

Application of Raman spectroscopy to forensic fibre cases[☆]

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Abstract

Five forensic fibre cases in which Raman spectroscopy proved to be a good complementary method for microspectrophotometry (MSP) are described. Absorption spectra in the visible range are indeed sometimes characteristic of a certain dye but this one can be subsequently identified unambiguously by Raman spectroscopy using a spectral library. In other cases the comparison of Raman spectra of reference fibres and suspect fibres led to an improvement of the discrimination power. The Raman measurements have been performed directly on mounted fibres and the spectra showed only little interference from the mounting resin and glass. Raman spectroscopy is therefore a powerful method that can be applied in routine fibre analysis following optical microscopy and MSP measurements.

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1. Introduction

In general, since Raman and infrared spectroscopies are based on vibrational modes, they are regarded as complementary methods. However, the fundamental processes behind these two techniques are completely different, the former being a scattering process while the latter is a pure absorption phenomenon. The spectroscopic selection rules for infrared and Raman activities are then different so both methods produce complementary vibrational data.

Forensic scientists are mainly interested in fast non-destructive, selective and sensitive examination methods. Raman spectroscopy already proved to be a promising technique in diverse areas of forensic science. For instance, it has been used for the examination of paint chips [1,2], inks [3,4], drugs [5,6], condom lubricants [7] and in the detection of anthrax residues [8].

Concerning forensic fibre examination, infrared spectroscopy is mainly used to determine the polymeric composition of

synthetic fibres, providing a generic fibre class and subclass. Usually no dyes are detected using infrared since the dye content of a fibre is in most cases lower than 5% in weight. On the other hand, for dyed fibres, Raman spectroscopy provides information mainly about the dyes due to enhancement by resonance [9–11]. Therefore it can be considered as a complementary technique to microspectrophotometry (MSP) in the visible and UV regions which is characteristic of the electronic absorption of the dye molecules.

The purpose of this paper is to highlight the added value of Raman spectroscopy in the field of forensic fibre examination and its operational implementation. This technique is really efficient in the discrimination of dyed fibres and to complete the fibre characterization sequence. Raman spectroscopy has been used by one of the authors for more than 40 years in research, both as a quantitative and qualitative method. The close cooperation between an analytical research laboratory and a forensic fibre laboratory resulted in Raman being included as a standard method for fibre examination. In addition to fundamental research, everyday casework samples are also a good way of evaluating Raman spectroscopy, since it is able to measure very different chemical dye classes on different fibre types. These samples also introduce questions about the sampling methods, the conditioning and obviously the order of Raman analysis in the fibre examination sequence.

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In this paper, the authors wish to report on some Raman and MSP results from fibre casework. The results confirmed the value of Raman spectroscopy as a powerful tool to forensic fibre examination. Measurements could be performed directly on mounted fibres without encountering much interference from the mounting medium or the cover glass. The initial routine results obtained from MSP were confirmed by Raman spectroscopy but this latter technique, since it provides a much more detailed dye spectrum, is likely to be more specific and allows identification with a higher degree of confidence.

2. Experimental method

2.1. General approach

All fibres were collected using the tape lifting method. The tapings were subsequently examined with low power microscopy in order to select crime relevant fibres or fibre tufts.

Those fibres were removed from the tapings and mounted on standard glass slides and cover slips for microscopy using a synthetic mounting resin (Histomount™, National Diagnostics). In some cases, *in situ* measurements were also carried out on non-mounted fibres. A tuft of these fibres was simply placed on a glass slide and single fibres were stretched and fixed at the extremities using regular scotch tape.

High power microscopy ($\times 400$) was then used to perform a first discrimination on the basis of morphology, colour, polarization and fluorescence of the fibres. Corresponding fibres were submitted to microspectrophotometry in the visible range (MSP Vis) and other methods to obtain information about the fibre dyes and the chemical fibre composition for man-made fibres. Raman spectroscopy was used for gathering information about the dye structure, for comparing references to fibre traces and for examining fibre collectives, comparing the Raman spectra with each other.

2.2. Raman spectroscopy

All Raman spectra were recorded using a LabRam spectrometer (Jobin–Yvon) coupled to an Olympus confocal microscope (a $\times 20$ objective lens was used for simultaneous illumination and collection) and a nitrogen-cooled Open Electrode 1024×256 CCD detector. The excitation wavelength was in all cases 514.5 nm (Spectra Physics argon-ion laser). The laser power at the sample was usually kept as low as 0.5 mW and, in some cases, was gradually raised to 10 mW in order to improve the Raman signal. Care was however taken not to alter the dye on the analyzed fibre, otherwise a sudden increase of a broad band at 1600 cm^{-1} indicates thermal decomposition.

Integration times ranged from a few seconds to a few minutes, depending on the sample. The positioning was performed by viewing the image of the sample using the CCD camera attached to the microscope. The laser beam was subsequently focused on the selected position, producing a spot of about $3\text{ }\mu\text{m}$ diameter.

Most Raman measurements in casework were performed directly on dyed fibres mounted with resin on standard glass

slides and cover slips. In some cases measurements were also carried out on non-mounted fibres.

Computer treatment of the spectral data was performed using home-made software. All spectra were baseline corrected in order to remove any fluorescence background using an algorithm based on a polynomial regression model.

When necessary, the spectrum of the mounting resin, obtained on a position next to the fibre, was quantitatively subtracted from the spectrum of the analyzed fibre. In order to keep the integrity of the data, no smoothing of the spectra was ever performed.

2.3. Microspectrophotometry

Absorption spectra were collected in the visible range between 380 and 800 nm using a Tidas 800 microspectrophotometer (J&M) coupled to a Zeiss microscope (Axioplan 2) and a diode array detector (type MCS 1024, range 190–1020 nm). Absorption spectra of dyed fibres were typically recorded using an integration time of 350 ms and 5 accumulations. The measurements were performed directly on the mounted fibres at a magnification of $400\times$ through an area of $5 \times 30\text{ }\mu\text{m}$. Reference data were taken just next to the mounted fibre (obtaining the spectrum of the W-halogen source) and were directly followed by measurements of the sample data on the fibre.

The acquisition of spectra was done using TidasDaq software and the raw data were exported as CSV files. No smoothing of spectra, nor baseline correction were ever performed. Most absorption spectra of dyed fibres show a large variability in intensities due to differences in fibre thickness and to uneven dye uptake for natural fibres. Ten spectra of references (known fibre samples) were typically recorded for natural fibres and five for man-made fibres. The spectra from fibre traces (unknown samples) were checked in terms of absorption profile and of belonging to the variability range of the reference spectra. For sake of clarity, the figures of reference fibres show only three spectra: the middle one is representative of the average recording and the others correspond respectively to the least and most intense recorded spectra. The figures of unknown fibres let only appear the least and most intense spectra for each trace.

3. Results from casework

3.1. Case 1

In a murder case an examination of fibres found on the stabbed victim was performed. Brown cotton was identified as a target fibre. Some 1500 individual fibres and a couple of fibre tufts were present on the victim. Bright field, fluorescence microscopy and MSP measurements in the visible range performed on some of these fibres suggested they come from a same fibre source. A suspect admitted the murder but claimed it to be the result of self defence. Confronted with the fibre results, he indicated that the source of these brown cotton fibres was a brown jacket which has been thrown away. A cap recovered on the crime scene which, according to the suspect, did not belong to him was then examined. Lots of extraneous brown cotton fibres were retrieved on this cap. These were similar to the target fibres found on the

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