

# FORENSIC DATING OF OFFICIAL DOCUMENTS: UTILIZING FTIR ANALYSIS OF STAMP PAD INK DEGRADATION FOR DOCUMENT AUTHENTICATION

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## Abstract

*This study delves into the deterioration of stamp pad ink found on official documents and explores its potential in dating these documents. The credibility of official documents relies on the application of an official seal or stamp using stamp pad ink. However, individuals with malicious intent may seek to manipulate the ink's appearance to deceive the document's perceived age. To counteract this, we propose a non-destructive method employing Fourier Transform Infrared (FTIR) analysis in Attenuated Total Reflection (ATR) mode to analyze the degradation of stamp pad ink. Through the application of FTIR analysis in ATR mode and the utilization of chemometric approaches like Principal Component Analysis (PCA), we have effectively established a connection between the degradation of stamp pad ink and the document's age. This methodology stands as a crucial tool in authenticating official documents and identifying fraudulent attempts to alter their purported preparation date. The implications of these findings extend to the realms of forensic document examination and legal contexts, offering a dependable means of dating documents through the analysis of ink degradation patterns.*

**Keywords:** Document Age authentication, Stamp pad ink, FTIR spectroscopy, Forgery Non-destructive analysis, Chemometrics

## INTRODUCTION

Sigillography, the study of stamps and seals, plays a crucial role in authenticating official and important documents, including legal ones, by impressing them with stamps using stamp pad ink. However, forgers often alter the stamp impressions to make documents appear older than they are. Consequently, the forensic examination of stamp pad ink becomes essential in determining the true age of questioned documents. Numerous research efforts have focused on tackling this issue using various analytical techniques such as UV-Vis spectrophotometry [1], Visible near infrared reflectance spectroscopy [2], High-Pressure Liquid Chromatography, GC/MS methods [3], digital microscope, and Raman spectroscopy [4], Gas Chromatography [5], MECC-DAD and CZE-ESI/MS [6], Confocal Raman Microscope [7], HPLC [8], FTIR [9], TLC [10] [11], and Raman Spectroscopy [12], LD-IMS [13].

Nonetheless, many studies using non-destructive techniques to demonstrate the aging of stamp pad ink over time remain limited. In this paper, we explore the non-destructive Attenuated Total Reflectance (ATR) mode of FTIR spectroscopy, a sophisticated and reliable technique used in document analysis to study the aging process of various materials, including paper, ink, and toner [14 - 19]. The chemometrics approach, particularly Principal Component Analysis (PCA), is employed to reveal the relationship between stamp pad ink degradation and its aging time.

## MATERIALS AND METHOD

In the course of this study, a comprehensive collection of 158 examples of stamped impressions was procured, specifically utilising stamp pad ink extracted from a school journal. All of these impressions were generated with a uniform stamp and ink pad throughout the course of a twelve-month duration. In order to conduct an analysis of the ink imprints, Attenuated Total Reflection (ATR) spectroscopy was utilised. The ATR spectra were measured using an FTIR Bruker Alpha P instrument that was equipped with OPUS software and a platinum diamond ATR crystal. The scans were performed throughout the spectral range of 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup>, with a scanning rate of 20 scans per second and a spectral resolution of 8 cm<sup>-1</sup>.

To get the ATR spectra, we ensured that the gauge pressure applied to the stamped section of the paper remained rather constant. Following each scanning process, we diligently employed methanol as a precautionary measure to maintain the pristine condition of the diamond crystal, hence mitigating the risk of any potential contamination. Following that, we implemented techniques such as smoothing, normalisation, and baseline modifications in order to improve the quality of the acquired spectra.

In order to create a dependable reference point, we further performed a calibration analysis by measuring the unmarked section of the paper (referred to as the blank measurement). In the context of this research, our

analysis primarily centred on data obtained from the first measurement, as well as stamp impressions that had undergone ageing for durations of one month, four months, eight months, and one year.

## RESULTS AND DISCUSSION

The analysis results relied on several critical factors, which encompassed Eigenvalues, Scree plots, Squared Cosine values, correlation circles, and biplots. These analytical tools played a pivotal role in interpreting the dataset and extracting insights regarding the underlying patterns and relationships within it.

Eigenvalues serve as a fundamental component of Principal Component Analysis (PCA) and furnish essential information regarding the variance explained by each principal component. In this particular study, it was determined that the Eigenvalues exceeded a threshold of one, thereby satisfying the Kaiser Criteria. This statistical criterion signifies that the chosen principal components hold statistical significance and are suitable for meaningful interpretation of the study's outcomes.

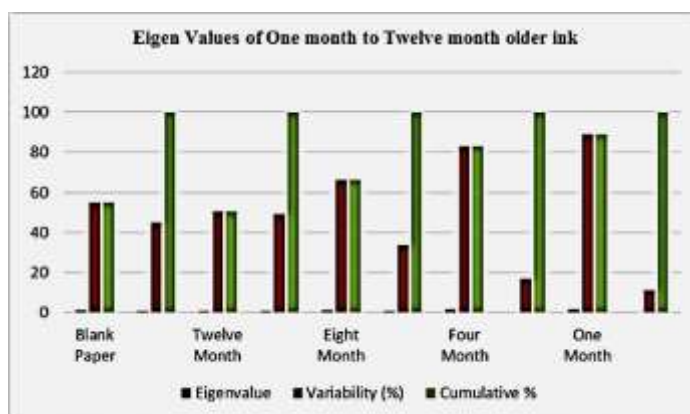


Figure 1: Eigen Values of one month to twelve month older stamp pad ink obtained in chemometrics analysis

In the PCA scatter plot (Figure 2), we observed intriguing patterns concerning the F2 variable, which exhibited a consistent decrease as we transitioned from older to fresher ink samples. This discovery underscores the pivotal role played by the F2 variable in discerning the age of the ink samples and elucidates its substantial contribution to the observed variability. In statistical terms, it accounted for a substantial 60% of the variability in older ink samples and 10% in fresher ink samples. These statistical insights emphasize the significance of the F2 variable in distinguishing between ink sample ages.

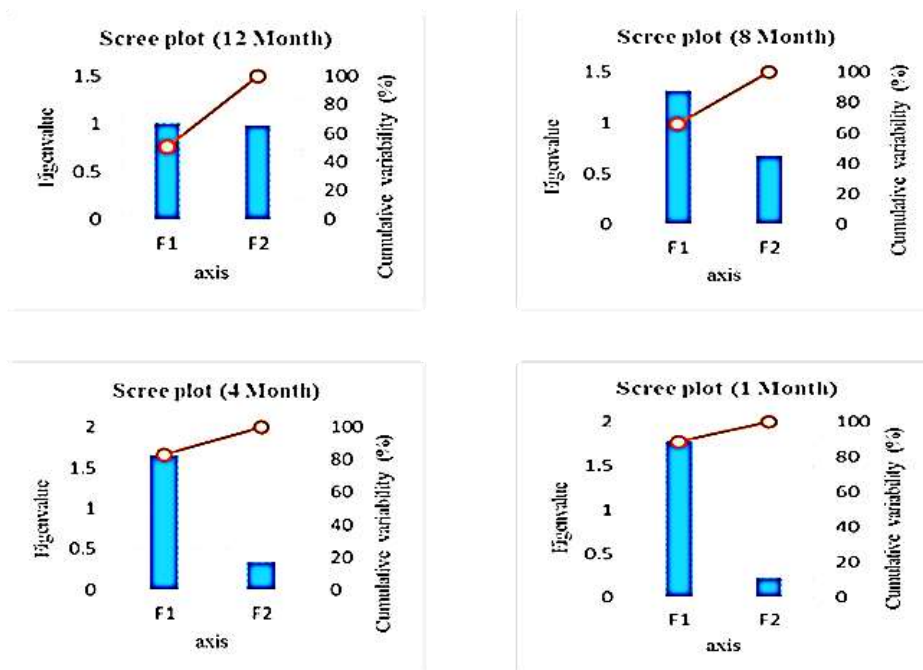


Figure 2- Scree plots various time duration showing decrease in F2 variables from older to fresher ink.

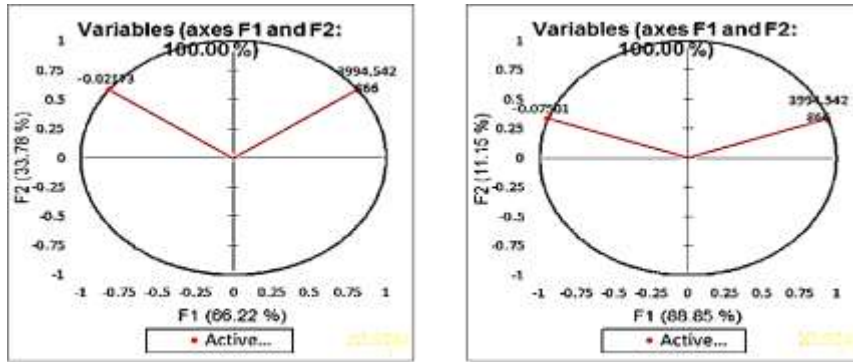


Figure 3- Correlation circle of Twelve Month and One Month older ink.

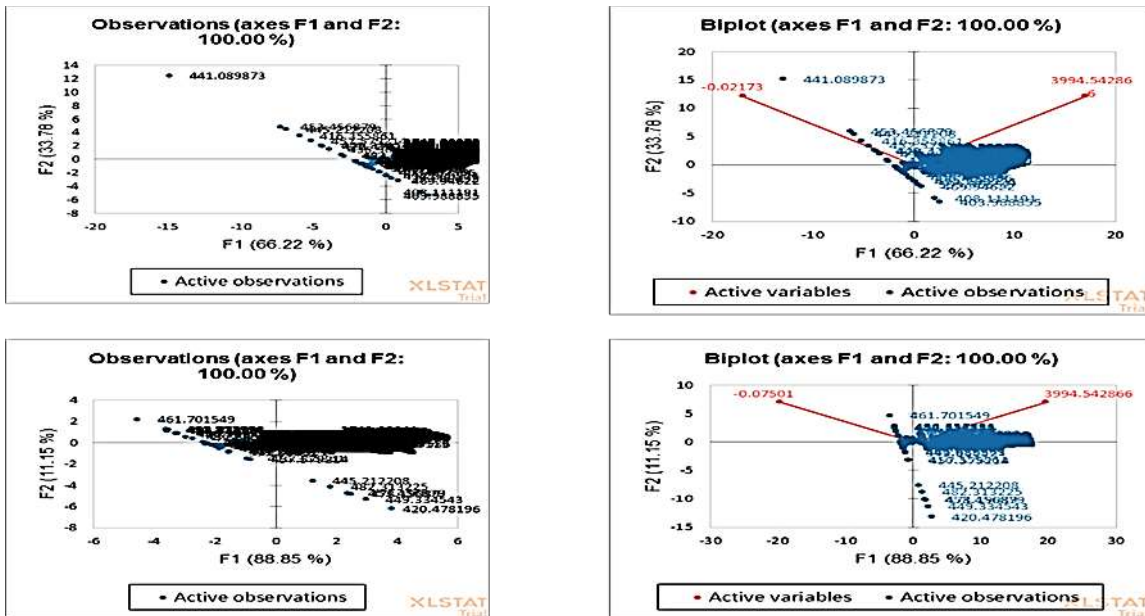


Figure 4- Biplots of 12 months and 01 month older stamp pad ink.

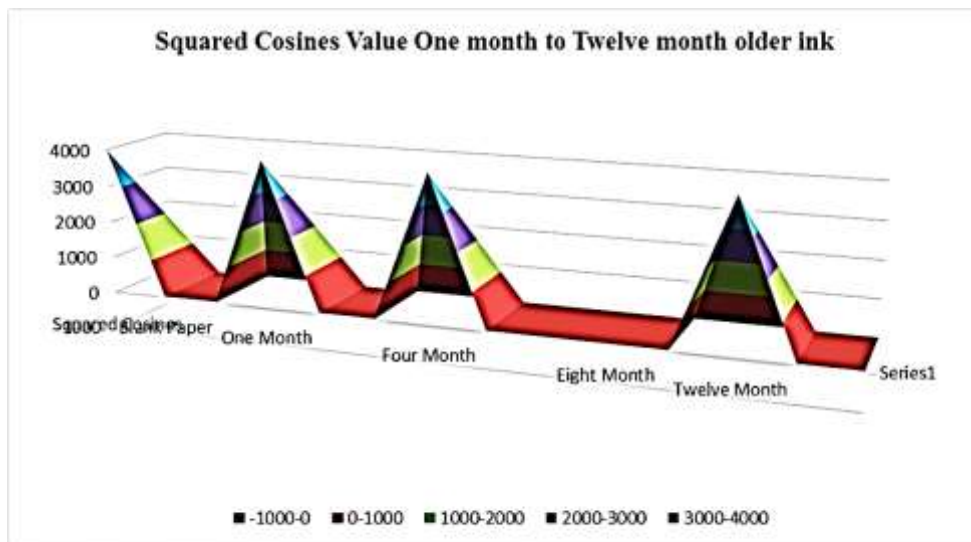


Figure 5- Squared Cosines Value of one month to twelve month older stamp pad ink obtained in chemometrics analysis

Upon further examination of the correlation circle and biplots (Figures 3 and 4), we gained significant insights into how the F1 and F2 axes influence the variability within the ink samples. The F1 axis was observed to explain a substantial proportion of the variability, contributing to 66% in older ink samples and 88.85% in fresher ink samples. Conversely, the F2 axis accounted for 33% and 11.15% of the variability in older and fresher ink

samples, respectively. These statistics underscore the critical roles of both axes in capturing the underlying variance, with F1 playing a more dominant role in fresher ink samples, and F2 being more crucial in older ink samples.

The Squared Cosine values (Figure 5) provided additional statistical insights into the variability of the F1 and F2 variables. These values signify the cosine of the angle between the original variables and the principal components, indicating how well each variable is represented by the principal components. In our study, the Squared Cosine values for the F1 variable decreased from 0.889 in fresh ink to 0.506 in older ink, revealing a diminishing representation of the F1 variable as the ink aged. Conversely, the Squared Cosine values for the F2 variable increased from 0.11 in fresh ink to 0.70 in older ink, indicating a stronger representation of the F2 variable in older ink samples.

Overall, the analytical results provided profound statistical insights into the variability and relationships within the ink samples. Leveraging PCA, alongside Eigenvalues, Scree plots, Squared Cosine values, correlation circles, and biplots, facilitated a comprehensive interpretation of the data. The study emphasized the significant role of the F2 variable in distinguishing between older and fresher ink samples, along with the varying contributions of the F1 and F2 axes to the overall variability in the dataset. These statistical findings significantly enhance our understanding of the ink samples and their characteristics, with potential implications in forensic or historical document analysis.

## CONCLUSION

The chemometric study, which notably utilises scree plots and eigenvalues, constantly highlighted the robust link that exists between the deterioration of stamp pad ink and its ageing length. The results obtained from the Fourier Transform Infrared (FTIR) spectroscopy performed in Attenuated Total Reflection (ATR) mode have presented convincing evidence, confirming the effectiveness and reliability of this non-destructive method in determining the age of a document by analysing the ink used in stamp pads.

Furthermore, the dense grouping of data points found in the biplots provided further evidence to support the dependability and accuracy of the approach. When considering the research as a whole, it becomes evident that the utilisation of FTIR in ATR mode is a highly valuable instrument within the field of forensic document evaluation. This method offers a non-invasive technique for determining the age of stamp pad ink, as well as serving as an efficient tool for identifying any fraudulent modifications made to important papers.

## REFERENCES

- [1] B. L. P. Z. X. G. C. W. Guoliang Ouyang, "Preliminary Studies on the Absorbance Ratio Method Used to Determining the Age of Stamp-pad Ink Seal," *Journal of Forensic Sciences*, vol. 64, no. 4, pp. 1203-1212, 2019.
- [2] X. Y. N. P. M. H. W. W. M. P. X. Z. Shuqiang Lyu, "Spectral heat aging model to estimate the age of seals on painting and calligraphy," *Journal of Cultural Heritage*, vol. 46, pp. 119-130, 2020.
- [3] J. S. J. Y. X. W. F. H. A. Z. Y. L. J. H. M. X. Ya-Tong Yao, "Differentiation and dating of red ink entries of seals on documents by HPLC and GC/MS," *Journal of separation science*, vol. 32, no. 17, pp. 2919-2927, 2009.
- [4] A. A. S. A. E. Y. M. M. A.-S. A. B. A. S. I. M. A. E.A. Samia Ibrahim Shraa, "Physical distinguishable of heterogeneous overlapping resulting from stamp-pad and laser printing inks," *Egyptian Journal of Chemistry*, vol. 62, no. 8, pp. 1391-1412, 2019.
- [5] B. Li., "Dating of Seals Produced with Stamp-Pad Ink Using Gas Chromatography Method," *Journal of Forensic Sciences*, vol. 59, no. 5, pp. 1403-1409, 2014.
- [6] A. K. a. P. K. Małgorzata Król, "Application of MECC-DAD and CZE-MS to examination of color stamp inks for forensic purposes," *Forensic Science International*, vol. 233, no. 1-3, pp. 140-148, 2013.
- [7] J. L. J. F. Y. L. W. Z. R. Chen, "Discrimination of seal inks used for seals by Confocal Raman microscopy," *Pigment & Resin Technology*, vol. 43, no. 6, pp. 389-393, 2014.
- [8] M. R. I. H. Y. A. Enein, "High Performance Liquid Chromatography Determination of Ethylene Glycol in Stamp pad ink," *Toxicological and Environmental Chemistry*, vol. 24, no. 3, pp. 181-184, 1989.
- [9] W. Z. J. F. a. Y. L. Jungang Lv, "Discrimination of red inks in seals by Fourier Transform Infrared Spectroscopy," *Analytical Letters*, vol. 47, no. 8, pp. 1392-1399, 2014.
- [10] A. K. S. S. B. O. P. Jasuja, "Thin Layer Chromatographic Analysis of Indian Stamp Pad Inks," *Forensic Science International*, vol. 42, pp. 255-262, 1989.
- [11] X. L. Zhen Li, "An Examination of Handwritten Signatures Forged Using Photosensitive Signature Stamp," *Forensic Sciences Research*, vol. 6, no. 2, pp. 168-182, 2021.



- [12] B. S. Ali Raza, "Application of Raman spectroscopy in forensic investigation of questioned documents involving stamp inks," *Science & Justice*, vol. 53, no. 3, pp. 332-338, 2013.
- [13] Y. Z. Y. W. J. Y. M. X. X. F. Wang, "Identification and differentiation of the red ink entries of seals on document by laser desorption ionization mass spectrometry," *Forensic Science International*, vol. 236, pp. 99-108, 2014.
- [14] M. M. B. R. P. M. Ashwini Kher, "Classification of Document Papers by Infrared Spectroscopy and Multivariate Statistical Techniques," *Applied Spectroscopy*, vol. 55, no. 9, pp. 1192-1198, 2001.
- [15] S. S. M. M. Ashwini Kher, "Forensic Classification of Paper with Infrared Spectroscopy and Principal Components Analysis," *Journal of Near Infrared Spectroscopy*, vol. 13, no. 4, pp. 225-229, 2005.
- [16] V. K. V. S. R. Kumar, "Fourier transform infrared spectroscopy and chemometrics for the characterization and discrimination of writing/photocopier paper types: Application in forensic document examination," *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, vol. 170, pp. 19-28, 2017.
- [17] W. N. S. M. D. & D. I. Muhammad Naeim Mohamad Asri, "Combined Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA): an efficient chemometric approach in aged gel inks discrimination," *Australian Journal of Forensic Sciences*, vol. 52, pp. 38-59, 2020.
- [18] A. S. V. S. Raj Kumar, "On the spectroscopic cum chemometric approach for differentiation and classification of inkjet, laser and photocopier printed documents," *Science & Justice*, vol. 60, no. 4, pp. 347-357, 2020.
- [19] M. A. Z. A. A. S. V. P. M. A. H. Z. E. Ahmed, "Laser-induced breakdown spectroscopy and chemometric analysis of black toners for forensic applications," *Journal of Chemometrics* 2021;35:e3334., vol. 35, no. 3334, pp. 1-13, 2021.