Nanosecond Time-Gated Spectroscopy of Laser-Ablation Plume of Human Hair to Detect Calcium for Potential Diagnoses

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We demonstrate the nanosecond time-gated spectroscopy of plume luminescence in UV laser ablation of human hair. Clear and sharp peaks of calcium ion (Ca+) appear in the spectrum although the Ca content is only 0.1% in human hair. Highly sensitive detection of Ca is thus possible. In the experiment, the peak intensity of Ca+ was measured for human hair samples of female subjects over a wide range of age, and compared to the bone mineral density of the lumbar vertebrae of the subjects themselves. Our experimental results suggest that this specific spectroscopy has the potential for novel diagnoses including monitoring of daily Ca intake and a screening diagnosis of osteoporosis. The spectroscopic system and time transition of plume-luminescence spectra are also described.

Key words: tissue laser ablation, plume luminescence, time-gated spectroscopy, calcium detection, optical diagnosis

1. Introduction

Laser ablation is used routinely in actual clinical application for evaporation and cutting of biological tissue in surgical operations. Besides the use for such a surgical knife, tissue ablation has been used for refractive corneal surgery1,2) and vascular surgery.3) To improve these operational techniques, dynamic analyses of tissue ablation were made by observing time-transitional images of the laser-ablation plume with a high-speed framing camera, stroboscopic photography and microscopy.4~7) These results contribute to the development of further therapeutic techniques based on laser ablation. Laser ablation also has potential as a diagnostic tool in which the time-gated spectroscopy of the laser-ablation plume, as reported by several research groups.8~11) The 308-nm XeCl excimer laser pulse of 20 ns illuminated a calcified plaque in an aortic wall and urinary stone to obtain the time-gated spectra of the laser-ablation plume, as reported by Andersson-Engels et al., where the time resolution was on the order of a few tens of nanoseconds.8) The time-gated spectroscopy of the plume was also used to study pulsed-laser fragmentation of biliary calculi.9) Luminescence spectra of ablation products of an atherosclerotic aorta were investigated using the 2.1-μm Holmium YAG laser pulse of 250 μs and the XeCl laser pulse of nearly 60 ns.10,11) All this research is still basically at the experimental stage, indicating the time-gated spectroscopy of the plume is useful for destructive characterization of biological tissue. There has thus been no proposal for actual diagnostic application.

In this paper, we demonstrate the nanosecond time-gated spectroscopy of plume luminescence in UV laser ablation of human hair for detection of calcium (Ca). In our experiment, the time-transient spectrum of the ablation plume can be obtained with a time slot (or gate time) of only 10ns; nevertheless, this specific spectroscopy clearly exhibits a sharp intensity peak of Ca+ of human hair. This spectroscopic method of Ca detection is minimally invasive because a single laser pulse illuminates the tissue surface, and it does not require any poisonous sensitizers like fluorescence dye. A preliminary experiment was made toward a possible diagnosis, where several tens of samples of female hairs were collected and tested to detect the Ca content. The experimental results suggest that our method may lead to novel diagnoses, including monitoring of daily Ca intake and a screening diagnosis for osteoporosis.

2. Time-Gated Spectroscopy of UV Laser Ablation

2.1 Experimental Setup

The experimental setup is shown in Fig. 1. The Q-switched Nd:YAG laser is used as the light source which supplies laser pulses of nearly 5 ns at the wavelength of 266 nm with the repetition rate of 10 Hz. An electronic shutter is placed in front of the laser to pick up a single laser pulse from a time series of pulses. The laser pulse is focused on a tissue sample where the focused spot size is around 150 μm in diameter. The laser-ablation plume is then ejected from the tissue surface, and grows up along the direction normal to the surface. The plume luminescence is captured by a fiber probe with 960-μm core diameter, then diffracted with the polychromator. The spectroscopic image is gated with a time slot as short as 10 ns in synchronization with the illuminating laser pulse, as shown in Fig. 1. The time slot is set at the desirable delay time t_d after the laser pulse illuminates the tissue sample. t_d is here adjustable with an accuracy...
of less than 1 ns because jitter of the trigger pulse is below 0.5 ns in the laser controller. The time-gated spectroscopic image is intensified and detected by a CCD camera. The time-serial image data from the CCD are fed into a frame grabber. To improve the signal-to-noise ratio, the image intensities are integrated along an array of pixels corresponding to a certain wavelength, resulting in the plume-luminescence spectrum in the wavelength range of 350 to 700 nm with a resolution of 1 nm.

### 2.2 Time-Transient Spectra of Laser-Ablation Plume

The UV laser pulse is suitable for the ablation of human hair to minimize differences in laser absorption due to hair color. In the experiment, the 266-nm laser pulse of 5.5 ns illuminated a piece of human hair where the pulse energy was 17 mJ. In the case of UV laser ablation, an air break occurred near the focal point of the lens, resulting in the dissociation of nitrogen. To avoid this air break, the hair sample was placed nearly 1 mm short of the focal point. The light spot size on the hair sample was roughly 200 µm which was almost twice the width of the human hair; therefore, optical alignment was relatively easy with respect to the hair sample. The time-transient spectra of the plume luminescence are shown in Fig. 2.

To understand the time transition of the plume-luminescence spectra shown in Fig. 2, the dynamics of laser ablation of tissue is here described briefly, according to our previous experiment. In tissue ablation, as soon as the laser pulse is loosely focused on the tissue sample, the leading edge of the laser pulse is absorbed instantaneously near the surface where air and water are then decomposed to form plasma. The plasma absorbs a considerable part of the pulsed laser energy, and grows rapidly in the reverse direction of the incident laser pulse. It looks like a spindle-shaped brilliant plume, whose spectrum includes several peaks of nitride ion (N⁺) over the wavelength of interest, as shown in Fig. 2. This plume-like plasma is a partial shield for the tissue sample against the laser pulse. The remaining energy of the laser pulse is absorbed via the plasma by the tissue itself, and as a result, the tissue ablation is made by gener-