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Biomedical and environmental applications of laser-induced breakdown spectroscopy

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Abstract. Laser-induced breakdown spectroscopy (LIBS) is an emerging analytical technique with numerous advantages such as rapidity, multi-elemental analysis, minimal sample preparation, minimal destruction, low cost and versatility of being applied to a wide range of materials. In this paper, we report the preliminary observations we obtained using LIBS for clinical and environmental samples. Elemental analysis has been done qualitatively in human teeth samples which show encouraging results. It has also been demonstrated in this paper that LIBS can be very well utilized in field applications such as plastic waste sorting and recycling.

Keywords. Laser-induced plasma; spectroscopy; teeth; plastic; principal component analysis.

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1. Introduction

In recent years, LIBS has been shown to be a versatile elemental analysis tool attracting increased attention because of its broad range of applications. LIBS can be used for analysis of both environmental samples (soil, water, etc.) and physiological samples (tissue and body fluids) [1–4]. Conventional spectroscopy techniques such as inductively-coupled plasma optical emission spectroscopy (ICP-OES), ICP-mass spectroscopy (ICP-MS), and atomic absorption spectroscopy (AAS) are good in analytical performance, but their sample preparation method is destructive and environmentally hazardous. These techniques normally involve the acid digestion of the silicate and organic matrix under conditions of elevated temperature and pressure, requires hazardous chemical use and disposal and is time-consuming as well. All these methods are capable of analysing only one element at a time. Compared to these methods, LIBS has numerous potential advantages such as simplicity in the experimental set-up, less sample preparation, less destructive analysis of sample, possibility of remote elemental analysis for hazardous or inaccessible targets, etc.

Also, LIBS technique has the advantage of measuring several elements simultaneously up to limits of parts per million. In view of the above, we have carried out some preliminary studies to develop a method for elemental analysis of clinical/environmental samples like teeth and plastic.

2. Methodology

In the present study, a LIBS system (figure 1) has been assembled and optimized using the following components: a pulsed Nd:YAG laser (Quanta-Ray PRO-230-10, Spectra-Physics/Newport, USA), a high resolution echelle spectrograph (Mechelle, ME5000, Andor, Ireland), an intensifier charge coupled device (ICCD) from iStar, (DH734-18U-03PS150) Andor, Ireland, embedded with gate/delay generator and optical/optomechanical components. The assembly was interfaced to a computer (Intel(R) Core (TM) Duo, Speed 3 GHz, 4 GB RAM, 520 GB memory) which controlled experimental steps, collected and stored the signal, and processed the data to give the final results. Further details about the experimental set-up are discussed elsewhere [5,6].

Teeth samples utilized for this study were obtained from Oral Surgery Department, Manipal College of Dental Sciences, Manipal. For the LIBS studies on plastics, only plastics with class number marked on it were used. From each class (namely polyethylene terephthalate (PET), high-density polyethylene (PE), polypropylene (PP) and polystyrene (PS)), 12 spectra were collected under identical conditions and air ambient. No sample preparation was involved in the study and no pre-processing of the spectra was done before statistical analysis, i.e. principal component analysis (PCA).

3. Results and discussion

3.1 *Biomedical application: LIBS studies on human teeth samples*

Elemental analysis of teeth after hard tissue Osteotome (figure 2) has been tried using LIBS. A typical sample (figure 2) was divided into three regions where the elemental com-

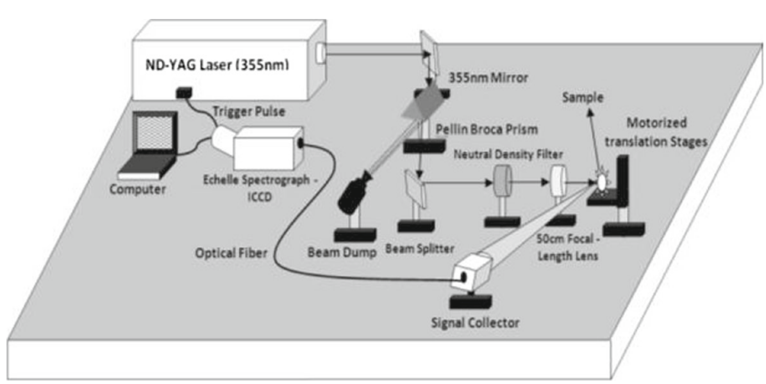

Figure 1. LIBS experimental set-up used for plastic identification.

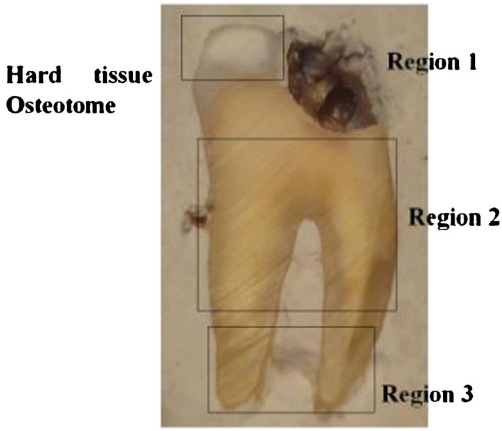

Figure 2. Hard tissue Osteotome image and the regions chosen for the current study.

position of the teeth is expected to vary. Generally in teeth, the calcium and phosphorus concentrations decrease from region 1 to region 3 (i.e. enamel to root) [7] but the magnesium concentration increases from region 1 to 3. To verify this, each region of the sample was exposed to laser (irradiance $\sim 10^{11}$ W/cm^2 for all three regions) and LIBS spectra were recorded for 500 ns gate delay and 3 μs gate width.

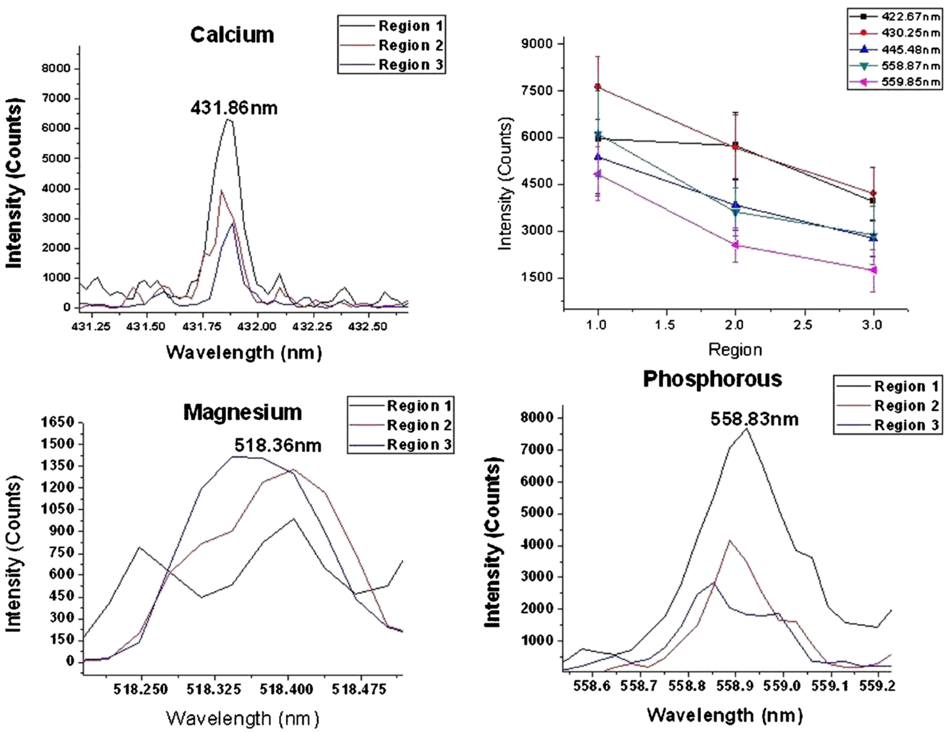

Figure 3. LIBS spectral variations of calcium, magnesium and phosphorus at different regions in calcified tissue sample.

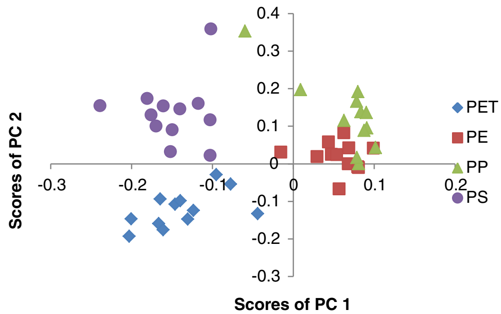

Figure 4. PCA results on LIBS studies using plastics, showing scores of PC1 vs. scores of PC2.

Further analyses of the recorded LIBS spectra of teeth gave rise to interesting results. Excellent correlation between literature [7] and results has been observed. The maximum intensity of the calcium emission line (431.86 nm) fell as we moved from regions 1 to 3. The same trend was observed in five different emission lines of calcium (422.67 nm, 430.25 nm, 445.48 nm, 558.87 nm and 559.85 nm) which confirmed the results. Also magnesium emission intensity was increasing from regions 1 to 3. Phosphorous spectral behaviour was matching with that of calcium. The results are shown in figure 3.

3.2 *Environmental application: LIBS studies for plastic classification*

When sufficiently intense laser (4.88×10^8 W/cm^2) is irradiated on the sample, plasma is generated whose emission spectrum can reveal the identity of the elements present in it. Plastics are no exception for this but different plastics behave differently depending on the composition of the polymer. The emission spectra can then be studied by different ways like calculation of different C, H ratios, pattern recognition (compared with a standard) or statistical methods for classification. Details of data processing and data analysis using Thermo Galactic GRAMS/AI (specialized spectroscopic data analysis software for principal component analysis (PCA)), with fluorescence, Raman and protein profile data, are given elsewhere [8,9]. The PCA results of LIBS spectra recorded from all four classes of plastic samples with scores of principal component 1 (PC1) against principal component 2 (PC2) are shown in figure 4. It can be seen that there is fairly clear clustering (classification) among different classes of plastics.

4. Conclusions

The presence and relative concentrations of major elements (calcium, phosphorus and magnesium) in human teeth can be easily determined using LIBS technique. The importance of this study comes in anthropology where teeth and bone are main samples from which reliable data can be easily retrieved. The results obtained from plastic studies show that statistical analyses of the LIBS spectra of samples can be used for successful classification of different classes of plastics, viz. PET, PE, PP and PS. This method, once automated, will be capable of accurately sorting plastics within seconds and saves considerable amount of time and energy in comparison to other existing methods.

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