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Analytical capability of LIBS method for carbon detection

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In this work, several applications about carbon detection by LIBS for identification and quantification purposes and for assistance during the surface cleaning of materials will be presented. The first set of applications focuses on the qualitative analysis of polymers where the interest was to determine the presence of carbon and other elements for identification of their compounds. In the second case, the carbon lines monitored during laser cleaning process allowed to control the removal of surface contaminants located on specimens covered by dense layers of hydrocarbons coming from oil spill residues. Finally, two examples of quantitative measurements were achieved on coal and fly ashes specimens coming from a coal-fired power station. In this last application, the utilization of an adequate procedure of data processing is crucial since quantification is one of the major difficulties which limit the progress of LIBS technique toward a mature analytical tool.

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1. Introduction

Carbon is a key element to examine in a large variety of sample types. Its detection and quantification lead to the determination of material types or distinguishing the products. Inorganic and organic carbon can be detected by laser-induced breakdown spectroscopy (LIBS) through its atomic spectral lines C(I) or molecular bands, C_2 (Swan) and CN, such as in the case of polymers, coal or cells.

LIBS measures the total abundance of an element in a sample because the plasma generated in this process breaks down the original target sample into its component parts. In principle, all information about the starting material structure and bonding is lost. However, the signal obtained from an element depends on the compound form of this starting material [1]. Hence, Eppler et al. observed differences in the emission signal from constant content of Pb and Ba ratioed to C (247.8 nm) in the analysis of soils. These differences were due to a chemical matrix effect in which the constituents in the compounds change the excitation and emission characteristics of Ba and Pb. Alternatively, it could be due to the difference in the mass of each compound ablated which possess different thermal and optical properties.

Characterisation of organic compounds like polymers using LIBS requires careful data processing. Due to their similar elemental compositions, it is necessary to carry out intensity ratios of various elements to distinguish one polymer from another. The ratios used by Anzano et al. [2] were: (i) H/C(I) ratio, this is the most important ratio for identifying [3] and differentiating [4] organic compounds; (ii) O/N ratio, under atmospheric conditions if the compounds studied have no nitrogen and oxygen then it will be constant; (iii) C_2/C(I) ratio, which relates the carbon-carbon bonds and number of carbon atoms. Other ratios studied, less important, are CN/C(I) and H/C_2.

The LIBS application to identify chemical stoichiometry usually relies on line ratios to determine molecular concentration. Sattman et al. used C/H line ratio and the chlorine line to identify polymers [5], while others have used combinations of C, H, O and N lines (and ratios) to determine stoichiometry. De Lucia and co-workers used C/P ratio to obtain the stoichiometry in chemical agent simulants [6]. Lopez-Moreno et al. determine whether a sample is explosive or not based on molecular emission of C_2 Swan bands and N, H, O, H/C_2, Na/C_2 emission lines and ratios [4]. Portnov et al. identified organic compounds in air based on intensity ratios of C, H, O, N, C_2 and CN [7].

The comparison of LIBS with standard combustion method for carbon content detection in soils showed satisfactory correlation for concentration range 0.16 – 4.32 % [8]. The existence of metals and other inorganic matter in the combustion products of boilers and industrial furnaces can have deleterious effects on furnace refractory materials and boiler convection pass heat transfer surfaces and can contribute to stack particulate-matter emission. Thus, the monitoring and process control is necessary. Applied in situ, LIBS offers a rapid time response relative to the other techniques and avoids some uncertainties associated with extractive probes used at high temperature and pressure [9]. Hohreiter et al. compared LIBS spectra of two carbon sources (particulate and gaseous) with the "same" concentration of atomic carbon. The observed emission signal was found to depend on the physical state of the analyte source [10]. Such findings challenge the widely held assumption that complete dissociation of constituent species within the highly energetic laser induced phase results in independence of the atomic emission signal on the analyte source.

The quantification of carbon by LIBS was carried out by many investigation groups and some of them can be found in Table 1.

Table 1. LIBS detection limits for carbon.

Emission line	Medium/ Matrix	LOD (ppm)	Reference
247.8	LiCl solutions	50	Cremers [11]
833.5	air	36	Dudragne [12]
193.1	Steel	65	Aguilera [13]
193.1	Steel	80	Aragon [14]
193.1	Steel	7	Sturm [15]
97.7	Steel	87	Khater [16]
247.8	Soil	300	Cremers [17]
193.1	Steel in air	3	Noll [18]
133.6	Steel	5	Hemmerlin [19]
97.7	Steel	1.2	Khater [20]
193.1	Steel in Ar	7	Sturm [21]
193.1	Steel	7	Radivojevic [22]
247.8	Soil, 7 Torr CO_2	0.24%	Radziemski [23]
193.1	Soil, 7 Torr CO_2	0.32%	Radziemski [23]
165.7	Soil, 7 Torr CO_2	0.51%	Radziemski [23]

The present study is based on the detection of carbon by LIBS through various types of applications: identification of polymers, monitoring of a laser cleaning process and quantification of carbon in coal and fly ash.

2. Experimental

Single-pulse LIBS instrumentation set-up consisted of conventional arrangement including pulsed Nd:YAG laser, focusing and collecting optics, spectrograph with detector and was described elsewhere [24]. The laser operated at its fundamental 1064 nm, second 532 nm and third 355 nm harmonic wavelengths. The maximum energy output was 300 mJ/pulse and pulse duration of 5 ns. The maximum repetition rate of used laser was 10 Hz, but due to the detection system speed capacity, the frequency of 2 Hz had to be used.

The laser beam was directed normally to the sample surface passing through a planoconvex quartz lens (focal length 300 mm). The sample was placed few millimeters away from the focal point of the lens in order to provide larger spot and increase the repeatability of the measurements. The microplasma created on the sample surface was collected by collecting lens placed in the distance of 4 cm from the sample surface and coupled to a quartz optical fiber and transmitted to an Echelle spectrograph coupled to an ICCD camera. The spectrograph spans the spectral region of 200–850 nm simultaneously with high resolution, thus it allows multi-elemental analysis under the same experimental conditions for each element. The spectral lines were chosen according to commonly used strategy, the interfered or self-absorbed lines were avoided. The detector delay time and integration time were set according to experimental needs. The experiment was operated using personal computer and temporal conditions were introduced with a pulse delay generator. All experiments were performed in air under atmospheric pressure.

The specimens investigated were of different nature: polymers, rocks contaminated by oil, coal and fly ash. Concerning the polymers category, four plastic sheets (red and yellow sample of polypropylen, silicone, metacrylate) of common use were used for comparison purpose. Moreover, a pigment sample of cadmium red mixed with linseed oil and spread over a wooden substrate was analyzed. The second set of specimens was rocks fragments and stones covered with different fuel thicknesses, collected from the Galician coast during the Prestige disaster. The fuel oil originated from the Prestige tanker is a very viscous water-insoluble product, basically composed of saturated hydrocarbons, resins, naphthalenes and polycyclic aromatic hydrocarbons [25]. In this case, owing to the rugged topography of the pieces, samples were situated in X–Y–Z stages and an alignment system consisting of two He–Ne lasers was used to help in sample positioning in terms of laser focal point situation, collection alignment and point-to-point clean-up. Finally, coal and fly ash samples were obtained in powder form from a coal fired power plant. Once the powder was mixed and homogenized with a KBr binder in ratio 1:4 in agate mortar, it was pelletized in a manual press.

3. Results

3.1 Identification of polymers

Carbon can be detected by LIBS trough its atomic emission lines (main at 247.8 nm), CN bands (385.4; 386.1; 387.1; 388.3; 416.7; 418; 419.6; 421.5 nm) and C_2 Swan molecular bands (469.5; 471.4; 473.6 nm). Molecular bands are observed in organic compounds or may ensue from the chemical reaction with surrounding atmosphere, while atomic line represents total carbon content. Material of the sample is almost entirely atomized when exposed to intense laser radiation, so the molecular information is lost. Peak ratio in combination with the analysis of molecular bands serve for identification of materials [2].

In the present work, one pigment and four polymer samples were analysed by LIBS. Fig. 1 depicts the LIBS spectrum of Cadmium red pigment sample with zooms in interesting regions of C(I) line and molecular bands. The objective of this experiment is the use of carbon lines (among other elements) for material identification which is interesting in the field of analysis of paints found in cultural heritage specimens and art objects. The detectability and quality of particular lines and bands are strongly dependent on LIBS experimental conditions, especially on detector timing.

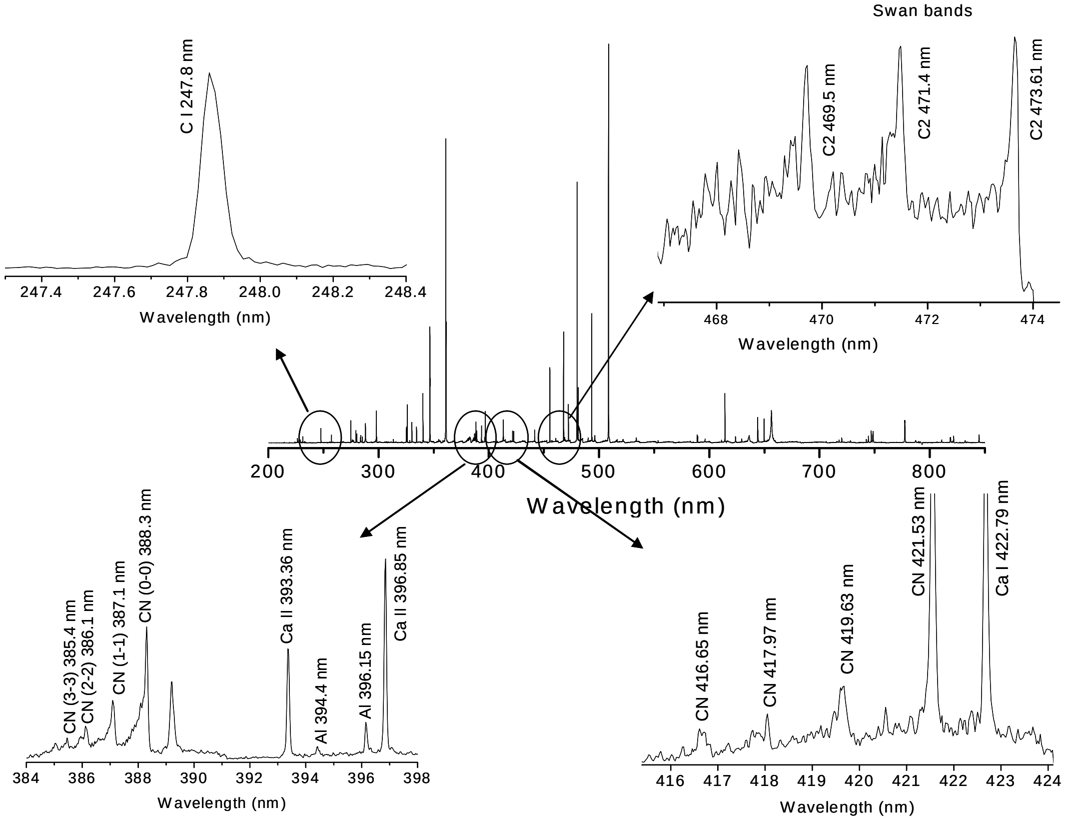

Fig. 1. LIBS spectrum of Cadmium red pigment with presence of C line at 247.8 nm, CN and C_2 Swan bands. The experimental conditions used for the spectrum acquisition were laser wavelength of 532 nm, energy of 130 mJ/pulse, delay and integration time both of 2 μs.

Polymer materials have usually similar elemental composition and are hard to distinguish qualitatively. The capacity of a chemical method to distinguish between polymers is important in the field of manufacturing process control and recycling. Except of Si present in silicone, the elements of all four polymers used in this work are C, H and O (PMMA – poly methyl methacrylate $(C_5O_2H_8)_n$, silicone $[R_2SiO]_n$, where R = organic groups such as methyl, ethyl, and phenyl; PP – polypropylen $(C_3H_6)_n$). Figure 2 shows a histogram used for distinguishing various polymers based on the spectral band and atomic lines ratios. Samples called red and yellow plastic are polypropylene based materials differenced in type and amount of organic additives. The heights of the histogram bars can be used to classify particular samples for process control or recycling category based on fast and easy LIBS method.

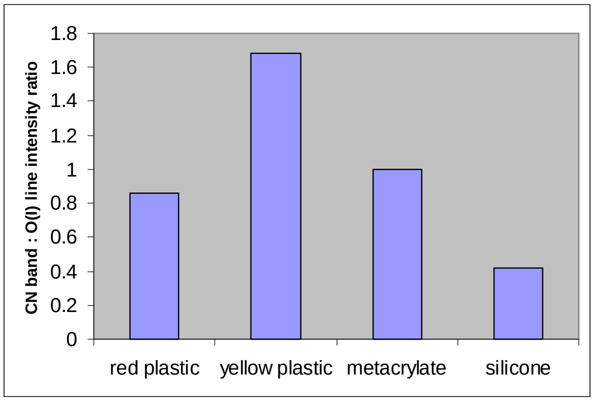

Fig. 2. CN bands signal divided by O signal to distinguish different polymers. The experimental conditions used for the spectrum acquisition were laser wavelength of 532 nm, energy of 130 mJ/pulse, delay and integration time both of 2 μs.

3.2 Cleaning monitoring

LIBS can also be applied for monitoring a cleaning process through the detection of the characteristic lines. As an example, the laser cleaning of oil spill residues on solid surfaces is presented in Figure 3. More about LIBS application on oil spills can be found in [26] and about laser cleaning in [27].

Fig. 3 shows the depth profiles of C and Si which are the elements of interest for the fuel and rock, respectively. A depth profile is the signal corresponding to the element charasteristic of the upper or lower layer material in dependence on depth or number of pulses fired to the same position on the layered sample. Such profile represents the process of upper material removal from the base layer. When the signal corresponding to the upper layer drops to a determined value and in the same time the signal of the base layer increases to a determined value [28], the removal speed and, consequently, the thickness of the layer can be obtained (see inset of Fig. 3). For the same reason, the ratio of the spectral lines corresponding to the upper and lower layer, respectively, can be directly recorded. These features are of interest for thickness determination and self-controlling cleaning processes of layered materials. This is illustrated in Figure 3 where the ratio of C and Si intensities is plotted, as well as the intensities of C and Si separately. Both cases indicate that about 75 pulses are required to fully remove the fuel crust from the rock surface.

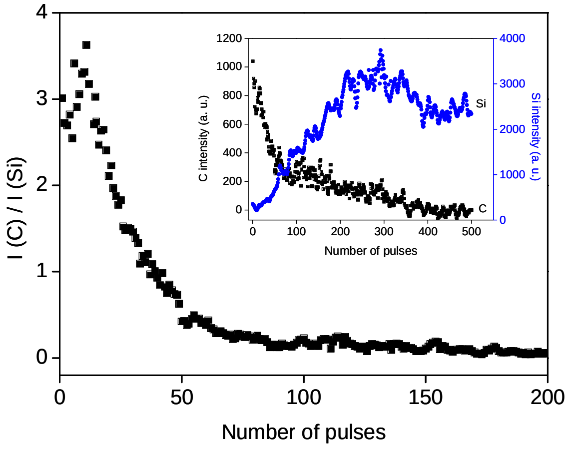

Fig. 3. LIBS depth profile C/Si intensity representing the removal of a fuel crust from a polluted rock. The inset of the figure corresponds to the depth profiles of C and Si intensities separately. The experimental conditions used for the spectrum acquisition were laser wavelength of 355 nm, energy of 200 mJ/pulse, delay and integration time both of 500 ns.

3.3 Quantification of carbon

Quantitative approach is not always possible with LIBS method. However, if an adequate procedure is applied for data processing, calibration curves can be obtained. In a previous paper, the authors presented the calibration curves of some elements of interest (Fe, Al, Si, Mg, Ca) in coal samples [29]. In the present paper, the carbon calibration curve was obtained from coal and is shown in Figure 4.

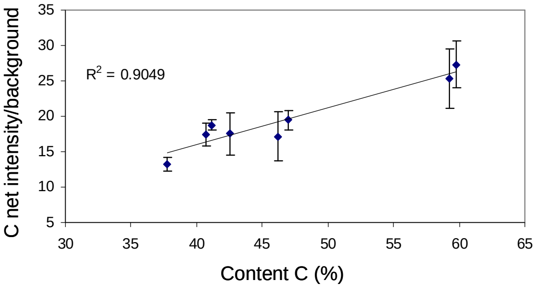

Fig. 4. Calibration curve of carbon in coal expressed as ratio C net intensity/background vs content of C in %. The carbon line used was C (I) 247.8 nm. The experimental conditions used for the spectrum acquisition were laser wavelength of 532 nm, energy of 180 mJ/pulse, laser repetition rate of 2 Hz, delay and integration time of 1 and 10 μs, respectively. Error bars correspond to 10 laser shots.

As the direct dependence of C spectral line intensity on carbon concentration did not result in linear dependence, it was necessary to apply data processing method. The net intensity of C line at 247.8 nm was divided by the background intensity in the proximity of carbon line and a linear dependence with a correlation factor of 0.9 was obtained. By this way, we can reduce shot-to-shot variations in the emission signal and hence improve measurement precision and correct nonlinear behaviour. The carbon content was determined using an automatic analyzer CHN.

The interest of coal fired power plant is to examine the elemental composition both in coal and in respective fly ash in order to control the combustion process. As described in the previous case of coal samples, the problem of non-linearity of calibration curves was observed as well in the case of fly ash samples. Each element behaves differently depending on experimental conditions of ablation and thus a different data processing method is suitable for each case. One of these methods is the use of an internal standard where a more precise quantification can be obtained. In this case, the analyte signal is divided by the internal standard element signal [30]. Carbon was already used as an internal standard in pharmaceutical industry for the analysis of organic materials in order to increase analytical precision for phosphorus quantification [31]. Cremers and Radziemski described also the internal standardization using silicon for the calibration curves construction of carbon in soil samples [17].

Various approaches of data processing methods were previously studied for the case of fly ash, as was gross intensity, net intensity, peak area and net intensity/total intensity ratio. Note that the “total spectra intensity” means the sum of the intensity recorded by the detection system used. The case presented in Fig. 5 shows the silicon calibration curve, where C(I) spectral line was used as an internal standard to obtain linear calibration curve for the analysis of fly ash.

“Limits of detection (LOD) obtained from presented LIBS measurements are rather high (0.12 % for carbon and 3.16 % for silicon), compared to other conventional quantification techniques, as a consequence of the naturally high content of Si and C in samples. LOD were calculated according to the IUPAC definition [32]. Consequently, LOD = (3.SDb) /S = (3.RSDb) / (S/B), where SDb is the standard deviation of the background, RSDb is the relative standard deviation of the background and S is the slope of the linear part of calibration curve. Background was measured in the proximity of the corresponding spectral line.”

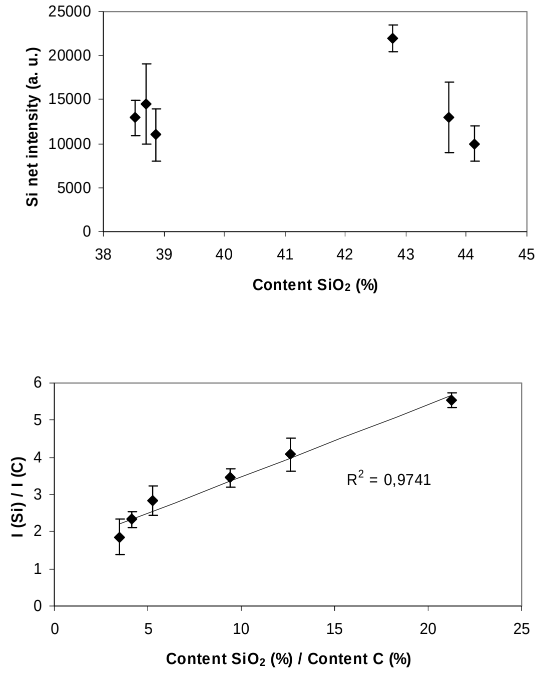

Fig. 5. Calibration curves of Si net intensity and of Si/C net intensity in fly ash samples. The spectral lines used for the detection were Si (I) 288.2 nm and C (I) 247.8 nm. The experimental conditions used for the spectrum acquisition were laser wavelength of 532 nm, energy of 100 mJ/pulse, laser repetition rate of 2 Hz, delay and integration time both of 1 µs. Error bars correspond to 10 consecutive laser shots.

Both coal and fly ash samples were prepared in the form of powders. For easy and fast LIBS analysis the samples were pelletized. Some difficulties may arise from samples preparation, such in the case of some pharmaceutical products, which are in tablet (pellet) form with the presence of binders. In one hand, the use of binder enables the sample cohesion, on the other hand, it may bring problems such as spectral interference. Our case of pellet preparation was much easier than pharmaceutical tablets. Indeed, fly ash was pelletized with KBr binder and coal did not need any binder to ease the pellet preparation. The reason of choosing KBr over more usual organic binders was mainly to avoid the interference of organic C in carbon quantification. The silicon oxide content displayed in Figure 5 was previously measured by authors with conventional technique Inductively-coupled plasma – Optical emission spectroscopy after sample fusion and dissolution. The carbon content was also determined using an automatic analyzer CHN.

4. Conclusions

Various approaches of LIBS were applied to examine carbon in a variety of specimens. At first, the spectral lines and molecular bands of carbon were detected in the case of polymers and a pigment sample for their identification. It was proved that materials having similar elemental composition can be distinguished based on carbon lines and molecular bands. In particular, polymers, namely poly methyl metacrylate and two polypropylenes with different organic additives can be distinguished by the relation between CN band and oxygen line.

Carbon detection by LIBS was also achieved in the cleaning process of rocks spilled with oil residues. The feature of LIBS is the self-controlled cleaning based on depth profiling of the oil layer represented by the carbon intensity. The cleaning process is stopped when the rock surface is reached, namely when the carbon line disappeared.

LIBS was found suitable for quantitative analysis of carbon in energetic industry. The elemental analysis of coal and respective fly ash is required opportune to control the combustion process in coal-fired power plants. Hence, it was showed that proper data processing may lead to linear calibration curves. Different data processing suits to each element. While the linear calibration curve for carbon in coal was obtained by dividing net intensity by the background, some elements of fly ash showed improvement of calibration curves when dividing its net intensity by the carbon intensity used as internal standard.

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