Т. 86, № 1 **ЖУРНАЛ ПРИКЛАДНОЙ СПЕКТРОСКОПИИ** ЯНВАРЬ — ФЕВРАЛЬ 2019
V. 86, N 1 **JOURNAL OF APPLIED SPECTROSCOPY** JANUARY — FEBRUARY 2019

LASER PLASMA SPECTROSCOPY USING A PULSED CO_2 LASER FOR THE ANALYSIS OF CARBON IN SOIL**

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Analysis of carbon (C) in soil has been successfully made by laser plasma spectroscopy using a pulsed carbon dioxide (CO_2) laser. Fine particles of soil sample were attached on a surface of the metal subtarget by adding a small amount of moisture; the metal was used to initiate the gas plasma. Experimentally, a pulsed laser was focused on the subtarget to induce a luminous plasma. The particles were vaporized and entered the plasma region. Dissociation and excitation happened in the high-temperature plasma region. The result certified that analysis of C in soil can be demonstrated. A further measurement revealed that a calibration curve of C was successfully carried out. The limit of detection of C in the soil was around 23 mg/kg.

Keywords: *laser-induced plasma spectroscopy, laser-induced breakdown spectroscopy, carbon analysis, soil sample.*

АНАЛИЗ СОДЕРЖАНИЯ УГЛЕРОДА В ПОЧВЕ МЕТОДОМ СПЕКТРОСКОПИИ ЛАЗЕРНО-ИНДУЦИРОВАННОЙ ПЛАЗМЫ С ПРИМЕНЕНИЕМ ИМПУЛЬСНОГО CO_2-ЛАЗЕРА

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УДК 533.9;543.42;546.26

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(Поступила 13 октября 2017)

Импульсный CO_2-лазер успешно применен для анализа содержания углерода в почве методом спектроскопии лазерно-индуцированной плазмы. Мелкодисперсные частицы образца почвы прикреплялись к поверхности металлической подложки путем нанесения небольшого количества влаги. Металл использован для возбуждения газовой плазмы. В результате при фокусировке излучения лазерного факела на подложку возникало светящееся плазменное образование. Частицы испарялись, и продукты испарения поступали в плазму. Процессы диссоциации и возбуждения происходили в высокотемпературной области плазмы. Полученные результаты подтвердили возможность проведения анализа углерода в почве, построить надежную калибровочную кривую для определения концентрации углерода. Предел обнаружения углерода в почве составил 23 мг/кг.

Ключевые слова: *спектроскопия лазерно-индуцированной плазмы, анализ содержания углерода, образец почвы.*

[**] Full text is published in JAS V. 86, No. 1 (http://springer.com/10812) and in electronic version of ZhPS V. 86, No. 1 (http://www.elibrary.ru/title_about.asp?id=7318; sales@elibrary.ru).

Introduction. Carbon (C) inventories in soils have altered recently due to the serious global climate change [1–3]. Soil C is a fundamental matrix of soil chemical and physical properties, such as nutrient contents, structure of soil, and capacity of water in the soil, which affect the ecosystem and soil quality [4, 5]. The use of more coal and oil for homes, factories, and transportation releases carbon dioxide (CO_2) and other greenhouse gases into the atmosphere, resulting in an increased temperature of the atmosphere. This increment of temperature influences the soil C dynamics and reduces the annual change of soil organic C [5]. Thus, an efficient technique of measuring soil C is required to estimate the terrestrial C inventories. Several analytical techniques were employed to analyze the C in soil. X. M. Zou et al. conducted a sequential fumigation-incubation for estimating C in soil [6]. Paul et al. used the method to predict the retention time and rates of C turnover in soils [7].

Emission spectroscopy by laser, which people usually call laser-induced breakdown spectroscopy (LIBS), has attracted many scientists for applications to rapid elemental analysis in various materials [8]. A Nd:YAG laser is usually employed as an excitation source. When the laser is directed and focused on a sample target, a high-temperature plasma is produced; the plasma contains atomic and ionic elements as well as molecules from the target. The plasma is then imaged to the optical spectrometer to obtain the emission spectrum. However, the standard LIBS cannot directly analyze the soil sample because once the laser is irradiated on the soil target, a blow off of soil seriously occurs. Therefore, to perform an analysis of soil using LIBS, the soil must be changed in the pellet. However, the pelletized sample is not hard like an ordinary solid sample; therefore, a plasma with high temperature cannot be induced [9].

In another direction, we have found that a pulsed CO_2 laser is very favorable for soil analysis because the laser has a long wavelength, which has high absorbance in the soil [10]. We proposed a sampling technique for the analysis of C in soils by using a pulsed CO_2 laser. A subtarget technique was suggested for sampling. A tiny amount of soil particles were faintly painted on a metal plate by adding moisture. When a pulse laser was irradiated on the subtarget, on which the thin layer soil was painted, a high-temperature plasma was induced, and the metal subtarget was not ablated and damaged. It is notable that the present preparation method is more convenient compared with the conventional LIBS by pressing the sample into the pellet. In the case of pellets, some additional agent is needed, such as KBr, to make a hard sample pellet to produce a strong plasma. Pellet preparation therefore is much more complicated compared with that of the present technique.

Method. Figure 1a displays the basic setup for this experiment. A pulse CO_2 laser (Shibuya SQ 2000, 10.6 μm, 200 ns, 3 J) was used as an energy source. The pulsed laser was directed and focused onto the sample by ZnSe lens (100 mm in focal length). The spot size of the laser on the sample was 1×1 mm^2, of which the laser fluence was 0.75 GW/cm^2.

A C soil sample collected from the garden was used as a sample in this research. For semi-quantitative analysis, a standard soil sample that contained various concentrations of C (200, 500, and 1000 mg/kg) was used. Prior to the analysis, the fine soil particles with moisture were directly attached to a nickel plate (0.1×20×20 mm), which served as a subtarget, as shown in Fig. 1b. The suitable thickness of the sample

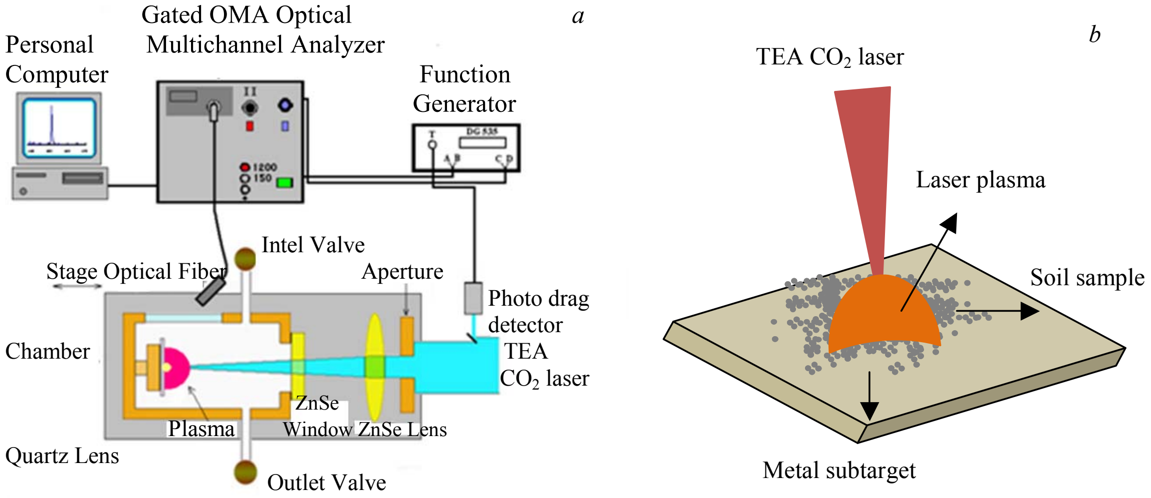

Fig. 1. Basic setup (a), and lustration of the sample holder employed in this study (b).

on the subtarget was 1 mm. Based on this experiment, if the sample was too thick, then plasma quenching would happen and reduce the plasma temperature and plasma lifetime. The sample was put in a steel chamber ($12\times12\times12$ cm^3). The pressure inside the chamber was kept constant at 1 atm of nitrogen gas. The emission spectrum from the laser plasma was obtained using an optical multichannel analyzer system (OMA), which consisted of a spectrograph and photodiode detector. An optical fiber connected to the OMA system was used to collect the plasma emission. The time integrated mode of OMA was used during the experiment.

Results and discussion. First, the soil C assessment was made using the present method. To this point, a small amount of soil fine particles (around 500 mg) with moisture were spread on the nickel plate, which played a role as a subtarget. Figure 2 displays the C spectrum obtained from the soil sample. High-intensity C I 247.8 nm clearly occurred with low background intensity. Furthermore, many typical atomic lines of Si showed that the characteristics of the soil sample could readily be observed on the right side of the spectrum.

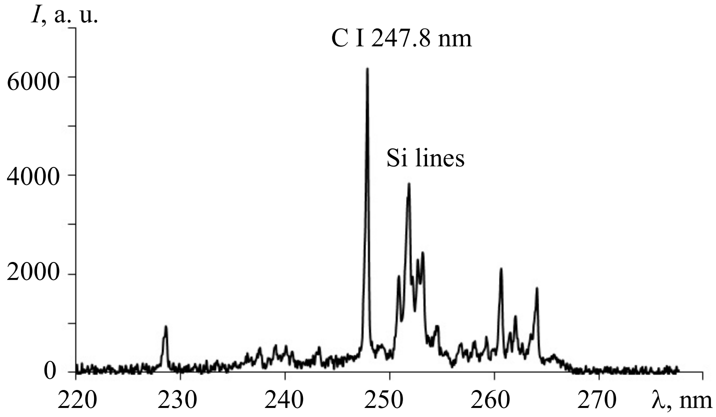

Fig. 2. C spectrum obtained from the garden soil.

The C atom is contained in garden soil at several thousand ppm (parts per million or mg/kg). The present technique is superior to the ordinary LIBS technique for conducting rapid and efficient measurements of total soil C. For the LIBS case, the soil sample should be made as a hard pellet to obtain high-temperature plasma. In the sample preparation, a chemical agent, such as KBr, is commonly used. Therefore, the ordinary LIBS required tedious sample pretreatment for soft sample or powder analysis.

In our present method, analysis can be made without sample pretreatment because we only directly painted the soil sample with moisture on the metal subtarget prior to the analysis.

An analysis of the company soil sample, which contained various concentrations of C, was further made using a present method. Considering the intensity ratio between C I 247.8 nm and Si I 251.9 nm was almost constant, the Si line near C was used as a standard. The curve with linear calibration was made from the soil, as demonstrated in Fig. 3. It should be noted that the use of silicon for standardization should be evaluated with regard to soil mineralogy because the Si content in soils varies with the mineralogy of soils.

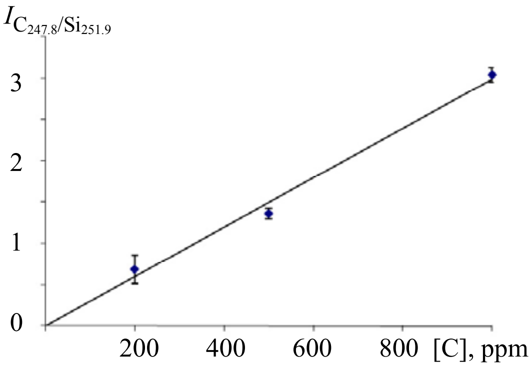

Fig. 3. C curve obtained from the soil containing various concentration of C by using metal-assisted laser-induced gas plasma spectroscopy.

To examine the sensitivity by using present technique, a C analysis in soil was conducted. Figure 4 shows the spectrum obtained from a company soil sample containing 500 mg/kg of C. The emission line of C I 247.8 nm can clearly be seen. Other lines of Si on the right side of the C also were detected. The detection limit of C was around 23 mg/kg; the calculation of the detection limit follows the equation reported in this work [11]. This result is superior to the case of ordinary LIBS, of which the detection limit of C was around 300 mg/kg as reported by other researchers [4]. Therefore, our present technique has the very potential to perform C analysis in soil C influenced by global climate change.

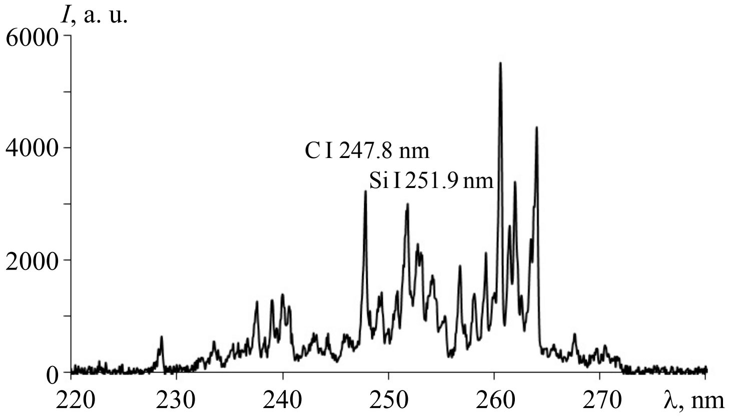

Fig. 4. Emission spectrum taken from the soil containing 500 mg/kg of C using metal-assisted laser-induced gas plasma spectroscopy.

Conclusion. Carbon analysis in the soil sample was demonstrated by laser-induced plasma spectroscopy using a pulsed CO_2 laser. In this experiment, fine particles of soil mixed with moisture were painted on a subtarget. A luminous plasma was produced when the laser beam was irradiated on the subtarget. The soil particles then moved and enter the plasma region. Dissociation and excitation processes of particles takes place in the plasma region. A semi-quantitative analysis was demonstrated for C element in soil sample. The limit of detection of C in soil was 23 mg/kg.

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