Comparison between femtosecond and nanosecond laser ablation of solution samples applied on a substrate

T Kato1,2, T Kobayashi2, Y Matsuo2, M Kurata-Nishimura1,2, R Oyama1,2, Y Matsumura1, H Yamamoto1, J Kawai1,2 and Y Hayashizaki1,2

1Genome Exploration Research Group, RIKEN Genomic Sciences Center (GSC), RIKEN Yokohama Institute, Yokohama, Kanagawa, 230-0045, Japan

2Discovery Research Institute, RIKEN, Wako, Saitama 351-0198, Japan

E-mail: tkato@riken.jp

Abstract. We have compared time-of-flight mass spectra for an inorganic and a biological macromolecular sample applied on a silicon substrate obtained by laser ablation with femtosecond and nanosecond lasers. Many fragment peaks appeared in the mass spectra for nanosecond laser ablation. In contrast, the samples were effectively atomized to monoatomic ions by femtosecond laser ablation. We find that femtosecond laser ablation has a great advantage in an elemental analysis of solution samples on a substrate. Silicon clusters \( \text{Si}_n \) (up to \( n=6 \)) from the substrate were also observed.

1. Introduction

Recently, studies of short-pulsed laser ablation have shown that a femtosecond laser pulse effectively atomizes and ionizes materials in the irradiated spot [1,2], and that the intensity ratios of produced ion species are precise and reproducible as compared with nanosecond laser ablation (LA) [3]. Those reports suggest that femtosecond laser ablation is more suitable for the ionization method in elemental analysis of solid materials over ns/LA. While the performance of fs/LA has been especially studied on solid materials, little is known about solutions applied on a substrate. Elemental analysis of solution samples is, however, very important for microelement analysis, the stable isotopic trace method and so on.

In the previous study, we have observed that solutions of organic macromolecules were simultaneously atomized and ionized by fs/LA and that the observed ratio of isotopes was consistent with the natural isotopic ratio [2]. The possibility of fs/LA as an ionization method for elemental analysis of macromolecules has been indicated by the experiment. However, the ability of fs/LA should be discussed in comparison with ns/LA. Studying differences in product ion species between fs/LA and ns/LA is a way to clarify the characteristics of each laser ablation technique.

In the present study, we observe mass spectra of ion species heavier than 50 amu produced by ablation, using femtosecond and nanosecond lasers, at the surface of solution samples applied on a flat substrate. The samples of an inorganic solution and a biological macromolecule contain the element of europium (Eu) as a control. We obtained single-shot ablation spectra using a pulsed laser, and a moving target, combined with time-of-flight (TOF) measurements with a mass spectrometer. This
study reports the difference of the product ions between fs/LA and ns/LA of a thin layer of the solution samples on a silicon substrate.

2. Experiment
Solution samples used in our experiment are shown in Table 1. The Eu standard solution was a commercial chemical for the atomic absorption analysis. The Eu-labelled deoxyribonucleic acid (Eu-DNA) was a huge biological molecule synthesized in our laboratory. The single stranded Eu-DNA consisted of about 1000 nucleic-acid bases. A drop consisting of 10 μL of each sample was put on a silicon substrate and then dried in vacuum. The sample size on the substrate was about 4 mm in diameter for each.

Table 1. Organic and inorganic solution samples used in the experiment.

| Sample Description                                | Composition formula | Solvent      | Concentration (mol/L) |
|---------------------------------------------------|---------------------|--------------|-----------------------|
| Eu standard solution                              | Eu(NO\textsubscript{3})\textsubscript{3} | HNO\textsubscript{3} | 6.6×10\textsuperscript{-3} |
| Eu-labelled deoxyribonucleic acid                 | C\textsubscript{186}H\textsubscript{213}N\textsubscript{65}O\textsubscript{104}P\textsubscript{16}Eu | Tris buffer | 10\textsuperscript{-7} to 10\textsuperscript{-8} |

Figure 1 shows a schematic of the experimental setup. Femtosecond laser pulses were supplied from a Ti:Saphire laser system (Spectra-Physics, Hurricane). The laser properties are as follows: 800 nm wavelength, 120 fs pulse duration, output energy 800 μJ/pulse, and 500 Hz repetition rate. The laser pulses were frequency doubled using a second harmonic generation crystal (BiBO crystal) of 1 mm in thickness shown in Figure 1. A nanosecond laser pulse was generated using a pulsed YAG laser system (New Wave Research, Tempest). The wavelength of the nanosecond laser was 355 nm. The laser pulse duration was 10 ns, with a typical output energy up to 3 mJ, and a repetition rate of 10 Hz. Each laser beam was alternatively focused by an achromatic lens, of focal length 250 mm, onto the sample surface at an incidence angle of 45 degrees through a magnesium fluoride window. The light intensity of each laser pulse was regulated with the laser generation system, and reduced through neutral density (ND) filters in the beam path to change the energy condition. The silicon substrate with its applied sample was mounted on an XY stage in a vacuum chamber connected to a reflectron TOF mass spectrometer. The positive ions produced by the laser ablation were separated by mass-to-charge ratio and then detected with a micro channel plate (MCP). The output signals were recorded with an oscilloscope (LeCroy, WaveRunner 6050) through a fast preamplifier (ORTEC, 9305). Since each sample was perfectly evaporated with a single laser pulse, after acquiring each spectrum, the target sample was moved with the XY stage a distance of 200 μm. This distance was sufficiently large to ensure the next laser pulse would irradiate a fresh sample surface. In order to perform a single shot measurement, a mechanical shutter was closed during a data recording for an induced event with one laser pulse. The laser ablation was carried out under vacuum conditions of 10\textsuperscript{-7} Torr.

\( ^a \) PH buffer solution.
3. Results and discussion

Typical mass spectra of the Eu standard solution obtained by single-shot fsLA and nsLA are shown in figure 2(a) and (b), respectively. The peaks at mass/charge of 151 and 153 are clearly identified as Eu$^+$ in both figures. The ratios between the signal intensity of $^{151}$Eu$^+$ and $^{153}$Eu$^+$ are consistent with the natural abundance of 48:52. A femtosecond laser pulse performs simultaneous atomization and ionization with no molecular fragments. In contrast, the mass spectrum obtained by nsLA is studded with a few small peaks probably corresponding to fragment ions.

![Figure 2. Typical mass spectra of the Eu standard solution for fs/LA (a) and ns/LA (b). The pulse energy of the femtosecond laser was 130 µJ/pulse, and 1 mJ/pulse for the ns/LA. In the experiment for ns/LA, the signal peaks did not stably appear with the lower pulse energy.](image)

Figure 3(a) shows a typical mass spectrum of Eu-DNA for single-shot fs/LA. Eu$^+$ ions were clearly detected without fragments, although some clear peaks were obtained in the mass/charge range < 100. In contrast, lots of fragment peaks of the organic molecules obtained at all channels from 50 to 300 in mass/charge are observed in a typical mass spectrum for nsLA of Eu-DNA (figure 3(b)). Two strong peaks standing on the fragment signals at the mass/charge of 151 and 153 in figure 3(c) are not identified as Eu$^+$ ions, because the signal ratio is incongruous with the natural abundance.

For the inorganic sample, the ns/LA performed sufficient simultaneous atomization and ionization to analyze the constituents of the sample. However, the organic sample was fragmented by the ns/LA, preventing analysis. Figures 2, 3 show that fs/LA is prominent for the organic sample. We also examined the ns/LA of Eu-DNA with various pulse energies. In the case of 130 µJ/pulse, the same pulse energy used in the fs/LA, no clear peaks were observed around the mass/charge ratio of 150. The molecules in the laser spot seemed not to be ionized due to low power density of the nanosecond laser pulses. In fact, lots of fragment peaks did not disappear even when 15 times higher pulse energy of 2 mJ/pulse was used for ns/LA. These results indicate that there is a great difference in the effectiveness of femtosecond and nanosecond lasers for producing simultaneous atomization and ionization of organic macromolecules. This characteristic is probably caused by differences of the ablation mechanisms [4,5]. Although ns/LA might achieve the same performance as fs/LA with a far higher pulse energy, we didn’t examine it beyond 2 mJ/pulse. The TOF spectra were dominated by too much ions from the substrate.

The equally spaced peaks of silicon cluster ions such as Si$_3^+$, Si$_4^+$, Si$_5^+$, and Si$_6^+$, appear with the each isotopic signal in figure 3(a). In the fs/LA, for a thin layer of the solution samples, the quantity of ablated molecules is determined by the size of the laser spot, because the samples in the laser spot are completely evaporated. Therefore, the fs/LA has an advantage in quantitative analysis. At the same
time, half of ablated atoms were constituents of the substrate. In addition to Si and the clusters, some impurities on the substrate were detected clearly by high amplification of the MCP.

![Image of mass spectra](image.png)

**Figure 3.** Typical mass spectra of Eu-DNA for fs/LA (a) and ns/LA (b). (c) is a zoom-in of spectrum (b) from 140 to 160 in mass/charge. The pulse energies were 130 µJ/pulse for fs/LA and 1 mJ/pulse for ns/LA.

4. Conclusion
In summary, the fs/LA effectively dissociated and ionized the solution samples of organic and inorganic molecules into the constituent atomic ions, while the ns/LA dissociated them into their fragment ions and fragment molecules. The constituent elements and the silicon clusters have been observed clearly all at once from a 10 µL drop of the samples on the substrate. We have confirmed that fs/LA is far superior to ns/LA for simultaneous atomization and ionization and that fs/LA is effectively applicable to the elemental analysis for small quantities of solution samples on a substrate, especially for elements heavier than 100 amu.

Acknowledgements
This work was supported in part by Presidential Research Grant for Intersystem Collaboration of RIKEN to J.K. and Y.M., Research Grant for the RIKEN Genome Exploration Research Project from the Ministry of Education, Culture, Sports, Science and Technology of the Japanese Government to Y.H., and Research Grant for Advanced and Innovative Research Program in Life Science to J.K. The authors would like to thank Dr. Bishop for reading the manuscript.

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