Solvent effect on the acoustic detection of laser-induced breakdown

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Abstract. Interaction between pulsed laser beam and nanoparticles in solution results in the breakdown of dielectric medium which accompanies the plasma formation. Acoustic detection of laser-induced breakdown uses the information of the recorded acoustic signal for the quantification of colloids. To this date, laser-induced breakdown detection (LIBD) is mostly applied to water-based colloidal systems. This study aimed to give an insight of the solvent effect on the acoustic LIBD. Various solvents, namely methanol, ethanol, toluene, xylene, hexane, ethylene glycol, and oil, were subjected to acoustic LIBD. The results showed that the breakdown threshold energies for the non-water solvents were shifted from that of water; thus calibration curves for nanoparticles quantification might need some corrections. In addition, the effect of solvent dilution on acoustic LIBD was also studied by varying the concentration of methanol and ethanol. It was showed that solvent dilution resulted in the shifting of breakdown threshold energy to a lower value. This study indicated that careful analysis has to be taken when quantifying nanoparticles in non-water solvents using LIBD technique.

1. Introduction

The rapid development of nanotechnology has led to various techniques available for the characterization of nanoparticles. Laser-induced breakdown detection (LIBD) is a laser-based technique for detecting nanoparticles in liquid medium, which is particularly sensitive for small-sized and low-concentrated colloids [1]. According to previous study, it is superior to other laser-based techniques by a factor of $10^4$ [2,3]. LIBD requires least sample preparation; however, high-concentrated sample might need dilution [1].

Acoustic LIBD is based on the detection of shock wave (breakdown) generated from interaction between pulsed laser beam and matter [1,4]. Solids, such as nanoparticle, have lower breakdown threshold energy compared to liquids. LIBD makes use of this fact and therefore is able to tell the presence of nanoparticle in solution [4]. Various studies have applied LIBD for detecting and quantifying nanoparticles, mostly in aqueous solvents [1,5–7]. Nevertheless, non-aqueous solvents are often involved in nanoparticle synthesis [8–14]. Therefore whether acoustic LIBD technique is applicable for non-aqueous solution or not is of interest.
In addition, nanoparticle quantification by LIBD technique needs calibration with standard reference materials. Ultrapure water is usually used for background (zero concentration) [15, 16]. It is of question if correction is needed for quantification of nanoparticles suspended in non-aqueous solvents. In this research, various non-aqueous solvents were subjected to acoustic LIBD to see the effect on the LIBD experiment.

2. Experimental Methods

Experimental setup for acoustic LIBD is shown by figure 1. Nanosecond pulsed laser beam from Nd:YAG laser (Q-Smart, Quantel) with a wavelength of 532 nm and a frequency of 10 Hz was focused into sample in a 3500 µl cuvette. The generated acoustic signal was detected by a microphone attached on the cuvette wall. The microphone was connected to a recording system which saved the recorded signal as an audio file. Each file contained the audio signal from one thousand laser shots interactions with the sample. A homemade program was used to process the file by dividing it into blocks and evaluating each of them for the presence of acoustic signal. The number of blocks was set to be the same as the number of pulsed laser shot. It was assumed that one block represented interaction between one pulsed laser beam and the sample. The signal peaked when a breakdown occurred and the number of peaks was counted as the number of breakdowns. The number of breakdowns which occurred for a certain number of pulsed laser shot was called breakdown probability [15].

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\text{Breakdown probability} = \frac{\text{Number of breakdown occurred}}{\text{Number of pulsed laser shot}} \quad (1)
\]

A series of acoustic LIBD experiment were carried out at increasing pulsed laser energies from 0 to 5 mJ. LIBD data was taken three times in each condition for statistical purpose.

At first, the feasibility to perform acoustic LIBD on non-aqueous sample is to be confirmed. Methanol and ethanol solutions with added natural colloids were subjected to LIBD and the results were compared to those without colloids addition. It was then followed by observation on the breakdown occurrences in various non-aqueous solvents without any colloidal addition. The non-aqueous samples were methanol, ethanol, toluene, xylene, hexane, ethylene glycol, and oil. Each sample was filtered through a 0.02 µm syringe filter (Anotop, Whatman) to remove any particulate. In addition, methanol and ethanol samples were also prepared in various concentrations, which were 33% and 67% by dissolution in filtered water. The resulted breakdown probabilities were compared to those of pure alcohol.

![Figure 1. Experimental setup for acoustic LIBD.](image-url)
3. Results and Discussion
Figure 2 showed the S-curves resulted from the LIBD experiment on methanol (left) and ethanol (right). They complied with the characteristics of LIBD S-curve which consists of three regions, namely threshold, slope, and saturated region [1]. The figure also depicted the shifting of LIBD S-curves after colloids addition. As solids, the natural colloids have lower breakdown threshold energy than the solvent (methanol and ethanol). As a result, samples with colloids addition had S-curves that were positioned more to the left than those from samples without colloids addition. This was another indication that acoustic LIBD is able to perform colloid detection in methanol and ethanol.

After confirming the feasibility of LIBD study in methanol and ethanol, another question that arisen was that whether the change of solvent will affect the nanoparticle quantification procedure in acoustic LIBD or not. This is important since the determination of colloidal size and concentration using acoustic LIBD needs calibration by standard reference nanoparticles. The common standard is polystyrene (latex) in aqueous solution. Therefore the zero-concentration (background) sample is water which contains no colloids. However, when the solvent is changed, the background S-curve might also change.

Figure 3 showed the shifts of LIBD curves from various non-aqueous solvents. Aside from methanol and ethanol, toluene, hexane, xylene and ethylene glycol showed typical LIBD S-curves (had three regions). This result indicated the possibility of LIBD to detect nanoparticles in such solvents. Only oil showed different trend of LIBD data, having a flat rather than an S-curve. There are two possibilities that can be inferred, that oil has a very high breakdown probability or that oil behaved in such a way that LIBD cannot be performed on it. To gain more insight in this specific matter, more studies are needed.

As previously hypothesized, careful analysis should be taken when dealing with the quantification of nanoparticles suspended in those solvents. The breakdown threshold energy of non-aqueous samples in figure 3 differed slightly from that of water, as shown by the shifted S-curves. The non-aqueous samples used are all without colloids addition. Therefore should serve as background in the quantification analysis. Shifting in background S-curve may result in errors during the determination of size and concentration of nanoparticles in non-aqueous solvents, if the calibration is not corrected. An example is that when an unknown non-aqueous sample is justified to be having large nanoparticles based on the breakdown threshold energy calibration in aqueous solvent, while in fact it contains no colloid. Determination of concentration will also face difficulties as there is discrepancy in breakdown probabilities of zero concentration in the calibration. For this reason, quantification should be performed against the calibration using same solvent as the sample.

![Figure 2](image)  
*Figure 2. Acoustic LIBD is able to detect colloids in methanol (left) and in ethanol (right).*
4. Conclusions
Colloids presence in methanol and ethanol solutions has been successfully detected by means of acoustic LIBD. Alcohol solutions containing natural colloids had lower breakdown threshold energy compared to those without natural colloids, thus resulted in S-curve shifting. Solvent change from water to methanol, ethanol, toluene, hexane, xylene and ethylene glycol also resulted in S-curve shifting. However, different behavior was shown by oil, in which no breakdown was observed during LIBD experiment in the designated energy range. Furthermore, the concentration of solvents also affects the background S-curve. For these reasons, nanoparticle quantification in non-aqueous samples against standard calibration curves should be corrected with the corresponding solvent used.
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