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Forensic Examination of Artificially Aged Document by Non-Destructive Technique.

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ABSTRACT:

Criminals adopted new techniques of ageing the document by treating it with different substances that disguised it to laymen as a naturally aged document. Forensic document examiners need to pay special attention to such artificially aged documents during laboratorial examination. In this paper, using VSC 6000-HS and FTIR-ATR, we discussed the non-destructive approach to the examination of artificially aged documents, which are treated with some chemical substances to accelerate the ageing process of the documents. The FTIR-ATR spectrum of such an artificially treated document shows the unique peak of chemicals or substances that were used to accelerate the age of the document. L*a*b* colour values obtained in VSC 6000-HS clearly show the degree of yellowness (ageing) in some artificially aged documents, which strongly indicate the sign of forgery. Further, the chemometric analysis also discriminates the artificially aged document treated with different substances.

Introduction:

A slow and time consuming process of paper or document ageing which depends mainly on environmental factors including surrounding temperature, humidity and storage condition of the paper as well as materials used in the paper manufacturing process and physical, chemical, mechanical, photochemical, biochemical, and radiochemical factor decreases the degree of brightness which causes the appearance of yellowing or browning colour (dull appearance) and deterioration of the physical and mechanical properties of the paper. For fraudulent purposes, the document or papers are often subjected to artificial ageing by forgers adopting various methods like Thermal ageing, Chemical ageing, etc. as well as keeping the paper in a moist atmosphere, in the oven, and most commonly treating the document with some chemicals, among which the popular one is the use of coffee or black tea. Even the Use of an Orthopteran insect, the cricket, to artificially age the paper is reported. [1]. It is one of the most challenging tasks for the Questioned Document Examiner to identify this type of fraud, which could be achieved by the detection of caffeine and other such substances or chemicals on the questioned document, which might be treated with some chemicals to show it is older than it really is.

The most prominent sign of ageing is the decrease in the brightness of the paper (yellowing of the paper) during the natural ageing process [2], [3], which is very different as compared to artificial ageing. The use of gas chromatography/Mass Spectrometry in SIM mode [4], time of flight secondary ion mass spectrometry (TOF-SIMS) [5], Liquid chromatography/mass Spectrometry (LC-MS) [6], UV-VIS Spectroscopy, Infrared Spectroscopy (IR), and Wet Chemical Analysis [7], accelerate light ageing as well as colour measurements. [8], kinetic analysis [9], modelling of dyes and solvents ageing using GC/MS [10], FTIR [11], Pyrolysis Gas Chromatography Mass Spectrometry (Py-GC/MS) [12], X-ray diffraction spectrometry paper [13], Neutron Activation Analysis (NAA) [14], Easy Ambient Sonic-

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spray Ionisation Mass Spectrometry (EASI-MS) and High Resolution Mass Spectroscopy (HRMS) [1], Size Exclusion Chromatography (SEC) [15], Headspace-Solid Phase Micro Extraction (HS-SPME) coupled with Gas Chromatography and Mass Spectrometry (GC-MS) [7], Paper Spray Mass Spectrometry (PS-MS) [16]. Hyperspectral Imaging [17]. Synchrotron Technology [18]. Gas Chromatography with Mass Spectrometry (GC-MS) and High Pressure Liquid Chromatography with Photodiode Array Detection (HPLC-DAD) [19], Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR), X-ray diffraction (XRD), Energy Dispersive X-ray Fluorescence (EDXRF) [20], and optical brightener examination [21] are commonly used techniques to find out whether the paper is naturally aged or artificially aged.

Eminent researchers focus on artificial ageing and the various techniques used; most of them are destructive or time-consuming. This paper focuses on the simple, non-destructive examination of artificially aged paper, which was treated with different solutions to accelerate the age of the paper.

Method:

In this study, six different artificially aged papers which were prepared by suspending six paper strips of plane A4-size paper of 80 GSM of equal length and width (Approximately 9.5 cm long and 2.5 cm broad) in the six different beakers numbered 1 to 6. Beaker 1 contains a standard solution of soya sauce, beaker 2 contains a solution of coffee, beaker 3 has an iodine solution, beaker 4 has a detergent solution, beaker 5 contains a tea solution, and beaker 6 contains a ferric chloride solution. All these soaked papers are air dried at room temperature, which then turns them yellowish or brownish, similar to naturally aged papers. (As shown in Figure 1). Using VSC 6000 HS (Foster + Freeman Limited, UK), the L*a*b* colouring and measuring system, which is reported by the Commission International de l'Eclairage (CIE), is used to find out the colour intensity of the paper. The ATR spectra of all these papers were measured using a FTIR Bruker Alpha P equipped with OPUS software and a platinum diamond ATR crystal. Scans were performed in the wavelength range of 4000 cm-1 to 400 cm-1, with 15 scans per second and 8 cm-1 resolution. The ATR spectra were acquired by applying nearly constant gauge pressure to the stamped region of the paper. After each scan, the diamond crystal was cleaned with methanol to prevent contamination. Smoothing, normalization, and baseline adjustments were applied to the resultant spectra. A calibration spectrum (Blank measurement) was also obtained by measuring the non-treated white area of the blank portion of the paper. Spectra of all the standard solutions of coffee, tea, iodine, soya sauce, detergent, and ferric chloride were also measured in similar conditions. Two naturally aged paper (seven year and seventeen year older) are compared with these artificially treated papers.

Result and Discussion:

In this analysis, naturally aged paper does not show any prominent sign of ageing even after seven years, but in paper before 17 years, a sign of ageing is clearly seen, which is encircled by a red colour as shown in figure 1. Artificially aged papers, which are treated with different substances, show signs of yellowness very prominently. Out of which the paper treated with detergent and iodine solution does not show any noticeable degree of yellowness, but it shows the sign of ageing like the dull texture of the paper surface. Paper treated with soya sauce shows a medium level of yellowness, while paper treated with coffee, tea, and ferric chloride solution shows the highest degree of yellowness. As shown in Figure 1 and Table 1 below.

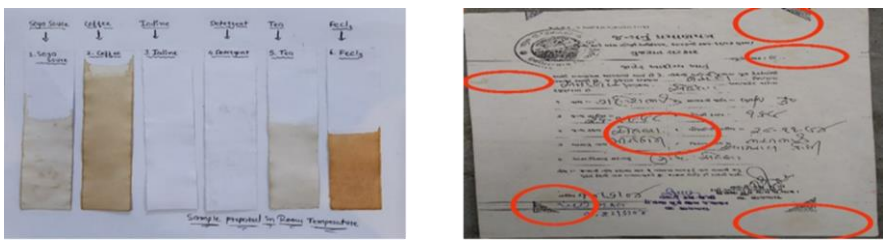

Figure 1: Artificially Aged Paper (Left) and Naturally Aged Paper (Right).

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SN	Paper treated with	Degree of Yellowness
1.	Blank Paper	Absent
2.	Seven year old Paper	Absent
3.	Seventeen year old Paper	Less
4.	Soya Sauce solution	Medium
5.	Coffee solution	High
6.	Iodine solution	Absent
7.	Detergent solution	Absent
8.	Tea solution	High
9.	Ferric chloride solution	High

Table 1: Degree of Yellowness in different papers

Transmission spectra of standard solutions of soya sauce, coffee solution, detergent solution, iodine solution, tea, and ferric chloride solution and paper artificially treated with these solutions are recorded by using Fourier Transform infrared (FTIR) in Attenuated Total reflectance (ATR) mode. The transmission spectra of the coffee solution and the paper treated with the same solution are shown in figure-2. As shown in figure-2 (left), two peaks are seen at 2361.11 and 1642.67, whereas, the peaks at 2361.14 and 1515.55 in artificially treated paper with coffee solution (right) are nearly close to each other, which clearly indicates that this paper is treated with coffee solution to accelerate the age of the document. Similarly, soya sauce, tea, and ferric chloride solutions are frequently used for forgery purposes to enhance the ageing process of a document.

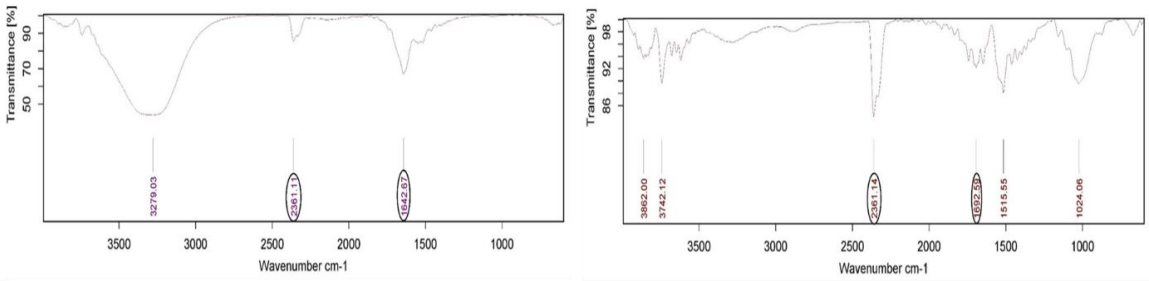

Figure 2: Transmission Spectra of Coffee solution (Left) and artificially forged paper treated with Coffee solution (Right).

Further, Chemometric analysis of the all these artificially treated document is carried out in which the Eigen values which are obtained in principle component analysis shows the linear combination of the initial variables of principle component analysis are also discriminate the artificially treated papers. (As shown in Table- 2 & Table-3).

Table 2: Eigenvalues of different artificially aged paper-

Paper treated with	Soya-sauce treated paper		Coffee solution treated paper		Iodine solution treated paper	
	F1	F2	F1	F2	F1	F2
Eigenvalue	1.016	0.984	1.026	0.974	1.064	0.936
Variability (%)	50.815	49.185	51.319	48.681	53.182	46.818
Cumulative (%)	50.815	100.00	51.319	100.00	53.182	100.00

Table 3: Eigenvalues of different artificially aged paper-

Paper treated with	Detergent treated paper		Tea solution treated paper		$FeFcl_3$ solution treated paper	
	F1	F2	F1	F2	F1	F2

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Eigenvalue	1.084	0.916	1.016	0.984	1.031	0.969
Variability (%)	54.202	45.798	50.806	49.194	51.548	48.452
Cumulative (%)	54.202	100.00	50.806	100.00	51.548	100.00

In this study, the first Eigen value of artificially treated paper with soya sauce equals 1.016 in the F1 factor and 0.984 in the F2 factor and represents 50.81 % of the total variability. This indicates that if we represent the data on only one axis, there is a possibility of finding 50.81% of the total variability. The Eigen values of all the artificially treated papers are shown in Tables 2 and 3, in which the paper treated with iodine solution and detergent solution shows 53 to 54% of the total variability of the data. The paper treated with iodine solution and detergent solution does not show a strong degree of yellowness in L*a*b* values, But with the help of chemometric analysis, one can find out whether such papers are naturally aged or artificially aged. The papers artificially treated with tea, coffee, and ferric chloride solution show more ageing, and their Eigen values are 1.016, 1.026, and 1.031, respectively.

The next parameter of principle component analysis is the correlation circle, which shows a narrow angle in each of the artificially treated papers that reflects the positive link between the variables. Biplots show the simultaneous representations of variables and observations in the PCA space. If the sum of the variability percentages associated with the axes of the representation space is sufficiently high (for example, 80%), then the representation can be considered reliable. Correlation Biplot interprets the angles between the variables, as these are directly linked to the correlations between the variables. The correlation circle, biplots, and scree plot of a paper treated with coffee and ferric chloride solution are shown in figures 3 and 4 respectively.

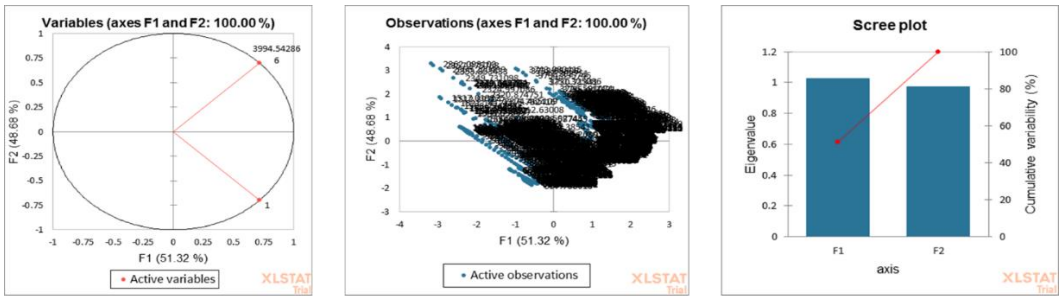

Figure 3: Correlation circle, Biplots and Scree plot of paper treated with Coffee solution.

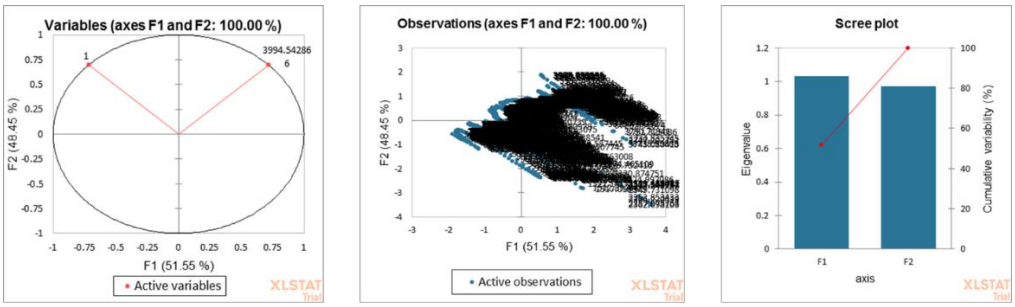

Figure 4: Correlation circle, Biplots and Scree plot of paper treated with Ferric chloride solution.

Dendrograms of artificially treated papers obtained in chemometric analysis are shown in Figure-5. The paper artificially treated with detergent solution and iodine solution which do not show any prominent mark of yellowness, in the dendrogram it shows a lower degree of dissimilarity at 100 points. The paper artificially treated with coffee solution and ferric chloride solution shows a prominent mark of yellowness; in the

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dendrogram, these two also show a greater degree of dissimilarity at 200 points (Figure-5).

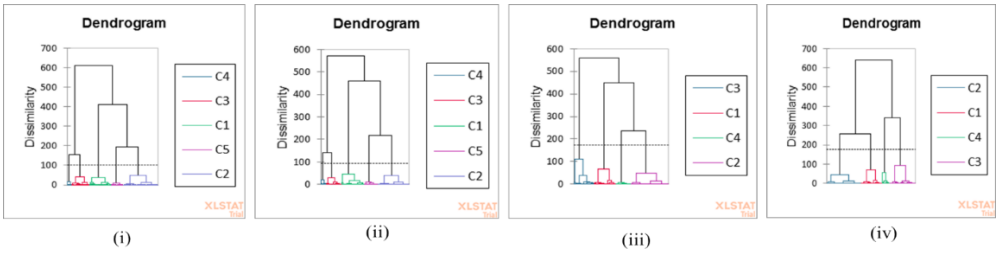

Figure 11: Dendrograms of paper treated with (i) Detergent, (ii) Iodine, (iii) Coffee, (iv) Ferric chloride solution.

Conclusion:

Artificially aged documents treated with coffee, tea, and ferric chloride solution show the highest degree of accelerated ageing and a high degree of yellowness. Iodine and detergent solutions do not show any prominent marks of yellowness, but the texture of the paper feels like an older one. Transmission spectra measured by FTIR-ATR show prominent peaks of these substances, which were used to artificially age the document. Thus, the non-destructive technique of FTIR ATR can be used for the detection of the age of a document in an artificially treated document to accelerate its ageing. In Principle Component Analysis, the correlation circle, which shows a narrow angle in each of the artificially treated papers, reflects the positive link between the variables. The dendrogram shows lower dissimilarity values for paper artificially treated with detergent and iodine solution and a comparatively high value for paper artificially treated with coffee and ferric chloride solution.

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