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Raman spectroscopy and capillary electrophoresis applied to forensic colour inkjet printer inks analysis

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ABSTRACT

Forensic laboratories are increasingly engaged in the examination of fraudulent documents, and what is important, in many cases these are inkjet-printed documents. That is why systematic approaches to inkjet printer inks comparison and identification have been carried out by both non-destructive and destructive methods. In this study, micro-Raman spectroscopy and capillary electrophoresis (CE) were applied to the analysis of colour inkjet printer inks.

Micro-Raman spectroscopy was used to study the chemical composition of colour inks in situ on a paper surface. It helps to characterize and differentiate inkjet inks, and can be used to create a spectra database of inks taken from different cartridge brands and cartridge numbers. Capillary electrophoresis in micellar electrophoretic capillary chromatography mode was applied to separate colour and colourless components of inks, enabling group identification of those components which occur in a sufficient concentration (giving intensive peaks). Finally, on the basis of the obtained results, differentiation of the analysed inks was performed.

Twenty-three samples of inkjet printer inks were examined and the discriminating power (DP) values for both presented methods were established in the routine work of experts during the result interpretation step. DP was found to be 94.0% (Raman) and 95.6% (CE) when all the analysed ink samples were taken into account, and it was 96.7% (Raman) and 98.4% (CE), when only cartridges with different index numbers were considered.

1. Introduction

The chemical composition of inks provides very important circumstantial evidence in cases of fraudulent documents and counterfeit banknotes. Nowadays, forging-counterfeiting of both documents and banknotes is committed by utilizing inkjet printers. Vouchers, receipts, prescriptions, banknotes, and other documents produced in such a way are characterized by close similarity to the originals due to the very high precision of modern digital technology and the high quality of inkjet printer inks. Inks normally used in the inkjet printing process have a rather complex composition: a very different one from that of regular pen inks. Forensic document examiners, due to the available technical literature, are well aware of the capabilities and discriminating power of many techniques, such as: ultraviolet–visible spectrophotometry (UV–vis), Fourier transform infrared spectroscopy (FTIR) [1], thin layer chromatography (TLC) [1,2], Raman spectroscopy [3,4], X-ray fluorescence (XRF) [4], mass spectrometry (MS) [5–8], high performance liquid chromatography (HPLC) [9], and capillary electrophoresis, but the studies relate only to writing inks from various kind of pens.

The basic way of investigating inkjet printed documents is to inspect questioned and specimen printing for class characteristics and machine specific characteristics, and record the similarities and differences between them. Many of the characteristics being examined – paper handling marks, black image, dot size and shape, print direction, print head size, sequence of colour printing – are linked with the basic operation of inkjet printers. Nevertheless, analysis of the ink constitutes one of the essential parts of this investigation. Printer ink examination involves testing the reaction of the ink under different lighting conditions (visible, UV, IR absorbance, and IR luminescence) and using various analytical techniques (e.g. TLC, HPLC [10], LD-MS [11], FTIR [12], Raman spectroscopy [12–15], and capillary electrophoresis [16,17]).

To the best of the authors' knowledge, no comparative report on Raman spectroscopy and capillary electrophoresis applied to

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discriminating analysis of colour inkjet printer inks has been published. Since knowledge of the DP of an analytical technique can be useful for examining questioned documents, the aim of this work was to determine the DP. In contrast to Raman spectroscopy, CE destroys the analysed document to some extent. However, if the CE procedure is specially optimized and validated for ink extraction from paper and further ink analysis [16,17], it requires only a minimal amount of printed sample and, therefore, can be considered as semi-destructive. The authors venture to claim that both methods would be very helpful when interpreting results and presenting them in court.

Very important from forensic point of view is to remember about aging of printer inks. This process can highly change the results of inks comparison. According to literature [18,19] and the authors' previous research [20] the degradation of ink on printouts is caused not only by time but it is strongly influenced by light. It was also revealed that humidity may play a part in the rate of ageing. Consequently, the best conditions for the preservation of a document are in a dark and dry environment.

In the paper, the comparison of the discriminating power of the two presented techniques was based on the analysis of 23 colour inkjet printer inks. This investigation is the first step towards building a database of inkjet inks, which is very important for the work of a forensic scientist.

2. Experimental

The chemicals used throughout the experiments were: sodium tetraborate decahydrate (borax) from POCH (Poland), sodium dodecyl sulphate(IV) (SDS) from Sigma-Aldrich (Germany), and acetonitrile (ACN), methanol (MeOH), hydrochloric acid, and sodium hydroxide, all produced by Merck (Germany). All reagents and solvents were of HPLC grade or p.a. purity. Every solution was made using high-purity, reverse osmosis filtered water.

The 23 printer inks considered in the present examinations are listed in Table 1. All examined inks were collected from different manufacturers or from different batches from the same producer. The test page for each of the printers listed in Table 1 was printed using a three-colour ink (yellow, magenta and cyan) in a rectangular rainbow pattern. The same ream of PolSpeed paper (International Paper, Poland) was used to minimize differences arising from the paper substrate. All printouts were stored in dark and dry conditions at room temperature [20].

2.1. Raman analysis of colour inkjet printing inks

Raman spectra were collected with a LABRAM Aramis confocal Raman microscope (Horiba Jobin Yvon, France). The confocal microscope was coupled with a 460 mm focal length spectrograph equipped with four interchangeable gratings turrets (300, 600, 1200, 1800 L mm^{-1} gratings). Different excitation wavelengths (532, 633 and 785 nm) were applied by up to three lasers. For investigation of small areas, the laser can be passed through an optical microscope, thus reducing the sample area. On the incoming path, the laser beam is reflected towards the microscope by means of a special filter. On the return path to the spectrograph, the Raman backscattered light is fully transmitted through the filter towards the confocal slit-hole located at the entrance of the spectrograph. The spectrograph disperses the multichromatic Raman signal onto the CCD multichannel detector.

This analytical method does not require any sample preparation; spectra can be recorded in situ on the paper surface, as the visual mode of the microscope is used instead of a separation process to localize the measurement points. However, owing to the pattern of the samples, determination of the measurement points for pure ink often came up against a difficulty. Namely, while this rainbow pattern was taking form, different colour inks were being mixed so as to create the perceived colours. For every sample, the spectrum of the white paper was recorded, so that peaks of the paper could be identified – if they appeared – on the spectrum of the inks. The samples were investigated with all the three lasers; the measurements were carried out in a spectral range of 200–2000 cm^{-1} with a 600 L mm^{-1} grating, and the measurement spot was ~1–2 μm. This allowed spatial resolution of the paper fibres and location of the ink on the fibres. The measurement of the pure inks of each sample were repeated from three to six times at different spots to keep a check on the experimental uncertainty in peak position and relative peak intensity (Fig. 1). The software used for the manipulation of spectra, e.g. baseline correction,

Table 1
Twenty-three inks considered in the present examinations.

Sample number	Printer type	Cartridge number		
		Yellow	Magenta	Cyan
s1	HP Officejet 5610		HP 22 (C9352A)	
s2	HP PSC 1410		HP 22 (C9352A)	
s3	HP Deskjet 895 Cxi		HP 23 (C1823)	
s4	HP Deskjet 5150		HP 57 (C6657)	
s5	HP Deskjet 3820		HP 78 (C6578)	
s6	HP Deskjet 930C		HP 78 (C6578)	
s7	HP Deskjet 950C/952C		HP 78 (C6578)	
s8	HP Deskjet F4280		HP 300 xL (CC644EE)	
s9	HP Photosmart C3100		HP 342 (C9361EE)	
s10	HP Photosmart C5280		HP 351 (CB337EE)	
s11	HP Photosmart C4280		HP 351 XL (CB338EE)	
s12	HP Deskjet Ink Advantage K209a-z		HP Deskjet 703 (CD888AE)	
s13	HP Photosmart B109a	HP 364 (CB320EE)	HP 364 (CB319EE)	HP 364 (CB318EE)
s14	Canon Pixma MP210		CL-38	
s15	Canon Pixma iP1800		CL-38	
s16	Canon Pixma iP1900		CL-38	
s17	Canon Pixma MP240		CL-511	
s18	Brother DCP-135C	LC-970Y	LC-970M	LC-970C
s19	Brother MFC-215C	LC-900Y	LC-900M	LC-900C
s20	Epson Stylus D92	T0714	T0713	T0712
s21	Epson Stylus Photo R340	T0484	T0483/T0486	T0482/T0485
s22	Lexmark x2530		35 Colour	
s23	Lexmark x3650		35 Colour	