Photo-acoustic emission measurements in liquid-based food and aqueous products

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Abstract

Pulsed laser light when of low to moderate intensity impinged into an aqueous media generates stress waves by thermoelastic mechanism. Referred to as photo-acoustic emission (PAE) these arise from sources during rapid laser liquid interaction that contains valuable information on the state of the composition and concentration of the liquid. Optical energy from a Q-switched Nd-YAG laser light source (wavelength of 1.064 µm, 50mJ maximum power) is lead into a Perspex cell (100 millilitres capacity) containing sample liquid-based food products and picked up using a piezoelectric (1MHz bandwidth) transducer 30mm distant from and in-line with the optical fibre. Spectral measurements of PAE generated in water, milk and other diverse liquid-based food and aqueous products provide distinguishable classes of power spectral density and frequency ranges. Grin rod lens fixed to the PAE cell improved the PAE signal-to-noise ratio by two orders of magnitude. Variation of milk concentration in water and influence of iron filings in oil are discussed.

1. Introduction

The present day food process industry is looking for new methods of monitoring the quality of food, chemical and pharmaceutical aqueous and liquid products. The photo-acoustic emission (PAE) method shows potential promise for their classification, characterisation and analysis. Photo-acoustics in liquids using pulsed laser light has been under investigation for biological and medical diagnostic applications in trace gas analysis, measurement of glucose in blood [1], measurement of tissue optical properties, tissue diagnostics and imaging [2], studying photosynthesis in plants [3]. Photo-acoustic spectroscopic measurements have been undertaken in the oil industry [4], and agricultural, food, nutrition and environmental applications because of demands for improved monitoring sensitivity, operation and alternate on-line use mechanically.

The process of conversion of optical energy, either from a chopped light source or a pulsed laser source, into acoustic energy has been named as opto-acoustic effect, the photo-acoustic effect or the pulsed photo-acoustic technique. The acoustic energy detectors are usually either in the form of an audio microphone or a high frequency piezoelectric transducer to provide signals whose amplitudes and frequencies characterise the liquids under examination. The process of conversion can be considered as an acoustic emission (AE) source mechanism occurring in the liquid. In conventional AE monitoring used in solids, stress or elastic waves are generated from damage sources such as cracks, defects, frictional rubbing, phase transformations and other dynamic processes occurring in materials components and structures. Similarly, pulsing laser light into liquid mixtures or aqueous fluids causes thermal effects leading to generation of localised elastic wave generation which manifest in the form of acoustic emission signals at the transducer output.

The PAE signal once obtained can be related to different conditions of the liquids to provide information, for example, for spoilage analysis of juices, for contamination monitoring of liquid-based foods, fuels and lubricating oils and quality analysis of dense liquids. This paper focuses on using photo-acoustic emission measurements to identify diverse but common food or pharmaceutical products.

2. Literature on Photo-acoustics

A broad survey of literature in the field of laser based sensing indicates that, interaction of pulsed laser light with small highly absorbing particles is common in wide variety of engineering process [4]. Beyond the thermo-elastic region, illumination of laser light in an aqueous medium results in ablation causing thermal stress confinement [5]. Further, it has been demonstrated that short-pulse ablation has a advantage of being reasonably efficient in terms of its detection sensitivities yet causing a minimum of thermal damage in the medium. There have been a number of experimental and theoretical attempts to understand and evaluate ablation mechanisms for water and water-containing media.

The increasing employment of pulsed laser sources for medical applications has fostered the study of photomechanical aspects of laser-tissue interaction [6]. In medical applications where laser pulses are delivered via optical fibres the fibre tip borders on an absorbing medium; the thermoelastic stress wave caused by absorption of laser energy is deposited over a volume that forms the acoustic source. In laser-tissue interaction studies it was found that the thermoelastic stress waves generated at fibre tip are subjected to diffraction effects that results in tensile stresses and causes cavitation near the rigid liquid glass interface both in the near and far fields of the acoustic source. The diffraction is found to influence the temporal profile of the acoustic stress wave and has important consequences when determining optical properties of the medium by opto-acoustic methods.

Fibre optic evanescent wave spectroscopy (FEWS) using an infrared light source using attenuated total internal reflection (ATR) is used for studying molecules in chemical and environmental related applications. In determining concentrations of carbon dioxide in soft drinks, glucose in food products and fat in milk sensitivities of the order of 1% has been achieved [7]. However, the main problem with this method is that there are overlapping spectral absorption peaks. Ultrasonic methods using piezo-electric transducers and pulse-echo methods have been used for characterising a variety of non-food and food emulsions which are concentrated, optically opaque, partially crystalline or compositionally complex [8]. The generation of acoustic waves by absorption of light in a liquid medium is known as the photo-acoustic effect. Near infrared-pulsed photo-acoustic spectral studies of crude oils and their detection in aqueous media show high levels of detection sensitivity [4]. However, applicability to in-situ measurement of concentration and composition in healthcare products and food industries appear to be limited or classified. Other methods include on-line ultrasonic density sensors for process control of liquids and slurries for monitoring the retrieval operations from radioactive waste storage tanks [9].

In PAE generation, it is assumed that the particles of the medium in the path of laser radiation are potential sites for absorption and later emitting stress waves to be picked up in the acoustical region. PAE technique can offer a simple indirect way (optical absorption) of measuring thermal properties (conductivity and/or diffusivity) in solid and liquid samples. A thermal property like conductivity and/or diffusivity unique for a liquid medium can be readily controlled in a pharmaceutical or food process plant that is in operation. PAE involves absorption of pulsed laser light by a liquid and non-radiative relaxation of the energy resulting in heating in the optical interaction region. Typically this is followed by a thermoelastic expansion of the material leading to the generation of a propagating acoustic pressure pulse. In the case where the thermal diffusion lengths during the period of the incident optical pulse are small in comparison to the geometry of the optical interaction region, then the resultant acoustic pressure pulse is independent of the sample boundary conditions, leading it to open cell applications [4].

3. Theoretical considerations

As an ultrasonic wave propagates through a medium its amplitude decreases or attenuates. There are several causes of this attenuation such as spreading of the wave front, change of acoustical energy to heat (absorption), and scattering from irregular surfaces [10]. One factor that affects attenuation is relaxation. This term describes the lag between an initiating disturbance and a readjustment of energy distribution induced by the disturbance- for example, heat flow from a region under compression to a lower pressure region. A finite time is involved and the exchange of energy approaches equilibrium value exponentially.

A study of relaxation phenomena yields considerable information regarding the nature of a solid or liquid. Relaxation absorption is most commonly observed at high ultrasonic frequencies (megahertz range). At low frequencies, absorption due to relaxation is negligible but as the frequency increases, the absorption also increases, rising to a peak at a relaxation frequency, and then decreases to zero at high frequencies where energy transfer has no time to occur. Relaxation type of absorption includes those due to conduction of heat, viscosity and rotation/vibration of atoms within a molecule. Therefore, it is possible to determine molecular structure if the correct excitation frequencies are chosen.

In spectroscopic methods of chemical analysis a series of peaks (or bands/lines) representing intense absorption or emission of light of solids in fact characterises the chemical structure and concentration of the sample under examination. This relates to the molecular activity that involves different types of energy that it possesses under a given state or condition [11]. These components include: a) translational energy arising from the movement of the centre of mass of the molecule; b) nuclear spin energy and electron spin energy associated with its spinning about the axes; c) rotational energy arising from the rotating molecules about its centre of mass; d) vibrational energy due to periodic contraction and expansion of the chemical bonds which involves potential and kinetic energy; e) electronic energy arising from the revolution of electrons to maintain its charge stability. Although the gross 'source energy' of a molecule can contain several components as listed above the energy changes that occur due to external perturbation can result in the three output energy states: light, heat and sound. It is a formidable task to theoretically define or quantify these individual partition functions for a given chemical compound, however these components contribute to physically measured data to provide substantial evidence characterising a molecular state or condition.

While chemical spectroscopic methods use absorption or emission of light in order to detect spectral peaks, pulsed laser light source energy can also activate liquid mixtures to produce acoustic emission outputs that can show characteristic bands in the frequency spectrum. For the liquids the laser pulsing gives raise to a method for chemical analysis and classification with the principal advantage being that it can be a non-invasive and in-situ technology for the food, chemical processing and pharmaceutical industries. Further it offers ample scope for traceable sensing and measurement of acoustic emission with reference to chemical standards and calibration methodologies that needs estimation of acoustic pulse pressure [12].

The theory of laser absorption by a liquid generating an acoustic pressure pulse is given by the equation [4].

$$P(r) = kE_0 \frac{\alpha\beta v^{\frac{1}{2}}}{c_p t_e^{\frac{3}{2}} r^{\frac{1}{2}}} \qquad (1)$$

Where E_0 is the incident optical energy, α is the optical absorption coefficient, β is the volumetric thermal expansion coefficient, v is the acoustic velocity, C_p is the specific heat at constant pressure, k is the system constant and t_e is the effective time parameter that relates the optical pulse width and the acoustic transit time across the optical beam, r is the distance from the optical axis.

The power spectrum is proportional to the square of the piezo-electric transducer voltage *V*, namely V^2. Power spectral density can be calculated from a power spectrum by dividing by the spectral bandwidth so the unit is V^2/Hz. The transducer output voltage is proportional to the impinging mechanical stress wave or acoustic pressure pulse. The signal power resulting in the work done by this pressure pulse acting over an area of the transducer base times the longitudinal wave velocity of sound is proportional to the sum of the various spectral density peaks in the frequency domain resulting in an equation that follows:

Power spectral density, $PSD \; \alpha \; P(r) \; AV_l \qquad (2)$

Where, *P(r)* is the acoustic pressure pulse at a distance r from the optical axis, 'A' area of the transducer facing liquid, 'V_l' is the longitudinal velocity of the sound in the medium. The estimated acoustic pressure in any given liquid media can be calculated using the equation (2) as follows:

$$P(r) = K\frac{PSD}{AV_l} \qquad (3)$$

Where K is the constant of proportionality and attributable to the impedance offered by the PAE measurement system. By experimentally obtaining the power spectral densities for a given transducer configuration, the acoustic pressure for different liquids can be easily estimated and can be compared with the theoretical acoustic pressure as obtained in equation (1). This verification forms part of another work and is not discussed here.

A multimode optical fibre was used to transmit laser light and four simple configurations were used for monitoring PAE generation and propagation in a liquid medium (Figure 1). (A) Unfocussed beam launched directly from the optical fibre in the liquid; (B) focussed beam with Grin rod lens embedded in the perspex cell wall. (C) focussed beam with Grin rod lens embedded and carrying a glass tube through which passes the liquid under examination. A 100 millilitres perspex test cell was used. A piezo-electric (0-1MHz flat frequency response) transducer was positioned in-line with the axis of the laser light source. (D) U-shaped aluminium rod, carrying pulsed laser light source on one end and AE transducer on the other to serve as a dipstick. This was used as a PAE wave-guide. In this paper results for configurations (A) and (B) are presented.

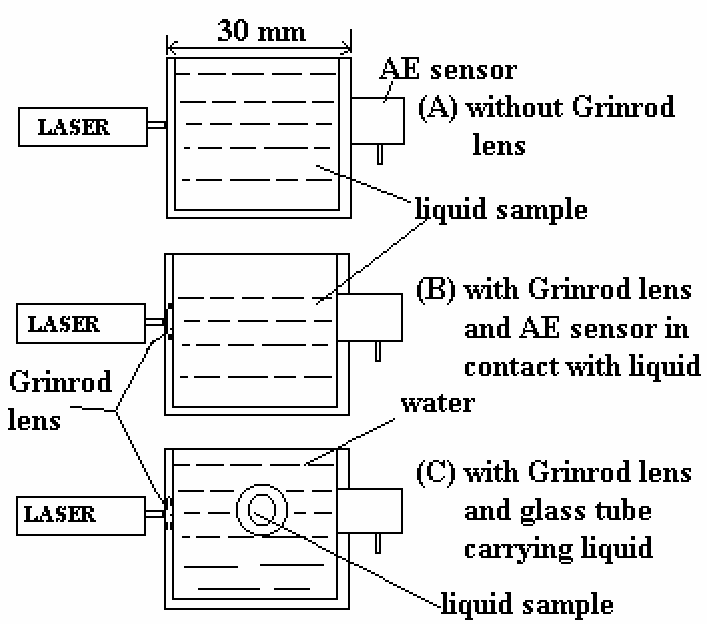


Figure 1. Three cell configurations

4. Experimental work

The experimental set-up used is shown in Figure 2. A Q-switched Nd-YAG laser (maximum energy of 50 mJ at a wavelength of 1.064 μm) has been utilised for the purpose of thermoelastic wave generation resulting in PAE. The laser light source is connected through a multimode silica glass optical fibre (core diameter 800 μm, a numerical aperture 0.25 and critical angle 5 degrees. The output light power used from the optical fibre was $2\mu w$. In the configuration (A), the broadband AE transducer is coupled to the outside surface of the perspex cell. The optical fibre is located in-line with the transducer axis with the perspex cell acting as a interface wall. The transducer was connected to a preamplifier and filter combination and the output was connected to an oscilloscope and a data-acquisition unit linked to a PC incorporating virtual instrumentation software (Labview). The amplitude data points chosen for data acquisition were 30,000 in number and the sampling rate maintained at 5MHz. Power spectral density estimate of the PAE was made using MATLAB software. The FFT length was specified as 2048 points and the signal vector used Welch's averaged periodogram method.

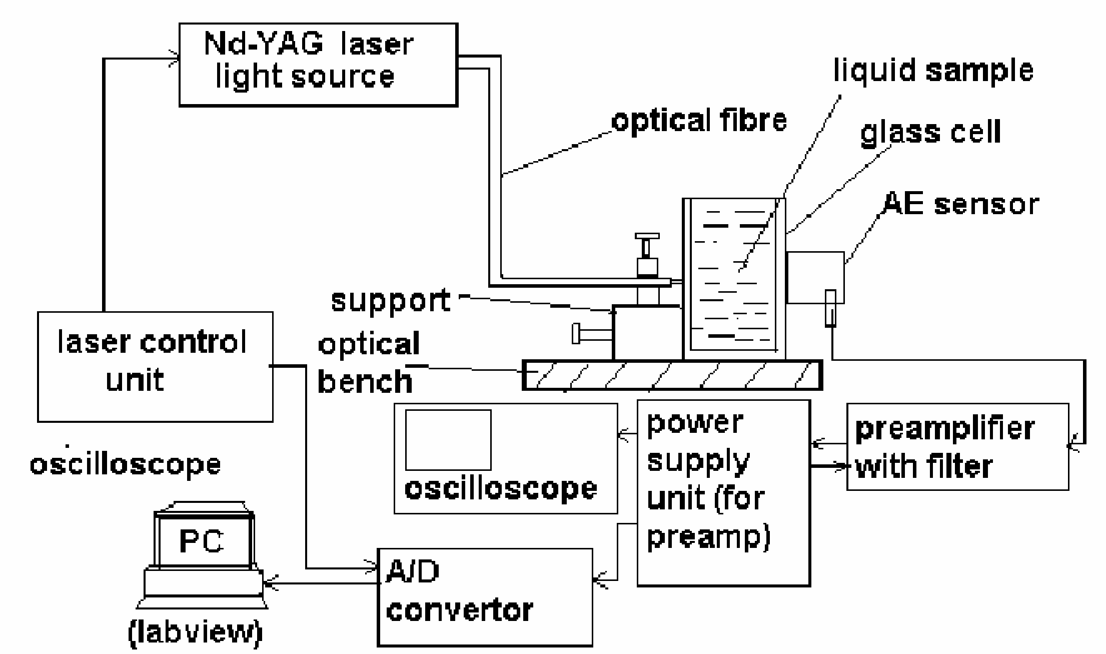


Figure 2. Schematic of experimental set-up

In the first experiment namely configuration (A), different dilution ratios of water and skimmed milk was added to the perspex cell, starting from 0 ml of milk (i.e. all water) to 100 ml of milk (all milk) in steps of 10 ml (Figure 1). In all experiments six repeat measurements were taken to establish variability. For Configuration (B), the optical fibre was kept in close contact with the grin rod lens and with the transducer directly in contact with the liquid. Diverse liquid samples chosen were water, milk, tea-in-water, apple orange juice, Pepsi, Cola, shower gel, sunflower oil, paint and follow-on-milk, apple-banana puree, creamy-pasta-brocolli, coffee, calcium-carbonate in water. Sunflower oil was doped with iron filing to get an understanding for impurity monitoring from the PAE signal. Configuration (C) was investigated to provide for in-situ monitoring.

5. Discussion of results

Most of the studies on photo-acoustics involve analysis of the frequency spectrum. The method adopted here involves the calculation of power spectral density that gives the fractional energy of emission due to thermal absorption in the liquid medium that would provide the much-desired information on the type and nature of the liquid under observation. Results of the experiment show that, the diverse liquids can be categorised based on the power spectral density as well as the frequency ranges (Figure 3 and Figure 4).

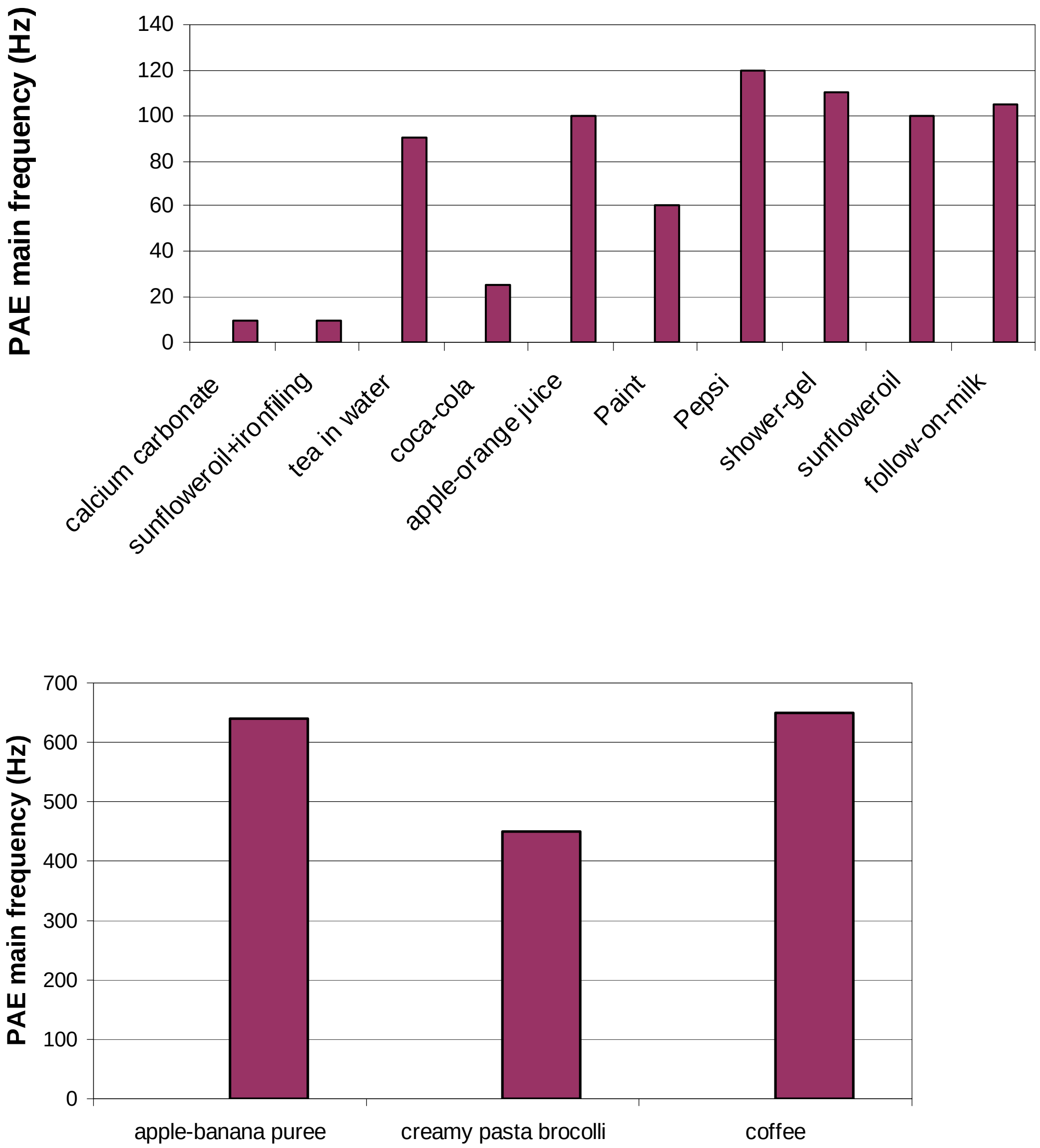
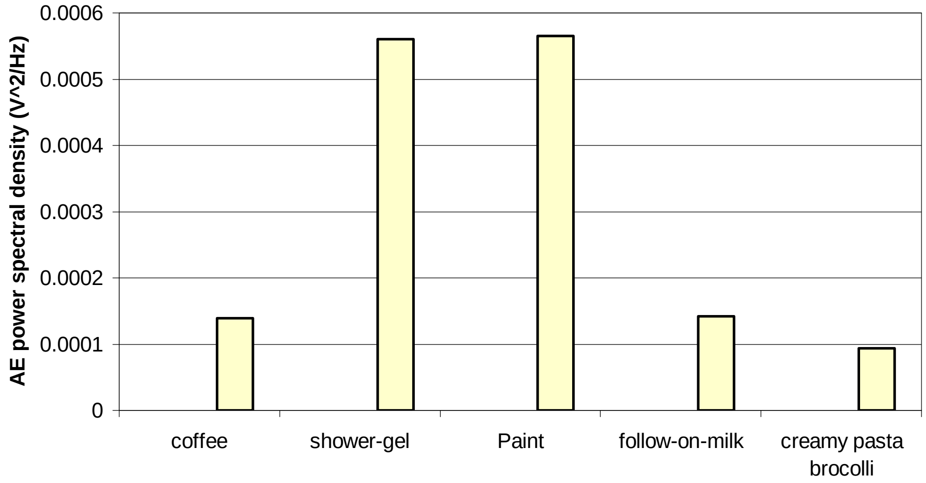
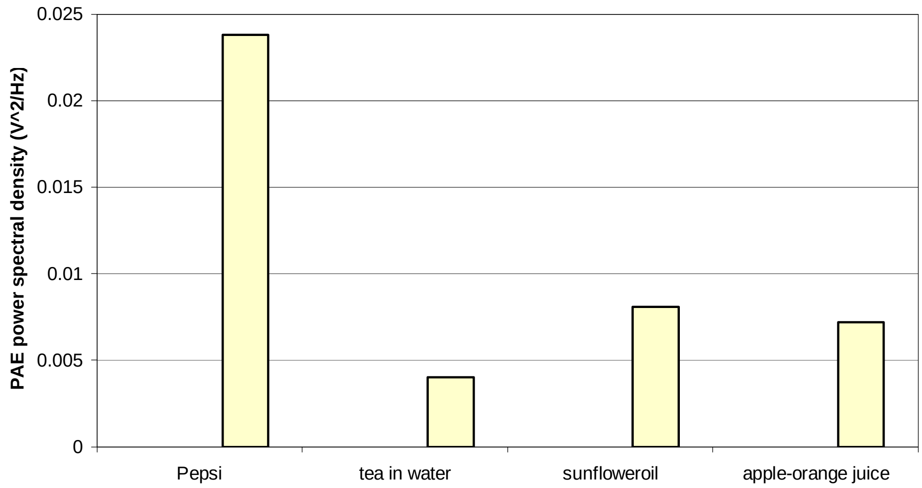
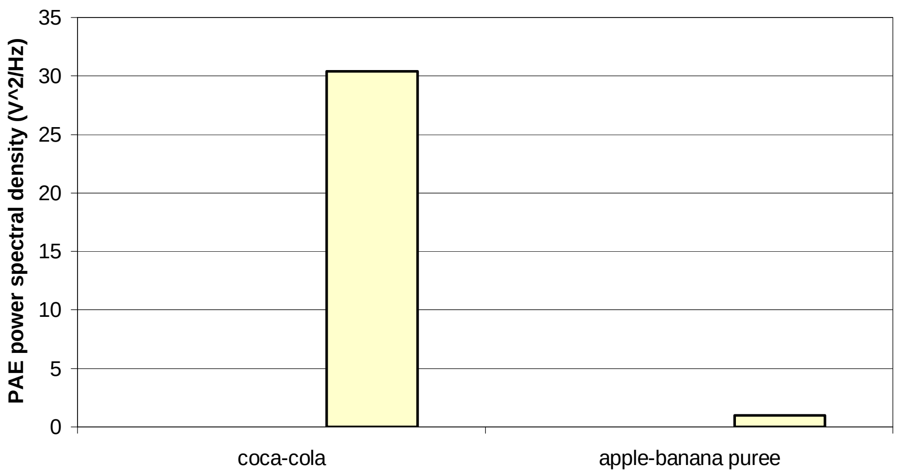


Figure 3. PAE main frequency (Hz)


AE power spectral density (V^2/Hz)
0.0006
0.0005
0.0004
0.0003
0.0002
0.0001
0
coffee
shower-gel
Paint
follow-on-milk
creamy pasta brocolli


PAE power spectral density (V^2/Hz)
0.025
0.02
0.015
0.01
0.005
0
Pepsi
tea in water
sunfloweroil
apple-orange juice


PAE power spectral density (V^2/Hz)
35
30
25
20
15
10
5
0
coca-cola
apple-banana puree

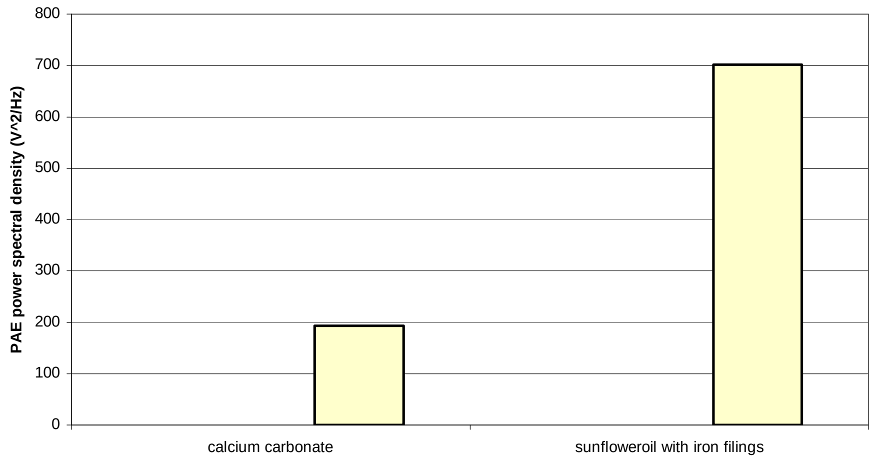


Figure 4. PAE power spectral densities for diverse liquids for configuration B

Lower frequency ranges are seen in samples of coca-cola, calcium carbonate in water and sunflower oil doped with iron filing impurities. Non-homogeneous mixtures like apple-banana puree, creamy-pasta-broccoli and coffee fall under a band of higher frequency in the ultrasonic range.

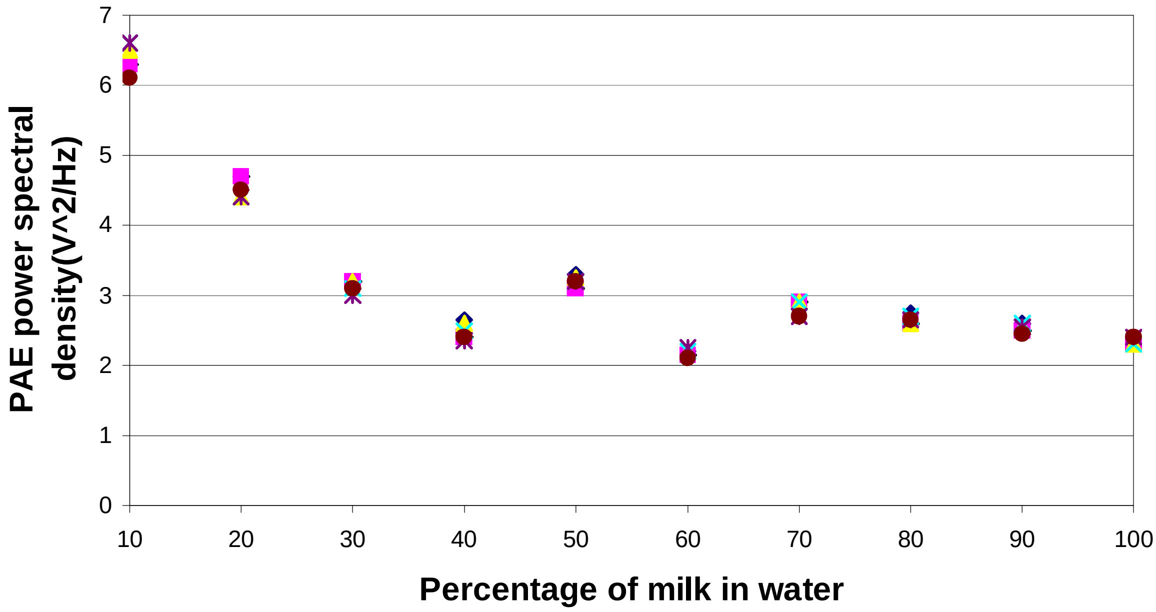


Figure 5. PAE spectral density variation in milk for 100ml cell for configuration C

Figure 5 shows the variation of power spectral density with percentage of milk in water. As readily seen the detection ability is up to 40% of milk in water after which power spectral density is probably not a best measure for such type of colloidal mixture. Literature indicates that the ultrasonic wave generated changes according to the laser pulsing energy. In the case of low energy pulses, the major mechanism of ultrasonic generation is due to the thermal stresses induced by the absorption of laser light. With an increase in this pulse energy, the mechanism changes to become dependent on the vaporisation pressure of the irradiated material. The two modes have different names the first one being thermal stress mode and the second one the ablative mode and have different directions of the force vector. In a thermal stress mode, ultrasonic waves originate at the edge of the laser-irradiated area where the thermal gradient is most significant. In the ablative mode the plane waves that are longitudinal in nature are generated from the irradiated area. In our case since the laser light intensity was low to medium the thermal stress mode was predominantly noticed. Over a much broader perspective the understanding of generation of acoustic wave by illuminating laser light in a medium occurs in four possible ways [13]. 1) If the light energy absorbed in the medium during illumination is greater than the boiling threshold (for water this is 537 cal/cc) the material will evaporate, and an explosion will be ignited in the medium. 2) If the total absorbed energy during illumination is small such that no evaporation may take place, there may still be a large acoustic wave generated in the medium by the thermal-elastic or thermal-expansion effect. 3) For some transparent material illuminated by Q-switched laser, the total absorbed energy in the material is too small to generate any appreciable wave, but the electric field in the laser may be as high as 10^7 V/cm, and this high electric field may generate a significant stress wave in the medium by means of electrostriction coupling of the electrostriction coefficients in the medium are high. Ex. Brillouin scattering of light in a medium.4) A large amplitude acoustic wave may be generated by di-electric breakdown of the medium owing to high intensity light (Ex. 500-atm peak). In fact, this type of wave generation involves a series of flashing spots along the light beam during illumination. Further, pulsed laser heating of highly absorbing particles results in the radiant energy absorption resulting in heat generation and transfer in the particulate medium system. This radiation heating can be highly non-uniform, and so cannot in general be treated as constant [14]. The significance of thermo elastic stress generation stems from the fact that low hydrodynamic pressure below the equilibrium vapour pressure can create cavities filled with either vapour or non-condensable gases from pre-existing gas pockets. The dynamics of the cavity growth and collapse can play a major role in the ablation process and the acoustic-pulse generation [15]. Attempts are on towards traces of hydrocarbon in water and non-invasive monitoring of glucose in blood [2]. An opto-acoustic source constituted by an optical fibre on whose tip a thin metallic layer is evaporated and is found successfully used as a ultrasonic source [16]. However fabrication and evaporation of the film at the tip is difficult and needs precision and might cause harmful back reflection of the laser radiation to damage the laser equipment if not fabricated properly. Photo acoustic spectroscopy has been used for measuring thermal properties (conductivity and diffusivity) in solid and liquid samples using 1000 W tungsten lamp, mechanical chopper and grating monochromator. Modelling non-linear absorption of photo-acoustic spectrometry of homogeneous fluids has been investigated which essentially occur due to effects like bleaching when the analyte has long-lived excited metastable states i.e., a triplet state [17]. Depending upon the wavelength of the impinging optical radiation, the particles in the liquid tend to absorb and emit stress waves at acoustical wavelengths resulting in either a point or line source. If the absorption of radiation by the liquid under investigation is high the path length of the optical radiation is small and the photo-acoustic emission source has can be treated as a point source from which spherical wave- fronts emanate. On the other hand, if a given liquid is transparent to the optical radiation the beam of radiation has a larger path length resulting in a line type of source. Generally liquids fall within the two extremes of line or point sources depending upon their optical absorption characteristics. Water shows a typical peak at about 250 kHz. The magnitude of this frequency peak decreases with increase in the stand off distance. Further this peak frequency at 250 kHz (called water frequency) appeared to be a reliable baseline and hence was used for analysing behaviour of other sample liquids mixtures.

6. Conclusions

The results of the experiments show that it is possible to characterise aqueous mixtures and measure their concentration in terms of photo-acoustic emission technique. However, a study of relaxation phenomena should yield considerable information regarding the nature of diverse liquids. Relaxation absorption tends to increase predominantly at higher ultrasonic frequencies in the megahertz range and is negligible at low frequencies. Relaxation type of absorption includes those due to conduction of heat, viscosity and rotation/vibration of atoms within a molecule. Therefore, it is possible to determine molecular structure if the correct excitation frequencies are chosen. Also, if the observation cell is designed appropriately and calibrated an instrument for liquid concentration measurement is feasible. In our experiments, photo-acoustic emission shows good promise to monitor common diverse liquids. Introduction of Grin rod lens in the cell improves the signal to noise ratio by two orders of magnitude for monitoring milk-water mixtures. Photo acoustic emission is sensitive to different types of liquids. Once developed it can prove to be a generic methodology for estimation of fruit juice spoilage over time, contamination of liquids based foodstuffs, degradation of fuel and machine oils.

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8. References

1. Mills TN, Biological and medical application of photo-acoustic and Photo Thermal Phenomenon, Photoacoustic and Phothermal Phenomenon, 10th International Conference, edited by Scudieri F, Bertolotti M, AIP Conference 463, 563, 1999.
2. Ashton HS, Mackenzie HA, Rae P, Shen YC, Spiers S, Lindberg J, Blood glucose measurements by photoacoustics. Photoacoustic and Phothermal Phenomenon, 10th International conference, edited by Scudieri F, Bertolotti M, AIP Conference 463, 570,1999.
3. Frandas A, Jalink H, van der Schoor R, Monitoring the photobaric component of green leaves by low frequency Photoacoustics, 10th International Conference, edited by Scudieri F, Bertolotti M, AIP Conference 463, 594,1999.
4. Hannigan J, Freeborn S S, Wilkinson A, Greig F, Suttie R A and Mackenzie H A, Pulsed Photoacoustic spectroscopic studies of crude oils and their detection in aqueous media for application in offshore instrumentation, Photoacoustic and

Photothermal Phenomenon, 10th International conference, edited by Scudieri F, Bertolotti M, AIP Conference 463, 365,1999.
5. Alexander A, Oraevsky, Steven, Jacques L, Mechanism of laser ablation for aqueous media irradiated under confined-stress conditions, Journal of Applied Physics, 78, 2, 1995.
6. Paltauf G, Schmidt-kloiber H, Frenz M, Photoacoustic waves excited in liquids by fiber-transmitted laser pulses, Journal of Acoustical Society of America, 104, 2, 1998.
7. Bormashenko E, Citron S, Eytan O, Kravcik S, Pogreb R, Reichlin Y, Sela B, Schulzinger E, Spector O, Vasserman I, Katzir A, Fiberoptic evanescent wave spectroscopy and its chemical environmental and medical applications, 14th International Conference on Optical Fiber Sensors, 11-13, SPIE vol. 4185, 2000.
8. Mc Clements DJ, Povey MJW, Jury M, Betsanis E, Ultrasonic characterization of a food emulsion, Ultrasonics, 28, 1990.
9. Greenwood M.S, Skorpik JR, Bamberger JA, Harris RV, On-line ultrasonic density sensor for process control of liquids and slurries, Ultrasonics 37, 159-171, 1999.
10. Asher R.C, Ultrasonic Sensors for Chemical and Process Plant, Institute of Physics Publishing, Bristol, 1997.
11. Jones B.E, Ravishankar SR, Photo-acoustic emission, Patent Application No.0100894.5, January 2001.
12. Ravishankar SR and Jones BE, Laser generated acoustic emission in water, NDT & E International (to be published).
13. Chia. Lau. Hu, Spherical model of an acoustical wave generated by rapid laser heating in a liquid, Journal of Acoustical Society of America, 46,3,1969.
14. Longtin JP, Qiu TQ, Tien CL, Pulsed laser heating of highly absorbing particles, Journal of heat transfer, 117, 785-788, 117,1995.
15. Kim M, Ye CP Grigoropolous, Pulsed laser-induced ablation of absorbing liquids and acoustic-transient generation, Applied Physics. A 67. 169-181, 1998.
16. Elena Baigi, Leonarado Masotti, Massimiliano Piercaccini, Fiber optic optoacoustic source, Proceedings of the 4th Italian Conference, Sensors and Microsystems, Roma, Italy, 3-5 February 1999.
17. Stephen E. Bialkowski, Photothermal Spectroscopy Methods for Chemical Analysis, Volume 134, Chemical Analysis: a Series of Monographs on Analytical Chemistry and its Application.