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PRAXIS—combined μ-Raman and μ-XRF spectrometers in the examination of forensic samples

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Abstract

Recently, two analytical techniques – Raman and XRF spectroscopy – have been often applied in criminalistic examinations of different kinds of trace evidences. In this paper, the application of the new combined μ-Raman and μ-XRF spectrometer in analysis of multilayer paint chips, modern inks, plastics and fibres was evaluated. It was ascertained that the apparatus possesses real advantages and could be helpful in the identification of examined materials after some modifications, i.e. by adding an extra laser and decreasing the spot size of the X-ray beam.

Keywords: Forensic analysis; Paint; Ink; Fibre; Raman spectrometry; XRF

1. Introduction

Physicochemical investigations of such criminalistic traces as paint samples (microchips, attrition on fabric), inks (in documents) and fibres are especially difficult. The reason is that the samples are often very small (thin) and, in addition, it is not usually possible to separate them entirely from the base. The preferred analytical tool in such cases is microtechniques that are non-destructive of the examined samples and may be used *in situ*.

In routine examinations of inks, non-destructive analytical methods, such as microscopic and optical ones, are primarily applied [1,2]. These methods allow chosen parameters of the ink to be characterized, such as its colour, luminescence and absorption of radiation. Samples may be differentiated on the basis of transmission, reflection and fluorescence spectra obtained for inks deposited on the surface of paper. However, in order to identify the ink, it is necessary to determine its kind and composition, using methods of chemical analysis. Among these methods, thin-layer chromatography, IR and capillary electrophoresis are applied most often [3–8]. They are simple to use, require only a small amount of sample for examination, and at the same time they are characterised by a high degree of selectivity and repeatability of results, but isolation of the sample from the substrate of the document (i.e. the paper) by means of solvent extraction is necessary, which leads to at least some damage to the examined document. So, Raman spectroscopy, due to its non-destructive nature, has been recently applied by forensic experts to differentiate of inks directly on documents [9–12]. Elemental content has not been taken into consideration during routine ink examination up till now, although it could certainly help in identification of ink pigments/dyes and in differentiation between examined ink samples. The fingerprint model was recently developed in order to discriminate between different iron-gall inks used in the production of historical manuscripts by means of micro XRF analysis which takes interference from the paper background and diffusion of the ink into the paper into account [27]. The modern inks do not include iron, but often contain very similar set of various elements. The observed differences between them are rather quantitative except so called security inks which are marked by lanthanides and could be easily differentiated.

Forensic analysis of paint samples usually encompasses optical microscope analysis, enabling definition of the layer structure of the paint sample (establishing the number of paint layers visible in a cross section of the sample, defining their colour, thickness and granulation) as well as spectrometric

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analysis (by FTIR, SEM-EDX or μ-XRF) enabling analysis of the chemical composition of particular layers in examined paint coat fragments on the basis of obtained spectra [13–16]. The above methods are frequently supplemented with microspectrophotometry in the UV/vis range, allowing objective determination of the colour of particular layers, and with the pyrolytic-GC/MS method, used for a detailed analysis of the paint binder composition [17,18]. Raman spectroscopy is also occasionally used as a method that provides information about pigments [20,23]. XRF yields elemental data of a very small paint sample which often enables identification of pigments and fillers. However, the X-ray beam diameter is typically not small enough to perform cross-sectional analyses. When multiple-layered chips are analysed in bulk, the obtained spectra represent the elements present in many layers of the specimen and not just one [29].

In the examination of other polymer materials like fibres and plastics, microscopic techniques supplemented by infrared spectroscopy yield results which are helpful in criminalistic identification. The morphological structure of the fibre, its colour, its appearance in polarised light and fluorescence in UV/vis are sometimes sufficient to identify and differentiate it from other fibres. Establishing the polymer composition is not problematic; however, identification of the dyes and pigments used requires extraction by solvents and application of chromatographic methods (TLC). Hence, interest in the Raman spectrometry method as a non-destructive method enabling study of the fibre *in situ* is growing [24,25].

Similarly in samples of plastics, the polymer content can be determined by IR spectrometry, but pigments and dyes cannot be identified due to their low concentration. Information about elemental composition obtained by the use of X-ray spectrometry can be helpful in defining the type of pigments used.

It has been shown that Raman spectroscopy has real potential as an analytical tool for forensic examinations of traces [19,20–23]. However, certain drawbacks of this technique can sometimes make meaningful spectrum analysis difficult. These difficulties are mainly linked to the intense background signal attributed to fluorescence effects, and sample heating leading to thermal degradation or even pyrolysis or photochemical reactions. Strong fluorescence produced by paint components may overwhelm the weaker Raman scattering peaks. In the face of these difficulties, information gained by the Raman spectrometry method should be supplemented by other analytical data, e.g. obtained by the XRF method.

X-ray fluorescence spectrometry as an analytical technique which non-destructively examines the elemental contents of a small sample and provides information about pigments and fillers, is more sensitive to higher atomic weight elements than SEM/EDX. Nevertheless the depth of X-ray penetration as well as the beam diameter influence on results obtained for multilayer materials. However, the recently applied TXRF technique is useful in layer profiling of paint samples and laminates. Additionally by the use of synchotron light source, the detection limits can be as low as fg level [26,28].

Table 1
Experimental samples of car paint

Model	Colour	Number of layers
Opel	Grey	4
Opel	White	7
Dewoo	White	4
Renault	Black	4
Fiat	Yellow	7
Renault	Yellow	5
Lada	Green	5
Dewoo	Green	4
Fiat	Red	4
Fiat	Red	5

The aim of this work was to assess the usefulness of the combination of μ-Raman and μ-XRF spectroscopy found in the PRAXIS apparatus, made within the European project,[1] in analysis of multilayer paint chips, modern inks and fibres. The application of two non-destructive analysis methods in one instruments seems to be very useful for the investigation of such criminalistic traces.

2. Materials and methods

Measurements were performed using a PRAXIS prototype—a combined μ-XRF and μ-Raman spectrometer which enables the determination of all elements heavier than Mg ($Z = 12$) with the help of X-ray fluorescence and additionally the analysis of complex molecules by Raman spectroscopy. The apparatus consists of two parts, i.e. a Raman spectrometer (Jobin Yvon, France) with 633 nm laser excitation and a fibre optic connection of the measuring head to the spectrometer, resolution approximately 3 cm^{-1} and also an energy dispersive micro-beam X-ray fluorescence spectrometer (IFG, Germany) with a fine focus X-ray tube (max. 50 kV, 30 W), a polycapillary optics with spot size of approximately 30 μm and a drift chamber detector with a sensitive area of 5 mm^2 with energy resolution of $<$140 eV. It enables analysis by means of two techniques which are normally used in identification of the kind of pigments and dyes in different materials creating traces on the scene of crime. Four groups of pigmented materials were chosen for examinations.

Ten fragments of multilayer automobile paint coats originating from street sample collection (Table 1), composed of 4–7 paint layers of similar/different colour and of which the individual layer thickness varies between 10 and 100 μm, were chosen for examination. A fragment of paint coat was embedded in appropriate resin (Technovit 2000LC) and after removing the top layer of the preparation with the use of a microtome, a smooth cross-section of paint was obtained. A sample prepared in this way was placed horizontally in the chamber of the apparatus. Raman spectra in the visible range (633 nm) were measured directly on a cross-section of the paint fragment. Examination of the elemental composition by XRF technique was possible after dividing the paint sample into single layers.

Examinations were also performed for 80 blue, red and black inks originating from ballpoint pens and gel pens of various brands and made by various manufacturers, commonly available in Poland (Table 2). For each of the investigated inks, lines were drawn or a short text was written on smooth white paper (IBM Laser Paper 90 g/m^3). The ink samples were examined by Raman spectrometry in the visible range and XRF spectrometry directly on the paper. Additionally, the ink samples were analysed by XRF after drying on glass plates.

An attempt was made to examine also a few fragments of different types of synthetic fibres (i.e. polyamide, polyacrylnitryl and acetate fibres) as well as

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