Application of Spectral Methods for Identification of Constituents of Documents

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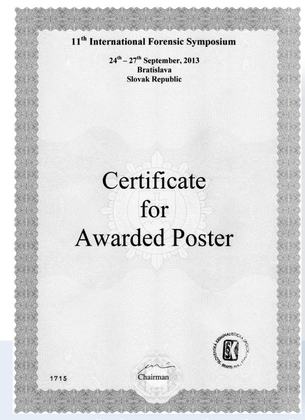
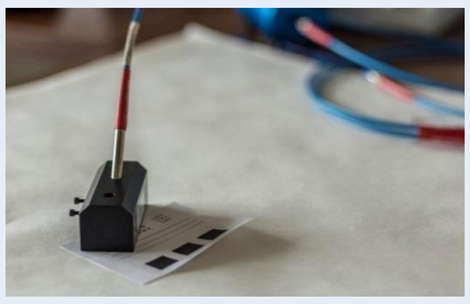


Introduction

The poster is a presentation of the results achieved in the framework of the applied research in the area of spectroscopic diagnostic of documents. The aim of the project is development of the methods of examination and evaluation of properties of documents and their constituents from the point of view of forensic analysis based on molecular spectroscopy in the IR, UV-VIS-NIR regions, Raman spectroscopy and x-ray fluorescence spectroscopy. The results of the analysis and identification of different kinds of paper substrates and writing and printing means - ballpoint pens, ink pens and gel pens, tonners of laser printers and inks of inkjet printers – obtained from model databases developed on the basis of survey of practical using of these writing means in the area of Slovakia are presented.

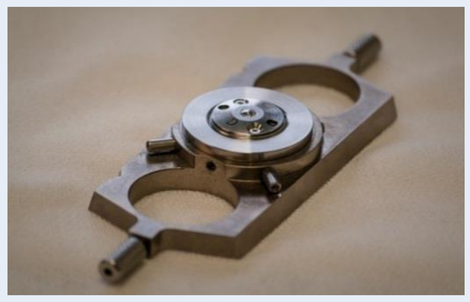
Experimental

UV-VIS-NIR spectroscopy



Fibre optics spectrophotometer system Ocean Optics, UV-VIS-NIR light source DH-2000-BAL

FTIR spectroscopy and μFTIR spectroscopy



FTIR spectrophotometer EXCALIBUR series, FTS 3000 MX (DIGILAB, USA)
μFTIR Varian 610-3R Series, FT-IR Microscope

XRF spectroscopy

XRF spectrometer X-MET5100, Oxford Instruments

Raman spectroscopy

Raman spectrometer JobinYvon Labram 300 with He-Ne laser (633 nm)

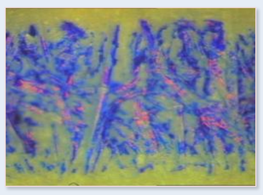
Results

Paper underlay

9 samples of different kinds graphic office papers

Based on the analysis of FT-IR spectra of paper samples was specified characteristic region of the spectrum, suitable for identification differences between the studied samples of office paper. It is a region of wave numbers between 1215-1562 cm^{-1}, where are located absorption bands pertaining to calcium carbonate, the filler being introduced into sheets of tested paper. Subsequent application of statistical methods to evaluate the measured absorbance values for this region was suitable to determine variability in the filler content for the individual sheets (back and front), for each sheet in the package and the packages representing the various types of paper, which were evaluated by comparing each other.

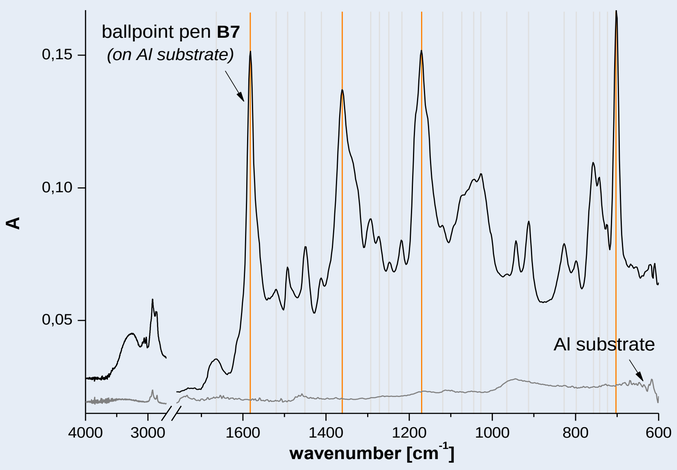
Variance of values A for different types of paper



Writing means

19 model samples of different kinds blue pens ballpoint (B), roller ball (R) and gel pens (G)

Combination of FTIR and Raman spectroscopy proved to be a useful tool in the analysis of the writing means. In examination of writing means by FTIR spectroscopy the measurement at least on three different positions is recommended. For measurement of spectra of solid areas the method of conventional ATR-FTIR (diamond crystal) is adequate, for measurement of spectra of lines micro-FTIR-ATR method using diamond and germanium tip is more suitable. Subtraction of spectra of substrate from spectra of writing means on substrate is feasible; however, the spectrum of substrate should be taken in closest proximity of the line.



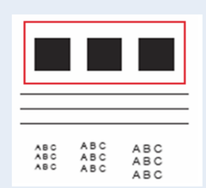
FTIR spectrum of ballpoint pen B7, measured on aluminium substrate

Watermarks

12 samples of original chemical watermarked paper sheets, true watermark and 4 laboratory counterfeits of watermark

This work was focused on detection of possible counterfeited chemical watermarks, created in laboratory conditions by using FT-IR spectroscopy. FT-IR method was used to observe selected paper samples containing real paper watermark and samples containing genuine chemical and laboratory counterfeited chemical watermarks.

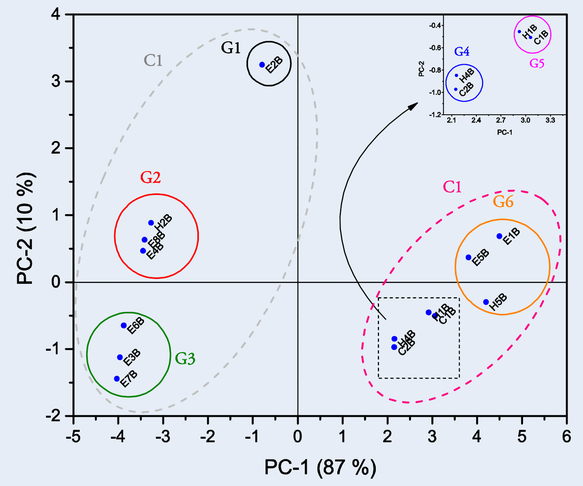
By this method it is possible to obtain evidence of the functional groups of different translucentizing agents present in the sample, which showed characteristic absorption bands on infrared spectrum. With these, it is possible to identify a specific part, a substance used to create the watermark, respectively distinguish an original print from a liquid substance used to imitate it. It also proved possibility to determine differences in their absorption spectra, whether in the case of real paper watermarks or genuine and counterfeited chemical watermarks, and ultimately to confirm the authenticity or falsity of subjects. FTIR method is suitable to distinguish between genuine chemical watermark and its imitations by comparison of specific shapes of spectra.



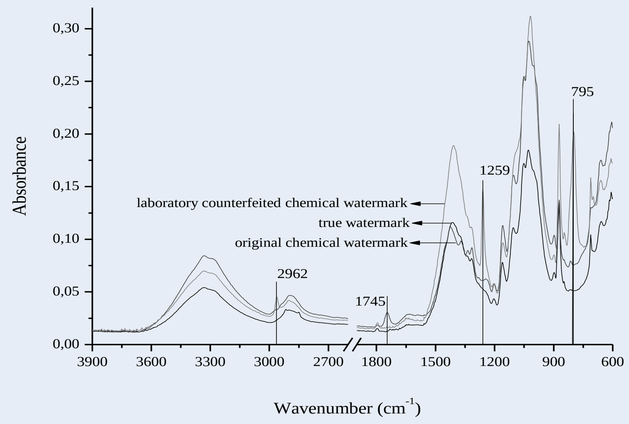
Laser and inkjet prints

The model target consisting of solid areas and lines corresponding to the thickness of the font size 8, 10 and 12 points

UV-Vis spectra of inkjet prints obtained from solid surfaces of model targets have been subjected to Principal Component Analysis (PCA). Figure shows a scatter diagram of the component scores for principal components PC-1 and PC-2. The samples can be divided into the clusters. Objects lying in a given cluster, are similar and simultaneously not similar with samples in the other clusters. The clumps lying close to each other are similar relatively. Based on the score values of the first principal component, which explains 87% of data variability, the printouts can be divided into the two groups (C1 and C2). Together with the other principal component of PC-2, describing 10% of the variance of data, it is possible to divide the sample into the six clusters (G1-G6).



The scatter diagram of the component scores for principal components PC-1 and PC-2



FT-IR spectrum of the real watermark, original chemical watermark and the laboratory counterfeit

Conclusions

The method of recognition of different sheets of printing papers in multi-sheets document based on FTIR spectra and statistical processing of the obtained spectra using method of Analysis of Variance (ANOVA) was developed. It was found, that the type of used filler, the content of the filler and two-sidedness of the sheet are the significant factors influencing the identification of differences of individual sheets of paper. The suitability of different techniques of measurement of FTIR spectra of writing and printing means – ATR-FTIR, micro-FTIR with tips of different materials (diamond, germanium) for study of composition of writing and printing means in solid areas as well as thin lines was experimentally examined. It was shown that the methods of SERS and XRF and their combination with FTIR can be utilized in identification of blue writing means. The spectra of inkjet inks on paper in the VIS-NIR region obtained using Fiber Optics Reflection Spectroscopy (FORS) were analyzed by multivariate statistical method Principal Component Analysis (PCA). This method allows create cluster structure of the spectra of reference set and then test whether the examined spectrum corresponds with one of these clusters. The spectral methods of examination of chemical water marks applied on safety and printing papers were studied and experimentally verified. The database of compounds used in production of chemical water marks was collected. This database is continually upgraded and supplemented.

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