

An application scheme of LIBS to detect trace ethanol and methanol



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ABSTRACT

Laser Induced Breakdown Spectroscopy (LIBS) is an alternative tool for chemical analysis of any given solid and liquid samples, especially of in-organic materials. If a reliable calibration can be performed, the technique is also acceptable for elemental quantitative analysis. However, LIBS has not been widely applied for organic chemical analysis, especially for organic molecular identification, although some trial investigations have been reported. In this paper, a scheme for detection and identification of trace methanol and ethanol using LIBS is reported. In the scheme, an intensive pulsed laser is used to breakdown gaseous trace alcohol samples and the optical emission spectra of the induced plasma are collected. In order to verify the scheme, trace alcohol samples are prepared deliberately by using pure ethanol or methanol bubbled with Argon as carrier gas and then mixed into matrix gases. The key issue for the scheme is to constitute indexes from the LIBS data. Two indexes are found suitable for alcohol detection and identification. One is the emission intensity ratio (as H/C) of the Hydrogen line (653.3 nm) to Carbon line (247.9 nm) for identification and the other is the ratio of the Carbon line (as C/Ar) or the Hydrogen line (as H/Ar) to Argon lines (866.7 nm) for quantitative detection. Calibration experiment result shows the index H/C is specific for the two congeners but almost independent on concentration. In detail, the H/C keeps specific constant of 34 and 23 respectively for ethanol and methanol. Calibration of the indexes C/Ar and H/Ar shows they are almost linearly related to concentration below 1300 ppm and therefore are competent for concentration measurement. With the indexes, trace concentration measurement achieves a limit of 140 ppm using laser pulse energy of 300 mJ.

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1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is a widely used spectroscopic technique to analyze the elemental composition of solid, liquid and gas [1–3]. And so far, the technique is known as the only spectroscopic method capable of detecting most chemical elements in almost any environment. Its merits as a chemical analysis technique include high efficiency, specificity, simplicity and remote sensing. Generally, LIBS employs a pulsed laser that is focused onto a solid sample or within a gas or liquid sample to heat the vicinity of the focus and ionize or dissociate the samples into plasma. Radiation from the plasma is then collected and spectrally resolved by a spectrometer to yield information on chemical compositions [4]. Except for chemical analysis, LIBS has also been applied in many fields ranging from industrial through environmental to biomedical fields [5–8].

Laser-induced breakdown spectroscopy (LIBS) is powerful for chemical element analysis especially of in-organics. However, it is less useful for organic molecules because the bonding structure instead of the chemical elements is the key for organic molecules and the laser induced breakdown can easily destroy the bonds. In fact, due to the high temperature (10,000–20,000 K) of laser induced plasma, organic molecules involved in the plasma are mostly fragmented and even decomposed into atoms. However, some researchers have still tried organic molecules using LIBS because of its fascination in simple operation and sample preparation, if compared with mass spectroscopy and chromatography. N. Melikechi and H. Ding [9] have shown that LIBS with a cooling system could be used to identify qualitatively alcohols and some proteins. M. Tram and Q. Sun [10] used LIBS to analyze the major elemental ratios in solid organic compounds. Therefore LIBS has the potential of a useful tool for organic chemical analysis. However the quantitative accuracy of the technique both for in-organic and organic chemical analysis is still one of the most important issues because it depends on the complexity of laser induced plasma formation, atomization, ionization and excitation processes. The

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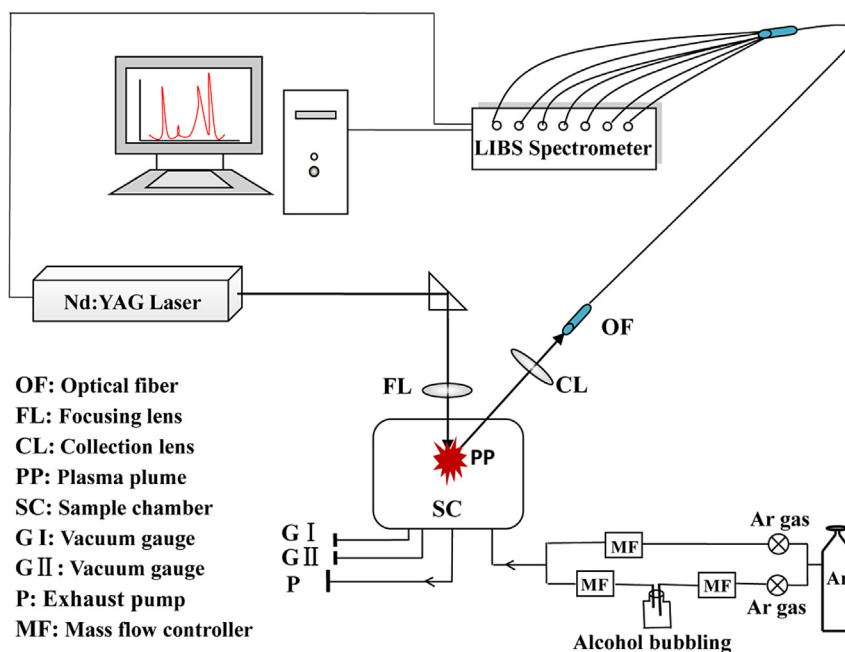


Fig. 1. Schematic of the LIBS experimental set-up.

most common approach to achieve LIBS quantitative analysis uses calibration curves generated with standard samples. Nevertheless, problems arising from laser fluctuation, fractionation in atomization and local thermodynamic equilibrium assumption should be properly addressed in order to obtain reliable calibration in laboratory. Commonly used spectrum intensity normalization method, as another important technique for quantitative accuracy, relies on the correlation between the spectrum intensity of some major elements and the plasma parameter especially the plasma electron density [11,12]. For gas LIBS, the matrix gas used as normalization reference that is competent for reducing the laser plasma fluctuation makes gas LIBS more accurate than solid or liquid LIBS, since the matrix takes the major of the laser plasma and the matrix portion is stable.

Generally speaking, laser induced plasma can commonly be thought under local thermal equilibrium (LTE) [13,14], which ensures Boltzmann–Maxwell and Saha equations to be true. Therefore the ratios of atomic products fractionized from the organic molecules in laser induced gas plasma depend mainly on the plasma temperature. Considering that the energy threshold for different atomic products, the LTE plasma circumstance with certain temperature will generate different atomic product distribution for different organic molecules. Therefore the atomic product ratios are possibly capable of recovering the organic molecules. In this paper, an LIBS scheme applied for methanol and ethanol detection and identification is presented and validated using calibration samples, because the two alcohol congeners are good representatives for popular organics without hetero-atom.

Methanol and ethanol are common chemicals for people to access in daily life. They have similar bonding structure, but different properties and applications. Ethanol is widely used in many important aspects, but methanol is normally used as organic solvent or fuel and sometimes used as the main component of adulterated wine which murders many people. Their similar chemical structure can only be separated from each other through some advanced techniques, such as mass spectroscopy or chromatography. Unfortunately, these techniques are relatively complex and expensive for real-time applications and therefore not

suitable for non-professional operation. Thus a simple technique is still crucial for quick detection of methanol and ethanol.

2. Experimental details

The LIBS setup used here has a configuration similar to that published [9] except the closed sample chamber and is shown schematically in Fig. 1. For more detail, the authors of Ref [9] directly used alcohol liquid as samples instead of alcohol steam with argon as carrier and matrix. The gaseous samples in our scheme escape from laser induced evaporation and therefore are much safer against laser fluctuation than alcohol liquid. Foremost, the gaseous sample preparation routine used in our scheme provides us a possibility to modulate sample concentration for calibration of quantitative measurement.

As common, the system consists of three parts: excitation laser, closed sample chamber and spectrometer. A Q-switched Nd:YAG laser (Brilliant Eazy, Quantel) generating fundamental wavelength (1064 nm) and 5 ns laser pulses at a repetition rate of 10 Hz is used as the excitation source. A quartz 5-cm focus length lens with diameter of 2.5 cm focuses the laser pulses into the sample chamber to breakdown the contained gas sample.

In order to isolate the working gas from air, the chamber is a closed room which consists of a quartz drum and two end flanges. The quartz window on the top end provides a channel for the laser coming into the gas sample and an access for the plasma emission recording. Two gauges are employed respectively for base vacuum below 1 Pa and working pressure up to 10^5 Pa. The gas filling is controlled with two mass flow controllers respectively for matrix gas Argon and alcohol agent with expected mixing ratio.

An integrated spectrometer is necessary for broadband spectrum concurrent recording. As the LIBS configuration commonly used, the optical emission of laser plasma is collected and focused onto the optic fiber inlet of the used spectrometer (LIBS2500 + Ocean Optics Inc, USA, in our case) by another 10 cm focus length lens with diameter of 5 cm. The spectrometer is provided with seven linear silicon CCD array detectors for recording broadband spectrum from 200 nm to 980 nm, and can achieve a

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