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LIPS spectroscopy for the contamination analysis and laser cleaning diagnostics of historical paper documents

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Abstract

The spectra of laser excited surface plasma (LIPS) recorded for historical, originally contaminated paper and also for model samples reveal reach structures which vary strongly for successive excitation pulses. The characteristic bands are ascribed to contaminants (Na I, Ca I) and pigments (e.g. V I, V II, Ti II, Fe I). Results confirm that the applied technique allows for nearly non-destructive identification of the composition of surface layers such as contaminations and pigments.

Keywords: LIPS; Spectral analysis; Pigments and paper contaminations; Artwork conservation by laser

1. Introduction

Recently, a growing interest in the application of radiative techniques for restoration and analysis of documents and artefacts on paper and parchment is observed (Kolar et al., 2000; Kautek et al., 2000; Kamińska et al., 2002). The potential of ablative laser cleaning is confirmed experimentally and the optimal interaction parameters such as wavelength (532 nm) and energy fluences ($<1\,\mathrm{J/cm^2}$) are specified. Kolar et al. (2000) showed that for the laser wavelengths applied so far the degree of polymerisation of the paper substrate reveals smaller changes for irradiation at 532 nm in comparison to irradiation at 308 nm due to the fact that the bond energies of main cellulose compounds are not accessible by the 2.33 eV photons. It is shown that spectroscopic measurements can deliver information on the chemical composition of the substrate, the pigments applied and the surface contaminants, and also the light-induced deterioration of these species can be studied in this way (Ochocińska et al., 2003).

It can be observed that laser induced plasma spectroscopy (LIPS) can become the frequently used technique in the analysis of artwork. Mainly the monitoring of laser cleaning of stone artefacts (for example, Maravelaki et al., 1997) and the pigment's identification (Castillejo et al., 2000, 2001; Martin et al., 2000) are reported. In contrast, there are only few literature data on the usage of LIPS for investigation of historical paper documents (Melessanaki et al., 2001; Ochocińska et al., 2002). It is in part due to the conservator's opinion that plasma together with a high-energy laser beam can damage the fragile paper objects. In fact, the LIPS technique is nearly non-destructive if properly applied.

In this work LIPS spectra of historical and model paper samples recorded under pulsed laser excitation at 248 nm (KrF excimer laser), and also 266 and 355 nm (Nd:YAG laser with FHG and THG modules) are discussed. Comparison of results with the reference spectra allows identification and analysis of composition

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of the contaminants, and of sufficiently large pigment layers as well. In addition, it is confirmed that a properly applied LIPS technique delivers useful results even for small pigment samples deposited on historical documents.

2. Experimental

2.1. Samples

Samples of historical documents originally contaminated and locally covered with various pigments and also, for reference, some model samples artificially coated with pigments were investigated.

The LIPS spectra of old paper and of the most typical surface contamination, i.e. dust on the back cover of the Leopolita's Bible (1561) and also archive documents both from XIX c. were measured, respectively. For measurements on locally applied pigments the marks of a red and blue pencil due to hand pagination made (most probably in XIX c.) on the archive documents as well as on the Bible pages and its back cover were selected. In the case of the blue pencil marks present on sample originating from the Bible's cover also laser cleaning was applied in an independent experiment and this was reported previously (Kamińska et al., 2002).

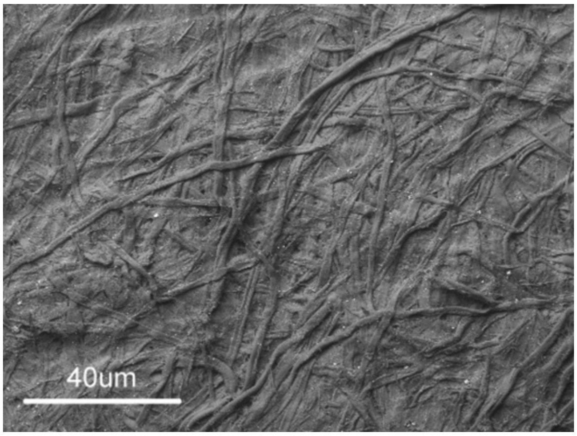

Fig. 1. SEM picture of the surface of model paper; main components: cotton + gelatine; the cellulose fibres form a semi-regular network; magnification 50 × .

The material of model samples (Fig. 1) was a high purity, hand-made, cotton/gelatine, non-bleached paper. It was carefully selected and prepared in order to match the chemical composition, morphology, and also length of the cellulose fibres of historical papers. For modelling of the artificial coatings the commercial soft pastels (Rembrandt® from Talens®) were used: red (Scarlet, 334.7), blue (Phthalo blue, 570.5) and also green (Cinnabar green deep, 627.3).

2.2. Experimental set-up

For excitation of the plasma emission the Nd:YAG laser Brilliant B (Quantel) of the pulse duration of 6 ns (FWHM) and operating in a single pulse mode was used at the IF-FM laboratory (Gdańsk). The frequency multiplication modules THG and FHG were utilised in order to select the excitation wavelength of 355 or 266 nm, respectively. Moreover, excitation by means of the KrF excimer laser at 248 nm was provided in the laboratory of ICP/CSIC (Madrid). In both cases the laser beam was focused onto the sample surface (applied spot diameters were in the range of 0.1–1.0 mm) and the average pulse energies for excitation of the original samples at 248, 266 and 355 nm were equal to 3.5, 39.0 and 50.0 mJ, respectively. The model samples were investigated under excitation at 266 nm and a constant pulse energy of 22.0 mJ was applied in this case. The plasma emission was collected by a focusing lens ($f = 50$ mm) and transmitted to the entrance slit of the 0.5 m (IF-FM) or 0.2 m (ICP/CSIC) spectrograph (Acton Res.) directly or by means of an optical fibre. For recording of the spectra and data processing the Peltier-cooled CCD camera SV-BIG (CVI) synchronized with the excitation pulse by the pulse-delay generator DGD535 (Stanford Res.) and the PC-based data acquisition unit were used. Spectra taken with the 0.5 m monochromator were averaged and the corresponding experimental details allowing for comparison and quantitative considerations are listed in Table 1.

Table 1
Data and settings of the experimental set-up

	Original samples		Model samples
Excitation wavelength	355 nm	266 nm	266 nm
Pulse energy	50 mJ	39 mJ	22 mJ
Grating type	300 gr/mm blaze 500 nm	1200 gr/mm holographic	1200 gr/mm holographic
Entrance slit	10 µm	100 µm	150 µm
Excitation pulses per record	5	3	10

3. Results and discussion

3.1. Spectra of contamination on historical documents

The LIPS spectra obtained for dust deposited on the surface of archive documents, performed and recorded under excitation at three different wavelengths are shown in Fig. 2. The spectra are not corrected for the detection response and represent averages of data recorded for 3 (266 nm) or 5 (355 nm) excitation pulses except for the single-shot spectra obtained under 248 nm excitation. Each individual spectrum corresponds to a

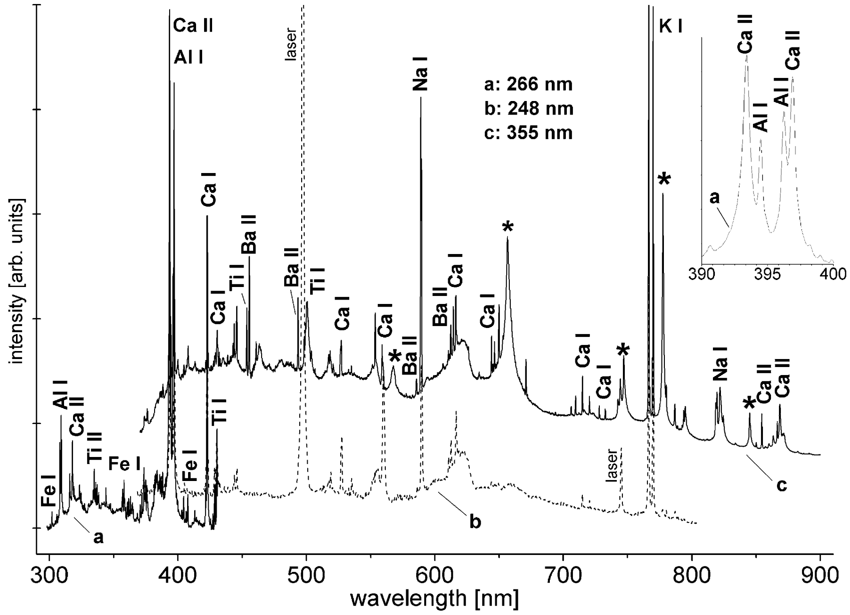

Fig. 2. LIPS spectra of historical sample contaminated by dust and excited at 266 nm (a), 248 nm (b) and 355 nm (c); with (*) marked peaks are characteristic for plasma induced in air (without sample); for clearance only selected assignments are given, intensities of (a), (b) and (c) are not comparable; for details see Table 2.

Table 2
Atomic and ionic lines identified from LIPS spectra of dusted paper

266 nm									
Fe I	302.06	Ti II	334.9	Fe I	371.99	Ca II	396.85	Ti I	430.59
Al I	308.22	Ti II	336.2	Fe I	373.49	Ti I	399.86	Fe I	432.35
Al I	309.27	Ti II	337.28	Fe I	374.83	Fe I	404.58		
Ca II	315.18	Fe I	358.12	Ca II	393.37	Fe I	406.36		
Ca II	317.93	Ti I	363.5	Al I	394.4	Ca I	422.67		
Ti II	323.45	Ti I	364.27	Al I	396.15	Fe I	427.18		
355 nm									
Ca II	393.37	Ca I	443.57	Ca I	518.88	Ca I	612.22	K I	766.49
Al I	394.4	Ti I	453.32	Ca I	526.22	Ca I	615.12	K I	769.9
Al I	396.15	Ba II	455.4	Ca I	526.56	Ba II	614.17	Na I	818.33
Ca II	396.85	Ba II	493.41	Ca I	527.03	Ca I	616.21	Na I	819.48
Ti I	399.86	Ti I	498.17	Ca I	534.95	Ca I	643.91	Ca II	820.17
Ca I	422.67	Ti I	499.11	Ca I	558.87	Ca I	644.98	Ca II	824.88
Ca I	428.3	Ti I	499.95	Ca I	559.45	Ca I	646.25	Ca II	849.8
Ca I	429.89	Ca II	500.15			Ca I	647.17	Ca II	854.21
Ca I	430.25	Ca II	502	Ca I	585.75	Ba II	649.69		
Ca I	431.86	Ti I	500.72	Na I	589	Ca I	714.81		
Ca I	442.54	Ti I	501.42	Na I	589.59	Ca I	720.22		
Ca I	443.49	Ca I	504.16	Ca I	610.27	Ca I	732.61		

fresh location on the sample surface which was previously not laser-illuminated. This is accomplished by a stepwise, small shift of the sample holder and assures constant reference conditions. In order to differentiate spectral bands originating from the ambient air, the spectrum of laser induced plasma without sample was measured and the corresponding lines are marked by stars in Fig. 2. With regard to contaminants, the positions of the characteristic and most intense peaks are in agreement independent of excitation and even laboratory conditions.

The atomic and ionic lines identified so far are listed in Table 2. The majority of the observed bands originate from chemical elements such as: calcium, sodium and potassium which are partly dissolved in water. The strong, partially overlapping lines of Ca II and Al I are characteristic, too (Martin et al., 2000), and are shown in the inset of Fig. 2. It is worth mentioning that the Ca emission lines observed in LIBS spectra of artwork are often associated with contamination (Castillejo et al., 2001). The frequently observed bands of Fe I are also ascribed to contaminants (Klein et al., 1999; Gobernado-Mitre et al., 1997). The presence of the titanium and barium lines is due to the white pigments such as titanium white (TiO_2) and fixed white ($BaSO_4$) used in paper production.

The above assignment and conclusions are both confirmed by the observation of spectra recorded for several consecutive excitation pulses applied to the same location at the sample surface. The corresponding decrease in intensity of bands originating from contamination results in their disappearance after prolonged irradiation—see Fig. 3. This result indicates clearly the contamination removal due to ablation and supports the correctness of the proposed assignment.

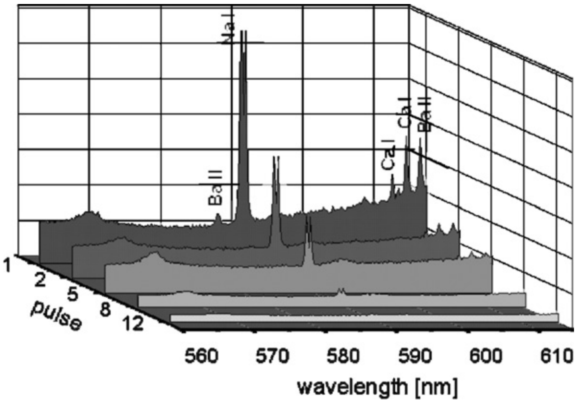

Fig. 3. A decrease of band intensities originating from the surface contaminant due to prolonged irradiation of the sample.

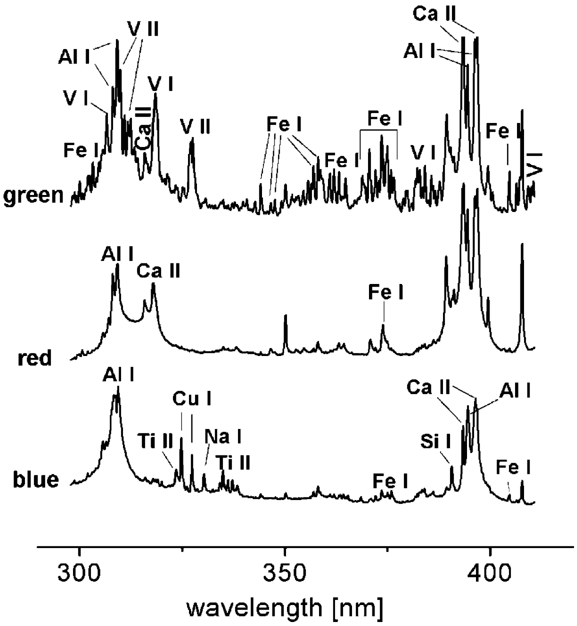

Fig. 4. The LIPS spectra of various, commercially available pigments on the model paper samples: excitation 266 nm.

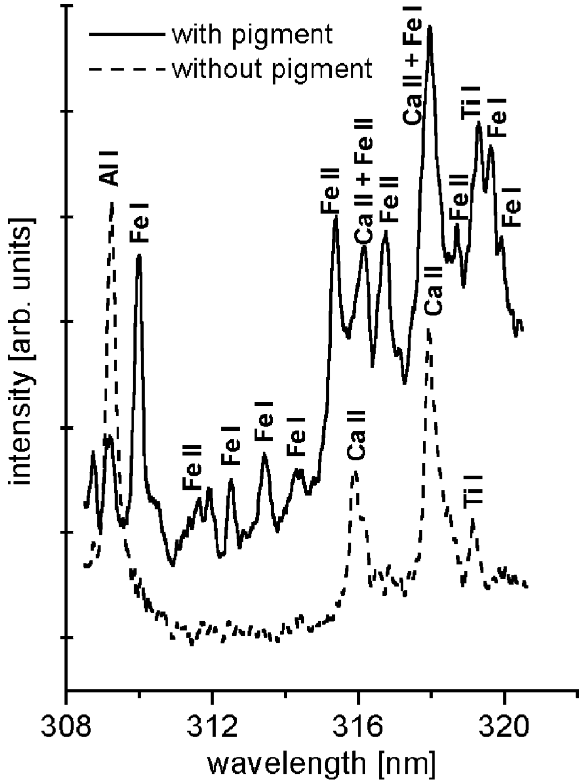

Fig. 5. LIPS spectrum of a real sample: red pencil mark on the dusted archive document (XIX c.)—solid line; non-coloured region—dashed line; plasma induced by a 266 nm laser.

3.2. Spectral characteristics of model samples and pigments

The spectra of the three different colour layers prepared by pigment application on the model paper surface were recorded under excitation at 266 nm and the results are presented in Fig. 4. For the reference spectrum of the model paper without any pigment applied no bands were detected. It allows to conclude that all peaks present in the spectra of Fig. 4 originate from pigments present on the paper surface and differences in spectral shapes of investigated pigments are clearly seen too. Strong peaks of Al I and Ca II, which are present in the spectrum of dust (see Fig. 2 for comparison), are observed in the spectra of all pigment-covered samples. It indicates that these species are components of the pigment's binding medium. In the spectrum of a green sample a number of iron and vanadium lines are observed. Conversely, the spectrum of a red pigment is characterised by a lower number of iron lines and the Ca band intensity is relatively high. The supposed presence of ultramarine (calcium aluminosilicate) and TiO_2 in the blue pigment composition can explain the shape of the lowest spectrum of Fig. 4. This result agrees with the literature data (Castillejo et al., 2000) and confirms that under suitable conditions the LIPS technique allows to identify pigments and also to analyse their specific composition for different layers on paper.

3.3. Examples of LIPS spectra of original pigments on historical documents

A similar spectral analysis applied to a real object represents a different task as there is often inconspicuous quantity of pigment covering a small area, e.g. in the form of a line, and a trace of a brush or pencil. In addition, the unquestionable value of historical objects requires application of the non-destructive analytical methods and most often only small samples can be provided for investigation. Under these circumstances, trials on two original samples were performed.

In both cases the pigment-covered area was relatively small and corresponded to a red and blue pencil trace. It required a precise positioning of the focused beam in order to measure the pigment signal. Spectra recorded under excitation at 266 nm (red pencil trace) and 355 nm (blue pencil) together with reference spectra of the bare substrate are shown in Figs. 5 and 6, respectively.

It can be easily observed that differences between the pigment spectra and the reference ones are for both pigments much smaller than in model situations, which is obvious. Nevertheless, the spectra are characterised by unquestionable differences.

In particular, for the red pigment a set of excellently resolved and intense Fe I lines is superimposed on the background signal in the narrow spectral range of the recorded emission of 308–320 nm (see Fig. 5). The

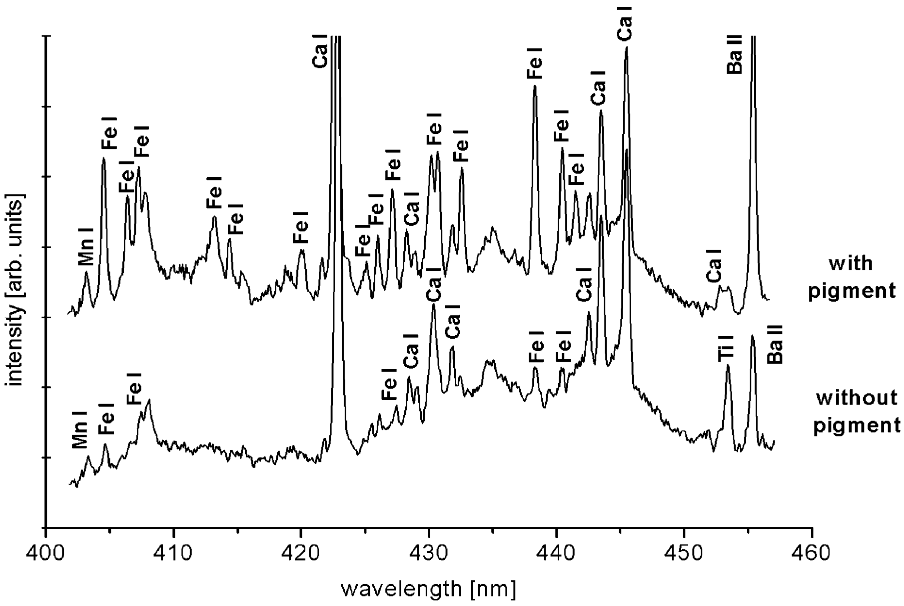

Fig. 6. LIPS spectrum of pigments originating from blue pencil mark on the back cover of Leopolita's Bible, and a spectrum of a non-coloured paper region; plasma induced by a 355 nm laser.

intensity increase of the Ti band can be ascribed to the component of the pigment. The small intensity of the Al band compared to the reference one requires more experimental data for discussion and confidence. A much wider area of considerable differences can be observed for the second sample (see Fig. 6). In this case the Ti band is absent in the pigment spectrum. Also a reach structure containing a number of Fe and Ba lines characterise the historical, blue pigment in comparison to reference.

4. Conclusions

LIPS spectra of dust-contaminated, historical paper samples are characterised by reach structure of numerous emission lines ascribed to Ca I, Ca II, Na I, K I, Al I and Fe I. The occurence of the Ti I, Ti II and Ba II bands can be explained by the usage of white pigments (TiO_2 and $BaSO_4$) in the production of paper as well as for pigment composition in the past. A strong decrease of the band intensities ascribed to contamination under prolonged sample irradiation confirms the assignment. The comparison of the spectra of the model samples and pigments agree with literature and support the conclusion on the application potential of the LIPS technique for analysis and identification of pigment layers on the paper substrate.

In particular, marked differences are observed for three model pigments whenever, for the historical samples characterised by a small quantity of pigment on the paper substrate, the proposed LIPS technique requires more precision and the measured signals are much weaker. Nevertheless, examples of spectra recorded for historical pigments on old documents reveal bands characteristic of pigments and support the usefulness of the applied spectroscopic technique.

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