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An investigation into the use of calculating the first derivative of absorbance spectra as a tool for forensic fibre analysis

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Abstract

A range of fibre samples was measured using J&M MSP400 and J&M MSP800 microspectrophotometers across the visible and UV/visible wavelength ranges respectively. The first derivative of the absorbance spectra was then calculated and studied. When the absorbance spectra produced for some samples were broad and featureless, the first derivative spectra provided more points of comparison that facilitated discrimination. For many of the samples, calculating the first derivative did not result in any additional discrimination due to the high number of points of comparison present in the absorbance spectra. However, for the samples that exhibited a high level of intra-sample colour variation (e.g. through uneven dye uptake common in cotton and wool, etc.), which was evident in the absorbance spectra, the associated first derivative spectra highlighted this variation between the fibres and could potentially have resulted in false exclusions. The results show that whilst calculating first derivative can be a useful aid in the comparison of spectra, a high degree of caution is required when applying this method to fibres which exhibit a large intra-sample variation in colour.

Keywords: First derivative; Fibres; Microspectrophotometry; Spectra; Comparison

1. Introduction

Since microspectrophotometry has been used as part of the analysis of coloured textile fibres in forensic fibre examination, the results have been generated in the form of transmission and absorbance spectra. Comparison of spectra routinely involves overlaying these to determine whether they match with respect to peak positions and general spectral shape.

Absorbance spectra that have multiple points of identification, comprising peaks, troughs and shoulders, can be successfully compared using this method. However, when an absorbance spectrum has little detail (e.g. only a single broad peak such as that obtained from an almost opaque fibre), this method is more problematic and less discriminating.

This study aimed to identify whether calculating the first derivative of absorbance spectra could provide a means of additional discrimination for fibre comparison and to determine under what circumstances it could be most effectively employed.

Derivative spectroscopy provides a means for presenting spectral data in a potentially more useful form than the zero order, untreated data. The technique has been used for many years in branches of analytical spectroscopy such as finding the end point for titration plots. Derivative spectra are usually obtained by differentiating the recorded signal with respect to wavelength as the spectrum is scanned. First, second and higher derivatives can now easily be generated using the software supplied with currently available instrumentation.

Analytical applications of derivative spectroscopy are numerous and generally owe their popularity to the apparent higher resolution of the differential data compared to the original spectrum. This can result in broad, apparently featureless peaks in the original spectrum being resolved to show distinct, measurable components. To date this technique has not been widely employed in the field of forensic fibre analysis and comparison and this is reflected in the limited amount of published data [1,2].

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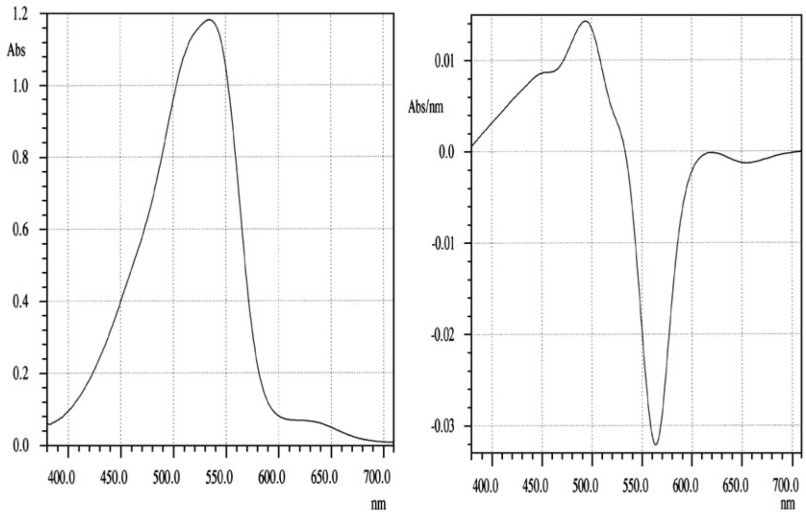

Fig. 1. Absorbance spectrum (left) and associated first derivative spectrum (right) of a red acrylic fibre.

Fig. 1 shows a visible wavelength range microspectrophotometry spectrum measured from a red acrylic fibre. The original absorbance plotted against wavelength spectrum shows a peak maximum at around 535 nm. This is the point at which there is no change in the peak gradient, and as such, this point appears at zero on the first derivative plot. Also, a subtle shoulder on the leading edge of the original peak at around 450 nm is displayed as a more distinctive feature on the first derivative plot, thus providing an aid to comparison.

Various mathematical procedures may be employed to differentiate spectral data. When data is recorded at evenly spaced intervals along the wavelength (λ), or other x-axis, the simplest method to produce the first derivative spectrum is by calculating the difference between two points, i and $i+1$.

$$\frac{\partial y}{\partial \lambda} = \frac{y_{i+1} - y_i}{\lambda_{i+1} - \lambda_i}$$

where y represents the spectral intensity.

A first derivative spectrum is produced when the results of such a calculation are plotted. This can emphasise differences between spectra, but will also enhance any noise present in the original spectrum. Subsequently, this can result in a noisy first derivative spectrum which will be difficult to interpret. Due to this observation, a polynomial line of best fit is plotted over a selected number of data points, to smooth the data before it is differentiated. This process is applied to all the data in steps until the entire spectrum has been processed. This was first used by Savitzky and Golay [3] based on the following equation:

$$\frac{\partial y}{\partial \lambda} = \frac{1}{10\Delta\lambda}(-2y_{i-2} - y_{i-1} + y_{i+1} + 2y_{i+2})$$

2. Experimental

2.1. Samples

A range of fibre types and colours reflecting those commonly encountered in casework, were used in this study.

Man-made fibre samples

- Red acrylic
- Orange polyester,
- Black polyester,
- Blue nylon,
- Blue “tigertail” acrylic,
- Blue polyester.

Natural fibre samples

- Dark grey lambswool,
- Yellow cashmere,
- Black cotton,
- Pink wool.

Dye batch fibre samples

- Brown acrylic (10 batches),
- Red acrylic (7 batches),
- Red acrylic (9 batches),
- Navy blue acrylic (10 batches).

2.2. Equipment

The microspectrophotometry was performed using two different instruments, both using Spectralys v1.82 software. One instrument – the J&M MSP400 microspectrophotometer – measured across the visible wavelength range (380–710 nm); the second instrument – the J&M MSP800 microspectrophotometer – measured across the UV/Visible wavelength range (250–710 nm). All measuring parameters used are given in Table 1.

3. Method

The Spectralys v1.82 software has the capability to calculate the first (and second) derivative of spectra (absorbance or transmittance) using the Savitzky–Golay smoothing algorithm