TITANIUM AND CARBON IN TEXTILE STRUCTURE BY LIBS METHOD

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Abstract
Laser induced breakdown spectroscopy (LIBS) is a serious method of chemical analyze of textiles. By the LIBS method we can estimate contain of more than 60 chemical elements in textile fibers. In this study is presented the interaction of laser beam with textile structure. The laser beam penetration into a textile structure is the topics of this study. The carbon and titanium concentrations were observed. This study present an influence of textile structure and quentitz of pulses on the estimated concentration of titanium in textiles.
Key words: LIBS, titanium, textile, TiO_2

1. Introduction

Laser Induced Breakdown Spectroscopy (LIBS) is a novel dynamically developing method of atomic spectroscopy with wide range of applications being described to this time. In the LIBS technique, a high power laser pulse is focused on to sample surface and plasma plume evolves as a result of interaction of incident beam with sample mater. The plasma created breaks down all sample chemical bonds and ionises many of constituent elements. The spectral emission occurs as a result of the subsequent relaxation of constituent excited species. Emission from the atoms and ions is collected by a lens of fibber optics and analysed by spectrograph and gated detector. Wavelengths of spectral lines emitted can be used to determine the elemental composition of the sample, intensities of characteristic lines corresponds to the elemental concentrations in the sample.

The most significant, representative and recent applications of LIBS described in the literature are analysis of alloys (molten samples, samples under water, detection of defects, surface analysis, analysis of light elements, fully automated systems with auto-samplers and so on), archaeological materials and art objects (low invasive analysis, possibility to perform *in-situ* measurements, high spatial discrimination, rapidity and capability for direct analysis without sample pre-treatment, connection of analytical and cleaning process), pharmaceutical products (fast multi-elemental analysis), aerosols (mobile systems for direct analysis of automatically acquired aerosol filter samples), military, homeland security and forensic samples [1].

In LIBS, a high power laser pulse is focused on a small spot of the sample which ablates the surface layer, and successively heats and ionises the vaporised matter, producing the plasma. The spectral emission, which occurs as a result of the subsequent relaxation of constituent excited species, is measured by an appropriate spectrometer. [2]

LIBS method is useful for the analyses of many elements in textile structure [3] and especially titanium contain is important from practical point of view. Titanium in the form of TiO_2 can be used not only as e delustring agent, but as a photocalalytic compound in smart and high-tech textiles. [4]

2. Experiment

Textile fabric

The experiment were realised on polyester fabric from delustred fibres (containing TiO_2 particles).Description of fabric structure: plain wave (weft: 200 per $10cm^{-1}$, warp: 410 per $10cm^{-1}$), areal weight $180g.m^{-2}$.

LIBS

The LIBS spectrometer (LEA S500, Solar TII Ltd., Belarus) used is fully described in [5]. The instrument integrates a dual pulse Q-switched Nd:YAG laser, operating at 1064 nm. The laser emits two colinear pulses of about 10 ns duration with energy per pulse variable between 80–150 mJ at maximum repetition rate of 20 Hz. The inter-pulse delay can be set from 0 to 20 ms. The spectrograph with focal length 500 mm and grating 1800 lines mm^{-1}. The wavelength range of the spectrograph is 170–800 nm. Recording of spectra is carried out by means of a back thinned and front illuminated CCD camera (2048 _ 14 pixels) with a minimal integration time of 1 ms.

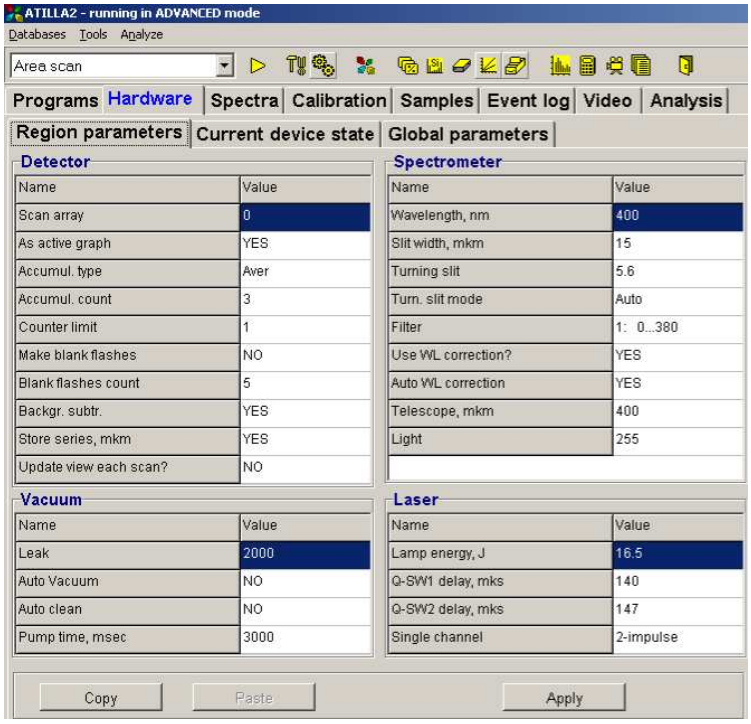

Figure 1. Parameters of LIBS

The adjusted parameters of LIBS (LEA 500) are visualized in Fig.1. From the measured spectra were extracted values connected with carbon concentration in sample (carbon peak at 388.340 nm), values connected with titanium concentration in sample (titanium peak at 399.864 nm). The background was measured near to the titanium peak – at the wavelength 399.796 nm.

The sample was irradiated by the laser in the instrument LEA 500 at 6 different places. Each place was measured (irradiated) 20-times.

3. Results and discussion

The values of background and both measured peaks (titanium and carbon) are decreasing with the quantity of shots. Background and the peak of carbon are decreasing linearly with the quantity of shots, but the titanium is nonlinearly. The average results values from all 6 measured places are presented the in graphical form in Fig. 2.

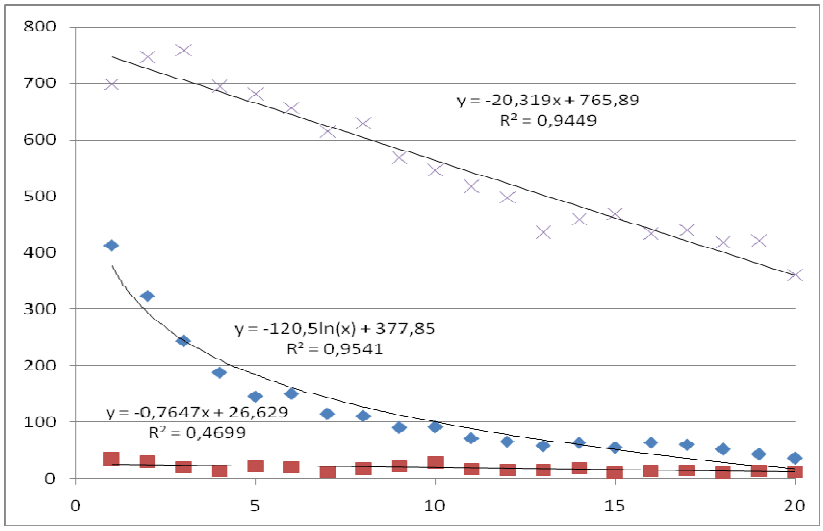

Figure 2: Change of measured LIBS values of bacground (squers), titanium peak (rhombs) and carbon peak (crosses), horizontal axes: quantity of shots, vertical axes: LIBS measured velues

The variation of results is relatively high. Each meseured dependence is diferent, bacouse the textile strcture is uneven (unhomogenic). The diameter of irradiated place in the instrument LEA 500 is maximal 0.4 mm. This value was used in this experiment, but 0.4 mm is not enought to obtain stable valuae on textile structure. Used diameter of spot is smaller then the size of structureal period in used fabric. So we can obtaine different ratio of polymer/air at different places of measurement. Samples of spot location on textile structure are presented in Fig. 3.

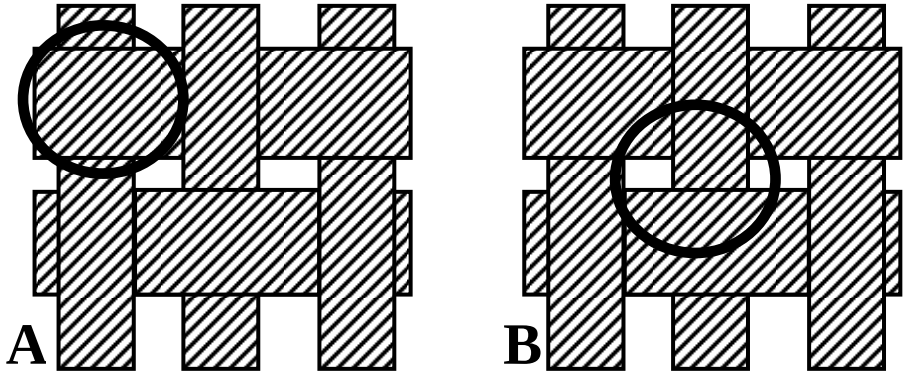

Figure 3: Adjustment of irradiated measured place (circle) on the model of used textile, A ... maximal quantity of fibres below the spot, B ... minimal quantity of fibres below the spot

The difference between irradiated places A and B on the Fig. 3 is not only in the air/polymer ratio on the surface, but in the thickness of polymer below the irradiated area (spot). The energy of single shots is enough high to decompose some fibbers and high quantity of shots can come through the textile structure. The minimal quantity of shots necessary to come through the textile is connected with the quantity of polymer below the irradiated area.

Experimental results we can theoretically divide to two groups. In the group A is the textiles show higher resistance to laser shots. Up to the 8th measurement we obtain stable values of carbon contend. This measurement were realised on the places A on Fig.3.

In the group B is the textiles show lower resistance to laser shots. Measured values are decreasing approximately linearly with the quantity of shots. This measurement were realised on the places B on Fig.3. The average dependences of measurement at places A and B are presented in Fig. 4.

In all cases (A and B) we obtain after 13 shots relatively stable value, which exhibits the coming of laser through the textile (creation of hole in structure).

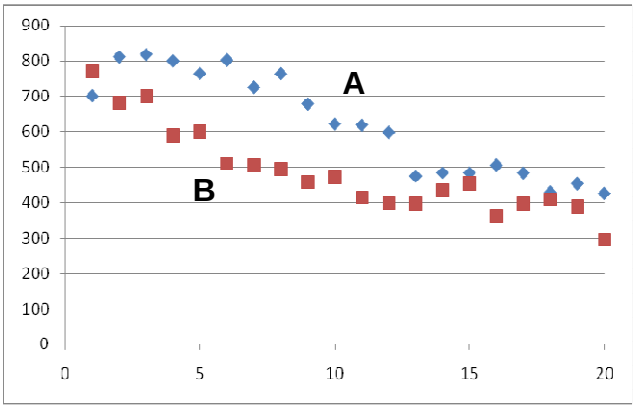

Figure 4: Dependence of LIBS measured values on the quantity of shots at the places with high quantity of fibres (A) and on the places with low quantity of fibres (B)

All measured values are presented in following group of graph (Fig. 5). The measured values of titanium peak, carbon peak and background are presented on graphical form to show possible connections.

Theoretically should be the connection between titanium and carbon peak linear, because the real ratio between this two elements in delustred fibres is stable.

The real dependence is different, probably because the carbon and titanium needs different energies of plasma for light emission and the property of plasma depend on the quantity of evaporated polymer.

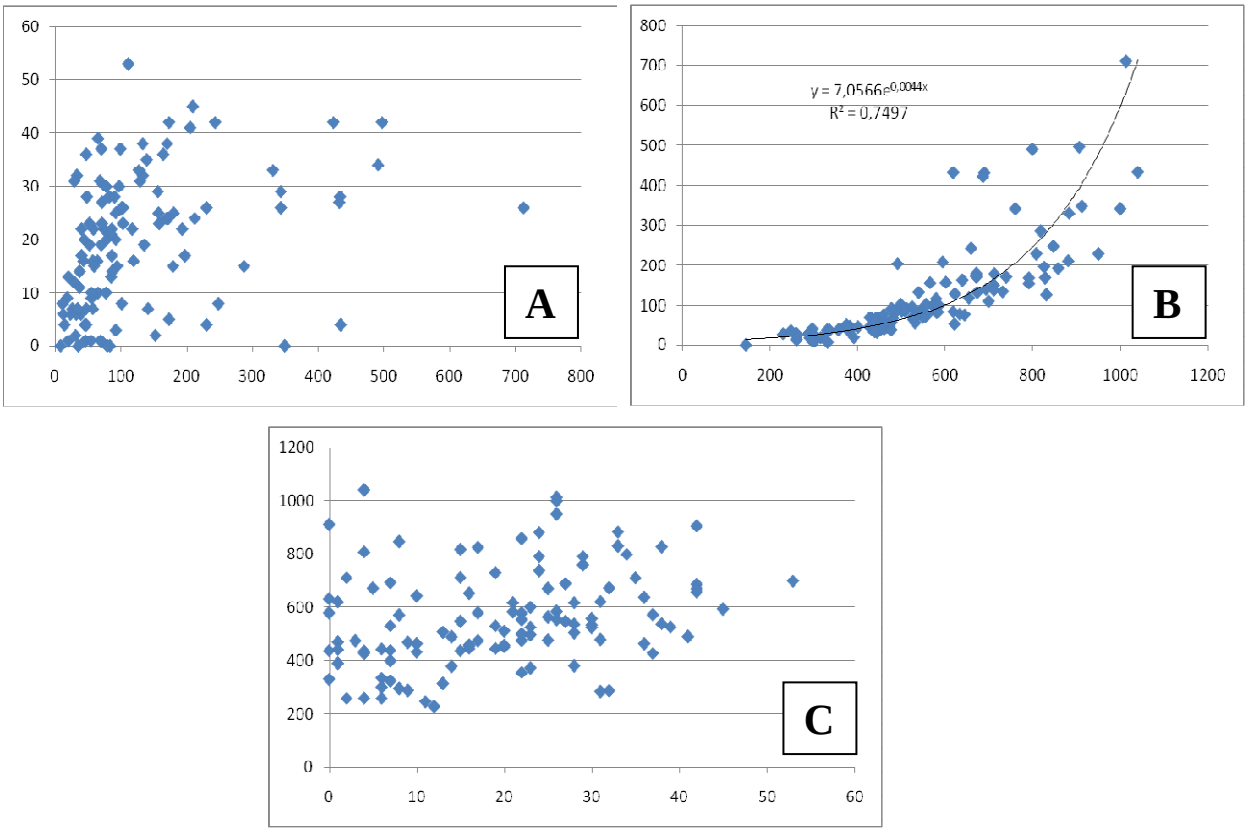

Figure 5: Connection between the measured values from LIBS
A: horizontal axes: Ti peak, vertical axes: background
B: horizontal axes: C peak, vertical axes: Ti peak
C: horizontal axes: background, vertical axes: C peak

4. Conclusion

Using of LIBS to analyze the elements in textile samples is possible. The results are highly connected with the position of spot on the textile; especially the size of irradiated place is smaller than the structural unit of textile. The first shot shows the relatively stable value in real connection with chemical composition of fibres. The next measurements in the same place are connected not only with the chemical composition of fibres, but with the structure (porosity, thickness...) of textile. If we would like to estimate chemical composition is necessary use only one shot on the one place.

5. Acknowledgement

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6. References

1. Pasquini, J., Cortez, J., Silva, L. M. C., Gonzaga, F. B.: *"Laser induced breakdown spectroscopy"*, Journal of the Brazilian Chemical Society, Vol. 18, No. 3, 2007, pp. 463 - 512.
2. E. H. Evans, J. A. Day, Ch. Palmer, W. J. Price, C. M. M. Smith and J. F. Tyson, J. Anal. At. Spectrom., 2007, 22, 663–696.
3. Pouzar, M., Průšová, M., Prokopčáková, P., Černohorský, T., Wiener, J., *„LIBS analysis of chromium in samples of dyed wool fabric"*, J. Anal. At. Spectrom., Vol. 24, No. 5, 2009, pp. 685–688
4. Průšová, M., Wiener, J., Pouzar, M.: *Estimation of Ti on textiles by LIBS method*, The Fiber Society Spring 2010 International Conference on Fibrous Materials, 12 – 14 May 2010 – Bursa, Turecko, ISBN 978-605591902-3
5. V. D. Kopachevskii and M. A. Krivosheeva, Refractories and Industrial Ceramics, 2007, 48(4), 255–258.