Chapter 15

Detection of Early Caries by Laser-Induced Breakdown Spectroscopy

Yuji Matsuura

Abstract To improve sensitivity of dental caries detection by laser-induced breakdown spectroscopy (LIBS) analysis, it is proposed to utilize emission peaks in the ultraviolet. We newly focused on zinc whose emission peaks appear in ultraviolet because zinc exists at high concentration in the outer layer of enamel. It was shown that by using ratios between heights of an emission peak of Zn and that of Ca, the detection sensitivity and stability are largely improved. It is also shown that early caries are differentiated from healthy part by properly setting a threshold in the detected ratios. The proposed caries detection system can be applied to dental laser systems such as ones based on Er:YAG lasers. When ablating early caries part by laser light, the system notices the dentist that the ablation of caries part has been finished. We also show the intensity of emission peaks of zinc decreased with ablation with Er:YAG laser light.

Keywords Laser-induced breakdown spectroscopy • Dental caries detection • Ultraviolet spectroscopy • Hollow optical fiber

15.1 Introduction

Visual observation and contact methods using a dental probe have been applied for diagnosis of dental caries although they sometimes cause misdiagnosis and pain. To improve diagnosis accuracy without pain, many non-contact methods based on radiation of electromagnetic wave have been developed [1–5]. In contrast to these methods that are usually performed as comparison between decayed and healthy parts, caries detection methods based on laser-induced breakdown spectroscopy (LIBS) enable absolute and quantitative analysis of elements contained in teeth. It is a method for elemental analysis which is based on spectral analysis of plasma

Y. Matsuura (✉)

Graduate School of Biomedical Engineering, Tohoku University,
6-6-05 Aoba, Aramaki, Aoba-ku, Sendai, Miyagi 980-8579, Japan
e-mail: yuji@ecei.tohoku.ac.jp

emission generated by irradiation of high-powered laser pulses [6]. LIBS is different from other element analysis methods such as inductively coupled, argon plasma-atomic emission spectroscopy (ICP-AES) [7], and LIBS needs no pretreatment of samples and, thus, it is capable of real-time analysis of very small amount. Recently, many groups applied LIBS methods to biomedical applications because they can be *in vivo*, less invasive diagnosis methods for a variety of soft and hard tissues [8–10]. For dental applications, many groups have proposed LIBS methods for caries detection by analyzing element contents in teeth [11, 12], and some groups have shown results of *in vivo* studies [13]. Enamels that are the outermost layer of the tooth are biochemical composite whose components are 96 % of inorganic materials including minerals, hydroxyapatites ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$), and a small amount of metals, 3 % of water, and 1 % of organics such as protein and fat. In decayed parts of tooth, the amounts of the above contents vary in accordance with degree of caries progress, and therefore, by analyzing these elements, one can detect caries and execute accurate diagnosis of decaying stages. These methods usually detect relatively strong emission lines of elements such as Ca and P in hydroxyapatite and C, Mg, Cu, and Sr in visible wavelengths. However, the sensitivity and the accuracy were not sufficient for detection of early caries.

We have built an optical-fiber-based LIBS system for *in vivo* and real-time analysis of teeth enamels during laser dental treatment using a dental Er:YAG laser system. These two systems are combined by using a hollow optical fiber that transmits both of Q-switched Nd:YAG laser for LIBS and infrared Er:YAG laser for tooth ablation. In this paper, we expand the spectral region under analysis to ultraviolet light to improve the sensitivity of caries detection and show that, by analyzing emission peaks of zinc (Zn) in ultraviolet, early caries are detected in high accuracy.

15.2 Experimental Setup

Figure 15.1 shows the schematic of experimental setup. A Q-switched Nd:YAG laser with an operating wavelength of 1,064 nm, a pulse width of 7–8 ns, and a repetition rate of 10 pps was used as the light source for plasma generation. The laser light was coupled to a hollow optical fiber with an inner diameter of 700 μm by a convex lens with a focal length of 250 mm. By using a hollow optical fiber for delivery of laser light to the sample surface, a system is capable of both of diagnosis based on LIBS and caries removal because the hollow optical fibers deliver high-powered infrared laser light for tooth ablation as well [14, 15]. Plasma emission induced by laser radiation was detected by a step-index, pure-silica-glass optical fiber with a core diameter of 400 μm and numerical aperture of 0.22. Detected emission was delivered to a fiber-coupled spectrometer (Ocean Optics HR2000+, slit width 10 μm , 1,800 lines/mm) to measure the power spectra of emitted light from 200 to 340 nm wavelength with a resolution of 0.14 nm. Experiments were performed at atmospheric pressure, and argon gas was injected onto the sample via the

Fig. 15.1 Schematic of experimental setup of fiber-based LIBS system

bore of hollow optical fiber to enhance emitted plasma intensities of low concentration elements [16].

As measurement samples, extracted human teeth in different levels of decay were prepared. The samples were divided into three stages: early stages of decay called “E1” and “E2” where the decays and cavities are stayed only in the tooth enamel, advanced stages called “D1” and “D2” where the cavities reach into the dentin, and healthy teeth without a decay or a cavity. More than ten samples in each stages including both of incisors and molars were prepared, and the samples were washed with brushes and pure water before being tested.

15.3 Results and Discussion

It is known that, usually, healthy teeth contain Ca and P that are main components of hydroxyapatite in high concentration. As tooth decay progresses, other inorganic elements such as Mg and Cu precipitate when crystals of hydroxyapatite are demineralized. Therefore, one can detect development of dental caries as increases of densities of minor inorganic materials in LIBS spectra. However, in our preliminary tests, we found that the differences in the intensities of these elements showing strong emission peaks in visible and near infrared wavelengths are too small between caries and healthy parts to detect early caries. Therefore, in this study, we focus on ultraviolet region where characteristic emission peaks of various minor components appear.

A measured LIBS spectrum of a healthy tooth in a wavelength region of 200–340 nm is shown in Fig. 15.2. This is an averaged spectrum of emissions by 50 laser shots, and the integration time of each emissions were 100 ms. Radiated pulse energy was 21–22 mJ. In the LIBS spectrum in Fig. 15.2, we found that, in addition to components in hydroxyapatite, minor inorganic components such as Mg were detected.

Figure 15.3 shows LIBS spectra of a healthy tooth and a decayed tooth. In the measurement of caries, radiated pulse energy was set to 15–16 mJ. We confirmed from the figure that, for the caries tooth, the densities of C were higher and that of Ca was lower than the healthy tooth. Based on this result, we firstly tried to set an evaluation standard for diagnosis of caries progress by using the peak intensity of C

Fig. 15.2 Measured LIBS spectrum of a healthy tooth in ultraviolet region

Fig. 15.3 LIBS spectra of a healthy tooth and a decayed tooth

and Ca that show relatively high peak intensities and large differences between caries and healthy teeth. We prepared five samples from each of healthy teeth, early caries (E1 and E2), and dentin caries (D1 and D2). We performed 30 measurements for each samples and calculated intensity ratios of C at 247.7 nm and Ca at 317.9 nm for quantitative evaluation that was not affected by fluctuation of the emission intensities [17, 18]. Figure 15.4 shows a scatter diagram of the measured results. From this result, we found that dentin caries were differentiated from the other levels. However, averaged values of the healthy teeth and the early caries were 0.0050 and 0.0059, respectively, and the difference was too small to distinguish.

Based on the above result, we repeatedly performed similar experiments while changing the combination of focusing elements to choose the optimum target elements for detection of early caries. In the spectra shown in Fig. 15.5, we found that the

Fig. 15.4 Scattered diagram of calculated intensity ratios of C at 247.7 nm and Ca at 317.9 nm for three different stages of caries development

Fig. 15.5 LIBS spectra of healthy tooth and decayed tooth in short wavelength UV region

Fig. 15.6 Scatter diagram of measured intensity ratios between Zn at 202.5 nm and Ca at 317.9 nm

peak height of Zn increases in caries teeth as well. It is known that, compared with other inorganic materials, zinc exists at high concentration in the outer layer of enamel [19, 20]. Although various inorganic elements precipitate when hydroxyapatite is demineralized, change in the concentration due to tooth decay is seen more obviously in zinc because early caries stays only at the very surface of the enamel layer. Therefore, we assume that zinc was strongly detected in early stage of dental decay.

Figure 15.6 shows a scatter diagram of measured intensity ratios between Zn at 202.5 nm and Ca at 317.9 nm. In this figure, average values of intensity ratios are

Fig. 15.7 Measured intensity ratio Zn/Ca as a function of number of radiated pulses of Er:YAG laser

0.0044 for the healthy teeth and 0.013 for the early caries. By setting a boundary at around 0.008, one can clearly distinguish between healthy teeth and early caries. Accuracies of diagnosis based on this result were as high as 98.2 % for the healthy teeth, 85.2 % for the early caries, and 96.6 % for the dentin caries. In additional experiments using more than five samples, the healthy parts and early caries are repeatedly tested. As a result, we confirmed that diagnosis accuracy for early caries was higher than 80 %.

Next, we evaluated feasibility of real-time analysis of the proposed method during laser treatment using an Er:YAG dental laser system. We utilized a dental laser system (J. MORITA, Erwin Adverl) and laser pulses with a wavelength of 2.94 μm and pulse energy of 100 mJ were radiated onto early caries by using a hollow optical fiber. Simultaneously, the LIBS analysis proposed above was performed. The results are shown in Fig. 15.7 as the measured intensity ratio Zn/Ca as a function of number of radiated pulses of the Er:YAG laser. For all of five samples that we tested, decreases in the intensity ratio were observed, and thus we confirmed that the proposed system is feasible for informing a practitioner finish of removal of caries parts.

15.4 Conclusion

We proposed a LIBS system for in vivo analysis of teeth enamels. The system utilizes a hollow optical fiber that transmits both of Q-switched Nd:YAG laser light for LIBS and infrared Er:YAG laser light for tooth ablation, and thus the system enables real-time analysis of teeth during laser dental treatment. By expanding the spectral region under analysis to ultraviolet light and focusing on emission peaks of Zn in the UV region, we largely improved the sensitivity of caries detection. We showed that, by using ratios of peak intensities of Zn and Ca, early caries were distinguished from healthy teeth with accuracies higher than 80 %. Then we applied this LIBS analysis to caries teeth while ablating the caries part with Er:YAG laser light and

have shown that the intensity ratio Zn/Ca decreases with radiation of Er:YAG laser pulses. Therefore, the proposed system is feasible for informing a practitioner finish of removal of caries.

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