Review Article

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Chemometric Approaches in Questioned Documents: A Mini Review

Devaseelan S[1], Vrinda J Bhat[2]

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Abstract

Some instances of papers that have been called into doubt include those that have been subject to identity theft, forged signatures or phrases, altered documents, and the forgery of banknotes or other security documents. For concerns involving paper or inks, chemical analysis is necessary, and following instrumental data collection in this field, multivariate analysis, also known as chemometrics, has arisen as a new approach for data evaluation and explanation. The goal of this research is to locate past studies that used forensic motivation to questioned documents using multivariate analysis. During the search, articles were discovered in four databases (Pubmed, Google Scholar, Scopus, and Science Direct). 26 research that have been selected in the last 10 years. There were 34 papers on pen inks, 14 pieces on printed documents, 4 articles on the study of banknotes, and 8 publications on paper. The analytical techniques used to get chemical data included multivariate image analysis, spectroscopy, chromatography, mass spectrometry, and thermo gravimetric analysis. Unsupervised pattern recognition, supervised pattern recognition techniques, and regression methodologies approaches were some of the chemometrics methods investigated. In order to emphasise how crucial it is for forensic professionals to be familiar with these procedures, this study summarised and discussed multivariate analysis techniques employed in a number of questioned document sub-areas. It also includes new research areas that aren't included in this report, such various printing and materials, inks, and security document analysis.

Keywords: Questioned documents; Inks; Paper; Chemometrics; Multivariate Analysis; Forgery.

INTRODUCTION

Analysis of document fraud, including identity theft, forgeries of words or signatures, document changes, and currency or security document fraud, is a significant field in forensic sciences. While physical inspection of disputed documents is often performed, chemical analysis of inks and support material is frequently necessary.[1-3]

The formulations for writing and printing inks are composed of pigments or dyes, resins, solvents, driers and drying oils, extenders, and additives like surfactants, conductive salts, biocides, composite carriers, or adhesion boosters.[4] Writing inks, or water based inks produced of dyes and ethylene glycol, may be found in a variety of writing implements, including ballpoint pens (oil-based inks made of dyes or pigments and organic solvents), felt tip pens, fountain pens, roller ball

Author's Affiliation: [1]Assistant Professor, [2]Professor, Department of Forensic Science, Srinivas University, Mangalore 575002, Karnataka, India.

Correspondence: Devaseelan S, Assistant Professor, Department of Forensic Science, Srinivas University, Mangalore 575002, Karnataka, India.

E-mail: devaseelan.s3@gmail.com

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pens, and gel pens.[4] The most widely used printing inks are toners and inkjets. Depending on the printer, inkjet inks may be UV curable, solvent-based, water based, or phase change; toner inks are dry powders or liquid dispersed powders that are mostly made of pigments and resins.[4]

The pulping and bleaching stages of the papermaking process from wood need the use of chemical agents such as sodium sulphide (Na_2S), sodium hydroxide (NaOH), chlorine monoxide (Cl_2O), calcium carbonate ($CaCO_3$), ozone, or oxygen, as well as metallic oxides. Because of this, each manufacturing batch specific specialised chemicals and cellulose are both present in the final paper products.[1]

Characterization and transformation of inks and sheets are typically needed in forensic analyses of questioned documents for distinction and age estimate, respectively.[2] Additionally, authentic papers and banknotes must be identified from counterfeit ones while dealing with security documents and money. This region has been studied using a variety of analytical techniques.[1,3,5-8] Numerous analytical techniques for chemically examining inks and paper provide enormous amounts of data, making it necessary to quickly and accurately interpret the findings. Chemometrics, also known as multivariate analysis in chemistry, is a statistical method used to analyse chemical data.[9,10] Additionally, it has the ability to arrange and simulate chemical experiments. For a wide range of chemical sample datasets, chemometrics offers accurate classification, discrimination, and model building tests.[11] Due to the fact that statistical and mathematical techniques can be used to supplement and correlate forensic analytical data in a variety of situations other than questioned documents (anthropology, biological, ballistic, toxicology, physical, and chemical sciences), chemometrics is becoming more active in the forensic sciences on a regular basis. In forensic document examinations, chemometrics may help with the interpretation of findings and data presentation even if a variety of analytical procedures are used to investigate inks and papers. Chemometrics is a helpful technique for database research and enhances the objectivity of data analysis in comparison studies. Forensics analysts must be familiar with chemometrics since it is increasingly used in the analysis of disputed documents.[3]

The objective of this study is to examine questioned papers that have undergone multivariate analysis or chemometrics analysis, highlighting their importance in the area. The research projects that utilised chemometrics to analyse contested documents are summarised in this publication, along with a brief overview of the most popular chemometrics techniques. Additionally, it lists the preceding analytical techniques used before the chemometrics analysis as well as the research topics that were most often mentioned in the publications in question. As a result, this study indicates areas and methodologies that might be explored further in the future.

MATERIALS AND METHODS

The phrases "multivariate analysis" and "chemometrics" were searched for in four databases and documents were cross-referenced. Within the previous ten years, the inquiry has taken place (2010-2020). The first search produced 62 publications after reviewing the titles and abstracts from PubMed (70 results; 10 articles chosen), Scopus (21 results; 18 articles chosen), Science Direct (190 results; 16 articles chosen), and Google Scholar (1610 results; 55 articles chosen). The inclusion criteria were satisfied by any study from the questioned documents area that included multivariate or chemometric data analysis. The search was restricted to the publications and questioned papers that detailed these processes. Original articles only in English or Portuguese were considered. 50 articles were selected and categorised by subject after duplicates and review papers were removed (paper, pen inks, printed documents, and banknotes analysis).

We conducted complementary searches on Google Scholar to locate as many articles as we could. The words "pen inks," "banknotes," "printed," "printing," "inkjet," "paper analysis," "toners," "packages," "prints," "packaging," and "stamps" were substituted for the descriptors "multivariate analysis" or "chemometrics" in these searches, and questioned papers were found by searching for specific terms relevant to each topic one at a time. In order to determine if any recent works using chemometric approaches were missing, the citations from the review papers in question[1,3] were examined. A total of 23 studies that employed multivariate analysis or chemometrics were taken into consideration in the area of the questioned papers.

RESULTS AND DISCUSSION

Multivariate analysis and chemometrics investigations took into consideration the four

main subject areas of the questioned papers. There were 34 articles in the ink for pens study field (57 percent from total studies). A total of 16 articles used mass spectrometry, multivariate image analysis, and spectroscopy to study the differentiation of ballpoint pen inks. Four studies used spectroscopy, multivariate image analysis, and mass spectrometry to evaluate various pen types or classes. These articles primarily used spectroscopy techniques to study ballpoint pen ink dating. Four studies examined pen ink that crossed over between ballpoint, gel, and ballpoint and gel pens using spectroscopic and mass spectrometric methods.

There were 14 studies (or 23 percent of all studies) on printed materials and printer inks. Among the papers taken were parcels of food and medicine as well as stamps. The printed inks included toners, inkjets, off-set, and intaglio inks. There were additional experiments with printing inks, sheets, and pen inks that included crossing lines. Although spectroscopic techniques were the most typically employed, mass spectrometry and multivariate image analysis were also examined. There were 8 studies, or 13% of all studies, that used paper analysis. While the other five studies concentrated on predicting paper age, three of them attempted to characterise or discriminate between various kinds of paper. Spectroscopy, analytical pyrolysis coupled with gas chromatography/mass spectrometry, and thermo gravimetric analysis were the most frequently used methods for paper testing. Money was present in the last batch of papers inspected. 7 percent of all studies classified banknotes (mostly Brazilian) and distinguished between genuine and fake ones using spectroscopy techniques, spectrometry, and multivariate image processing.[12]

Prior to the development of multivariate analysis, spectroscopic methods were most often used to extract chemical information from contested documents. Additionally, investigated were x-ray based techniques, thermal gravimetry, chromatography, and mass spectrometry. With a few notable exceptions, the majority of these techniques are non-destructive, which is advantageous when it comes to questioned papers since it preserves the integrity of the document for counterproof.[13] Additionally, Laboratories are able to provide a wide range of document analysis solutions because to the diversity of methodologies. In order to undertake suitable results interpretation and data presentation in reports, forensic professionals, on the other hand, must be acquainted with chemometrics data analysis.

Prior to multivariate analysis, all chemical data produced by analytical procedures (or multivariate image analysis) must be organised into a matrix. Supervised pattern recognition methods include linear discriminant analysis (LDA), partial least squares discriminant analysis (PLS-DA), k-nearest neighbour (kNN), and soft imputation.[14] Unsupervised pattern recognition methods include hierarchical cluster analysis (HCA) and principal component analysis (PCA); b) regression techniques include partial least squares (PLS) and multiple linear regression (MLR); and c) (SVM).[12] There were other methods utilised as well, including multivariate analysis of variance (MANOVA), spectral angle mapper (SAM), multivariate curve resolution with alternating least squares (MCR-ALS), and multivariate curve resolution (MCR).[15]

This research uncovered and summarised a sizable number of papers employing chemometrics approaches in the questioned publications.[16] These researches over the last 10 years have shown a growing trend in the importance of chemometrics in the field. In this instance, it is crucial that specialists in questioned documents know how to perform data analysis and give the findings for forensic use.[17] As a result, our study gave a brief overview of the most popular chemometric techniques that forensic experts should be aware with. The challenge of analysing chemical data for a document examiner scientist was highlighted by Deviterne-Lapeyre.[18] The author emphasised the need of experts comprehending chemometrics theories and ideas in order to appropriately interpret the results.[19]

The bulk of the research presented here classified and/or distinguished samples using chemometrics. While analytical techniques may provide trustworthy inks and paper chemical data for the comparative research, chemometrics analysis can increase the approaches' discriminating ability.[20] To highlight the limitations of the approach, however, intra-variability analysis should be included as an aim in research publications. Another crucial use of chemometrics in the sphere of questioned documents is the creation of databases[21], notably for sample identification, such as pen or paper brands. Chemometrics based study on the disputed papers may be useful in this particular situation. Until total standardisation is established, chemical document dating will remain a research topic.[22] Chemical document dating will continue to be a study topic until full standardisation is reached. A

few papers employed chemometrics to analyse the ageing of pen inks[23, 24] and paper.[25,26]

Chemometric techniques for ballpoint pen inks are often the subject matter that has received the greatest investigation in the articles that have been subjected to review. Although many different kinds of pen inks, printing inks, papers, and banknotes have been studied, these subjects have not yet been thoroughly researched. More study using various analytical techniques and chemometrics data processing is required.

CONCLUSION

This study compiled a sizable number of studies that used chemometrics to the domain of the in-question documents, giving a brief summary of the most often applied chemometrics approaches. These studies show the use of various analytical techniques in the investigation of writing instruments, printed materials, paper, and money. Regression methods, unsupervised and supervised pattern recognition techniques were used to analyse data in forensic science for a variety of purposes, including sample discrimination and classification, ageing estimation, establishing the chronological order of crossing lines, and identifying fake currency. These studies highlight the significance of chemometrics in contested documents, and forensic expert training need to include this information. Chemometric methodology for database building and implementation, inks and paper ageing studies, and innovative analytical methods for banknotes, non-ballpoint pen inks, other security papers, paper, and printing inks are all fascinating research topics for questioned documents.

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