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Original research article

Measuring of naphthalene fluorescence emission in the water with nanosecond time delay laser induced fluorescence spectroscopy method



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ABSTRACT

In this paper, the time resolved laser induced fluorescence emission of naphthalene ($C_{10}H_8$) has been measured by both a time delay method and a high pass method. The sample was excited by laser pulse at 266 nm wavelength and Fluorescence emission was detected by an ICCD. In the high pass method, a high pass filter is placed in front of a spectrometer to eliminate the laser pulse scatter. On the other hand, in the time delay method, instead of a high pass filter, a nanosecond time delay is used between the incident laser light and the detection of fluorescence emission. An enhancement was observed in the S/N ratio in time delay method compared to the high pass method. The fluorescence lifetime and the limit of detection (LOD) quantities of naphthalene in water were determined in the time delay method. Linear calibration plot has provided detection limits in the ppb range.

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1. Introduction

Due to their ubiquity and confirmed carcinogenic properties, Polycyclic Aromatic Hydrocarbons (PAHs) are common water pollutants. It is estimated that most PAHs in environmental water are not dissolved but rather in particulate forms. The concentration of dissolved PAHs in water is often an order of magnitude lower than its particulate concentration [1,2]. PAHs are generally formed during incomplete combustion, pyrosynthesis, or pyrolysis of hydrocarbons and are released to the environment by both natural and anthropogenic sources.

The highly fluorescent nature of PAHs has made molecular fluorescence spectrometry a popular technique for PAHs analysis [3]. In fluorescence measurement, the samples are not affected or destroyed in the process [4]. PAHs are composed of two or more condensed aromatic rings containing only carbon and hydrogen. Naphthalene ($C_{10}H_8$) is the simplest two ring PAH, which is the most volatile PAH and therefore present mainly in gaseous state. While naphthalene itself is not carcinogenic, it is the most abundant PAH in polluted urban areas [5,6]. The main sources of naphthalene in the urban atmosphere are motor vehicle exhaust and residential heating [7].

There is a strong interest in the automotive industry where researchers use fluorescence measurements on aromatics such as naphthalene to measure fuel concentration or equivalence ratio in internal combustion engines. Because naphthalene is

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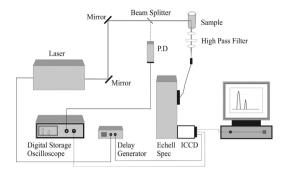


Fig. 1. Schematic figure of the experimental setup.

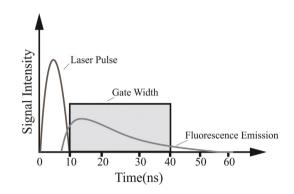


Fig. 2. Schematic diagram of the fluorescence emission.

naturally present in gasoline or diesel fuels, information about fuel evaporation and its subsequent mixing with air in the combustion chamber may be obtained by recording fluorescence signals from these species. Time resolved fluorescence provides a method for enhancing the specificity of fluorescence-based measurements of PAHs. The use of this method for analytically separating different chemical constituents, based on differences in their fluorescence decay times, has been described by several investigators [8].

In the time resolved laser induced fluorescence spectroscopy, the sample is excited by a laser pulse, and fluorescence emission is measured by a detector. Since the detection of scatter laser pulse can damage the detector, different methods are used to remove it. In one of the most common methods, a high pass filter, which passes the fluorescence emission, was placed in front of the spectrometer to filter the incident laser light [9–18]. Rudnick and Chen [19] employed a spectrograph whose spectral range did not cover the laser wavelength. In order to detect the fluorescence of petroleum accelerants, Saitoh and Takeuchi [20] applied them with an appropriating delay time for the elimination or reduction of background fluorescence, and they used a high pass filter to remove the laser light.

In this work, we study both a time delay method and a high pass method for the detection of fluorescence emission spectrum of naphthalene in water. In the time delay method, fluorescence emission is detected after the time delay at the range of laser pulse width and in the other method, a high pass filter is used. The S/N ratio in these two methods is calculated. Also, the fluorescence lifetime and the limit of detection (LOD) quantities are determined in the time delay method.

2. Experimental

2.1. Sample

A sample is prepared by dissolution of dry weighed naphthalene in water to obtain a concentration of 25 mg/l. Contrary to naphthalene, water is a polar molecule. Thus, to dissolve naphthalene in water completely, a mixer is used at 60 °C for 30 min.

2.2. Instrument

A schematic diagram of the experimental set-up is shown in Fig. 1. A Q-Switched Nd YAG laser (Continuum Surelite) with a wavelength of 266 nm, a 6 ns pulse width, a repetition rate of 10 Hz and the max pulse energy 5 mJ was used to pump the sample. This laser has a BNC connector that provides a negative going TTL signal (3.5 V) approximately 100 ns before Q switching of laser. Five percent of laser pulse was guided by a beam splitter to a photodiode (DET 10A) for timing of the

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