

## Determination of hydrocarbon levels in water via laser-induced acoustic wave



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### ABSTRACT

Hydrocarbon contamination in water is a major environmental concern in terms of foreseen collapse of the natural ecosystem. Hydrocarbon level in water was determined by generating acoustic wave via an innovative laser-induced breakdown in conjunction with high-speed photographic coupling with piezoelectric transducer to trace acoustic wave propagation. A Q-switched Nd:YAG (40 mJ) was focused in cuvette-filled hydrocarbon solution at various concentrations (0–2000 ppm) to induce optical breakdown, shock wave generation and later acoustic wave propagation. A nitro-dye (ND) laser (10 mJ) was used as a flash to illuminate and frozen the acoustic wave propagation. Lasers were synchronised using a digital delay generator. The image of acoustic waves was grabbed and recorded via charged couple device (CCD) video camera at the speed of 30 frames/second with the aid of Matrox software version 9. The optical delay (0.8–10.0  $\mu$ s) between the acoustic wave formation and its frozen time is recorded through photodetectors. A piezo-electric transducer (PZT) was used to trace the acoustic wave (sound signal), which cascades to a digital oscilloscope. The acoustic speed is calculated from the ratio of acoustic wave radius (1–8 mm) and optical time delay. Acoustic wave speed is found to linearly increase with hydrocarbon concentrations. The acoustic signal generation at higher hydrocarbon levels in water is attributed to supplementary mass transfer and impact on the probe. Integrated high-speed photography with transducer detection system authenticated that the signals indeed emerged from the laser-induced acoustic wave instead of photothermal processes. It is established that the acoustic wave speed in water is used as a fingerprint to detect the hydrocarbon levels.

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### 1. Introduction

Unquestionably, water is one of the gifted fundamental resources on earth to prevent from being polluted. Hydrocarbon, being one of the major pollutant factors in water, needs to be accurately monitored. The hydrocarbon contamination of water that results from the fuel burning emissions, industrial separator discharge, storm water run-off, water cooling systems, spills from road asphalts, fuelling depots, transportation and haulage, manufacturing facilities (automotive, plastics and steel production) and etcetera, continues to be a very burning issue due to its damaging impact on the environment [1–7]. Certain hydrocarbon compounds that are more detrimental than others require constant detection and close monitoring for human safety. Hydrocarbons being common and naturally occurring compounds usually exist with varying concentrations in storm water and effluent water.

Generally, hydrocarbons in water are free floating, emulsified, dissolved, or adsorbed to suspended solids.

Categorically, the presence of a hydrocarbon molecule is typically dictated by its size. The bigger molecules, being more buoyant and free, are readily alienated from water by natural separation or enhanced through oil/water separators including dissolved air floatation or coalescing systems. However, the smaller structures tend to emulsify with the water and are more complicated to eradicate from water. Naturally, the microbes in the soils and water are capable to breakdown hydrocarbons. Hydrocarbons that are exposed to the air have strong affinity to volatilise. In addition, hydrocarbon transformation through photochemical reaction often enhances their decomposition. Industrial processes and human activities frequently result in an augmented hydrocarbon loading in water. Consequently, the natural abilities of the water to

decompose the hydrocarbons become overwhelmed, which in turn generates environmental concern [2].

Irrespective of catastrophic or chronic discharges, oil spill in the environment poses diverse environmental risks and causes wide public concern [1]. An oil spill means the release of liquid petroleum hydrocarbon into the environment and is certainly a form of pollution. Primarily, it happens due to the release of crude oil from tankers; offshore platforms; drilling rigs and wells as well as spills of refined petroleum products (such as gasoline and diesel) and their by-products; heavier fuels used by large ships such as bunker fuel, and the spillage of any oil refuse or waste oil [2]. Liquid–liquid separation technique is the conventional method to determine the concentration of oil dispersed in water [3–6]. However, this method is limited by certain constraints, including high time consumption, can only be performed in a laboratory, and uses hazardous chemicals such as N-hexane and Freon, which are carcinogenic. Moreover, Fourier transform technique has similar shortcomings [7]. Based on intensive literature survey and on an established know-how in the field, an in situ fast and easy laser-based technique to determine the amount of oil spilled (hydrocarbon contents) in water is proposed [8–10].

A Q-switched laser-mediated breakdown in the liquid phase, so called the pulse laser ablation in liquid (PLAL) method has many applications [11–18]. The PLAL method is based on the conversion of optical energy into mechanical energy. The generation and detection of acoustic waves in solid and liquid media are performed using a short laser pulse. This technique is demonstrated as an important tool and used in several fields such as medical and applied sciences. Furthermore, it is used for soil characterisation [19–21], laser surface alloying [22,23], cleaning contaminated surface [24], laser tissue ablation, corneal sculpting [25], and indirect gall stone fragmentation [26]. The interaction of laser energy with material surface (solid media) causes rapid heating, thermo-elastic expansion, and phase change. Conversely, the interaction between the laser and liquid media results in strong ultrasonic or shock wave emission [27,28]. Depending on the applied laser energy, the interaction with the surface of an absorbing or a transparent liquid in contact with a solid boundary induces an explosive phase change and thereby generates a shock wave [29–31]. Despite a few dedicated efforts, an accurate laser-induced acoustic LIA based method for hydrocarbon concentration quantification in water is far from being realised.

Based on LIA shock wave generation, a new technique called laser-induced acoustic wave is proposed to determine the hydrocarbon level in water. The hydrocarbon level is quantified by measuring the speed of the acoustic signal generated from the shock wave. The detection of hydrocarbon level via sound amplitude is reported elsewhere [8]. This method offers several advantages in terms of speedy hydrocarbon identification with high accuracy, no requirement of chemicals, and technologically cleaner or greener without involving any waste management. This indigenously developed novel LIA system (invariably termed photo-acoustic and ultrasound) integrates a Q-switched laser with a piezo-electric transducer.

## 2. Experimental procedure

### 2.1. Sample preparation

YAMALUBE oil manufactured by YAMAHA Malaysia in cooperation with the USA is used as a hydrocarbon source. The solution is prepared by mixing 100 mg of oil in one litre of distilled water. An accurate measurement of oil (hydrocarbon) is accomplished using a micropipette. Thus, the concentration for this particular hydrocarbon solution is  $100 \text{ mg l}^{-1}$  or the equivalent of 100 ppm

(ppm). The solution is acidified with 2 ml of hydrochloric acid 2 N (QReC 37%) for finely dispersed droplets formation. The mixture is vigorously shaken and preserved upon achieving a homogeneous solution of pH 2 levels. Identical procedure is followed for preparing other solutions at different hydrocarbon (oil) concentrations. The solution is stored into a Pyrex cuvette of dimensions  $(3 \times 3 \times 3) \text{ cm}^3$  to carry out further measurements.

### 2.2. Synchronisation lasers system

A Q-switched Nd:YAG laser (IPL-Amyni) with fundamental wavelength of 1064 nm, peak energy of 40 mJ and pulse duration of 10 ns was focused inside the mixture to induce an optical breakdown. Two lenses were employed, one with a focal length of  $-25 \text{ mm}$  (to diverge the laser beam) and another (wide angle camera lens) with a focal length of  $+28 \text{ mm}$  (to converge the beam). This combination ensured the creation of a point source required to generate a spherical shock wave. The dye laser (module LN2C) was pumped using a Photonic PRA Nitromites Nitrogen Model LN 102C (LASER PHOTONICS). The Coumarin-500 organic dye laser (dye concentration of  $1 \times 10^2 \text{ mol}$ ) with output wavelength of 500 nm and ethanol as a solvent was used. The wavelength was tuned to 510 nm with the pulse duration of 300 ps and energy per pulse is less than 12 mJ. The dye laser was triggered from external with an input voltage of 5 V. The developed system was synchronised via a delay function generator (DG535 digital delay/pulse generator, Stanford research system). The Q-switched Nd:YAG laser plays a role to induce acoustic wave and the dye laser acts as an illumination source. Tektronix Oscilloscope (Model TDS3052C with 500 MHz bandwidth sample rates up to 5 GSa/s) with two channels was employed to manifest the delay between the two laser beam signals. An Olympus NDT (USA)-U8 421038 immersion transducer operated at a frequency of 5 MHz having surface diameter of 5 mm was used as an ultrasonic probe to detect the acoustic signal. A CCD camera (Model CBS2000P, SAMSUNG) was used to visualise and record the image of the acoustic wave.

Fig. 1 illustrates the schematic diagram of the experimental setup for the acoustic signal detection and shadowgraph technique. The dashed line indicates the path of the nitro-dye (ND) laser or Nd:YAG laser beam. Initially, a part of the Nd:YAG laser beam was detected by a photodiode (AP). The signal was used to be an input signal to trigger the function generator system (DG 535). Then, the function generator was set a delay before sending an output signal to trigger the dye laser. The ND laser beam was enlarged by two beam expanders (EB 1 and EB 2), to be able to cover the whole observation region. The CAM is a CCD Camera (Samsung SCB 2000), PD1 and PD2 are two identical photodiodes

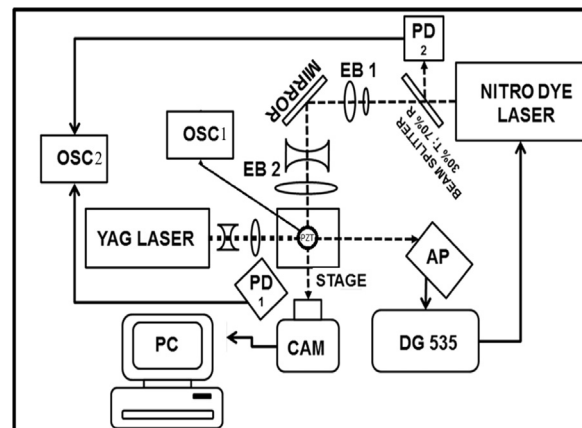


Fig. 1. Schematic diagram of the experimental setup.

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