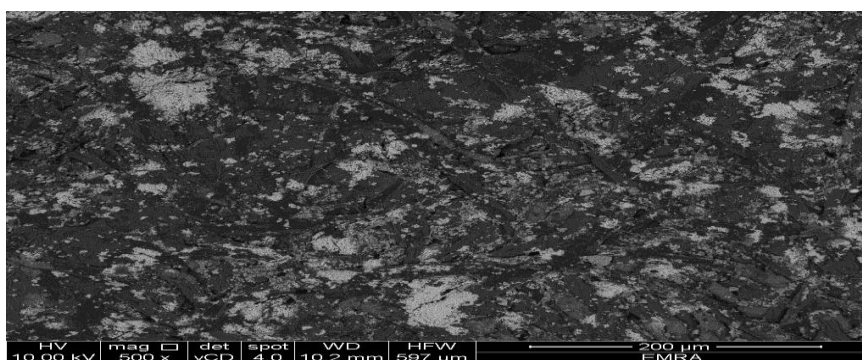


Figure 3: The scanning electron microscope of disappearing ink inside the layers of paper

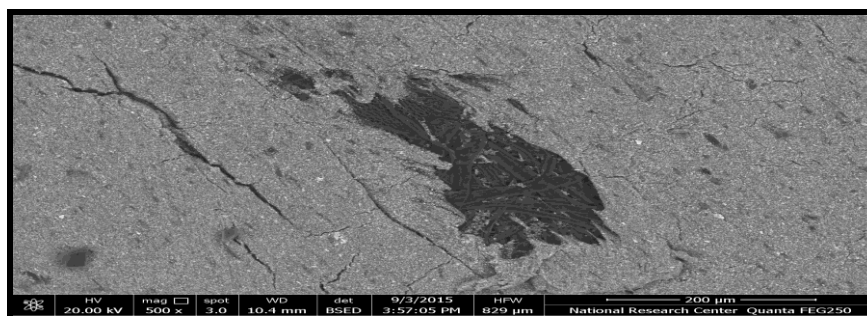


Figure 4: The scanning electron microscope of erasable ink on the surface of paper

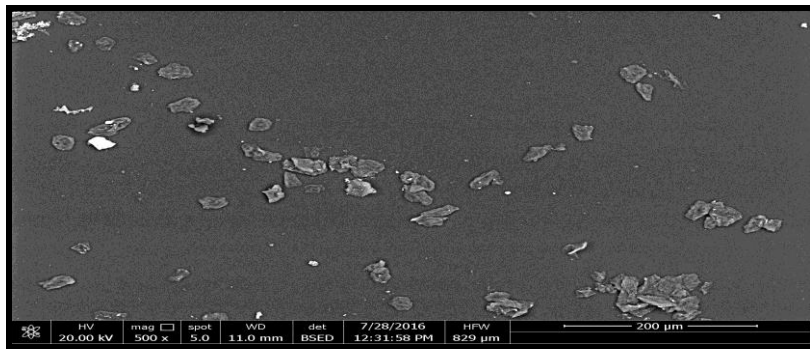


Figure 5: The scanning electron microscope of blue erasable ink on surface polycarbonate sheet

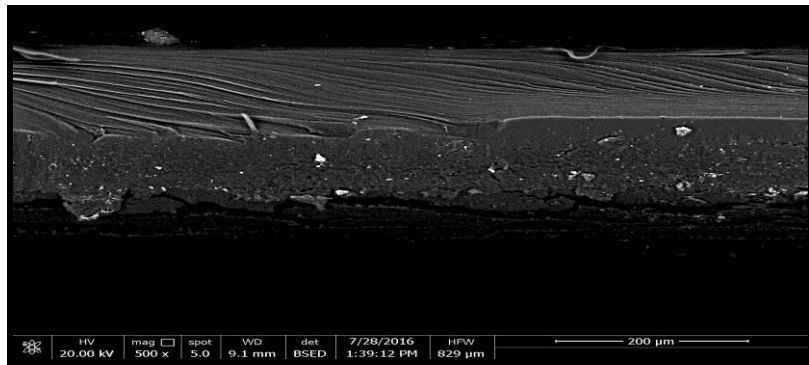


Figure 6: the scanning electron microscope of cross section for blue erasable ink on polycarbonate sheet

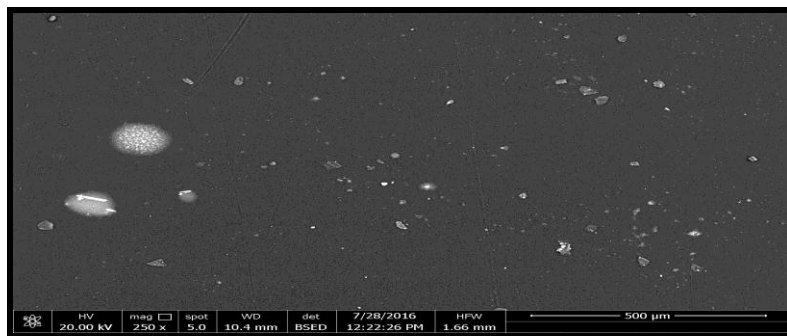


Figure 7: The scanning electron microscope of blue disappearing ink on surface of polycarbonate sheet

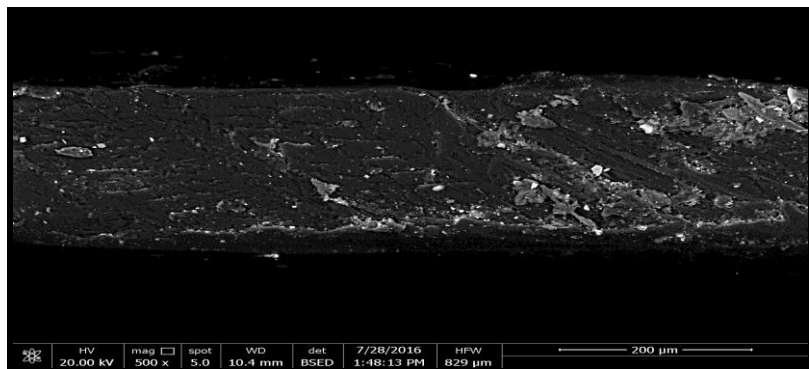


Figure 8: The scanning electron microscope of cross section for blue disappearing inks on polycarbonate sheet

3.5. Elemental differential analysis by X-ray (EDAX)

Elemental differential analysis by X-ray for polycarbonate sheets with erasable and disappearing inks explore the elemental constitution and percentage of each element in both of them, which represented in Tables (3) and (4) and graphically represented in Figures (9) and (10).

More information from EDAX analyses were obtained for the present elements in polycarbonate sheet with blue erasable ink, Figure (9) and Table (3). The oxygen present in polycarbonate sheet with high percentage 71.1% indicates the presence of dioctyl phthalate. (DOP), where this non volatile solvent present in the components of blue erasable ink.

Polyisopropene elastomeric polymer present in erasable ink is joined by chemical bonds with polycarbonate polymer leading to the stability of the ink on this polymer [18].

Table 3: Elements of blue erasable ink on polycarbonate sheet

Element	Weight %	Atomic%
C K	26.3	32.61
Na K	0.94	0.61
Si K	0.14	0.07
P K	0.18	0.09
Mo L	0.32	0.05
Cl K	0.51	0.21
K K	0.36	0.14
Oxygen	71.1	66.18

More information from EDAX analyses were obtained from the present elements in polycarbonate sheet with blue disappearing ink, Figure (10) and Table (4). The presence of about 0.08% Ti can be attributed to the presence of the TiO_2 pigment in the formation of disappearing ink [19]. While, the presence of element 1.4% nitrogen can be attributed to the basic ammonium hydroxide present in the components of blue disappearing ink [20]. The oxygen percentage is about 72.5% which is related to thymolphthalein. The additions of Ti element in the preparation of disappearing ink act as tag at examination when used in forgery because the Ti diffuses inside the polycarbonate sheet on writing liquid disappearing ink.

Table 4: Elements of disappearing ink on polycarbonate sheet

Element	Weight %	Atomic%
C K	25.92	31.53
N K	1.4	1.47
Mo L	0.02	0.03
Ti K	0.08	0.02
Oxygen	72.5	66.9

3.6. Comparison between erasable and disappearing inks

From the previous study we can compare between erasable and disappearing inks Table (5).

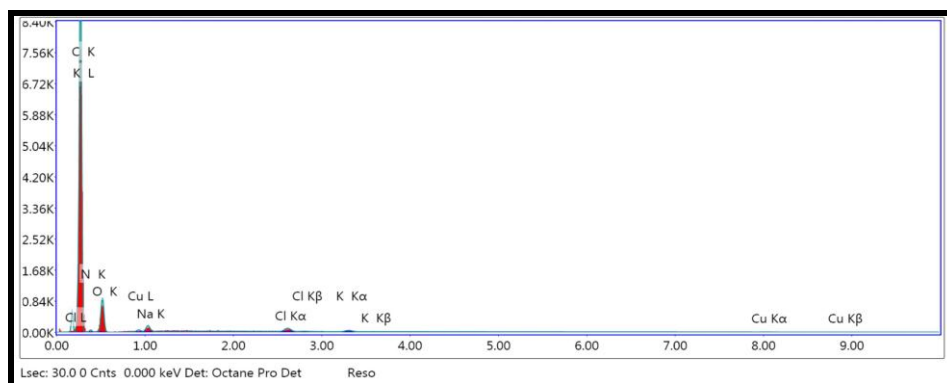


Figure 9: EDAX spectra of polycarbonate sheet with erasable ink

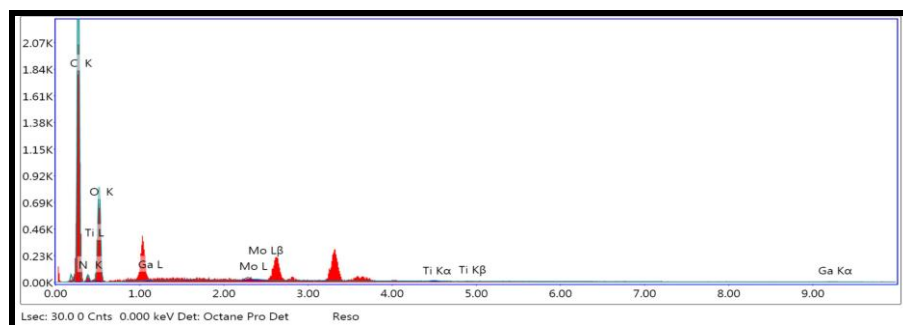


Figure 10: EDAX spectra of polycarbonate sheet with disappearing ink

Table 5: Comparison between erasable and disappearing ink

Item	Disappearing inks	Erasable inks
Type	Liquid writing materials (fluid)	Viscous writing materials (dry)
Color	Blue and Pink(red)	All color
Method of erasing	A Spontaneous erasure	by erasure or heat
Pressure of writing	Rough writing	Smooth writing
Shape of strokes	Ink penetrates the paper	Ink still on surface of paper
Effect of alkali solution on ink	reappearing the ink	No affect
State of ink on paper	Penetrable	On the surface of paper
Colorant materials	indicators	Dyes and pigment

4. CONCLUSION

- The research work is about the difference between the erasable and disappearing ink, in which the admittance of the inks to be used in written transactions of different documents expanded the likelihood of raising alerts to the forensic science community.

- Disappearing inks which contains phenolphthalein loses its color by time faster than that contains thymolphthalein.

- The color of erasable ink did not generally change by time at room temperature but changed on exposure to UV light.

- The disappearing ink is absorbed by paper while erasable ink remains on paper surface.

- The two types of ink are more stable on polycarbonate polymer sheets.

- The polymer component of erasable ink is chemically bonded with polycarbonate polymer leading to ink stability.

- The addition of some elements as Ti during their preparation of disappearing ink acts as tag at examination when used in forgery.

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ملخص عربي

دراسة مقارنة بين الأحبار القابلة للمحو والأحبار المتأطيرة (القابلة للاختفاء) المستخدمة في تزوير المستندات

الهدف من هذا البحث هو المقارنة بين الأحبار القابلة للمحو والأحبار المتأطيرة (القابلة للاختفاء) ودراسة دورها في تزوير المستندات المختلفة. أظهرت النتائج التي تم الحصول عليها اختلافات بينهما والتي تساعد فاحص المستندات على التعامل معها عند تقديمها في القضايا. يفقد الحبر القابل للاختفاء والذي يحتوى على الفينول فتالين لونه مع مرور الوقت بشكل أسرع من ذلك الذى يحتوى على ثيمولفتالين. فى حين أن لون الحبر القابل للمحو لم يتغير بشكل عام بمرور الوقت فى درجة حرارة الغرفة ولكنه تغير عند التعرض لضوء الأشعة فوق البنفسجية. من ناحية أخرى ، يتم امتصاص الحبر القابل للاختفاء بواسطة الورق بينما يبقى الحبر القابل للمحو على سطحه. يكون هذان النوعان من الحبر أكثر ثباتاً على البوليمرات المصنوعة من البولى كربونات. حيث أن البوليمر الموجود بمكونات الحبر القابل للمحو مرتبط كيميائياً مع بوليمر البولى كربونات الذى يودى إلى استقرار الحبر. وجود التيتانيوم فى الأحبار القابلة للاختفاء يعمل كدليل عند فحص حالات التزوير بسبب وجوده داخل البولى كربونات .