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Identification of inks and structural characterization of contemporary artistic prints by laser-induced breakdown spectroscopy☆

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Abstract

Identification of the inks used in artistic prints and the order in which different ink layers have been applied on a paper substrate are important factors to complement the classical stylistic aspects for the authentication of this type of objects. Laser-induced breakdown spectroscopy (LIBS) is investigated to determine the chemical composition and structural distribution of the constituent materials of model prints made by applying one or two layers of several blue and black inks on an Arches paper substrate. By using suitable laser excitation conditions, identification of the inks was possible by virtue of emissions from key elements present in their composition. Analysis of successive spectra on the same spot allowed the identification of the order in which the inks were applied on the paper. The results show the potential of laser-induced breakdown spectroscopy for the chemical and structural characterization of artistic prints.

Keywords: Laser-induced breakdown spectroscopy (LIBS); Artistic prints; Inks; Scanning electron microscopy (SEM)

1. Introduction

A print is a shape or mark made from a block or plate that is covered with wet colour (usually ink) and then pressed onto a flat surface, such as paper or textile. The basic materials used in the production of artistic prints are high quality papers, usually made with cotton fibers mixed with inorganic extenders and organic binders, printing inks constituted by artistic pigments together with agglutinants and other additives, and the pencils used for the author's signatures and series numbers [1–6].

The process of production of artistic prints includes the use of an original matrix containing the artist's design and one or more layers of ink of different colors organized according to artistic criteria. Most prints can be produced over and over again by re-inking the printing block or plate matrix. This method, by which multiple original prints can be produced from the same matrix, facilitates the dissemination of this type of artwork, but it has also stimulated the introduction in the market of many non-original prints whose quality ranges from bad imitations to illegally produced prints using the original plates. *Catalogues Raisonnés* of most important artists compile the formal information of the different print series. However neither chemical analysis of their components, nor data about their structural organization is ever quoted [7–9]. Formal characteristics are, in many cases, enough to establish the artistic origin of the artworks; however these are insufficient when the quality of the fake or fraud is high or when the original plates have been reused. Additional chemical and structural information are needed for these authentication purposes [10–12]. In this scenario restrictions are derived from the minute or almost negligible amount of sample available. Structural knowledge is important because it informs about the printing order of the different inks

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involved in the original production process. Changes introduced in further production batches could not necessarily imply changes in the appearance of the prints but could provide indicators of the lack of originality.

Pigments and dyes used in artworks can be identified using destructive techniques such as mass spectrometry (MS) or gas chromatography coupled with mass spectrometry (GC–MS). Alternatively, analytical techniques for non-invasive pigment identification are based on elemental analysis, such as X-ray fluorescence spectrometry (XRF), or on the analysis of the molecular structure by Raman spectroscopy. XRF has become quite attractive with the development of portable instruments which allow in situ analysis of art objects [13]. On the other hand Raman microscopy is an effective technique for the identification of pigments in paints or inks [14,15] because it is highly specific (each compound has its own Raman fingerprint) and provides good spatial resolution and sensitivity. Although both XRF and Raman are powerful non-destructive methods for pigment identification, they are unable to provide depth profiling information which is crucial in the analysis of multilayer structures.

On the other hand, laser-induced breakdown spectroscopy (LIBS) is a micro-destructive technique that yields elemental composition data from the spectroscopic analysis of the light emitting plasma plume that accompanies the laser ablation of a substrate. When applied to pigment characterization in artworks, LIBS data suggest the presence of certain pigments and, in addition, provide information on the stratigraphy of the substrate layers [16–19]. In particular LIBS has been used previously to study depth profiles of elemental composition of papers and paper coatings and of pigments and binders on paper [20,21].

In this work, we present results on the application of LIBS for the identification and determination of the stratigraphy of ink layers of prints prepared on a paper support. The LIBS technique has been applied for the analysis and characterization of many types of artworks [16], but to our knowledge this is the first time this technique is used for the characterization of artistic prints. In this work LIBS analysis has been combined with scanning electron microscopy (SEM) that is a powerful technique to determine elemental composition but has limited capacity to detect minor components and to resolve stratigraphical distributions.

In this work, we present results on the application of LIBS for the identification and determination of stratigraphy of ink layers of prints prepared on a paper support. LIB spectra have allowed discriminating among the different inks by virtue of specific emissions from atomic elements (or diatomic species in some cases). In samples with two layers of ink recording of spectra upon irradiation on the same spot of the sample with successive laser pulses have revealed the stratigraphy of ink layers and allowed the identification of the order in which these were applied on the paper substrate. This information, obtained by consuming a micrometric amount of sample, is of high relevance for the authentication of artistic prints. It is concluded that LIBS is a suitable technique for the chemical and structural characterization of this type of artwork.

2. Experimental

The LIBS system used for the experiments is described in detail in Ref. [22]. In short, LIB spectra were collected upon laser excitation at 1064 nm (Q-switched Nd:YAG, Quantel Brilliant B, pulse 5 ns, 10 Hz) in the 275–600 nm range with a 0.30 m spectrograph (TMc300 Bentham, 1200 grooves/mm) coupled to a time gated ICCD camera (2151 Andor Technologies). Spectra were recorded at a resolution of 0.25 nm with a gate delay and width of 1 and 50 μs respectively. Experiments were performed in ambient air. The laser beam was focused on the surface of the sample at an incidence angle of 45° onto a spot of 150 μm diameter with fluences up to 40 J/cm^2. The plume emission was collected by a f=4 cm quartz lens and imaged onto the entrance slit of the spectrograph. This non-orthogonal geometry was chosen in order to maximize the collection efficiency of the plume emission that could be reduced by interference with the edge of the sample in a normal irradiation configuration. Irradiation at 45° also improves the depth resolution by reducing the crater depth by a factor of cos 45° [23].

SEM analyses were carried out on a Cambridge Instruments Stereoscan 360 microscope equipped with microanalysis equipment INCA Energy 200. Results were processed with Oxford INCA software. Spectra were recorded at 20 kV, with a current of 1 nA, at a working sample to detector distance of 20–35 mm and integration time of 100 s. The areas analyzed ranged between 20 and 50 μm and punctual spots. For measurements, a small particle of ink (approximately 100 μm size) was extracted from the prints. Particles or fibers covered with ink were carbon coated and deposited on carbon adhesives over

Table 1
Analysis of inks commonly used in artistic prints by SEM and LIBS

Pigment, composition	SEM	LIBS
Arches Paper	Ca	Ca, Ca_2, Al, Na, CN
Faust Lamp black, C, $CaCO_3$, oil	Ca, Al, Si	Ca, Ca_2, Al, Na, Si, CN, **C_2**
Gamblin Bone black, C, $Ca_3(PO_4)_2$, oil	Ca, Si, P	**Ca**, Ca_2, Na, Si, Mg, P, CN
Charbonnel Ultramarine blue, Na_{8-10} Al_6 Si_6 O_{24} S_{2-4}, oil	Ca, Al, Na, Si, K, S	Ca, **Al**, **Na**, Si, K, S, C_2
Charbonnel Ocean blue, Ultramarine blue, TiO_2, $Cu(C_{32}H_{16}N_8)$, $CaCO_3$, oil	Al, S, Cu	Ca, Ca_2, Al, Na, Si, S, **Cu**, Ti, CN, C_2
Charbonnel Prussian blue, Fe_4 $[Fe(CN)_6]_3$, oil	Mg, K, S, Fe	Ca, Na, Mg, K, **Fe**, CN, C_2

Distinctive emitting species of each ink are marked in bold.

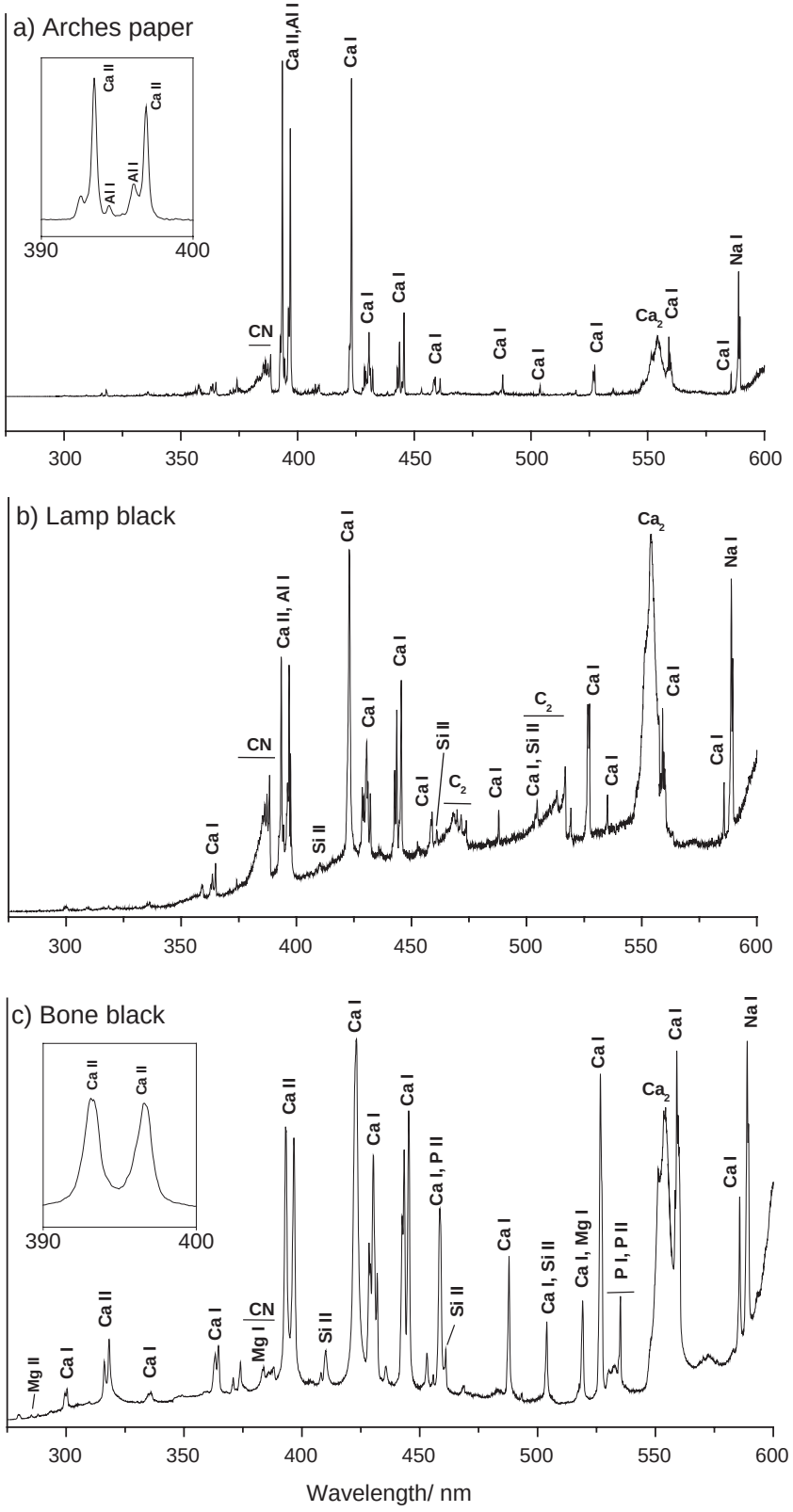

Fig. 1. LIB spectra of a layer of ink applied on Arches paper. Laser excitation at 1064 nm and fluence of 40 J/cm^2: a) Arches paper; b) Faust lamp black; c) Gamblin bone black; d) Charbonnel ultramarine blue; e) Charbonnel Ocean blue; f) Charbonnel Prussian blue. Insets in a) and c) show an enlarged view of the 390–400 nm range.

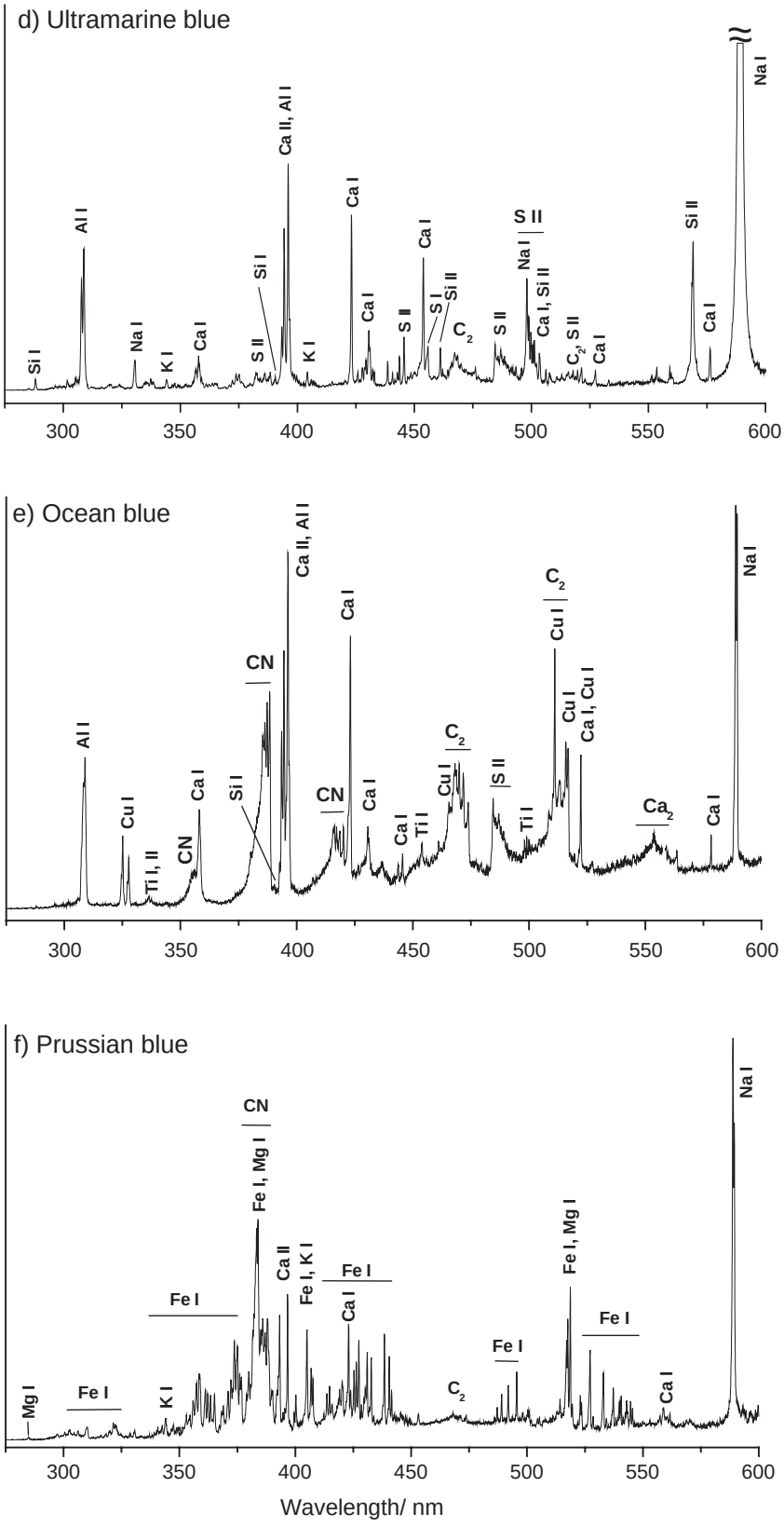

Fig. 1 (*continued*).

stubs of aluminum. Various extractions were made in each case in order to check the reproducibility of the measurements.

Two types of model prints on Arches paper were prepared for this study. In the first type one layer of ink was applied on the paper substrate. Ink was spread over the linoleum matrix with a roller and then transferred to the paper through a printing press. For the second type, an additional ink layer was overlaid onto the first layer with the same methodology. The inks of black and blue colors were selected among the most used in the manufacture of artistic prints. These included Faust lamp black, Gamblin bone black, Charbonnel ultramarine blue, Charbonnel Ocean blue and Charbonnel Prussian blue. According to

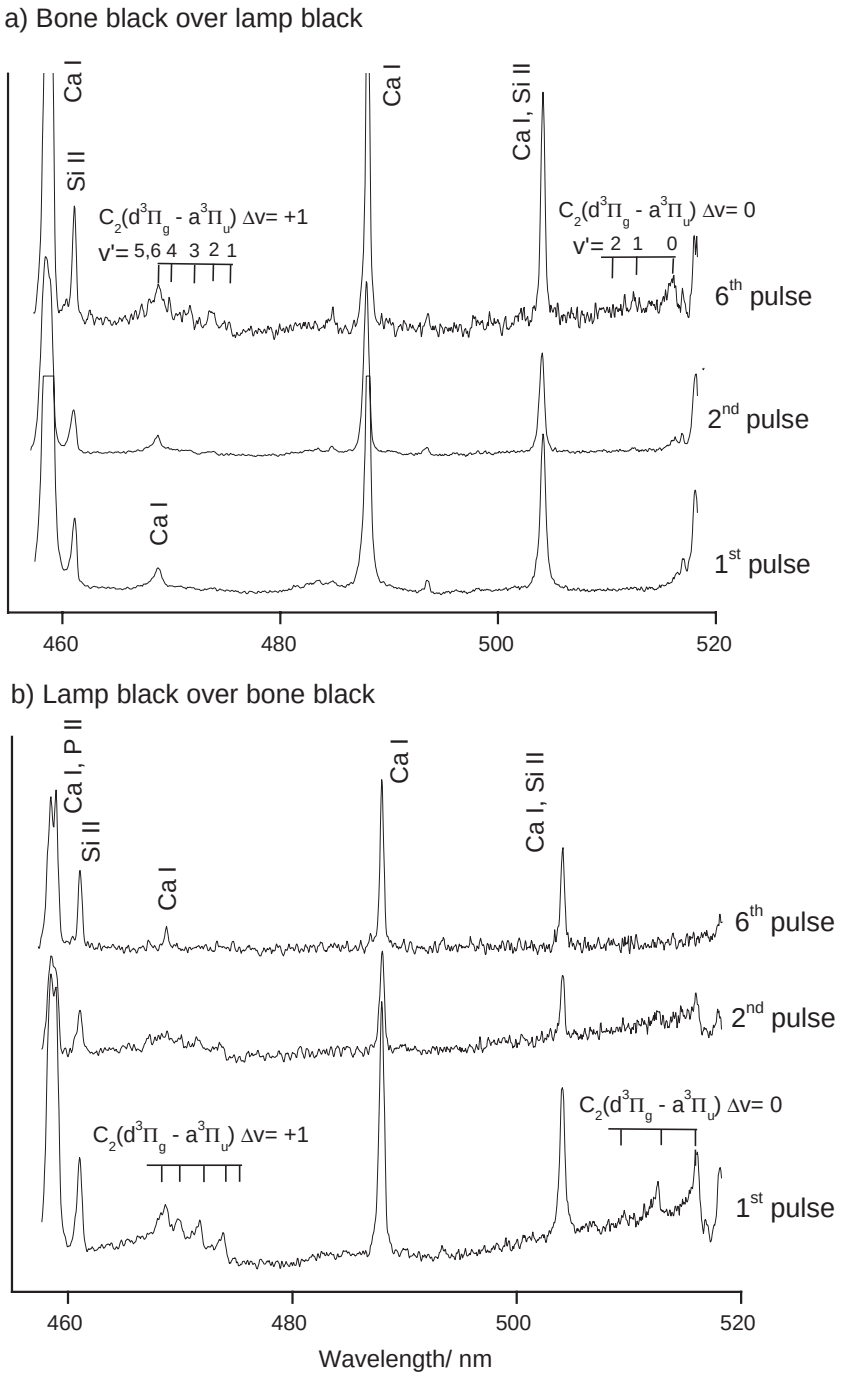

Fig. 2. Successive LIB spectra for stratigraphic analysis of prints constituted by two layers of ink on Arches paper upon laser excitation at 1064 nm and fluence of 40 J/cm^2: a) Gamblin bone black over Faust lamp black; b) Faust lamp black over Gamblin bone black; c) Charbonnel Ocean blue over Charbonnel Prussian blue; d) Charbonnel Prussian blue over Charbonnel Ocean blue. Al lines are marked with an asterisk.

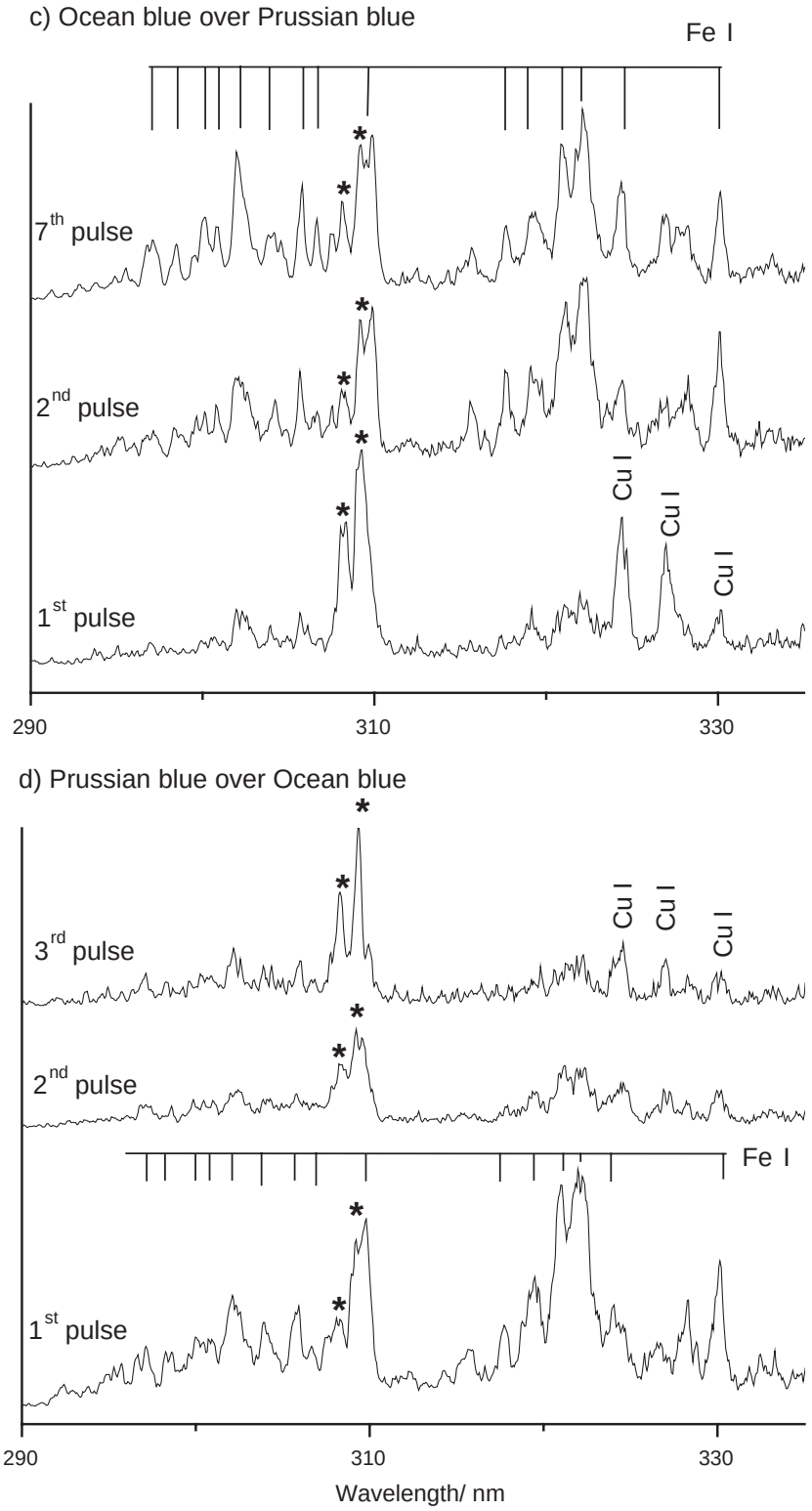

Fig. 2 (*continued*).

the manufacturer the composition of the inks is as follows: Faust lamp black: lamp black (C), oil and $CaCO_3$; Gamblin bone black: ivory black (C and $Ca_3(PO_4)_2$) and oil; Charbonnel ultramarine blue: ultramarine (Na_{8-10} Al_6 Si_6 O_{24} S_{2-4}) and oil; Charbonnel Ocean blue: a mixture of ultramarine blue, TiO_2, phthalocyanine blue ($Cu(C_{32}H_{16}N_8)$, $CaCO_3$ and oil; Charbonnel Prussian blue: Fe_4 $[Fe(CN)_6]_3$ and oil.

3. Results and discussion

SEM analysis of the different raw materials (Table 1) was performed, first, to check the information quoted by the supplier in the ink labels and, second, to compare these results with those obtained by using LIBS. It is interesting to notice that SEM results confirm the presence of some elements not included in the declared composition. This is the case of Si and Al in Faust lamp black, of Si in Gamblin bone black, of K and Ca in Charbonnel ultramarine blue and of K, Mg and S in Charbonnel Prussian blue. As SEM analysis was carried out in small ink particles taken from the samples, we can conclude that these elements are probably present in the ink binders. For the Arches paper the presence of Ca identifies the calcium carbonate as extender.

LIB spectra were taken on the Arches paper substrate and on the samples, constituted by one layer of black or blue ink on the paper substrate, in order to identify the elemental components and to find out distinctive emission lines that could be used as markers of each type of ink. At the highest fluence of ablation used in the experiments, the samples, of 200 μm thickness, constituted by one or two layers of ink over the paper substrate could stand up to 100 shots before a hole could develop. This allowed estimating an ablated depth per pulse of 2 μm.

Fig. 1 displays the spectra of the Arches paper and of the five inks of this study. Each spectrum shown was obtained by adjoining partial spectra acquired with a spectral window of 70 nm. All inks and the paper substrate display a line-rich spectrum containing neutral (I) and ion (II) atomic emissions. Diatomic species (Ca_2, CN and C_2) were also observed. Molecular emissions could result from interactions in the plume between electrons and atomic and ion species ejected from the substrate. Table 1 lists the species that were identified by assignment of the corresponding emissions, together with those obtained from SEM analysis. From the comparison one can see that LIBS allows ascertaining the presence of all the elements detected by SEM and of a number of additional elements that SEM failed to identify. From the assignment, it was possible to select a number of marker species for each ink (bold in Table 1), according to the intensity of their emission lines in the spectra and to their singular presence in the ink considered.

In the LIB spectrum of the Arches paper substrate (Fig. 1a), the presence of neutral and singly ionized calcium lines, in correspondence with the SEM finding, is due to calcium carbonate used as an extender. Al lines appear at 394.40 and 396.15 nm and Na lines at 588.99 and 589.59 nm. These two elements, not observed by SEM, could be present in the paper or arise from dust particles deposited in the surface. The violet system of CN ($B^2\Sigma^+ - X^2\Sigma^+$, $\Delta v = 0$) is observed around 388 nm. CN radicals are formed in the plume by collisions between carbon particles ejected from the ablated paper and nitrogen of ambient air. The emission near 554 nm is attributed to the ($B^1\Sigma_v^+ - X^1\Sigma_g^+$) transition of Ca dimers [24] also formed by collisions in the plume.

For inks, elements identified are clearly related to the pigments and extenders included in their composition. In the case of Faust lamp black (Fig. 1b), the LIB spectrum contains all the emissions observed in the spectrum of the paper (Ca, Ca_2, Al, Na and CN). Additionally the spectrum of this ink displays Si lines at 413.08 and 462.17 nm and in the region of 505 nm overlapping with Ca and C_2 emissions. C_2 ($d^3\Pi_g - a^3\Pi_u$) Swan bands observed around 474 nm ($\Delta v = +1$) and 516 nm ($\Delta v = 0$) are hardly seen in the spectrum of Arches paper. The amorphous carbon present in the ink composition is related to the observed molecular C_2 bands. Due to the distinctive and intense C_2 emissions, this diatomic species is chosen as a marker for Lamp black ink.

Gamblin bone black ink spectra (Fig. 1c) reveal the presence of Ca, Ca_2, Na, Si (at 413.08, 462.17, 504.10 and 505.59 nm), Mg (by virtue of lines at 285.21, 383.23, 383.82 and 518.36 nm), CN and P (emissions at 460.20, 529.35, 529.61, 531.60 and 534.47 nm). Phosphorous can be unambiguously assigned to the bone black pigment as this element is present in its composition. However, Ca was preferred to P as marker in this case, because of the high intensity of Ca I and II lines in comparison with the corresponding lines in the spectra of paper or the other inks.

Emissions from sodium, aluminum (at 308.21, 309.27, 394.40 and 396.15 nm) and silicon (288.12, 390.55, 462.17, 504.10, 505.59, 568.44 and 569.04 nm) identify the Ultramarine blue ink (Fig. 1d). Spectra taken on samples of this ink also display Ca, K (with lines at 344.63, 344.73, 404.41 and 404.72 nm), and C_2 emissions. The presence of sulfur, elemental component of the pigment, cannot be confirmed, although groups of emission lines around 385, 445, 458, 490, 501 and 514 nm suggest the presence of this element. Na and Al emission lines are very intense in the spectrum of Ultramarine blue ink. Consequently these two elements were selected as markers to ascertain the presence of this ink layer.

Spectra taken on samples of Ocean blue ink on paper (Fig. 1e) reveal the presence of copper (with emissions at 324.75, 327.39, 465.11, 510.55, 515.32, and 521.82 nm), titanium (several lines around 336, 453 and 500 nm), sodium, aluminum, silicon and sulfur. Intense CN violet bands (around 359 nm, $\Delta v = +1$, around 388 nm, $\Delta v = 0$, and around 421 nm, $\Delta v = -1$) are observed. These emissions come from the mixture of pigments (Ultramarine and phthalocyanine blues and titanium white) declared at the Charbonnel Ocean blue label. Some of these atomic elements are only detected by LIBS. Among these, Cu was chosen as a marker for Ocean blue ink.

Numerous iron lines dominate the spectrum of the Prussian blue ink (Fig. 1f). Emission from the CN group, also a constituent of the pigment, contributes to the spectral region around 388 nm. Emissions from Ca, Na, Mg, K and C_2 are also observed. The presence of sulfur, detected by SEM, is difficult to confirm through the LIBS analysis.

For the second type of samples, consisting of two ink layers overlaid in a given order, successive LIB spectra were

Table 2
Number of laser pulses and criterion for detection of inks in two-layer samples

Inks (number of pulses to go through the layer)	Pulse number	Criterion for discerning transition between ink layers
Blacks		
Gamblin Bone (3) over Faust Lamp (5)	3rd	C_2 ($d^3\Pi_g - a^3\Pi_u$), $\Delta v=+1$($\approx$474 nm) and $\Delta v=0$ ($\approx$516 nm) appear
Faust Lamp black (2) over Gamblin Bone black (18)	2nd	C_2 ($d^3\Pi_g - a^3\Pi_u$), $\Delta v=+1$, 0 disappear
Blues		Relative intensity of Fe(322.57 nm)/Cu(324.75 nm)
Charbonnel Ocean (2) over Charbonnel Prussian (6)	1st 2nd 7th	0.5 2.9 3.6
Charbonnel Prussian (3) over Charbonnel Ocean (30)	1st 2nd 3rd	2.9 1.3 0.8

recorded by applying a number of laser shots on the same spot of the sample until the characteristic spectra of the ink layer underneath was recognized. Fig. 2 shows two examples of superposition of two black inks and of two blue inks in changing order. Fig. 2a and b correspond to the case of superposition of Faust lamp black and Gamblin bone black, whereas Fig. 2c and d display the case of superposition of Charbonnel Ocean blue and Charbonnel Prussian blue.

For superposition of two black inks, the region between 455 and 520 nm is used to determine the transition between ink layers (Fig. 2a,b, Table 2). The appearance, or disappearance, of C_2 molecular Swan bands (used as marker of lamp black) with band heads around 470 and 516 nm is the most suitable indicator of the transition between the two black ink layers.

For the blue inks, distinctive atomic emissions in the 290–335 nm region are used as indicators of each layer (Fig. 2c,d). The presence of iron, by virtue of the high number of emission lines in this range, indicates the presence of Prussian blue, whereas copper emissions are associated with Ocean blue ink. The relative intensity of the Fe line at 322.57 nm to the Cu line at 324.75 nm as a function of the number of laser shots is shown in Table 2. This ratio increases on samples of Charbonnel Ocean blue over Charbonnel Prussian blue and decreases on the opposite case, providing a reliable indicator for the transition between layers.

Table 2 also resumes the number of laser pulses that have to be delivered to the surface of the sample in order to go through a particular ink layer. It is interesting to remark that, whatever the composition of the upper layer, it is passed through in few laser pulses, whereas the lower layer is detected during many more pulses. This behavior could be related to the morphology and composition of the components of prints. The network of cotton fibers of the paper produces an irregular non-flat surface. Onto this surface, the first printed ink will penetrate into the paper substrate in some extension, depending on the affinity of its chemical components, especially solvents, with the quite polar substrate of cotton fibers. The second overlaid ink will find a different situation due to the presence of the less permeable first layer. In this scenario, the thickness of the upper layer could be expected to be smaller and stand fewer laser pulses than the lower layer. On the other hand, the morphology of the substrate will produce some important lack of homogeneity on the total thickness of the ink layers and will contribute to the changes observed on the registered intensity of the different lines depending on the position probed by the laser beam.

4. Conclusions

LIBS analysis of model prints has allowed the identification of the elemental composition of a range of black and blue inks that is commonly used in the manufacture of artistic prints. Comparison with SEM indicates that LIBS is more sensitive for the detection of elements that are present in minor concentrations. For each ink studied it was possible to identify one or several atomic or diatomic emissions that could be used as distinctive markers in the model prints constituted by two layers of different inks. In those samples, the order of application of ink layers could be correctly established by monitoring the appearance of the selected markers by analysis of successive LIB spectra taken on the same spot. These results show the potential of LIBS for the chemical and structural characterization of artistic prints. Furthermore, due to the microscopic amount of sample that is consumed in the analysis, the technique could be used for authentication purposes on these artworks. Work is in progress to apply LIBS to real artistic prints.

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References

[1] B.L. Browning, Analysis of Paper, Marcel Dekker, Inc., New York, Basel, 1977.
[2] M.C. Sistach, Scanning electron microscopy and energy dispersive X-ray microanalysis applied to metallogallic inks, Proceedings from the 9th Triennial Meeting of ICROM Committee for Conservation, Dresden, 1990.

[3] A. Vila, N. Ferrer, J.F. García, Chemical composition of contemporary black printing inks based on infrared spectroscopy: a tool for prints characterization and discrimination, J. Cult. Herit., (2005) in press.
[4] S. Turner, The Book of Fine Papers, Thames and Hudson, Slovenia, 1998.
[5] S. Turner, About Prints: A Guide for Artist Printmakers, The Camberwell Press, London, 1993.
[6] B. Gascoigne, How to Identify Prints, Thames and Hudson, London, 1986.
[7] R. Santos Torroella, Dalí: época de Madrid: catálogo razonado, Ed. CSIC, Madrid, 1994.
[8] J. Dupin, Miró Engraver, Polígrafa, Rizzoli, 1989.
[9] G. Schor, The Prints of Barnett Newman 1961–1969, Hatje, 1996.
[10] M.T. Romero, N. Ferrer, Fourier transform infrared spectroscopy applied to the characterisation of 17th–20th century calcographic and xylographic inks, Mikrochim. Acta 131 (1999) 237–245.
[11] D. Van der Reyden, Recent scientific research in paper conservation, J. Am. Inst. Conserv. 31 (1992) 117–138.
[12] D.A. Scott, N. Khandekar, M.R. Schilling, N. Turner, Y. Taniguchi, H. Khanjian, Technical examination of a fifteenth-century German illuminated manuscript on paper: a case study in the identification of materials, Stud. Conserv. 46 (2001) 81–92.
[13] B. Hochleitner, V. Desnica, M. Mantler, M. Schreiner, Historical pigments: a collection analysed with X-ray diffraction analysis and X-ray fluorescence analysis in order to create a database, Spectrochim. Acta, B 58 (2002) 641–649.
[14] I.M. Bell, R.J.H. Clark, P.J. Gibbs, Raman spectroscopic library of natural and synthetic pigments (pre- ≈1850 AD), Spectrochim. Acta, A 53 (1997) 2159–2179.
[15] L. Burgio, R.J.H. Clark, Library of FT-Raman spectra of pigments, minerals, pigment media and varnishes, and supplement to existing library of Raman spectra of pigments with visible excitation, Spectrochim. Acta, A 57 (2001) 1491–1521.
[16] D. Anglos, Laser-induced breakdown spectroscopy in art and archaeology, Appl. Spectrosc. 55 (2001) 186–205.
[17] M. Castillejo, M. Martín, M. Oujja, D. Silva, R. Torres, C. Domingo, J.V. García, S. Sánchez-Cortés, Spectroscopic analysis of pigments and binding media of polychromes by the combination of optical laser-based and vibrational techniques, Appl. Spectrosc. 55 (2001) 992–998.
[18] M. Castillejo, M. Martín, M. Oujja, D. Silva, R. Torres, V. Zafiropulos, O.F. van den Brink, R.M.A. Heeren, R. Teule, A. Silva, Analytical study of the chemical and physical changes induced by KrF laser cleaning of tempera paints, Anal. Chem. 74 (2002) 4662–4671.
[19] I. Borgia, L.M.F. Burgio, M. Corsi, R. Fantoni, V. Palleschi, A. Salvetti, M.C. Squarcialupi, E. Tognoni, Self-calibrated quantitative elemental analysis by laser-induced plasma spectroscopy: application to pigment analysis, J. Cult. Herit. 1 (2000) S281–S286.
[20] H. Häkkänen, J.E.I. Korpi-Tommola, Laser-induced plasma emission spectrometric study of pigments and binders in paper coatings: matrix effect, Anal. Chem. 70 (1998) 4724–4729.
[21] H. Häkkänen, J. Houni, S. Kaski, J.E.I. Korpi-Tommola, Analysis of paper by laser-induced plasma spectroscopy, Spectrochim. Acta, B 56 (2001) 737–742.
[22] M. Castillejo, M. Martín, M. Oujja, E. Rebollar, C. Domingo, J.V. García Ramos, S. Sánchez-Cortés, Effect of wavelength on the laser cleaning of polychromes on wood, J. Cult. Herit. 4 (2003) 243–249.
[23] C.C. García, M. Corral, J.M. Vadillo, J.J. Laserna, Angle-resolved laser-induced breakdown spectrometry for depth profiling of coated materials, Appl. Spectrosc. 54 (2000) 1027–1031.
[24] V.E. Bondybey, J.H. English, Laser-induced fluorescence of the calcium dimer in supersonic jet: the red spectrum of Ca_2, Chem. Phys. Lett. 111 (1984) 195–200.