A Photoacoustic Study on Trichloroethylene in Water

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Abstract

Photoacoustic study carried out here on (trichloroethylene mixed) water reveals that this method can be efficiently used as a tool to estimate the presence of this hazardous chemical in drinking water to a level of 0.005mg/L.

Key words: Photoacoustics, trichloroethylene, ultrasonics, thermal diffusivity.

1. Introduction

Contamination of hazardous waste into ground and surface water would lead to lot of problems demanding great attention. Trichloroethylene (TCE) is one of the most frequently reported organic contaminant in water which is probably widely distributed in the environment due to industrial discharges of waste water streams. TCE is a volatile organic compound which has been extensively used as a metal degreaser, a solvent in adhesives, textile manufacturing, paint stripping, and dry cleaning etc. On the contrary TCE is toxic and carcinogenic for the human body. Intake of water having large amounts of TCE may cause nausea, liver damage, unconsciousness, impaired heart function or death. Because of these potential health hazards the United States Environment Protection Agency (U.S.E.P.A) has set a drinking water limit for TCE in drinking water as 0.005mg/L [1]. Hence the determination of TCE in water is of great interest because of the environmental impact and toxicity. There are a number of techniques available for the quantitative measurement of TCE in water including colorimetry, infra-red spectroscopy, gas-liquid chromatography (GLC), and gas chromatography/mass spectrometry. These analytical methods are often cumbersome, being both time consuming to set up and run, and often requiring bulky, expensive equipment. In order to overcome the above stated problems and limitations, alternative techniques are being attempted to exactly find the concentration of TCE in water in a simple way. Photothermal (PT) methods have recently been identified for the above mentioned requirements. Among the various types of PT techniques the photoacoustic (PA) method is widely used for measurement of thermal and optical properties of liquids [2,3]. Recently Lima et al [4] have carried out PA measurements by open photoacoustic cell for the determination of Chromium (VI) in water. They have drawn a calibration graph connecting Cr (VI) concentration and normalized photothermal amplitude by which they could estimate the molar extinction coefficient comparable to optical spectrometry. Similarly we have also carried out PA measurements for the determination of chromium (VI) in water using photoacoustic technique [5]. In the present work an attempt is made to measure the thermal diffusivity of TCE in water for various lower concentrations using the same technique with the aim of finding the minimum concentration for which the PA measurements are effective.

2. Sample Preparation

De-ionized water (DW) and TCE are taken to prepare water samples with various concentration of TCE. A stock standard solution of (0.2 -1 mg/L) TCE contaminated water (TCEW) was prepared and the experiments were carried out with this solution.

3. Ultrasonic measurements

Ultrasonic methods are being extensively used to study molecular interaction in pure liquids and liquid mixtures [6], as the ultrasonic measurements are non-invasive and proven techniques for such measurements. The ultrasonic velocities were measured using an ultrasonic interferometer of fixed frequency 2 MHz (accuracy2%) for the above TCE contaminated water samples and are given in Table.1. The results indicate that such a low concentration of TCE cannot be determined efficiently by ultrasonic technique, as there is no change at all in the speed of sound in these water samples.

Table.1.
Variation of ultrasonic velocity with concentration of TCE in DW water

Concentration of TCE in DW water (mgl/L)	Ultrasonic velocity (m/s)
0.2	1491
0.3	1491
0.4	1500
0.5	1500
0.8	1505
1	1505

(Error ~2%)

4. Photoacoustics (PA)

The present photoacoustic spectrometer consisted of a 400W Xe- lamp, an electro - mechanical chopper, a monochromator ,a digital storage oscilloscope and a PA cell. The principle of this technique is that when a modulated light is absorbed by the sample located in a sealed PA cell, the non-radiative decay of the absorbed light produces a modulated transfer of heat to the surface of the sample which produces pressure waves in the gas inside the cell that can be detected by the microphone attached to the cell [7]. A digital storage oscilloscope (DSO) was used to monitor the signal from the microphone.

5. Photoacoustic (PA) Cell

The PA cell here is unconventional in the sense that it is made up of glass funnel of length 10 cm, diameter 5 cm and it is completely blackened inside by carbon black and the wider end is sealed with a concave watch glass. Along the surface of the funnel on the top conical side a small hole of diameter of 1.5 mm is drilled. Let it be the position (2B). The liquid is taken into a needle shaped cell (cuvette) of diameter 1mm and length of about 5cm as given in the Fig: 1a. The designed cuvette (2A) is now inserted into this hole (2B) and sealed with paste, as in the complete set up , Fig:1b. At the end of the stem of the funnel a condenser microphone is inserted and closed airtight and kept very close to the cuvette and the complete set up is shown in Fig:1b.The whole compartment, the PA cell, should be airtight and soundproof. As a result of the periodic heating of the sample, some or all of it is converted into heat. If this heat warms up a gas (often air) in contact with the sample, the gas will expand, and a sound wave will be generated. The strength of the sound, detected with a microphone, is a measure of the amount of heat produced in the sample. The resulting PA signal depends not only on the amount of heat generated in the sample, but also on how this heat diffuses through the sample. Therefore, by analyzing the magnitude of the acoustic wave, thermal diffusivity of the sample (TCEW) is obtained.

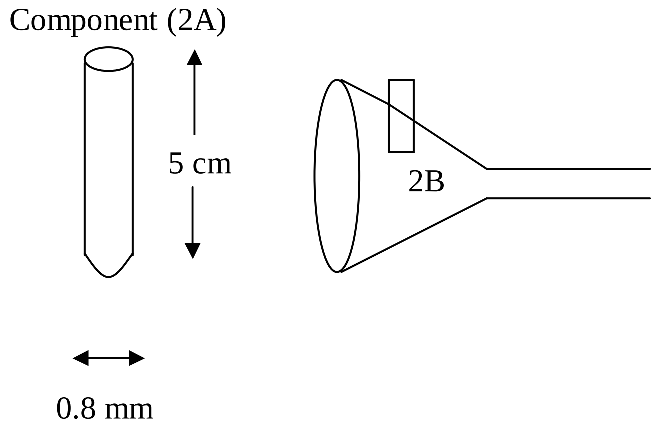
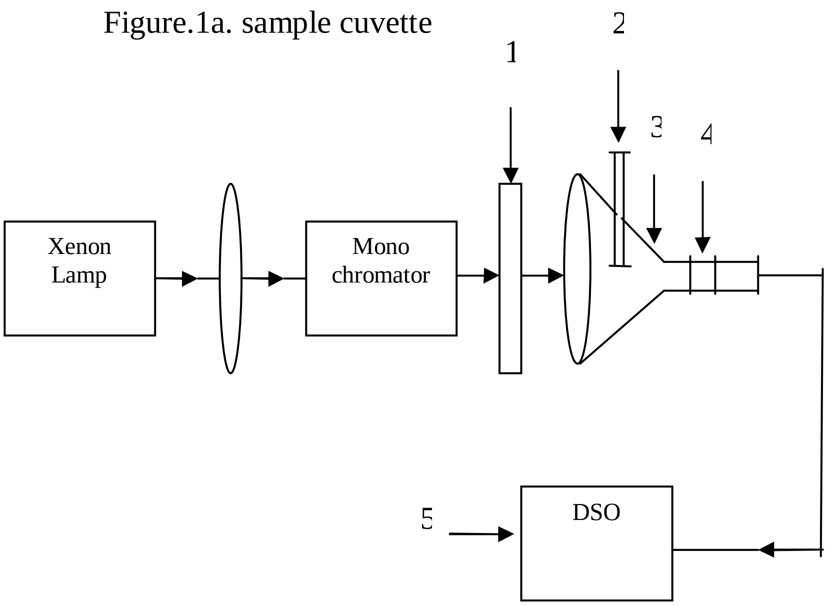


Figure.1a. sample cuvette



1.Mechanical chopper 2.Glass cuvette in the form of needle 3. Glass funnel
4.Microphone 5. Digital storage oscilloscope (DSO)

Figure. 1b.Experimental setup

6. Photoacoustic measurements

Thermal diffusivity is measured by studying the variation in the amplitude of the PA signal for various chopping frequencies for a fixed wavelength of the incident light. Even though the PA signal was traced for different chopping frequencies, this is shown here for a particular chopping frequency in Figure 2.Following Rosencwaig’s theory of photoacoustics [8], the intensity at the centre of the beam that is coming out of the PA cell can be expressed as

$$= \frac{- \quad \infty}{} = \quad = \frac{}{\left(\quad + \quad \frac{}{} \right)} \qquad (1)$$

$$= \quad = \frac{\infty \quad -}{}$$

where I_{∞}, I_0, I_t are the steady state PA signal, signal at time t = 0 and signal at time t respectively.

The PA signal produced by the sample, (TCEW) was measured for different chopping frequencies. The variation of reduced PA signal $\sqrt{\frac{S_0}{S}}$ (where S_0 - signal at time t = 0 and S - signal at time t) as a function of time is shown in Fig.2 for a particular concentration and chopping frequency. From the slope (of $\sqrt{\frac{S_0}{S}}$, as a function of time), of this graph, the characteristic time constant (t_c) corresponding to the liquid sample is found out.

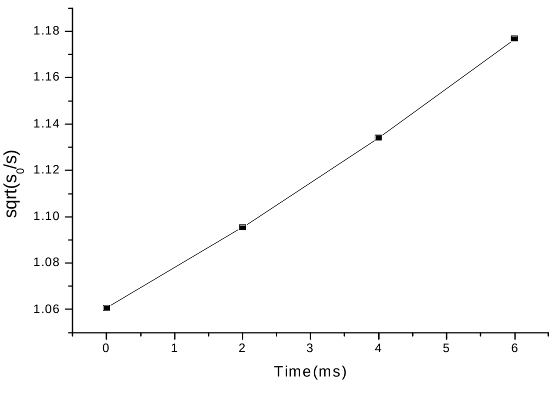


Figure.2. Reduced photoacoustic signal amplitude as a function of time for a particular concentration of TCE in water(0.8mg/L)

The characteristic time constant t_c is related to the thermal diffusivity (D) and beam radius (ω) through the relation [8]

$$t_c = \omega^2/4D \tag{2}$$

To eliminate the uncertainty in the determination of beam radius, a reference sample (water) with known thermal diffusivity is used to determine the thermal diffusivity of the unknown sample. Thus,

$$= \overline{\qquad\qquad} \tag{3}$$

where D and t_c correspond to thermal diffusivity and characteristic time constant of TCEW.

The present experimental set up was first calibrated by measuring the thermal diffusivity of acetone, water and toluene. The measured values of t_c and thermal diffusivity for water, acetone, and toluene were in good agreement with those reported in literature [8,9]. Then such measurements for the various contaminated water samples for the time constants and hence thermal diffusivities were carried out. The observed values of time constant (t_c) and thermal diffusivity (D) of TCEW for various concentrations are presented in Table.2. When a graph is drawn for concentration of TCEW and thermal diffusivity as in Figure.3, it is found that as the concentration of TCE in water increases, thermal diffusivity decreases. This can be understood from the fact that more and more impurity ions will scatter the incident energy in all directions of the liquid and so there is a possibility in the reduction of thermal diffusion. This graph clearly shows that, very small concentration of TCEW to the level of 0.005mg/L can be easily found out using the present technique by extrapolating the graph.

Table.2.
Variation of thermal diffusivity with concentration of TCE in DW water

Concentration of TCE in DW water(mg/L)	Thermal diffusivity (x10^{-7} m^2s^{-1})
0.2	0.73
0.3	0.68
0.4	0.61
0.5	0.49
0.8	0.37
1	0.28

Error ~3%

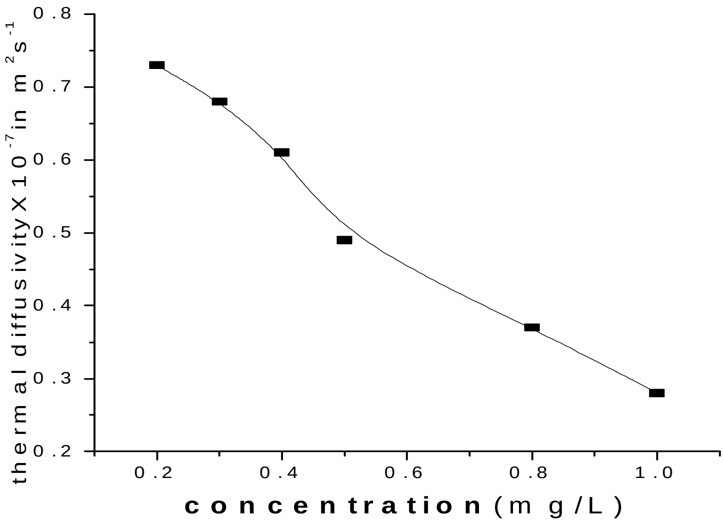


Figure.3. Variation of thermal diffusivity with concentration of TCE in DW water

7. Results and discussion

TCE is a hazardous waste, particularly for populations living near industrial areas and hazardous waste sites. There are many sophisticated analytical techniques (like atomic absorption spectroscopic activation analysis, chromatography, mass spectroscopy, emission spectroscopy etc) are mostly used for the detection of impurities that are present at very low concentration in water. But these techniques are usually expensive and require sophisticated laboratory equipments. Here a simple photoacoustic technique is used to find the TCE concentration in water which can be made portable. The present measurements on thermal diffusivity with TCE concentration are very useful to find (Figure.3) any lower concentration of TCE in water down to a level of 5μg/L. Since the thermal properties of TCE in water for the concentration (0.2-1mg/L) have not been reported in literature, a direct comparison of the present results could not be made. The results from the Table.2 suggest that if a graph connecting the thermal diffusivity and concentration is arrived, then the presence of TCE in any water sample can be immediately found out down to the threshold value of TCE in water. To the best of our knowledge this is the first report on thermal diffusivity for the mixtures of TCE and water for the concentration 0.2-1mg/L using the present setup.

8. Conclusion

A simple photoacoustic technique is proved to be very successful to find out the TCE concentration in water as other methods are not only complex in measurements but also the amount of sample needed would be much more compared to the present PA technique. This method is characterized by high sensitivity, good accuracy and can be successfully applied in routine analysis of TCE in water samples. This technique appears as a promising tool for environmental studies to trace contaminants in liquid samples.

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