

Laser Induced Breakdown Spectroscopic Analysis of Dental Elastomeric Impression Materials

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Abstract: Laser-induced breakdown spectroscopic analysis was done for 4 different dental elastomeric impression materials (polyvinylsiloxane) to evaluate the feasibility of new, fast, accurate, non contact and simple technique which is now a frequently suggested method for qualitative and quantitative elemental analysis in various environments. This technique uses Nd: YAG laser in conjunction with MS257 Spectrograph to record the data. The results showed that the elemental composition and the relative abundance of elements in each elastomeric impression material were found to be quite similar. Varying amounts of silica, oxygen, carbon, aluminum, magnesium, platinum, titanium, nickel were found. The laser induced breakdown spectroscopic elemental analysis was later compared with Energy-dispersive X-ray (EDX) spectroscopic elemental analysis and scanning electron microscopic images of laser induced craters on elastomeric impression materials were taken to see the laser ablated areas.

Key words: Laser-induced breakdown spectroscopy % Polyvinylsiloxane elastomers % Energy-dispersive X-ray spectroscopy % Scanning electron microscopy

INTRODUCTION

Laser induced breakdown spectroscopy (LIBS) is a simple technique to determine the relative abundance of the elements in the particular sample [1, 2]. In other words, it determines the chemical composition of the sample. Materials in any state like solid, liquid and gas can be analyzed using this technique [1]. This is relatively easy and fast method of analysis, the basic experimental set up consists of Q switched Nd:YAG laser (Brilliant-Quantal) which applies a high power laser beam on to the surface of the sample. The energy of the laser is sufficient not only to vaporize the material but also to break all the chemical bonds and ionize the elements present in the sample creating a small plasma plume from the ablated area [3, 4]. This luminous plasma emits light which is observed in ultraviolet, visible and near infrared region.

The light from the plasma is collected by lens and spectral analysis is carried out by spectrograph.

In recent years the rapidly-emerging technique of LIBS has been applied widely due to increasing success for the qualitative and quantitative analyses of a number of metals in soils, gases and liquids with relevant simplification of the conventional methodologies [5-7]. Many studies are done to measure the carbon and other nutrients in the soil and to control the cleaning of sandstone and stained glass [4, 6]. In the field of dentistry, researchers used this technique to analyze the teeth affected by caries and to determine the trace elements accumulation in teeth, quantity of mercury in the silver dental amalgam was also determined [1, 7-13].

The present investigation was performed to evaluate the feasibility of LIBS to determine the chemical composition of four different dental elastomeric

impression materials. Furthermore, the accuracy of LIBS was compared with the Energy-dispersive X-ray spectroscopic (EDX) elemental analysis and scanning electron microscopic (SEM) images of the laser shot are taken.

MATERIALS AND METHODS

Four light-body elastomeric (Polyvinylsiloxane) impression materials of different brands namely 3M ESPE Express (3M ESPE Dental Products, St. Paul, MN 55144-1000) Affinis Perfect impression (Coltene whaledent, Feldwiesenstrasse 20,9450 Altstätten, Switzerland), Aquasil (Dentsply DeTrey GmbH, 78467 Konstanz, Germany) and GC Exafast (GC Europe N. V, Interleuvenlaan 13B-3001 Leuven), were selected for this study. Standard split stainless steel mould was used to fabricate disc shaped specimens of 3.8mm diameter. The mould comprised of a base that is highly polished smooth surface, a steel ring that can be accurately positioned over the base and the perforated steel plate used to apply pressure after loading elastomers. Perforations were created for retention purposes and to allow the escape of excess material. After placing the ring on the base of the mould, the light body material is directly injected onto the platform. The perforated plate was pressed against the ring with sufficient force to remove the excess material. Specimens were allowed to set in a thermostatically controlled water bath at 37°C and retrieved after the manufacturer's recommended setting time.

The fabricated samples were then used in LIBS experiment. The LIBS apparatus as presented in Fig 1 consists of Q - switched Nd:YAG laser (Brilliant-Quantal), Spectrometer MS257 (Oriel instruments) equipped with CCD camera, delay unit, optical cable, DC motor for rotation of samples and a PC. The laser beam of wavelength 1064 nm at repetition rate of 10Hz is used in this experiment. In order to initiate plasma, 50 mJ laser beam of 6 mm diameter and 6 ns pulse duration is focused on the sample with quartz lens of 15 cm focal length. Sample was placed at rotating motor. LM-P10 optical cable, 1 meter long, 600 mm wide was used to collect Plasma emission at a distance of 5 cm from the sample and recorded after delay of 2.5 μ s with ICCD camera (iStar, Oriel instrument) connected to computer controlled spectrometer. 2400 lines/mm grating was used in spectrometer. The spectrometer was calibrated in wavelength by recording well known spectral lines of

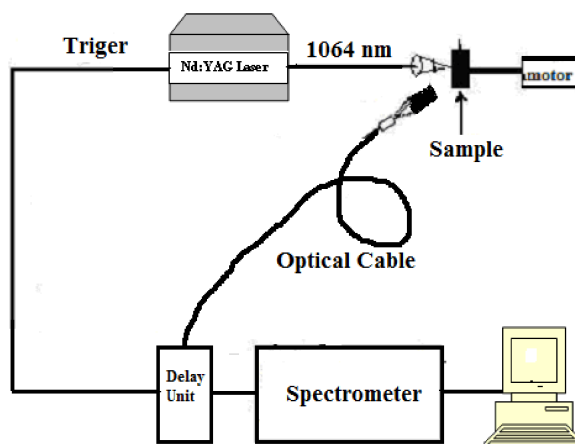


Fig. 1: LIBS Experimental Setup

neon and mercury. The uncertainty measured in wavelength during calibration was 0.01nm. All data was taken with 10 short averaging under identical experimental conditions. The samples were placed on a rotating stage which continuously rotated at 6 Hz in the diameter of 6mm to provide a fresh surface for every laser shot for the LIBS analyses. The elemental analysis of the sample is based on the emission spectra of the neutral and ionized excited species.

The surface topography of the laser shot area was analyzed with a Scanning electron microscope (JSM, 6360LV, JEOL, Tokyo, JAPAN). The specimens were air dried in a desiccator and were gold sputter coated up to 200A (Polaron E-5200 Energy Beam Sciences, Agawan, MA, USA) and examined by SEM in high vacuum conditions. Images were taken at 250X.

RESULTS

The spectral data is recorded in the range of 250nm to 550nm in 11 steps. Each step contains 30nm spectrum. The data is analyzed using software "Spectrum Analyzer 1.7" and graphs are drawn with Origin 8.0. Spectra of samples 3M ESPE Express, Coltene Affinis, Dentsply Aquasil and GC Exafast material are presented from 250nm-550nm in Figure 2, Figure 3, Figure 4 and Figure 5 respectively. The integrated intensities of the strongest lines of each detected element of the sample are considered as their abundance. Plots of the relative abundance against the pertinent elements of the samples are shown in Figure 6.

The elemental composition and the relative abundance of elements in each elastomeric impression material are found to be quite similar. Varying amounts of

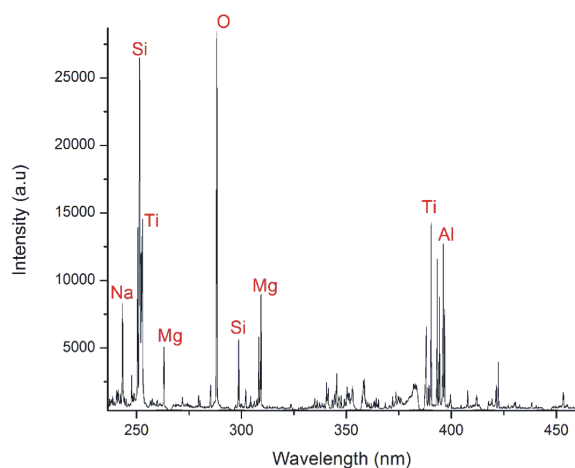


Fig. 2: Spectrum of 3M ESPE Express sample

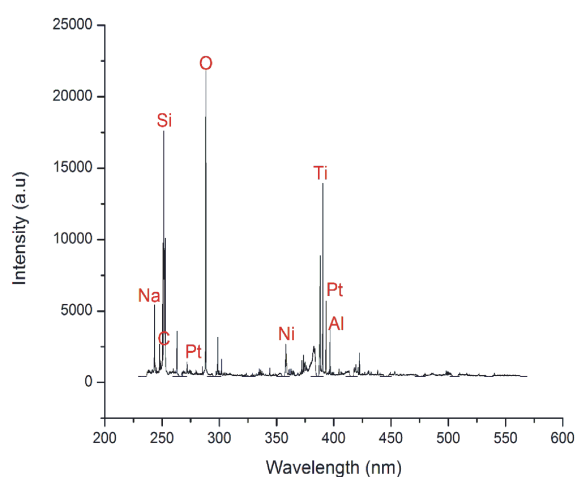


Fig. 5: Spectrum of GC Exafast sample

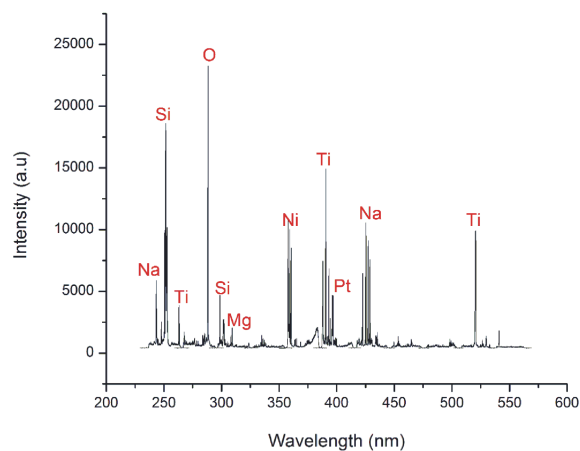


Fig. 3: Spectrum of Coltene Affinis sample

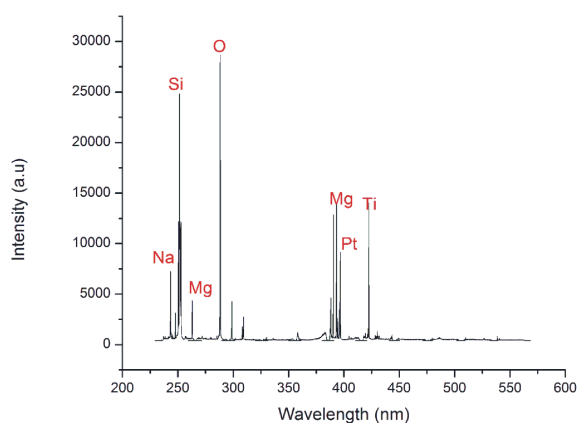


Fig. 4: Spectrum of Dentsply Aquasil sample

silica, oxygen, carbon, aluminum, magnesium, platinum, titanium, nickel were found. But similar elements were not detected when analyzed using EDX spectroscopic elemental analysis.

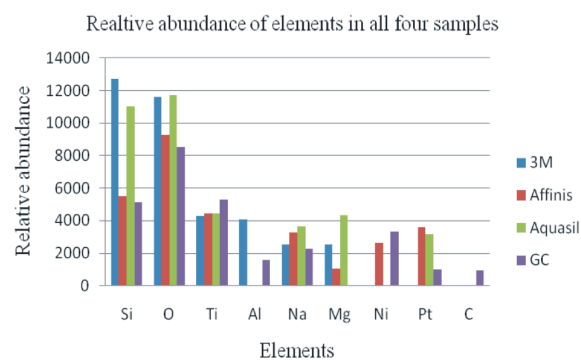


Fig. 6: Relative abundance of Elements in all elastomers Samples

Spectroscopic Analysis

3M Express Sample: The LIBS detected silica at 251.431 nm, oxygen at 288.380 nm, titanium at 390.478 nm, aluminum at 396.152 nm, sodium at 247.256 nm and magnesium at 311.258 nm. Relative abundance of these elements is shown in Figure 2. Silica is highest in quantity whereas sodium and magnesium are in lowest quantities. Whereas EDX analysis detected only 2 elements silica in 98.98% and Nickel in 1.02%.

Coltene Affinis Sample: The LIBS detected oxygen at 288.380 nm, silica at 251.431 nm, titanium at 390.478 nm, nickel at 357.723 nm, sodium at 247.256 nm and 426.139 nm, platinum at 396.645 nm and magnesium at 311.258 nm. Relative abundance of these elements is shown in Figure 3. Oxygen is highest in quantity and platinum and magnesium are in lowest quantities. Three elements were detected by EDX analysis; they are silica in 98.12%, Nickel in 1.10% and Aluminum in 0.77%.

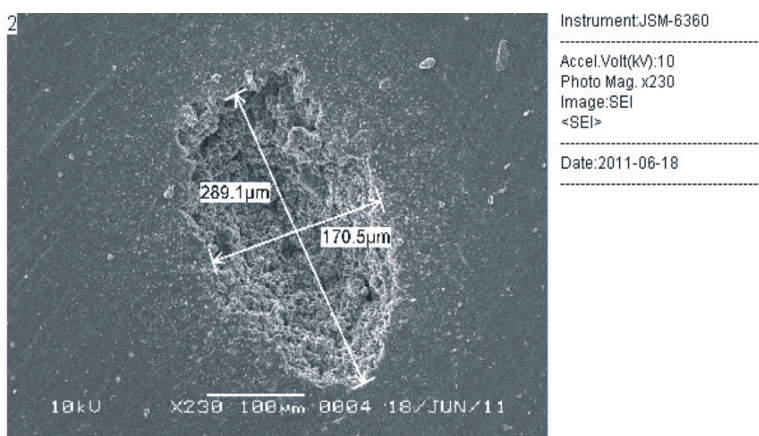


Fig. 7: SEM pictures of laser shoot area

Dentsply Aquasil Sample: The LIBS detected oxygen at 288.380 nm, silica at 251.431 nm, titanium at 422.479 nm, magnesium at 390.385 nm, sodium at 247.256 nm and platinum at 396.645 nm. Relative abundance of these elements is shown in Figure 4. Oxygen is highest in quantity whereas sodium and platinum are in lowest quantities. Silica in 99.93% and Nickel in 0.07% were detected by EDX analysis.

GC Exafast Sample: The LIBS detected oxygen at 288.380 nm, silica at 251.431 nm, titanium at 390.478 nm and 388.139 nm, sodium at 247.256 nm, carbon at 250.124 nm, platinum at 396.645 nm, nickel at 459.258 nm and aluminum at 396.152 nm. Relative abundance of these elements is shown in Figure 5. Oxygen is highest in quantity whereas nickel and aluminum are in lowest quantities. Four elements were detected by EDX analysis they are silica in 99.04%, Titanium in 0.50%, Aluminum in 0.31% and Nickel in 0.15%.

Scanning electron microscopic images of the specimens were taken at 230X which shows oval shaped laser shot areas measuring around 289.1 μm length and 170.5 μm wide (Figure 7).

DISCUSSION

The elemental analysis by any analytical instrument is to detect the trace amounts of individual elements present in the sample. This ability to detect in LIBS will vary according to the transitional strength of the elemental line, delay time (time between the firing of the laser pulse and the opening of the camera shutter) and the gate width (time for which the shutter is open) selected during the measurements, the sample matrix and collection optic geometry [14].

Lazic *et al.* [15] carried out a similar study for compositional analysis on the marbles of different countries. This technique has also been applied to perform elemental analysis of aluminum alloy and soil targets [16, 17]. In this study dental elastomeric impression material (polyvinylsiloxane) samples were analyzed and later the samples were subjected to Energy-dispersive X-ray spectroscopic elemental analysis in order to evaluate the feasibility of the LIBS technique. Varying amounts of silica, oxygen, carbon, aluminum, magnesium, platinum, titanium, nickel were found through LIBS analysis and similar elements were detected in varying concentrations and few elements like carbon, oxygen, sodium, magnesium and platinum were not detected by Energy-dispersive X-ray spectroscopic elemental analysis.

Since 1970s, electron microscopy is the most widely used and an extremely useful tool for analytical approach to determine elemental concentration. However analysis using EDX requires mounting of the specimens for gold coating to make the surface conductive. Detection of the chemical elements lighter than sodium by standard EDX and usual procedures for SEM is not easy and sometimes prevents accurate detection of carbon and aluminum when mounted using aluminum stubs and carbon tapes or carbon coat. Apart from the above mentioned problems there are various ways in which the electron beam can adversely affect a sample during examination which includes heating, electrostatic charging, ionization damage and displacement damage [18]. Moreover, carbon is the key element in the carbonate systems and polymers, the inherent difficulties of the EDX using SEM analysis in detecting these light elements makes its use difficult for carbon containing materials like polymers.

On the other hand LIBS offers unique capability for online elemental analysis of the sample in any state. The plasma can be produced from any sample state like liquid, gas, as well as from conductive and non conductive solids. The application of the LIBS into the various fields has grown enormously in the past 10 years. Laser induced breakdown spectrochemical analysis has proven extremely versatile, providing multi element analysis in real time without any sample preparation.

In the field of dentistry, Samek *et al.* [1] analyzed healthy and carious teeth to identify caries using LIBS. The goal was to determine the decrease of Ca and P and/or the increase of non matrix elements of carious and healthy teeth. The researchers concluded that the technique was easy and obtained near 100% identification of materials of both healthy and carious tooth sections [1]. The same research team also conducted quantitative analysis of trace metal accumulation in teeth using LIBS; they investigated the natural teeth taken from different age groups starting from infant to adult to identify the effect of environmental factors on the accumulation of trace elements in teeth. They found the close relation between the trace elements present and the tooth paste used by the patient [7]. Singh and Rai investigated the density of the different minerals in healthy and carious teeth and they mentioned that the technique is the potential technique for rapid identification of the carious teeth. They noted the decrease in the minerals like calcium and phosphorous in caries affected part when compared to non carious part of the natural teeth [12]. Similarly the LIBS technique was used to quantitatively analyze the mercury present in the silver amalgam restoration and to monitor the amount of mercury leaves from the restoration and enter the body [13].

Gregoire *et al.* applied LIBS technique on different polymers families like polyethylene, polypropylene, polyvinyl chloride to identify the organic materials present. They concluded that they were able to differentiate aliphatic and aromatic polymers and many polymers could be separated despite their similar chemical structures [19]. The results of the study shows that the light elements in the elastomers like carbon, oxygen, sodium, magnesium and platinum were not detected by the EDX analysis but it was possible to determine by LIBS analysis. Determining the exact chemical composition of the materials used in the dentistry is critical because the constituents if exceeded may cause harmful reactions when absorbed into the body and analysis also helps to modify the physical and biocompatible properties of the materials to suite the oral environment. Hence LIBS

analysis provides accurate qualitative analysis of the materials in any state within seconds without any sample preparation and elements lighter than sodium can also be easily detected by this technique. In analyzing polymers, since the polymers contains principally of carbon and which cannot be detected by usual EDX technique can be easily detected by LIBS.

CONCLUSION

The LIBS technique represents non contact and fast way of elemental analysis without any sample preparation. The plasma existing during laser ablation can be analyzed in real time and results obtained are near 100% accurate. The important finding of this study is the elements lighter than sodium can also be detected easily and especially the carbon being principal component of polymers which cannot be detected easily using EDX analysis can be detected using LIBS.

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