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Comparative study on fast classification of brick samples by combination of principal component analysis and linear discriminant analysis using *stand-off* and *table-top* laser-induced breakdown spectroscopy☆

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ABSTRACT

Focusing on historical aspect, during archeological excavation or restoration works of buildings or different structures built from bricks it is important to determine, preferably in-situ and in *real-time*, the locality of bricks origin. Fast classification of bricks on the base of Laser-Induced Breakdown Spectroscopy (LIBS) spectra is possible using multivariate statistical methods. Combination of principal component analysis (PCA) and linear discriminant analysis (LDA) was applied in this case. LIBS was used to classify altogether the 29 brick samples from 7 different localities. Realizing comparative study using two different LIBS setups — *stand-off* and *table-top* it is shown that *stand-off* LIBS has a big potential for archeological *in-field* measurements.

1. Introduction

Laser-Induced Breakdown Spectroscopy (LIBS) [1] is a method capable of fast classification, qualitative and semi-quantitative analysis of samples under investigation. Briefly, high energy laser pulse is focused on the sample surface, small amount of the sample is ablated and luminous laser-induced plasma (LIP) is created. The persistence of LIP is in the order of microseconds. When the plasma plume starts to cool down the best conditions for realizing LIBS measurements occur because intensive ionic and atomic emission lines can be observed in the spectra. Plasma radiation is collected and transported to the spectrometer by an optical setup. The signal of elements can be processed in real time using various chemometric analyses.

LIBS has a great potential in many fields (including industrial, environmental, cultural heritage and extraterrestrial applications), because of its particular advantages over other analytical methods, like quasi-nondestructivity, minimum or no need of sample preparation, relatively low instrumentation cost, experimental setup flexibility including the possibility of in-situ measurements [2]. Moreover, LIBS is a very promising technique for the elemental analysis of many types of cultural heritage objects [3], such as pottery, sculptures, pigments of paintings, glass, calcified tissues, geological samples or metals; as proved before [4–18].

For the analysis of historical walls or historic buildings the possibility of in-situ measurement has many advantages, including the preliminary determination of the origin of brick clay and estimation of chemical composition. The in-situ LIBS analysis of historical building material was presented by Laserna et al. [19], dealing with analysis of the Málaga cathedral walls with a *man-portable* LIBS and later in [20] with a *stand-off* LIBS. Remote sensing is a great advantage in this point, sometimes it might be even necessary. *Stand-off* LIBS could be the solution. In our work we focus on the analysis of historical walls in order to develop a simple and fast method for classification of bricks in-situ.

Focusing on building materials Xia et al. [21] used successfully multivariate analysis (partial least squares discriminant analysis PLS-DA and the hybrid combination PCA–Adaboost) to classify LIBS spectra of various materials for the purpose of concrete recycling.

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Generally, classification of bricks can be done by detailed investigation of their chemical composition. This composition can be revealed by LIBS, but it should be noted that due to the complicated brick matrices the LIBS spectra are very complex. Much information is ignored during the univariate analysis therefore multivariate methods were used with a great success. The chosen method for our purpose is LDA with a subset of PCA scores as inputs.

PCA, method generally applicable as a classification method, was applied here only to reduce the dimensionality in the data set and to discover latent variables among samples. This linear transformation of variables into lower number of so called principal components (PCs) filters out the irrelevant information about measurements and removes highly correlated variables [22]. Using scores of limited number of principal components as inputs for LDA prevents the overfitting [23].

LDA is a multivariate statistical method for discrimination of objects up to a finite number of categories, based on a certain subset of all objects (training set). The principle of this method is maximizing the ratio of the between-class variance to the within-class variance. The decision rules obtained by classification of training set are later applied to the testing set [24,25]. LDA was applied on LIBS measurements before, concerning alloys [26] and historical buildings [27]. The closest application to ours was the classification of IR spectra by means of LDA with principal components as inputs [28,29].

In our previous work [30] combination of PCA and LDA was introduced as an effective method for classification of LIBS spectra of archeological samples. The goal of work was to distinguish 7 types of materials (soil, brick, mortar, ceramics, shell, bone, bear tooth, and human tooth). Now, instead of classifying several different materials, we use the same method for only one of them — bricks, to see how specific this method can be among samples of similar composition, which differ in locality of origin.

The methodology was tested on both, data obtained by *stand-off* and *table-top* LIBS setup. The *table-top* arrangement used for experiment was chosen with respect to possible construction of portable device for in-field measurements. Lower pulse energy was used (as an alternative for diode-pumped laser) and CCD detector — such a device would be portable, low-cost and still effective enough for this kind of classification.

2. Experimental

2.1. Samples

Set of samples consisted of 29 samples containing bricks from 7 localities. 9 samples were laboratory manufactured for testing (localities Šlapanice, Hranice na Moravě and Tallinn) and the other 20 samples come from an archeological experiment, where bricks were prepared using different firing temperatures (localities Skalka u Velimi, Těšetice, Strážovice, Pohansko). Samples are listed in Table 1.

All samples were measured using two setups

- *stand-off* LIBS setup at Central European Institute of Technology (CEITEC), Brno University of Technology, Brno, Czech Republic,
- *table-top* LIBS setup at Department of Thermal Engineering, Tsinghua University, Beijing, China.

2.2. Stand-off LIBS instrumentation

The experimental setup was described in details elsewhere [31]. The *stand-off* LIBS setup contains a pulsed Nd:YAG laser (Solar Laser Systems, LQ 916) working on its second harmonic frequency (532 nm). Three-lens Galilean telescope optimized to have a focal spot with the smallest spherical aberration at the distance of ~10 m was used as a focusing system. The focusing system was projected to have the optimal spot size in the middle of the expected range of utilization (5–15 m) the *stand-off* LIBS apparatus is designed for. Using these parameters the diameter of ablation spot was ~1 mm at the analysis distance of 6.2 m. The emission was collected by a Newtonian telescope (Sky-Watcher, Synta), with a primary mirror diameter of 10″, and then transported through the optical cable (500 μm in diameter) to the spectrometer in Echelle configuration (Andor, Mechelle 5000) coupled to the ICCD detector (Andor, iStar 734i). The spectral resolution (λ/Δλ) of the spectrometer (corresponding to 3 pixels FWHM) for a 50 μm in diameter entrance slit used in these measurements is about 4000. Measuring conditions were optimized in order to get the best signal to noise

Table 1
List of samples.

Sample number	Sample type name	Locality	Firing temperature (°C)	Sample set
S1	SL	Šlapanice	910	Training
S2	SL	Šlapanice	950	Training
S3	SL	Šlapanice	950	Test
S4	HR	Hranice na Moravě	1050	Training
S5	HR	Hranice na Moravě	1050	Test
S6	TA	Tallinn	950	Training
S7	TA	Tallinn	1050	Training
S8	TA	Tallinn	1100	Training
S9	TA	Tallinn	1060	Test
S10	SK	Skalka u Velimi	1000	Training
S11	SK	Skalka u Velimi	900	Training
S12	SK	Skalka u Velimi	800	Training
S13	SK	Skalka u Velimi	700	Training
S14	SK	Skalka u Velimi	600	Test
S15	SK	Skalka u Velimi	500	Training
S16	SK	Skalka u Velimi	400	Training
S17	SK	Skalka u Velimi	300	Training
S18	TE	Těšetice	900	Training
S19	TE	Těšetice	600	Training
S20	TE	Těšetice	500	Test
S21	TE	Těšetice	400	Training
S22	TE	Těšetice	300	Training
S23	ST	Strážovice	900	Training
S24	ST	Strážovice	800	Training
S25	ST	Strážovice	700	Test
S26	ST	Strážovice	600	Training
S27	ST	Strážovice	300	Training
S28	PO	Pohansko	600	Training
S29	PO	Pohansko	300	Test

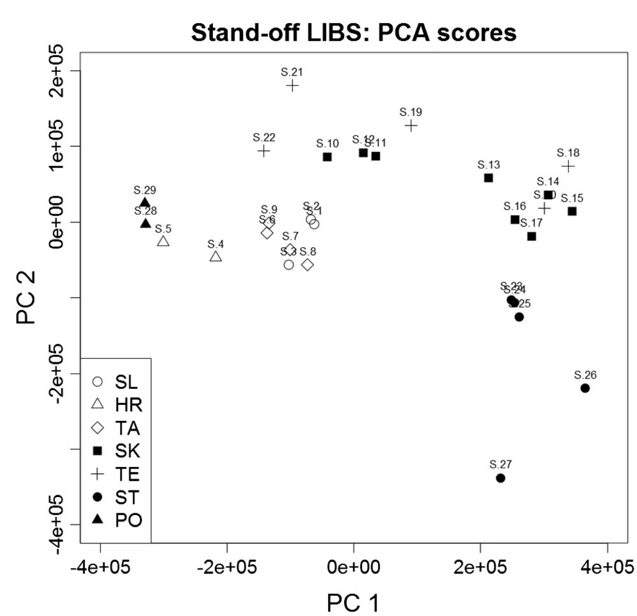

Fig. 1. *Stand-off* LIBS results: clustering of localities on the first two principal components (projection pursuit method) counted from whole spectra of all samples.