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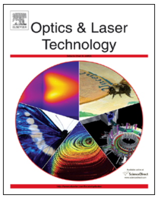

Development of a portable laser-induced fluorescence system used for in situ measurements of dissolved organic matter

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ABSTRACT

A portable laser-induced fluorescence system (total weight about 1.7 kg) has been developed for detecting the level of dissolved organic matter in water. The portable system consists of a high pulse repetition frequency (10-kHz) microchip laser at 405 nm, a reflective fluorescent probe and a broadband micro spectrometer. The stability and sensitivity of the new instrument were studied. The detection limit of this new instrument was 0.75 ug/L, and its baseline drift was only 0.45% per hour. Field results showed that the portable system can work as well as commercial laboratory spectrophotometers. A significant correlation ($R^2=0.96$) was found between measurements taken by the new instrument and thoses measured by laboratory spectrophotometer. In addtion, influence of temperature variation on measurements by the new instrument was investigated. The portable system is promising for monitoring dissolved organic matter in water, especially in the field.

1. Introduction

Chromophoric dissolved organic matter (CDOM) represents the colored fraction of dissolved organic pool, which absorbs lights in the visible as well as the UV ranges. CDOM can strongly influences ocean optical properties, remotely sensed spectra and biogeochemical processes. The significance of CDOM to biogeochemical processes has been studied by many researchers [1–3]. CDOM is operationally defined as the colored fraction of material passing through a 0.2 μm filter and quantified by the absorption coefficient, $a_g(\lambda)$, as measured on filtered samples using a spectrophotometer or absorption meter [4]. Like other absorption measurements, fluorescence measurement is another well-known tool for determining CDOM, which can be acquired more rapidly and with greater sensitivity in a variety of marine and freshwater applications. Various light sources, such as lasers, light emitting diodes, and lamps, can be used to stimulate fluorescence of aquatic constituents. The spectrally narrow laser emission provides improved selectivity and efficiency of excitation, and reduces the spectral overlap between the water Raman scattering and fluorescence bands of aquatic constituents [5]. The laser-induced fluorescence (LIF) technique is a well-known analytical technique for rapid water environment monitoring, which is based on the measurements of laser-induced water emission spectrum, to obtain qualitative and quantitative information about the in-situ fluorescent constituents. In the past two decades, a variety of shipboard, shore-based, and airborne laser fluorescence systems were developed for analyzing oil pollution [6–8], phytoplankton [9–13], water transparency and turbidity [14–16], and characterization of CDOM [17–22]. However, many such instruments are too bulky for routine use in the field, and some detectors use only one or a few channels to measure one specific parameter (e.g., chlorophyll-a, CDOM, oil, or variable fluorescence) and do not provide full and detailed spectral information about other fluorescent constituents for more comprehensive characterization of aquatic environment [23,24].

To our knowledge, the utilization of LIF technique in the East China Sea (ECS) has rarely been studied. The ECS water belongs to Class II water, influenced by outflows from the Yangtze River and the Hangzhou Bay, which contain high concentration of suspended sediment. The optical properties of Class II water are significantly influenced by constituents such as phytoplankton, mineral particles, CDOM, or microbubbles, whose concentrations do not covary with phytoplankton concentration. They are often affected by terrigenous material output. Class II water are normally encountered present in coastal zones (estuaries, shelf areas, inlets, etc.) and possibly far from the coast in the case of extended shelves or shallow banks [25,26].

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Compared with traditional measuring methods for CDOM monitoring, LIF technique has the advantage of rapidly acquiring high-resolution in situ profiles [27]. Studying the utility of LIF technique in the ECS is, therefore, of significance. The goal of this paper is to describe a novel portable LIF system and to utilize it for monitoring CDOM level in Chinese coastal and inland waters. A light-weight (about 1.7 kg) LIF system for fluorescence measurements was developed, which consists of a high pulse repetition frequency microchip laser at 405 nm, a reflective fluorescent probe and a broadband micro spectrometer. The signal to noise ratio of fluorescence spectroscopy instrument can be increased using high pulse repetition frequency laser [28]. A reflective fluorescent probe containing a dichroic beamsplitter could effectively eliminte the elastic scattering from fluorescence spectra. A broadband microspectrometer could provide full, detailed spectral information about fluorescent constituents in complex aquatic environments. In order to assess the performance of this new system, we compare the measurements taken by the instrument to those by laboratory absorption spectrophotometer or by spectrofluorometer. In addtion, the stability and sensitivity of the new instrument are studied in the lab. Influence of temperature variation on LIF measurement is investigated as well. Applications of the new system for water monitoring studies are illustrated by in situ measurements obtained in the Yangtze River Estuary and its adjacent sea and those obtained in the West Lake.

2. Instrument and methods

2.1. Experimental setup

Fig. 1 shows the schematic of the setup of the portable LIF system. It consists of an excitation source module, a fluorescent probe module, a sample holder module, and a detection module. A micro violet laser with 405 nm wavelength (MM-405-100, Boson Tech) is selected as the excitation source, which is a mini size laser with the excitation wavelength in violet band. The laser has high pulse repetition frequency rate (greater than 10 k-Hz) and low power consumption (about 10 w); the size of the laser is 85 mm × 32 mm × 31 mm, and the weight is about 0.3 kg. A power supply module (PSU-H-FDA, Boson Tech) is used to provide stable power and to control the temperature of the laser source; it weighs 0.8 kg. A broadband microCCD spectrometer (USB4000, Ocean Optics) is integrated to record complete visible LIF emission spectra with a range from 360 to 1000 nm, and with a full width at half maximum of 10 nm; its weight is about 0.2 kg. A fiber-optic fluorescent probe is used as the receiver in the fluorescence measuring system. A dichroic beamsplitter in the fluorescent probe is used to eliminte the elastic scattering from the laser-stimulated emission. Three focusing lens are used for excited light collimation, and a collecting lens is used for emission collection. A sample pool is made from a quartz of the size 12.5 mm × 12.5 mm × 45 mm. The length of the internal optical path of sample space is 10 mm. Its four sides are polished and transparent. A reflecting mirror (74-msp, Ocean Optics) under the sample pool is used to enhance fluorescence signals. The SpectraSuite software (Ocean Optics software Inc.) is used to record fluorescence spectra. It provides a complete control of setting the parameters for all system functions, such as acquiring data, designing graph display and using spectra overlays. During measurement, the output of the laser is focused though a fluoresent probe into the quartz sample cell; then the emitted fluorescence light passes through a dichroic beamsplitter in the fluorescent probe and is collected by a collection quartz lenses onto the entrance slits of a spectrometer, which is interfaced to a computer through a USB port. The LIF spectral integration time is typically preset to 0.1–1 s, and the number of acquisitions is typically preset to 5–25, in order to average the fluorescence spectra. Each sample measurement typically takes 30–50 s. The corresponding water Raman signal is used for fluorescence normalization that accounts for highly variable optical properties of natural waters [29–32]. A photograph of the optical system is shown in Fig. 2. One can see that the whole system is light in weight, and is small in size. It is easy for transport and can be used aboard a small boat to sample organics and other fluorescing compounds in waters.

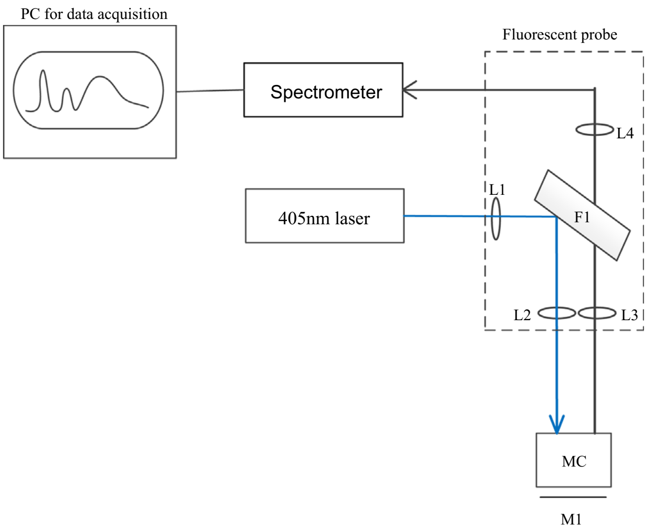

Fig. 1. System chart of the LIF system. MC – measurement cell; F1 – Dichroic beamsplitter; L1, L2 and L4 – focusing lenses; L3 – collecting lens; M1 – reflecting mirror.

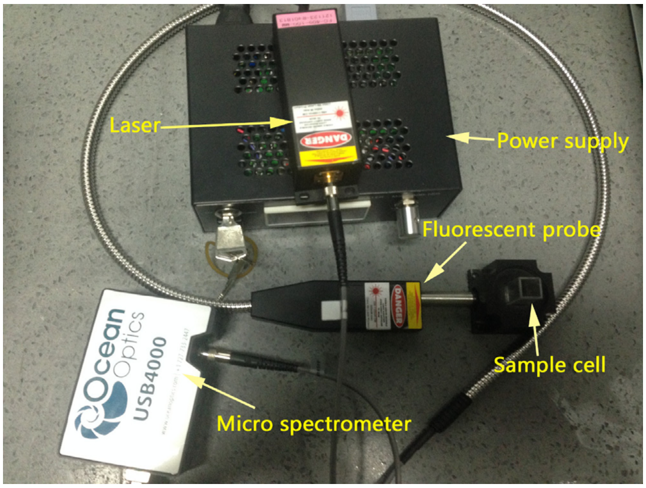

Fig. 2. Photograph of the optical system.

2.2. Sensitivity and stability studies

A fluorescence standard reference material, quinine sulfate [21,33], was used to measure the performance of the new fluorescence system. To measure the detection limit of the portable LIF system, the fluorescence of quinine sulfate (dissolved in 0.1-N sulfuric acid) was measured by varying the concentration of the sample from 0.15 to 15 ug/L. Replicate measurements were taken to create calibration curves of quinine sulfate at various concentrations. In addtion, in order to verify the stability of the LIF system, the baseline drift was measured, which is time variation of the peak baseline from a straight line. Measurements of Milli-Q water by the system were carried out once every second for one minute, and once every minute for one hour.