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Technical note

Laser induced breakdown spectroscopy: A potential tool for atmospheric carbon dioxide measurement

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ABSTRACT

Carbon dioxide (CO_2) is a main contributor to global warming, making up approximately 80% [1] of the greenhouse gases in the atmosphere. Therefore, a precise measurement of the atmospheric CO_2 concentration is essential. Although a number of analytical techniques are available for measuring CO_2 in air samples, laser induced breakdown spectroscopy (LIBS) offers a relatively simple and straightforward analysis which is why it was utilized in this study. LIBS requires a simple experimental setup and offers real-time carbon dioxide measurement. The strong C(I) emission line at 247.85 nm was selected for CO_2 measurement, which yielded a detection limit of 36 ppm with a pulse energy of 145 mJ. Real-time measurement has been demonstrated: a single measurement can be made in 40 s with a relative standard deviation (RSD) of 3.6%.

1. Introduction

Carbon dioxide (CO_2) is the predominant anthropogenic greenhouse gas responsible for continuous rise in global surface temperature and ocean acidity: relevant impacts being coastal flooding, eradication of wet lands, diminished glacial water sources, and damage to ocean ecosystems. A number of governing bodies recognize these threats and are beginning to mitigate CO_2 emissions; therefore, better measurement techniques are crucial for producing rapid and accurate results.

Currently, CO_2 is measured by various methods [2]. The two commonly used methods are GC–MS and infrared spectroscopy. The working principle of GC–MS is based on selective adsorption and elution of the gas molecules of interest in the GC column and the subsequent analysis by the mass-spectrometer. Within the sample gas is bombarded with a high-energy electron beam which causes causing fragmentation of the molecules in the sample. These fragmented molecules are accelerated by a magnetic field and separated by virtue of their different mass to charge ratios. Infrared (IR) absorption spectroscopy is an optical technique, which is the most commonly used technique for CO_2 detection. Carbon dioxide has a non-zero dipole moment which causes it to absorb specific wavelengths of light in the infrared region. Thus, analysis of absorption spectral bands gives the CO_2 concentration in the sample. This technique has a distinct disadvantage in the form of interference from water vapor and carbon monoxide.

In the present work we have applied laser induced breakdown spectroscopy (LIBS) for measurement of CO_2 in air. LIBS is a promising detection tool for solid, liquid and gaseous samples [3–5]. A LIBS set up essentially comprises of a high intensity laser as an excitation source and a time-gated spectrometer to collect the signal. Generally, a laser beam is focused onto a solid sample or within a gaseous or liquid sample to create high temperatures, dissociating the sample to form plasma. Radiation from the plasma is then collected by the spectrometer. Subsequent analysis of the radiation gives qualitative and quantitative information of chemical species present in the sample. Various authors have used LIBS for detection of gaseous samples [6–11]. While Hahn et al. [6] have used LIBS for hydrogen leak detection, Winefordner et al. [7] and McNaghten [8] have utilized it for detection of gaseous/particulate fluoride and helium, and argon in binary and ternary gas mixtures with nitrogen, respectively. Recently, Eseller et al. [9] used the technique for monitoring Ar, He and oxygen impurities in hydrogen. Ferioli et al. [10] have applied LIBS to measure the equivalence ratio of a spark-ignited engine where they showed that the ratio of either C(711.3 nm) or CN(707–734 nm) peaks and any of the N(746.3 and 743.8 nm) or O(776.6 nm) spectral lines can be used to estimate the equivalent ratio. In fact, the LIBS calibration curve of gaseous samples shows a better linearity and reproducibility than solids and liquids. This may be attributed to weak interactions relevant to the matrix effect in low density gas sample at atmospheric pressure and to the homogeneity of the gaseous sample.

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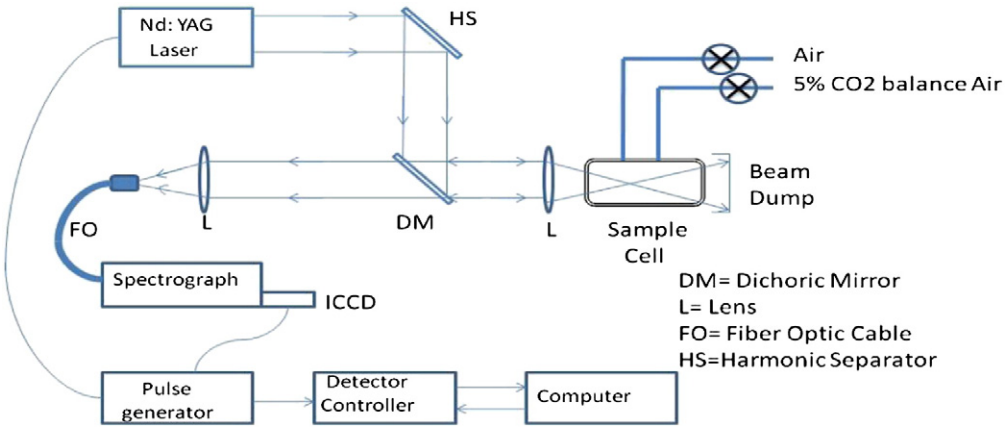

Fig. 1. Schematic of experimental set up for CO_2 measurement.

The purpose of this study is to investigate whether LIBS can be used as an analytical technique to detect carbon dioxide in air. Our working hypothesis is carbon dioxide concentration in air can be measured by creating a spark in the air and subsequently measuring the carbon signal at C-247.85 nm; a line used by other researchers [12,13] for carbon measurement in soil. We assume that the main source of the carbon signal in air is from carbon dioxide, considering the approximate concentrations of CO_2, methane, and carbon monoxide in air are 390 ppm, 1.79 ppm, and 0.1 ppm respectively (current values are available online at http://gaw.kishou.go.jp/cgi-bin/wdcgg/catalogue.cgi). Though in highly polluted cities some interference might come from the soot (black carbon) present in the air. Soot concentration in the atmosphere is highly inhomogeneous. Typical soot concentration in big cities is 0.46 μg/m^3 [14]. Generally, soot concentration may be neglected. However for those cases where this contribution cannot be neglected, this interference can be removed through the use of a commercial particulate filter (Diesel Particulate Filter has a removal efficiency of 85% to 100%). Alternatively, soot concentration can be measured separately and its contribution can be subtracted from the LIBS signal to get the contribution due to CO_2 only.

To our knowledge, the research reported here constitutes the first study utilizing LIBS for atmospheric carbon dioxide measurement.

2. Experimental

A schematic of the experimental set up is shown in Fig. 1. A two-way cylindrical cell was used to hold the gaseous sample during the measurement. The cell was fitted with two quartz windows at both ends to allow the laser beam to enter and exit the cell. The sample cell contained ancillaries to allow inflow and venting of gases, and measurement of the cell pressure. A rotary vane pump (Edwards E2M2) and a Baratron absolute pressure gauge (MKS 122A) were connected to the cell. The Nd:YAG laser (Big Sky Inc. CFR400) with a wavelength of 532 nm was used in this investigation. It was operated in Q-switched mode with a pulse repetition rate of 10 Hz. The pulse width (FWHM) and the maximum pulse energy were 8 ns and 180 mJ respectively. The beam diameter was 6.5 mm and had a Gaussian beam profile. A spherical plano-convex fused silica lens of focal length 10 cm was used for focusing the laser beam into the center of the sample cell to create a plasma spark within the gas mixture. The emission from the laser-induced plasma was focused into a fiber optic cable by a fused silica lens of focal length 10 cm. The other end of the optical fiber was coupled to a UV–visible Echelle optical spectrograph (LLA Instruments, GmbH, ESA 3000 EV/I, Berlin, Germany). The spectrograph had the spectral range of 200–780 nm (though it had some spectral gaps). It had a linear dispersion of approximately 5–19 pm/pixel. A 1024×1024 element intensified charge-coupled device (Kodak KAF-1001) with a pixel width of 24 μm was cooled by Peltier elements and attached to the exit of the spectrograph which was used to detect the light from the laser spark. The detector was operated in gated mode using a dedicated high-voltage fast-pulse generator (Stanford DG 535) that was synchronized with the laser pulse. The data acquisition and analysis were performed on a personal computer using ESAWIN software. Two certified gas mixtures supplied by Nexair were used in the experiments. These comprised a cylinder of compressed air and another of carbon dioxide (5% CO_2 balanced with air). The certified gas mixtures were used to prepare the gas sample for the system calibration.

3. Results and discussion

The initial efforts were concentrated on investigating the effect of experimental parameters (laser energy, gate delay, and choice of focusing lens) on the intensity of the carbon 247.85 nm line (Fig. 2). In addition, the use of a signal enhancement device that employed a metal substrate was also evaluated. The objective of the metal substrate was to improve signal-to-noise ratio of the analyte carbon line for better CO_2 detection. Finally, the optimized experimental conditions were used to record LIBS spectra for instrument calibration and CO_2 concentration measurement of ambient air.

3.1. Optimization of experimental parameter

Optimization using the available instruments and experimental setup is necessary to get the best signal. The most persistent carbon line that could be read with the spectrometer (LLA ESA 3000) was found to be C-247.85 nm. Intensity of the selected line was read directly from accompanying software (ESAWIN), which calculated the intensity by subtracting the background from the peak maximum. First, the effect of focusing lenses on the signal strength was investigated. The laser beam was focused with a 10 cm focal length lens and a spark was created in air. On-chip accumulation was found to be 40 to get the best signal-to-noise ratio without saturation.[1] The signal intensity was recorded with different pulse energies and gate delays. The whole procedure was repeated with a 20 cm focusing lens. The use of a 10 cm lens gave a stronger signal than the use of the 20 cm lens (Figs. 3 and 4). The plasma spark size observed in the experiment was smaller in the case of the 10 cm lens. The tight focusing of the laser beam in a small volume by a 10 cm lens had

[1] On-chip accumulation refers to adding of multiple exposures right on the interline ICCD before a single readout.