Experimental investigations of stained paper documents cleaned by the Nd:YAG laser pulses

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Abstract

The historical paper samples from XIII–XIX c. are characterised by means of techniques of the optical spectroscopy. The influence of pulsed laser cleaning by means of the Q-switched Nd:YAG laser at 532 nm on the spectra and also cleaning results of stained paper documents are reported and considered. In the absorption spectra, the minima around 280 and 370 nm are identified and luminescence reveals a characteristic band centred around 430 nm. The laser cleaning diagnosed by the recording of the LIF spectra with 266 nm excitation shows a profile of increasing intensity and preserved structure. The LIPS spectra reveal sharp emission lines recorded at 612.5, 644.2, 646.5, 671, 714.9, 720.2 nm (Ca I), 589.4, 616.4, 780 nm (Na I), and 766.5: 769.9 nm (Mg I) which are ascribed to the surface contaminations. The intensity decrease of these peaks is in accordance with successive laser pulses and monitors the cleaning progress of the stained paper. © 2003 Éditions scientifiques et médicales Elsevier SAS. All rights reserved.

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1. Introduction

The cleaning process represents one of the most important tasks in the restoration of old documents and works of arts on paper. The conventional cleaning methods are frequently characterised by the use of mechanical action on the object surface, which can be often supported by the application of chemicals. The aqueous and other solvents remove discoloration, dirt encrustation and improve the physical and chemical property of the paper material. Unfortunately, the use of chemicals and also water cleaning methods can lead to partial damage of the fragile paint and print layers or even brittle the original paper substrate, too. The application of the laser radiation for restoration of paper is expected to avoid the above problems. Hence, for laser treatment, the penetration depth as well as the dose of energy delivered can be controlled and therefore the risk of possible damage to the treated object can be markedly reduced.

Recently, intensive investigations devoted to the application of the laser based techniques for restoration of artefacts on the paper and parchment have been carried out [1–5]. Attempts are made for the model systems of contaminant/pigment/substrate [1,2], original samples [1,3,6], and the reference ones [4,5]. In particular, an extensive analysis of the chemical constituents and properties of the parchment and also its possible light-induced deterioration is performed [2]. From the experimental selection of the laser cleaning parameters, consistent results are obtained and also the less destructive wavelength (532 nm) and energy fluences (<1 J/cm^2) are derived [5].

In this work, the paper samples of old documents from XIII–XIX c. are characterised by spectroscopic techniques and the influence of pulsed, ablative cleaning by means of the Nd-YAG laser at 532 nm on the spectral results is considered. The experimental results obtained by using such techniques as photometry, fluorimetry, the laser-induced fluorescence (LIF) and plasma spectroscopy (LIPS), the study of colour metric and infrared spectroscopy applied for diagnostic of the sample properties before, during and after the laser cleaning process are presented and discussed.

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2. Experimental

The investigated paper samples were: a blotting paper taken as reference and made of cellulose with no additives (A), a rag, gelatine-sized, hand-made paper attacked by fungi (B1, B2) from XVII c., the magazine printed papers from XIX c. (C1, C2 and H), the rag, gelatine-sized paper from XVIII c. with traces of fungi and dark-grey stains (D1, D2), hand-made paper with dark yellow glue stains from XVI c. (G). (E1, E2), heavily soiled paper from XVIII c. discoloured and covered by a layer of solid, dust-like contamination (F), and also hand-made paper from XII-I–XIV c. (G).

The laser cleaning of paper samples was realised by means of the pulsed Nd:YAG laser (Quantel) operating with the SHG module at a wavelength of 532 nm. Fluences from the range 0.3–3 J/cm^2 were selected and controlled by means of the beam expander together with a focussing lens (f = 200 mm) and a joulemeter (Gentec).

For recording of the absorbance spectra in the range 200–800 nm, and for the overview spectra of the paper luminescence due to the selected excitation wavelengths of 266 and 355 nm, the UV/VIS spectrophotometer Lambda 25 (Perkin-Elmer) and the spectrofluorimeter LS50B (Perkin-Elmer) were used, respectively.

The fluorescence spectra (LIF) of the paper were obtained for samples excited at 266 nm by the Nd:YAG laser operating with the FHG module at frequency of 1 Hz. The constant pulse energy of 32 mJ was measured on the sample surface. The laser beam was not focused, so the energy density was below 0.02 J/cm^2 assuring mild excitation. The emission signal was collected by a lens (f = 50 mm) for transmission by an optical fibre and was dispersed by a 0.5 m spectrograph (Acton Res.) equipped with a 300 l/mm grating (blaze at 500 nm). For detection, the cooled CCD camera system ST-V SBIG (CVI) was applied. In order to capture the relatively weak signal, the camera was synchronised with the laser pulse by a delay/pulse generator DGD 535 (Stanford Res.). The overall system resolution was

1.2 nm and the spectra were recorded and averaged over 10 excitation pulses.

The LIPS spectra of the paper samples were recorded during the laser cleaning process under the single-pulse mode and the fluence applied to the paper surface was equal to 0.5 J/cm^2. The detection system was the same as that applied for LIF measurements.

The infrared spectra (DRIFT) were obtained by means of the FTIR spectrometer (Perkin-Elmer) equipped with the diffuse reflectance unit.

The colour metric studies were performed by using the DMS apparatus (Autronic) with an illuminant D65 (CIE) applied, and characterised by a spot diameter of 1.25 mm, and also by a bandwidth and sampling interval both equal to 10 nm. MgO was used as the standard white reference. Measurements were carried out in conformance with the CIE 1931 standard. Changes in colour were obtained from averages of three measurements.

The investigated paper samples together with the characterisation methods applied are listed in Table 1.

3. Results and discussion

3.1. Spectroscopic characterisation of the samples

An example of the paper absorbance vs. excitation wavelength obtained by the scanning of a continuous light source for samples A, B1 and C1 is representative for most investigated samples (Fig. 1a). An intensity increase is observed in the UV region and only the slight modulations in the range over 500 nm are in agreement with the literature [4]. Minima around 380 (A, B1 and C1) and 280 nm (B1) are caused by the sample emission. This is confirmed by the negative absorption of the reference sample (A) in this region. Excitation at 266 and 355 nm which agree both with the absorption bands results in the expected, characteristic broad emission centred around 420 nm. This is shown in Fig. 1b for sample A only, due to the fact that all the

Table 1

Description of the historical paper samples and methods of their spectroscopic characterisation applied in experiment

| Sample	Description	Diagnostic methods
A	Blotting paper, used as reference sample, made from pure cellulose without addition of pigments, bleaching substances, etc.	Spectrophotometry, spectrofluorimetry, spectrocolorimetry
B1	Gelatine-sized, hand-made, rag paper from XVII c.	Spectrophotometry, LIF
B2	As above, attacked by fungi (*Serpula lacrymanas*), which results in brown stains	LIF, DRIFT, spectrocolorimetry
C1	Magazine printed paper from XIX c.	Spectrophotometry, spectrocolorimetry
C2	As above, with organic discoloration (greasy stains)	Spectrophotometry, spectrocolorimetry
D1	Rag, gelatine-sized paper from XVIII c.	Spectrophotometry
D2	As above, attacked by fungi, with grey/black stains	Spectrophotometry
E1	Rag, hand-made paper from XVI c.	Spectrophotometry, spectrocolorimetry
E2	As above, with dark yellow glue stains	Spectrophotometry, spectrocolorimetry
F	Rag paper from XVIII c., heavily soiled, discoloured and cover by a layer of solid, dust-like contamination	LIPS, LIF, DRIFT
G	Rag, hand-made paper from XIII-XIV c.	DRIFT
H	Magazine printed paper (XIX c.), heavy stained at the edges (brownish stains)	Spectrocolorimetry

a)

b)
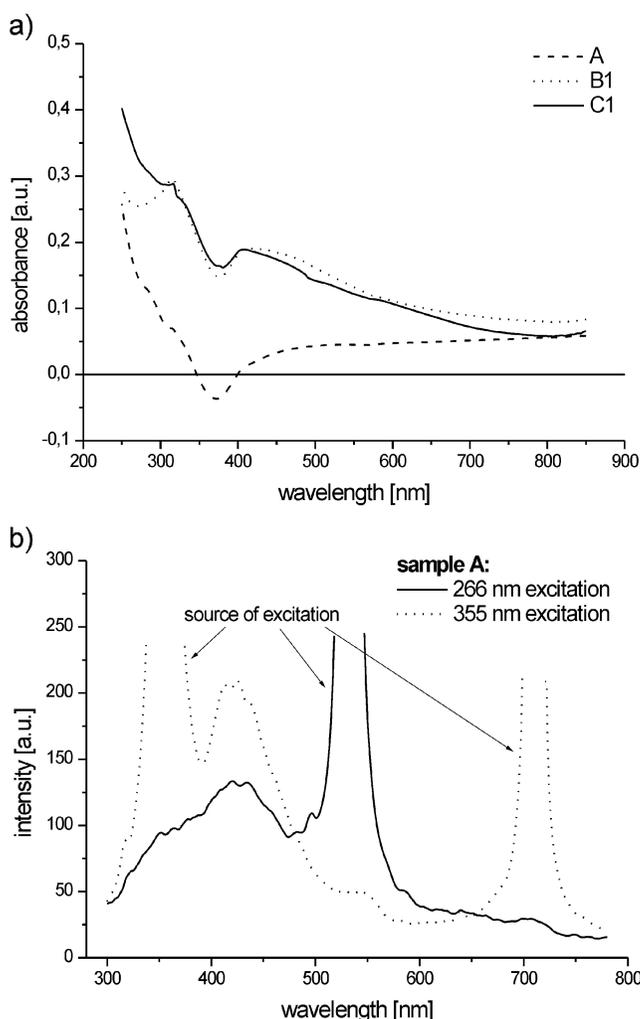
Fig. 1. The dependence of absorbance vs. excitation wavelength from photometric measurement for samples A, B1 and C (a), and the emission spectra of the reference sample A at under mild excitation at 266 and 355 nm obtained by means of the fluorimeter (b).

recorded emission spectra have the same shape with peaks due to stray light from excitation superimposed and differ only by intensity. It was observed too, that the emission signal of paper samples excited at 532 nm is negligibly small, which agrees with the results of other authors and confirms that this laser wavelength is less destructive for the paper than those of 266 and 355 nm [4,5].

In order to come to a conclusion on the stain absorption, two different regions of samples E and D with and without stain were examined, and for each sample, the recorded spectrum of the stain-free paper was extracted from that of the stained one and the difference spectra are shown in Fig. 2. The results reveal that in the near-UV region and in the case of sample E the stain absorption is greater than absorption of the paper. This agrees with the known emission band around 400 nm characteristic for the dark yellow glue stain which is present on sample E. Similarly, the dark-grey stain of sample D originating from fungi results in the broad absorption band in the entire visible region which is also confirmed by the spectrum in Fig. 2.
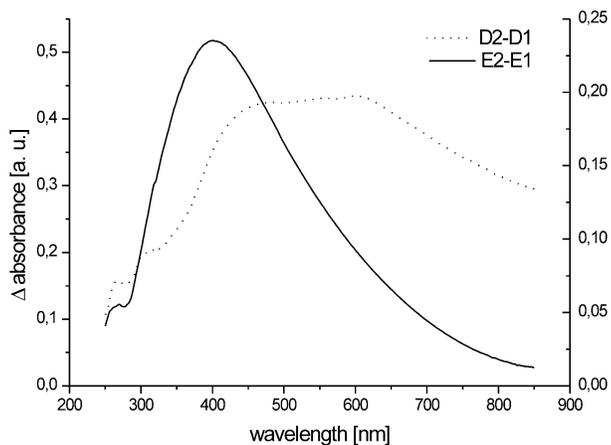

Fig. 2. Dependences of the absorbance differences between the stained and stain-free fragments of the same paper on the excitation wavelength under mild excitation.

From the relation of the absorption coefficient which is inversely proportional to the value of threshold fluence for the laser removal of a given substance [1], the conclusion follows that this value for stain should be smaller than that of paper. This indicates the laser cleaning potential of stained paper documents and its selectivity in the visible and near-UV region. The presence of dust and dirt in the form of micro-particles did not influence the shape of emission bands obtained by fluorimetry.

The LIF spectra deliver more detailed information about the shape and structure of the emission bands as expected and allow to analyse the differences between the well-preserved and damaged paper. The results obtained for samples B1 and B2 as spectral profiles averaged over 10 excitation pulses of the 266 nm laser are shown in Fig. 3. All the characteristic peaks are reproduced for both samples and can serve for the characterisation of a given paper together with contamination. The damaged paper B2 shows a lower intensity than B1 in the emission range up to about 520 nm which results from stain coverage of the paper. In the red and near-IR region, the emission of B1 becomes relatively lower than that of B2 which is due to the organic contamination of the first.

3.2. Laser cleaning of paper with subsequent diagnostic

It was observed that the interaction of the 532 nm laser results in less destructive changes of the paper than the interaction of the shorter ones of 266 and 351 nm. This followed from the surface inspection and was also demonstrated through a lower degree of polymerisation after interaction of the 532 nm laser in agreement with the literature data [4,5]. Therefore the value of 532 nm was selected for the cleaning experiments. Moreover, the 532 nm laser coincides with the water absorption window of a minimum around 500 nm, and its use is preferred because of the lowered damage risk of the paper structure due to the residual H_2O content in the paper. Moreover, this selection
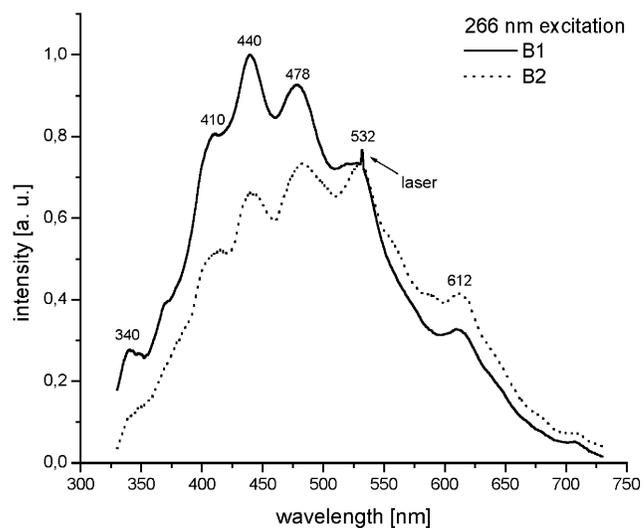
Fig. 3. The LIF spectra of sample B: the well-preserved fragment—solid line, and damaged by stain—dotted line; excitation at 266 nm.

is advantageous in comparison to shorter wavelengths because the bond energies of main cellulose compounds are not accessible by the 2.33 eV photons [5].

An example of the single-shot LIPS spectra, recorded during laser cleaning of sample F which was heavily soiled and covered by a dust layer, is shown in Fig. 4. Spectra (a), (b) and (c) correspond to the first, second and third cleaning pulse, respectively, and they are corrected for the spectral response of the detection system. The sharp emission lines at 612.5, 644.2, 646.5, 671, 714.9, 720.2 nm (Ca I), 589.4, 616.4 and 780 nm (Na I), and 766.5, 769.9 nm (Mg I) are ascribed to the surface pollutants. The broad band centred at 620 nm, originates most probably from the substrate fluorescence with superimposed, strong contamination peaks. This assignment is supported by the band position which agrees with that observed in the LIF spectra of this sample. The decrease in intensity of the contamination bands with successive pulses clearly demonstrates the effectiveness of the laser cleaning. This method of paper characterisation delivers valuable results immediately and during the cleaning process. Moreover, a commercially available, industrial version of spectrometer together with a transportable data analyser can be applied and could serve for the conservation practice.

In order to compare the potential of paper characterisation by means of both the LIPS and LIF techniques for the laser cleaning process also the LIF spectra of the same paper (F) were recorded under 266 nm excitation after laser cleaning by means of pulsed irradiation at 532 nm (10 pulses, ~ 0.5 J/cm^2). The results obtained so far for the stained paper as well as for the laser cleaned one are shown in Fig. 5. Some peaks, e.g. the one at 612 nm, are reproduced in accordance with the LIPS spectrum of the same sample F (Fig. 4) and even with the LIF spectra (Fig. 3) of other samples B1 and B2 indicating occurrence of the paper and contamination bands which can be obviously observed.
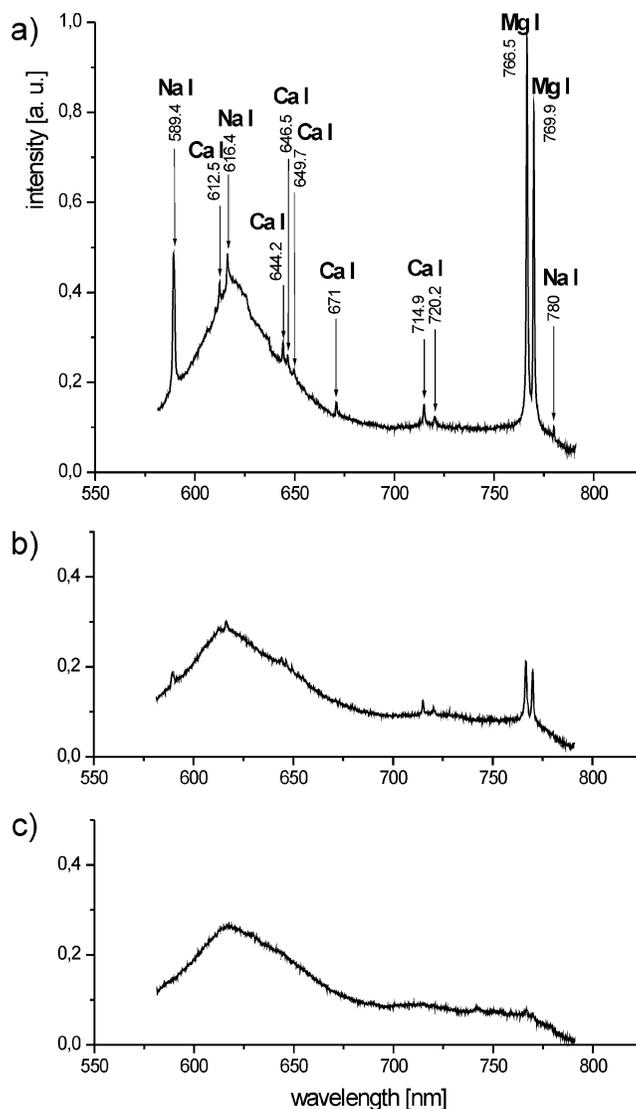

Fig. 4. The single-shot LIPS spectra recorded in situ for sample F during laser cleaning at 532 nm; (a), (b) and (c) correspond to the 1, 2 and 3 cleaning pulse, respectively.

3.3. Changes in the colour metric

For the investigated samples B2,3, C2, E2 and H, the colour metric study was performed before and after the laser cleaning at 532 nm with the beam energy densities from the range of 0.5–2.5 J/cm^2. The number of applied laser pulses was adopted in the range of 3–30 in order to obtain the cleaning effect. The changes in the paper brightness ΔL, colour coefficients a and b, and also colour difference ΔE are summarised in Table 2. The most impressive changes due to laser interaction were observed by the naked eye for sample E2, and they are confirmed by the results of measurements. The originally yellow paper (E2) has been bleached and this is reflected by the estimated values of $\Delta a = 50\%$ and $\Delta b = 30\%$. On the contrary, sample B2 did not show a noticeable colour change due to laser pulses applied but the measurements indicate a slight growth in
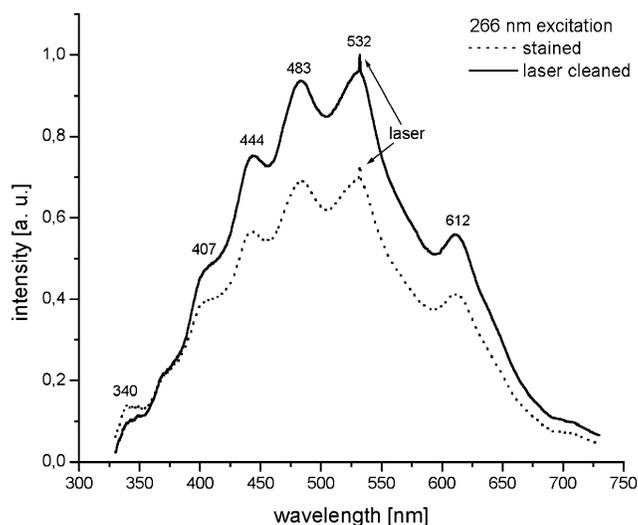
Fig. 5. Comparison of the LIF spectral profiles for the stained part of sample F before—solid line, and after laser cleaning with 10 pulses at 532 nm and fluency of 0.5 J/cm^2—dotted line.
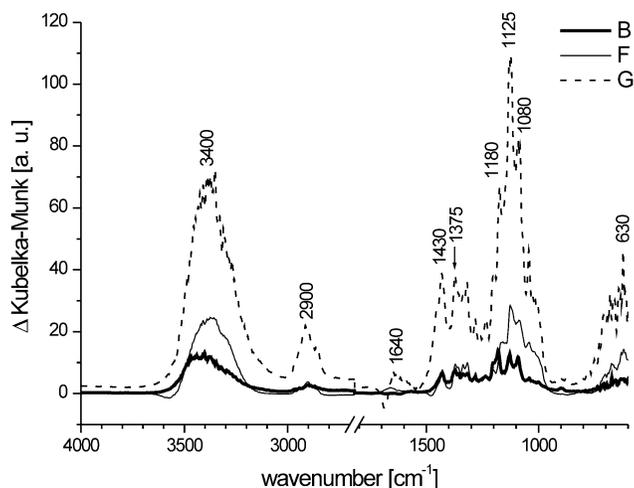

Fig. 6. IR diffuse reflectance spectra of samples B—solid line, F—dotted line, and G—dashed line, due to pulsed laser cleaning at 532 nm (B: 30–40 pulses, 2.5 J/cm^2; F: 40 pulses, 3 J/cm^2; G: 1–2 pulses, 0.5 J/cm^2).

Table 2
Results of the colour metric study obtained for selected samples: ΔL, Δa, Δb and ΔE—changes of the brightness, colour coefficients and relative colour, in percentages

Sample	ΔL (%)	Δa (%)	Δb (%)	ΔE (%)
B2	−1.15	32.88	−5.67	2.56
B3	−11.63	20.89	25.09	23.33
C2	−3.06	1.46	10.4	4.66
E2	−9.93	51.8	30.44	24.08
H	−4.92	−60.62	1.17	8.67

brightness accompanied by a green shift (about 30%) and a growth in the blue intensity.

3.4. Paper characterisation in the infrared region

The IR spectra of the untreated paper samples B, F and G were subtracted from their laser cleaned counterparts in order to arrive at a conclusion on the laser interaction effect. The single-pulse laser treatment at 532 nm was performed as long as a visible effect of laser irradiation appeared (sample B: 2.5 J/cm^2, 30–40 pulses; sample F: 3 J/cm^2, 40 pulses; sample G: 0.5 J/cm^2, 1–2 pulses). The difference spectra obtained in this way are represented by the wavenumber dependences of the standard Kubelka–Munk parameter KM and are shown in Fig. 6. All samples reveal measurable differences in the spectra due to laser cleaning.

The most impressive changes reproduced for all samples are observed in the strong OH oscillation band of 3200–3600 cm^{-1} and indicated on broken bonds between the cellulose molecules [7]. An increase of the stretching mode oscillations of the CH groups (2850–2960 cm^{-1}) indicates on formation of the intramolecular bonds. This conclusion is confirmed for sample G by the presence of the intensity minimum and maximum between 1600–1700 cm^{-1} resulting from the shift of C=O bond (from 1700 to

1640 cm^{-1}) after cleaning. Also an increase of band intensities corresponding to cellulose bonds–COC– (1080–1300 cm^{-1}) and –CO– (1000–1200 cm^{-1}) can be observed. This can indicate that the cellulose structure becomes less compacted after later cleaning.

It is necessary to notice that the changes due to laser cleaning and observed in all the spectra can be caused by: (1) changes in molecular structure of the paper (cellulose or other components); (2) molecular changes of the contaminants; (3) removal of the contaminants – if they absorb sufficiently the radiation.

The bands which can be ascribed certainly to the stains are not resolved in the spectra. Nevertheless, the sample contamination can absorb some part of radiation. This in turn can result in the observed differences and in the intensity increase of the peaks corresponding to cellulose bonds after cleaning. From the other hand the largest changes are observed for the less contaminated sample G. The heavily stained samples F and B indicate much smaller differences between their spectra before and after cleaning. This lead to the conclusion that the contaminants do not absorb significantly so the peaks in the resulting differential spectra can be finally ascribed to the structural changes of the paper.

Moreover, it is interesting that the largest changes in the spectra are observed not for samples treated with highest energy and largest number of laser pulses but for these revealing the lowest damage resistance because of worst production technology or ageing. The DRIFT technique due to its sensitivity seem to be an efficient tool for the study and identification of the paper structure and for finding the fluence threshold of cleaned paper objects.

4. Conclusions

Samples of paper from various historical periods (XIII–XIX c.) were characterised by means of methods of the optical spectroscopy in the spectral range from near-UV up to IR in order to validate the reliable pre-, in situ and post-processing diagnostics required for the laser cleaning which is extensively studied recently. The experimental data obtained by means of spectrophotometry, spectrofluorimetry, LIF, LIPS, DRIFT and colour metric measurements revealed the usefulness of laser-supported spectral diagnostic (LIF and LIPS) at various stages of the storage and conservation process of historical paper docu ments. The photo- and fluorimetric studies delivered information on the wavelength selection for the laser cleaning process and the 532 nm laser has been chosen in agreement with the literature. Also the DRIFT and colour metric techniques appeared as powerful and sensitive tools for investigation and identification of the molecular structure of the paper, and for absolute colour measurements, respectively. Changes in LIPS spectra recorded during laser cleaning showed the accordance with the cleaning progress and confirmed that this spectroscopic technique can be applied for monitoring of the surface contamination removal on paper documents.

Acknowledgements

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