ATR-FTIR: a chemometric approach to ink and paper discrimination (review)

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INTRODUCTION

Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) is a non-destructive technique used for analysing questioned documents. Fourier transform infrared spectroscopy (FTIR) is one of the most versatile analytical techniques for non-destructive chemical characterisation of documents [1,2,3,4]. This technique makes it possible to identify the functional groups present in the compound being analysed, as each molecular bond (e.g. C-H, O-H, C=O) vibrates at a certain frequency in the infrared (IR) region, which corresponds to a specific peak in the IR absorption spectrum. This technique is often used in conjunction with chemometrics to provide crucial information in forensic investigations.

AIM

The main objective of the present work was to carry out bibliographical research to update information of ATR-FTIR in forensic documents analysis.

BIBLIOGRAPHIC RESEARCH METHODOLOGY

This literature search was carried out in April 2024 using the PubMED and Google Scholar as databases. The keywords used were: 'document', 'pen inks', 'analysis', 'examination', 'FTIR', 'chemometrics'. For the search, a filter was applied which only selected publications from 2018 to 2024, with the articles selected being those which carried out analyses of documents and/or inks by ATR-FTIR and which clearly reported the instrumentation, the conditions used in the method and the power of discrimination. In this way, a total of 5 articles published in the last 5 years were selected, which met the intended selection criteria and whose results are relevant to the topic under study.

RESULTS

Figure 1 – Ink samples

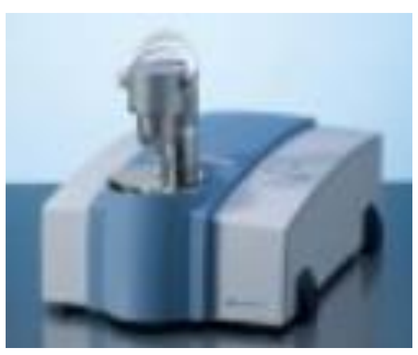

Figure 2– ATR-FTIR equipment

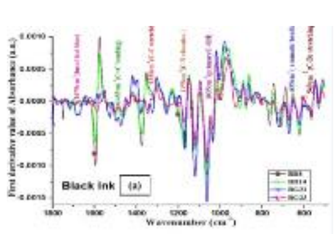

Figure 3 – ATR- FTIR spectra

Table 1 - Main results of the literature review of different ATR-FTIR document analyses.

Samples	Equipment and conditions	Results	Ref.
Paper relics: 15 different types of paper	Spectrometer: Nicolet iS5 (Thermo Scientific) Cristal ATR: Diamond Resolution: 2 cm^{-1} Spectral range: 4000 a 650 cm^{-1} Scans: 16	It was not possible to distinguish the paper by visual analysis due to severe overlapping of the spectra. To optimise the classification results, the following were combined with chemometrics: 100 % (LS-SVM, PLS-LDA), 98.67 % (PCA-LDA), 97.33 % (PLS-DA) and 95.56 % (SIMCA).	[5]
Types of document printing: 15 by inkjet, 15 by laser and 15 by photocopier	Spectrometer: Spectrum Two (Perkin Elmer) Cristal ATR: Diamond Resolution: 4 cm^{-1} Spectral range: 4000 a 400 cm^{-1} Scans: 8	The discrimination of printed documents was obtained by combining HCA and PCA: from HCA a discrimination of 89.19 % was obtained, while with PCA it was 99.90 %.	[6]
Fibre-tip pen inks: 12 black, 12 green, 12 blue, 12 green and 12 blue	Spectrometer: Alpha ART-FTIR (Bruker) Cristal ATR: ZnSe Resolution: 4 cm^{-1} Spectral range: 4000 a 600 cm^{-1} Scans: 24	Visual analysis of the spectra resulted in sample discrimination of 77.20 %, 98.40 %, 96.60 % and 96.60 % for black, red, green and blue fibre-tip pen inks, respectively, while with PCA the percentages rose to 69.75 %, 86.25 %, 97.25 %, 97.25 %, respectively. With the LDA model, the discrimination power for the four different colours was 100 %.	[6]
Stamp inks: 16 brands of blue inks and 12 brands of red inks	Spectrometer: Alpha eco-ATR FT-IR (Bruker) Cristal ATR: ZnSe Resolution: 4 cm^{-1} Spectral range: 4000 a 600 cm^{-1} Scans: 24	In the qualitative or visual analysis, the power of discrimination was calculated at 96.6 % and 93.9 % for blue and red stamp ink samples respectively. In conjunction with the PLS-DA and PCA-LDA models, it tended to be as high as 100 %.	[8]
Thermal papers: 255 papers from 15 different manufacturers and brands	Spectrometer: Spectrum Two (Perkin Elmer) Cristal ATR: Diamond Resolution: 4 cm^{-1} Spectral range: 4000 a 400 cm^{-1} Scans: 16	The power of discrimination was calculated at 83.82 % (HCA) and 95.64 % (PCA) for different thermal papers with different chemical compositions.	[9]

Legend: ZnSe - zinc selenide; SIMCA - soft independent modelling of class analogy; LS-SVM - least squares support vector machine; PLS-LDA - partial least squares linear discriminant analysis; PCA-LDA - principal component analysis linear discriminant analysis; PLS-DA - partial least squares discriminant analysis; HCA - hierarchical cluster analysis; PCA - principal component analysis.

CONCLUSION

The present bibliographical research revealed that application of the ATR-FTIR technique, combined with chemometrics, enabled the classification of different types of pen and stamp inks, as well as distinguishing different types of paper and printing inks. It also showed its association with different statistical methods such as LS-SVM, PLS-LDA, HCA, PCA and LDA, where high discriminatory power was obtained.

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