Forensic Science International 209 (2011) e26–e30

Contents lists available at ScienceDirect

Forensic Science International

journal homepage: www.elsevier.com/locate/forsciint

Case report

The analysis of dyes in ball point pen inks on single paper fibres using laser desorption ionisation time of flight mass spectrometry (LDI-TOFMS)

Broderick Matthews [a], G. Stewart Walker [a], Hilton Kobus [a,*], Paul Pigou [a,b], Carolyne Bird [b], Glyn Smith [b]

[a] Forensic Science Program, School of Chemical and Physical Sciences, Flinders University, GPO Box 2100, Adelaide, SA 5001, Australia
[b] Forensic Science South Australia, 21 Divett Place, Adelaide, SA 5000, Australia

ARTICLE INFO

Article history:
Received 12 January 2010
Received in revised form 11 March 2011
Accepted 25 March 2011
Available online 23 April 2011

Keywords:
Ink analysis
Document examination
Mass spectrometry

ABSTRACT

An important requisite for the forensic analysis of inks on documents is that damage to the document is avoided or minimised. This paper describes a technique for dye identification in ballpoint pen inks using LDI-TOFMS on single ink bearing paper fibres and its application to a case. A single ink bearing paper fibre can be prised from the surface of the document under a stereo microscope and presented to the instrument for analysis without further treatment. This sampling process causes imperceptible damage to the surface of the document. Clear mass spectrometric identification of the ink dyes is obtained. A case example is provided to illustrate the practical application of the technique.

1. Introduction

The analysis and comparison of inks can play an important part in the examination of forgeries. An important requisite for the forensic analysis of inks on documents is that damage to the document is avoided or minimised. This is why optical techniques that exploit the spectral properties of the ink to produce images based on the fluorescence or absorption of light at specific wavelengths are widely used. These properties are related to the molecular structure of the dye component of the ink and while providing excellent comparative evidence do not identify the dye molecule or differentiate between dyes with similar chemical groups.

Laser desorption ionisation (LDI) is an energy transfer process that produces both desorption and ionisation of sample molecules from a surface. An ultra-violet laser (337 nm) provides the energy source and ions produced are transported to a time of flight mass spectrometer (TOFMS). LDI is a soft ionisation process producing mainly molecular ions with none of the fragmentation associated with other ionisation techniques and its combination with the accurate mass measurement of TOF-MS provides identification of the molecular ions.

LDI is particularly well suited to the analysis of dyes due to their ionic nature and their strong UV absorption. The fact that the dyes are present as ions means that a matrix to enhance the energy transfer process such as is used in Matrix Assisted LDI (MALDI) is not necessary and dye containing materials such as inks can therefore be analysed directly with no sample preparation and no interference from the matrix. The matrices used in MALDI produce many peaks in the 100–500 m/z region and therefore are not a suitable ionisation technique for analysis of pens as many dyes used in ballpoint pens have a molecular weight below 500. Another advantage of LDI for dye analysis is that neutral components of the ink and the paper substrate will not be detected thereby improving the specificity for the dye, with the mass spectrum likely to be free from interfering peaks.

LDI-TOFMS has been used in archaeology and forensic science for the identification of pigments and dyes in inks [1–7] and for the identification of pigments in paint [8]. Analysis of inks by DART-MS (direct analysis in real time mass spectrometry) [9] and DESI-MS (desorption electrospray ionization mass spectrometry) [10] have also been reported. Weyermann et al. [3] have shown that LDI-TOFMS was a powerful technique for the discrimination of ball point inks. They separated 31 randomly selected blue ball point pens into 26 classes showing a discriminating power of 99%.

LDI-TOFMS offers the potential to analyse inks directly on paper surfaces to determine the molecular identity of the dyes [3]. The small area of interaction of the laser beam with the sample surface (typically 3 μm) means that very small samples can be analysed. This led to the concept of analysing individual ink bearing paper fibres that could be prised from the surface of a document causing imperceptible damage and providing a practically non-destructive technique for the analysis of the dyes in inks. In previously reported methods for ink analysis using LDI samples were obtained by cutting a 5 mm by 8 mm piece of ink bearing paper from the document [3] or by punching a 1.25 mm hole in the document [2].

* Corresponding author. Tel.: +61 8 8201 3225.
E-mail address: Hilton.Kobus@flinders.edu.au (H. Kobus).

0379-0738/$ – see front matter © 2011 Elsevier Ireland Ltd. All rights reserved.
doi:10.1016/j.forsciint.2011.03.033

This paper reports on the capability of LDI-TOFMS to determine the dye components in ball point inks on single paper fibres using a case study as illustration.

2. Experimental

2.1. Extraction of single ink bearing fibres from a document

Extraction of the fibre was a two-step process performed under an SZ-ST Olympus stereo microscope at 63× magnification. The fibre was prised loose using a chemically sharpened 0.2 mm tungsten wire (the tungsten wire was chemically sharpened by placing it in a solution of 1 M sodium hydroxide. A voltage of 20 V was applied in a circuit through the wire and solution until the wire was etched to a fine point). The released fibre was then removed using tweezers with super-fine points (ProSciTech, Australia) and attached to a modified sample plate (see Section 2.2) using double-sided carbon tape.

2.2. LDI-TOFMS analysis

A Waters Micromass M@LDI-LR TOF-MS (Micromass LTD, Cheshire, UK) with a pulsed nitrogen UV laser was used (λ = 337 nm, pulse rate 5 Hz). The instrument performed positive ion analysis using an accelerating voltage of +15,000 V with a delay of 600 ns for extraction and a sampling rate of 0.5 ns. The instrument was operated in reflectron mode with a reflectron voltage of 2000 V and an extraction pulse voltage of 2600 V. The software running the instrument was *MassLynx* version 4.1, 2005.

Calibration of the instrument was performed before each analysis using a saturated solution of caesium iodide (CsI) in water. This yielded m/z peaks of $(Cs_nI_{(n-1)})^+$.

Ink on paper samples were mounted on a modified conventional stainless steel MALDI sample plate (original MALDI plate sourced from Micromass LTD, Cheshire, UK). A rectangular portion of the plate centre was milled to a depth of ~2 mm to ensure that all pen samples on paper were at the level of laser focus. Samples were attached to the modified plate using double-sided carbon tape (ProSciTech, Australia).

2.3. Method validation

2.3.1. Ink discrimination

A range of randomly selected blue, black and red ball point pens were analysed to confirm that a similar level of discrimination to that reported by Weyermann et al. [3] could be achieved on our instrument. Twenty three blue pens, 15 black pens and 12 red pens were selected.

Samples were prepared by drawing a straight line with a single stroke of the pen on Reflex Pure White A4 80 GSM paper. A portion of this line was then extracted using an 11 mm long "I"-shaped hole punch (Francheville Cassette Craft Punch, Letter I). The removed ink line was then trimmed to approximately 5 mm and attached to the modified MALDI plate. Spectra were collected as the combination of 50 laser shots on a single point of the ink line. The spectra of three separate points on the same ink line were then combined to give a final spectrum.

2.3.2. Single fibre analysis

The samples were presented to the Waters/Micromass M@LDI and analysed using the same optimised settings described in Section 2.2. Spectra were collected as the average of 50 laser shots on a single fibre. The spectra from three separate fibres were combined to give a final spectrum. Results were compared to the solid line analysis described above.

3. Results

3.1. Ink discrimination

The 23 blue inks were classified into 10 classes, the black into 5 and the red into 3. The range of dyes detected in the inks is shown in Table 1 and clearly shows that the technique could detect the dyes present in the various inks and discriminate between inks

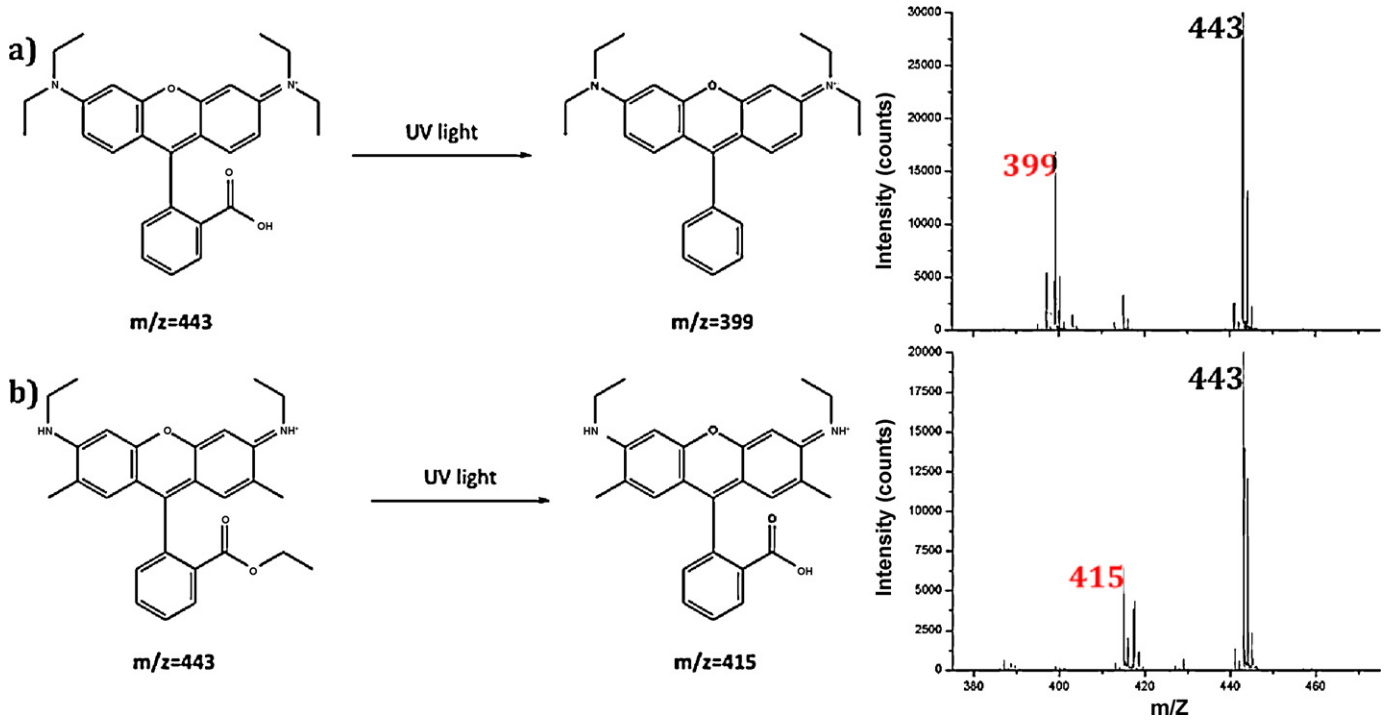

Fig. 1. Formation of degradation products of (a) rhodamine 6G and (b) rhodamine B.