J2 The Use of Attenuated Total Reflectance Fourier Transform Infrared Spectrometry (ATR-FTIR) in the Analysis of Paper

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After attending this presentation, attendees will understand the potential for the use of the Attenuated Total Reflectance Fourier Transform Infrared Spectrometry (ATR-FTIR) spectrometer in the field of forensic science in discriminating different brands of white multi-use and copier paper. Attendees will also understand the use of principal component analysis (PCA), hierarchal cluster analysis (HCA), and discriminant analysis (DA) in analyzing infrared spectra.

This presentation will impact the forensic science community by introducing questioned document examiners and other forensic scientists to the power of ART-FTIR combined with multivariate statistical methods such as principal component analysis and linear discriminant analysis.

Determining the sources of sheets of paper can facilitate in cases involving fraudulent documents, threatening letters, ransom notes, and other cases of questioned documents. A number of methods have been applied to the analysis and comparison of paper samples, including transmitted light imaging, laser speckle imaging, light microscopy, scanning electron microscopy, X-ray diffraction, pyrolysis-gas chromatography, Raman spectroscopy, ultraviolet-visible-near infrared spectrometry, FTIR, and ATR-FTIR. Some of these methods require the destruction or significant alteration of the sample examined. Some of the methods are also lengthy and time-consuming. ATR-FTIR has many attributes that commend its use for the analysis of paper: it is non-destructive; it can analyze small areas (thus avoiding areas of paper which bear printing or writing); it requires virtually no sample preparation; and, it is very fast (individual spectra being obtained in under one minute). Moreover, ATR-FTIR instruments are becoming more widely available in forensic science laboratories.

ATR-FTIR has been applied in the past to paper pulps and to a limited number of finished papers. This study involved the analysis of ten reams of white multi-use and copier paper, representing seven different brands. The brands of paper were ones that are widely available in office supply stores, big-box department stores, and online. These brands are those that would be encountered in many offices and homes, in use as computer printer paper, copy paper, or stationery. Such papers consist of cellulose, often with fillers such as calcium carbonate, sizing agents such as starch, and optical brighteners (fluorescent compounds that contribute to the whiteness of sheets of paper). All of these components have infrared absorptions in the range $600cm^{-1}$ to $4000cm^{-1}$. Samples taken from each ream included the top five, middle five, and bottom five sheets. Each paper sample was pressed against the ATR crystal of the FTIR spectrometer and a spectrum was scanned. The spectra obtained from this procedure were then converted to/from percent transmittance units and absorbance units. Only the infrared region from $600cm^{-1}$ to $1800cm^{-1}$ showed significant absorption peaks; therefore, only this region was analyzed further. Some of the infrared spectra displayed anomalous baseline offsets. To deal with these, all of the spectra in the $600cm^{-1}$ to $1800cm^{-1}$ range were smoothed and then converted to first derivative spectra using the Savitsky-Golay method. The first derivative spectra from $604cm^{-1}$ to $1300cm^{-1}$ were analyzed using principal component analysis (PCA), hierarchal cluster analysis (HCA), and discriminant analysis (DA). Features of interest in the first derivative spectra were confined to this spectral range.

It was observed that there the infrared spectra displayed a high degree of consistency within a ream of paper. In PCA eight factors were required to account for more than 90% of the variance in the data. The factor plot of the first two extracted factors indicated that the ten reams of paper could be placed in four groups: a group of seven and three groups of one each. DA using the first eight extracted factors and these four groups resulted in 94.3% correct classification of the infrared spectra and 93.8% correct classification on cross-validation. Two paper brands could be differentiated from the others and two different grades of paper belonging to the same brand could be differentiated from each other. While ATR-FTIR proved not be highly discriminating among paper brands, the simplicity of the technique, its non-destructive nature, and the increasing availability of ATR-FTIR instruments make this technique a useful addition to the methods of paper analysis.

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