



Differentiation of blue ballpoint pen inks by positive and negative mode LDI-MS

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ARTICLE INFO

Article history:

Received 1 May 2009

Received in revised form 25 May 2010

Accepted 29 May 2010

Available online 1 July 2010

Keywords:

Criminalistic

Questioned documents

Ballpoint

Ink

Mass spectrometry

LDI

Discrimination power

ABSTRACT

Usually, the differentiation of inks on questioned documents is carried out by optical methods and thin layer chromatography (TLC). Therefore, spectrometric methods were also proposed in forensic literature for the analysis of dyes. Between these techniques, laser desorption/ionization mass spectrometry (LDI-MS) has demonstrated a great versatility thanks to its sensitivity to blue ballpoint ink dyes and minimal sample destruction. Previous researches concentrated mostly on the LDI-MS positive mode and have shown that this analytical tool offers higher discrimination power than high performance TLC (HPTLC) for the differentiation of blue ballpoint inks. Although LDI-MS negative mode has already been applied in numerous forensic domains like the studies of works of art, automotive paints or rollerball pens, its potential for the discrimination of ballpoint pens was never studied before. The aim of the present paper is therefore to evaluate its potential for the discrimination of blue ballpoint inks. After optimization of the method, ink entries from 33 blue ballpoint pens were analyzed directly on paper in both positive and negative modes by LDI-MS. Several cationic and anionic ink components were identified in inks; therefore, pens were classified and compared according to their formulations. Results show that additional information provided by anionic dyes and pigments significantly increases the discrimination power of positive mode. In fact, it was demonstrated that classifications obtained by the two modes were, to some extent, complementary (i.e., inks with specific cationic dyes not necessarily contained the same anionic components).

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1. Introduction

The main goal of the forensic examination of inks is to highlight a material heterogeneity on a questioned document. In fact, the presence on a single document of two or more different inks (i.e., the use of different writing instruments) may indicate a forgery. Ballpoint pens are certainly wide used by people and many analytical methods were proposed to discriminate between different ballpoint ink formulations on paper [1–10]. The standard examination procedure for these inks includes first a study of the optical properties of the ink (e.g., absorption and luminescence) [11] followed by the separation of the dyes by thin layer chromatography (TLC) [1], a technique showing a good discrimination power [12–14]. The problem of this methodology is that it requires a local destruction of the questioned document to extract ink samples. Moreover, the sample preparation and analysis are time consuming procedures. Alternative non-destructive optical methods such as microspectrophotometry (MSP) were also proposed [2,3]; these techniques are however less discriminating [14].

Lately, mass spectrometric methods were evaluated because they seemed more promising in terms of sample destructivity, analysis time and discrimination power than previous analytical tools. Like TLC, mass spectrometric methods focus on the analysis of colored compounds. This ensures high discrimination power considering that combinations of organic dyes and inorganic pigments are highly variables in ink formulations [15]. Secondary ion mass spectrometry (SIMS) [4], field desorption (FD) [5], electrospray ionization (ESI) [7], laser desorption/ionization (LDI) [6,12,16–20], matrix-assisted laser desorption/ionization (MALDI) [19,21], direct analysis in real time (DART) [8] and desorption electrospray ionization (DESI) [22,23] were proposed for ballpoint inks examination. In addition to classical methods, mass spectrometry may yield information on the structure of the analyzed molecules (i.e., mass or/and fragmentation pattern). More specifically, the interest regarding the application of LDI-MS to ballpoint ink examination is high, because it is able to guarantee minimal sample destruction and to ionize ink dyes and pigments directly from paper with very little fragmentation and without sample preparation.

With LDI, both positive and negative ions can be obtained from a complex mixture. Previous researches in the domain of questioned documents concentrated mostly on the LDI-MS positive mode and have demonstrated that this analytical tool offers higher discrimination power than high performance TLC

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(HPTLC) for the differentiation of blue ballpoint inks [12]. Regarding LDI-MS negative mode, forensic literature reports numerous applications in different domains to extend the capability of positive mode; examples are identification of pigments used in works of arts [24,25], in illuminated manuscripts [26], in automotive paints [27], in rollerball pens [28] and in inkjet printers [29]. Nevertheless, its potential for the identification of pigments and dyes used in ballpoint inks and for the discrimination of ballpoint pens was never studied before. Application of LDI-MS negative mode should allow the detection of anionic dyes used in ink formulations in addition to cationic ones, providing in this way new information for ballpoint pen discrimination. The purpose of this study is to evaluate the potential gain of discrimination power in blue ballpoint inks analysis by considering both LDI-MS positive and negative modes. After optimization of the method in both modes, reference substances were analyzed in order to identify signals in the mass spectra originating from dyes. Additionally, the use of relative peak areas allowed to further optimize classification. HPTLC analyses of reference substances and representative inks were also performed to confirm the identifications obtained by LDI-MS.

2. Experimental

2.1. Materials

33 blue ballpoint pens were randomly chosen from the German and Swiss market between 2001 and 2006. These pens were used to prepare entries on multifunction white paper from Xerox® (Business Laser-Copy-Inkjet A4 80 g/m², Rochester, NY, USA). The straight lines were made with a ruler applying normal hand pressure. Reference solutions of organic dyes and inorganic pigments were also prepared to identify peaks in mass spectra of inks. Each colorant was dissolved in ethanol from Fluka® (Absolute Ethanol, Buchs, Switzerland) at a concentration of about 1 mg/mL inside polypropylene laboratory tubes from BD Falcon® (Blue Max® Conical Tubes 50 mL, Franklin Lakes, NJ, USA). These solutions were stocked inside a refrigerator at a temperature of 5 °C, safe from direct light. In total 33 reference solutions were prepared (Table 1).

2.2. LDI-MS method

Sample preparation. Concerning the pen entries, small pieces of paper measuring about 4 mm × 10 mm each, bearing a single fresh stroke running parallel to the longer edge, were cut and fixed directly on the metallic sample plate using an adhesive roller from Henkel KGaA® (Pritt® Glue-it® Permanent, Düsseldorf, Germany). For the reference solutions, an aliquot of 30 µL of each solution was simply deposited on the metallic sample plate.

Instrumentation. Positive and negative mass analyses were conducted on a commercial Axima-CFR® Plus matrix-assisted laser desorption/ionization (MALDI) time-of-flight (TOF) mass spectrometer from Kratos Analytical Ltd® (Kyoto, Japan) outfitted with a pulsed nitrogen laser (337 nm, 3 ns, with an operating spot size diameter of about 0.1 mm). This laser delivered pulses with maximal energy of 300 µJ per shot. The beam energy reaching the sample was adjusted by a step motor interposing different portions of a gradient mirrored disc (position from 0 to 180). Spectra were generated by averaging 150 scans in order to generate a single averaged mass spectrum; scans were performed by moving continuously the laser on the sample in order to avoid local dye degradations. The ion gate was adjusted so that only the spectral range comprised from $m/z = 100$ and $m/z = 1500$ were considered. External mass calibration was performed using known molecular peaks of specific dyes in pure solutions; these dyes were BV3 ([C₂₅H₃₀N₃]⁺; $m/z = 372.243$) and BB26 ([C₃₃H₃₂N₃]⁺; $m/z = 470.259$) for positive mode and AY36 ([C₁₈H₁₄N₃SO₃]⁻; $m/z = 352.080$) for negative mode. Samples were immediately introduced into the MS after their preparation and three averaged mass spectra were acquired in different locations of the sample for each analytical mode (positive and negative) in order to take into account the heterogeneity of the ink strokes and allow error measurements. Paper and glue blank analyses were performed to insure that no signal interference was produced by other sources than the ballpoint ink lines.

Optimal laser irradiance. The effect of the ionization process was evaluated for positive and negative modes by studying the effects on mass spectra of increasing laser irradiance, such as induced photodegradation of the dyes or loss of resolution of the mass signals. It was previously demonstrated that too high laser irradiance can cause photodegradation of cationic dyes, while too low laser irradiance is insufficient to provide exploitable spectrum intensity [19]. Therefore, the use of optimal laser irradiance is necessary to prevent these problems and insure reproducibility. It is important that the laser irradiance be kept the same for each acquisition of different samples in order to ensure results comparability. Empirically, optimal laser irradiance was evaluated by testing the effects of increasing laser nominal values on the spectra recorded from the analysis of strokes prepared with a reference ballpoint pen (BIC® Cristal Medium) that contained two cationic dyes, BV3 and BV4, and one anionic dye, SB38. Criteria were spectrum

Table 1
Reference substances analyzed by LDI-MS positive and negative mode, and HPTLC, in order to identify the compounds detected in ballpoint pen entries.

C.I. name	C.I. number	Abbreviation	Commercial name	Furnisher
Unknown	–	–	Fast Black K Salt	Fluka®
Acid Black 2	50420	AB2	Nigrosin Water Soluble	Fluka®
Acid Blue 9	42090	AB9	Duasyn Acid Blue AE02	Hoechst®
Acid Blue 92	13390	AB92	Cyaninsäure Blau R	Chroma®
Acid Orange 7	15510	AO7	Duasyn Acid Orange P01	Hoechst®
Acid Orange 10	16230	AO10	Orange G	Fluka®
Acid Red 52	45100	AR52	Duasyn Acid Rhodamine B-SF	Hoechst®
Acid Violet 17	42650	AV17	Acid Violet 17	Aldrich®
Acid Yellow 36	13065	AY36	Metanil Yellow	Fluka®
Basic Blue 7	42595	BB7	Victoria Pure Blue BO	Sigma-Aldrich®
Basic Blue 11	44040	BB11	Victoria Blue R	Aldrich®
Basic Blue 26	44045	BB26	Victoria Blue B	Aldrich®
Basic Green 1	42040	BG1	Malachitgrün	Chroma®
Basic Green 4	42000	BG4	Malachite Green Oxalate Salt	Sigma®
Basic Red 1	45160	BR1	Rhodamine 6G	Fluka®
Basic Violet 1	42535	BV1	Methyl Violet	Fluka®
Basic Violet 3	42555	BV3	Crystal Violet	Fluka®
Basic Violet 4	42600	BV4	Ethyl Violet	Fluka®
Basic Violet 10	45170	BV10	Rhodamine B	Sigma®
Pigment Blue 15	74160:4	PB15	Irgalite Blue GLVO	Labor Dr. Ph. Bugnon
Reactive Red 106	–	RR106	Reactive Red 106	Town End®
Reactive Yellow 145	–	RY145	Reactive Yellow 145	Helion Chemie®
Solvent Black 3	26150	SB3	Neptun Schwarz X60	BASF®
Solvent Black 7	50415 B	SB7	Nigrosin B Alcohol Soluble	Fluka®
Solvent Blue 2	42563:1	SB2	Neptun Blaubase 634	BASF®
Solvent Blue 38	74180	SB38	Luxolechtblau MBS	Chroma®
Solvent Blue 136	–	SB136	Orasol Blau BL	Cibe Speciality Chemicals Inc®
Solvent Brown 1	11285	SB1	Fat Brown RR	Aldrich®
Solvent Green 1	42000:1	SG1	Malachite Green Carbinol Base	Aldrich®
Solvent Orange 3	11270	SO3	4-phenylazo-M-phenylenediamine	Sigma-Aldrich®
Solvent Red 49	45170	SR49	Rhodamine B Base	Aldrich®

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