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Sensitive cesium measurement in liquid sample using low-pressure laser-induced breakdown spectroscopy ☆

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ABSTRACT

The environmental pollution by trace heavy metals is a severe problem for the environment and human health. In this paper, the liquid jet of $CsNO_3$ solution employed was introduced to the measurement chamber and detected using laser-induced breakdown spectroscopy (LIBS) directly at low pressure to determine the detection features of trace Cs element in liquid. The distinct and round plasma can be acquired when reducing the pressure. The interaction between the plasma core of the liquid jet and the surrounding gas can be controlled to enhance Cs detection ability. Cs emission was mainly in the surrounding area in the plasma. The influences of laser focal point and plasma measurement area on the measured signals were studied under low-pressure condition. When employing the defocus mode and varying the measurement area within a certain range, Cs signal and the signal-to-background ratio were improved. Cs detection limit can reach to 22.8 ppb ($3\sigma/m_s$) at pressure of 26 kPa in this paper. According to the discussion, the detection limit will be enhanced when improving the experimental conditions using this method, which shows the great application potential of liquid sample measurement.

1. Introduction

With the development of economy, the environmental pollution is becoming increasingly severe and much more attention should be paid to the issue. The pollution by trace heavy metals is a serious problem for the environment and human health. The importance of nuclear power, a proven means to supply the growing demand for clean energy in our energy future, is obviously depending on the basis of safe and rational utilization. As is well known, after the Fukushima nuclear power plant accident in Japan, there are several serious pollutions for the environment and human not only in the surrounding area of the nuclear power plant but also in the outlying regions [1–3]. This contamination released from the nuclear power plant is one of the main sources, as well as the nuclear weapons testing fallout, some industry waste discharge, etc. [4,5]. The atmosphere, water, and soil are polluted by these contaminants [6–8]. The pollution of cesium element becomes very serious after the Fukushima nuclear power plant accident. Simultaneously, the determination of the rare and valuable cesium is of crucial importance for the exploration and development. One of the focal researches is the measurement and treatment of trace elements contained in contaminants in the ocean or water [1,7]. Therefore, it is necessary to detect the trace element for monitoring and treatment. Gamma-ray spectroscopy and beta-ray counting method are the physical and chemical methods to detect the radioactive cesium in aquatic products. In addition to the physical and chemical analyses, the methods based on the analytical equipment have been developed in recent years [9,10]. Methods for determining cesium in waters with high-concentration salt (salt lake brine, under-ground brine, and oilfield water) consist of electrochemical analysis, chemical analysis, and spectrum method [11,12]. Inductively coupled plasma–atomic emission spectrometry (ICP-AES), atomic fluorescence spectrometry (AFS), and atomic absorption spectrometry (AAS) have also been employed to analyze the liquid materials. However, the complex pre-treatment of measurement samples is necessary for these methods.

Laser-induced breakdown spectroscopy (LIBS) is an analytical detection technique based on atomic emission spectroscopy for the qualitative and quantitative measurement with the advantages of non-contact, fast-response, high sensitivity, real-time, and multi-element detection [13]. With the development of laser and detection system, LIBS has become a focus of research in spectrometric field and has been applied in various fields, especially in the areas of combustion, metallurgy, and the harsh environment [14–17]. The measurement and analysis methods of LIBS for the qualitative and quantitative applications have been developed and studied extensively. The correction, normalization, and other methods have been proposed to reduce the signal uncertainty and to improve the measurement accuracy [18–21].

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The processes involved in laser-induced plasma formation are quite complex and different in the solid, gas, and liquid phases. One of the challenge targets for trace species measurement is to enhance LIBS detection limit. Several strategies, such as double-pulse, short pulse width breakdown, and low-pressure LIBS, have been employed to enhance the detection limit in different applications [22–26].

Compared with that of solid and gas phases, the plasma lifetime of liquid sample is shorter and the temperature becomes lower due to the pressure, volatility, and quenching effects of water. Sputtering of liquid water by a LIBS plasma often raises the problem of the measurement windows. The sensitivity, stability, and repeatability of LIBS signal are much lower than that in the solid sample, leading to the greatly increasing difficulty of its analyses. Numerous papers have reported LIBS measurement of different forms of liquid phase materials including the solidification, liquid bulk, liquid surface, and others [27–32], which shows different detection features and detection limit. The comparison between single- and double-pulse LIBS for the quantitative elemental analysis has been performed [27,33], which shows the enhancement of detection limit using double-pulse LIBS. Based on an overall consideration of various factors, however, double-pulse LIBS yielded a relatively minor benefit, while adding substantially to the complexity and cost of the system. The comparison of liquid jet and bulk liquid measurement has been studied to improve the detection limit of trace elements [34–36]. Detection limit in liquid jet was enhanced compared with that in bulk liquid. Low-pressure LIBS has been employed to measure the gas phase samples in our group. The detection limits were enhanced significantly in the trace element measurement of mercury and iodine [25,26]. Therefore, in this study, the element of Cs in liquid jet was measured using low-pressure laser-induced breakdown spectroscopy (LIBS) to enhance the detection limit. The experimental conditions and detection features will be studied and discussed exhaustively in this paper.

2. Theory

In the generation of plasma, the core of plasma is firstly produced by the absorption of the incident laser energy, such as multi-photon ionization in solids, liquids, or gasses. The creation of the plasma core induces the rapid plasma growth through the absorption of the laser energy by electrons and the electron impact ionization process in it. After the termination of the laser pulse, the plasma continues expanding because of its high temperature and pressure gradients (the high initial number density of plasma) compared with the ambient conditions. At the same time, recombination of electrons and ions proceeds because of the collision process and the temperature decreases gradually compared with the plasma generation process. LIBS signals arise in the plasma cooling period.

The dominant phenomena in the laser-induced plasma process of gas phase samples consisting of electron diffusion, multi-photon ionization, electron impact ionization, and recombination [37]. However, the effect of these processes is dependent upon the pressure. At atmospheric pressure (100 kPa), the electron diffusion and electron impact ionization processes are the major sources of the plasma generation. When reducing the pressure (a few kPa), the effect of electron diffusion and electron impact ionization decreases compared with that under high pressure condition. The plasma signals of measured atoms, such as Hg, iodine, and so on, are mainly produced by the multi-photon ionization process [25,26,38]. There are several interferences with target signal in LIBS process, generally including the continuum emission from plasma itself, coexisting molecular and atomic emissions, noise from detectors, and so on. The intensity of the continuum emission from plasma itself is produced by the bremsstrahlung process and its intensity depends on several factors such as electron number density, electron temperature, and so on. The interference of coexisting molecular and atomic emissions appears from the products of plasma generation process concerning the electron impact ionization process. Therefore, the interferences of the continuum emission from plasma itself and coexisting molecular and atomic emissions decrease at low pressure. According to the experimental results of Hg and iodine in gas phase samples, the detection ability can be enhanced using low-pressure LIBS [25,26].

The plasma generation mechanism of liquid sample is complex. When the liquid jet was irradiated by the laser beam, the creation of the plasma core induces the rapid plasma growth of the surrounding gas. The plasma of surrounding gas is also induced by the laser irradiation. The intensity of plasma emission becomes strong at atmospheric pressure (100 kPa) compared to those at reduced pressure, which indicates the importance of the pressure to get a maximum signal-to-noise ratio. In general, the enhancement of plasma emission intensities, which includes both the emissions from atoms and ions (signal) and the continuum emission (noise), does not mean the enhancement of the signal-to-noise ratio. The reduction of pressure usually causes the decrease of plasma emission intensities; however, it increases the signal-to-noise ratio in some condition by reducing the continuum emission [25,26]. In this study, the element of Cs in liquid jet was detected using the method of low-pressure LIBS.

3. Experimental apparatus

Schematic diagram of measurement system in this study is shown in Fig. 1(a). The apparatus fundamentally consisted of sample input system, laser, vacuum chamber, lens, spectrometer, ICCD camera, and auxiliary equipment. The beam from a Q-switched Nd:YAG laser (LOTIS TII, LS-2137U, beam diameter: 8 mm) operated at 1064 nm with 6–8 ns

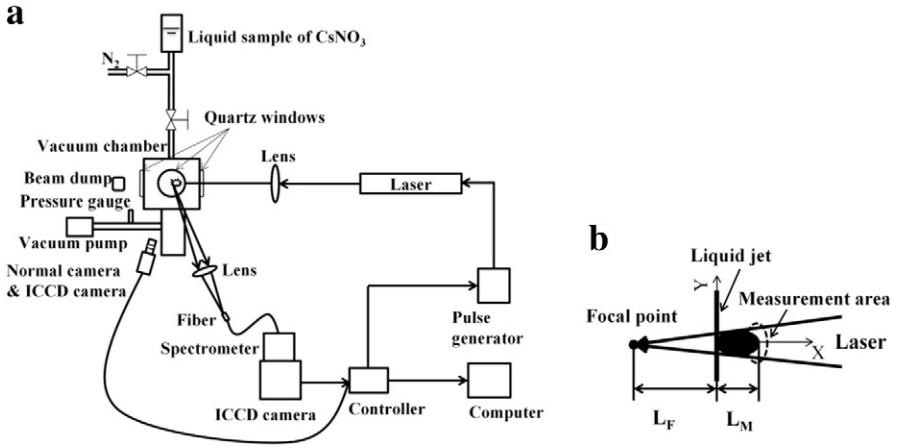

Fig. 1. Experimental system of liquid phase sample. (a) Schematic diagram of measurement system; (b) Laser focal point and plasma.