Sonochemiluminescence as a novel analytical method for the determination of some pesticides in water samples

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Abstract

We found that sonochemiluminescence (SCL) can be used as an analytical tool to determine some pesticides. At a given ultrasonic frequency (1.7 MHz) and under suitable conditions, the collapse of the bubbles can result in light emission (sonoluminescence, SL). Hydroxyl (OH) radicals generated during bubble collapse can react with luminol to produce sonochemiluminescence (SCL). SCL intensities were recorded for several pesticides solutions and compared with their blank SCL signal. Based on the results of the comparison of the SCL intensity of luminol methanolic solution (blank signal) with the SCL intensity of methanolic solutions of pesticides (sample signal) it was established that some pesticides play an antioxidant role and can react with OH radicals and inhibit the SCL of luminol. This strategy has potential to be used for the determination of some pesticides in environmental waters.

Keywords: Sonochemiluminescence, Ultrasonic waves, Luminol, pesticides

Introduction

Due to lack of state of the art instruments and lack of regular monitoring (Otieno, Owuor et al. 2013), it is not possible to completely treat wastewater and prevent the endocrine disruptive compounds (EDCs) passage through wastewater treatment plants into the environment. These flaws allow the harmful compounds to re-circulate in clean water sources, thus, they can reach living organisms (Fent, Weston et al. 2006). Each of these EDCs have different and harmful effects on living organisms. Triazole fungicide is one of the most important and widely used fungicide, acting by inhibiting fungal ergosterol biosynthesis (Pederson 2007). Penconazole(Fig.1) is a typical triazole fungicide, and it is commonly used in agricultural, horticultural, and forestry industries (Kenyon, Dixon et al. 1997). In agriculture, it is widely used on grape, apple, vegetables and tea plants to control powdery mildew (Pose-Juan, Rial-Otero et al. 2010). The maximum residue limits (MRLs)(European Food Safety Authority, 2018; Institute for the Control of Agrochemicals, Ministry of Agriculture, 2018; Chinese Ministry of Agriculture, 2018) for penconazole in agricultural products in China range from 0.01 mg kg^{-1} to 0.5 mg kg^{-1}. It is a highly toxic compound and especially harmful for unborn children according to some studies presented in literature (Polledri, Mercadante et al. 2018). Thus, residue of penconazole in agricultural products and environment should be monitored strictly.
Ultrasonic irradiation of liquids provides a unique chemical environment originating from acoustic cavitation bubbles (McMurray and Wilson 1999, Hatanaka, Mitome et al. 2002). The extreme conditions in the bubbles can give rise to the phenomenon called sonoluminecence (SL), i.e., the light emission of acoustically driven bubbles, and can lead to the formation of reactive species such as •OH, H•, and H_2O_2 in aqueous liquids. These species are
capable of inducing secondary oxidation or reduction reactions (Jin, Kumeta et al. 2009). It has been known that an alkaline luminol solution emits light when irradiated with ultrasound of sufficient intensity. The phenomenon is called sonochemiluminescence (SCL), which is believed to occur through an oxidative chemiluminescence (CL) process induced by sonochemically generated •OH. The SCL of luminol has been used to investigate the mechanisms of acoustic cavitation under different sonication
conditions (Tuziuti, Yasui et al. 2008, Rivas, Ashokkumar et al. 2012) .
Only a limited number of researches have been reported for analytical application of SCL. For example, determination of antioxidant capacity of tea extract and some vegetables has been reported using SCL (ZHANG, HU et al. 2009, Nie, Chen et al. 2010). Therefore, SCL methods have great potential to be used in analytical chemistry.
The aim of this work is evaluating SCL methods from luminol solutions to determine the amount of pesticides in environmental waters.

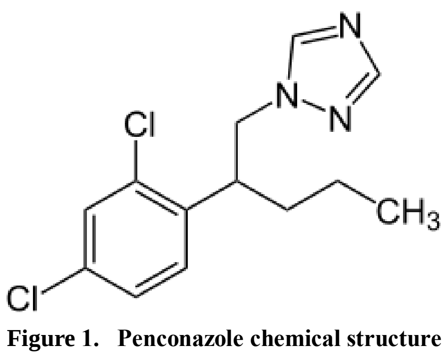

Figure 1. Penconazole chemical structure

Experimental

Material and solutions

All solutions were prepared using deionized water. Luminol and pecticides were purchased from Sigma-Adrich Co. The main solution of Luminol (10^{-3} mol L^{-1}) was prepared by transfering 0.0170 g luminol and 0.106 g of sodium carbonate into a 100.0 mL volumetric flask and diluting with deionized water. pesticide solutions (10^{-3} mol L^{-1}) were prepared with water or methanol in a 25.0 mL volumetric flask.

SCL Instrument

We used a lab-made SCL analyzer. The ultrasonic waves were produced by a piezoelectric device (1.7 MHz) submerged in a 250 mL water bath and the reaction cell was mounted on it. The light emitted by the SCL reaction was detected with no wavelength discrimination with a head on photomultiplier tube (PMT) located inside a darkroom. Reaction cell was a test tube. The block diagram of the instrument is shown in figure 2.

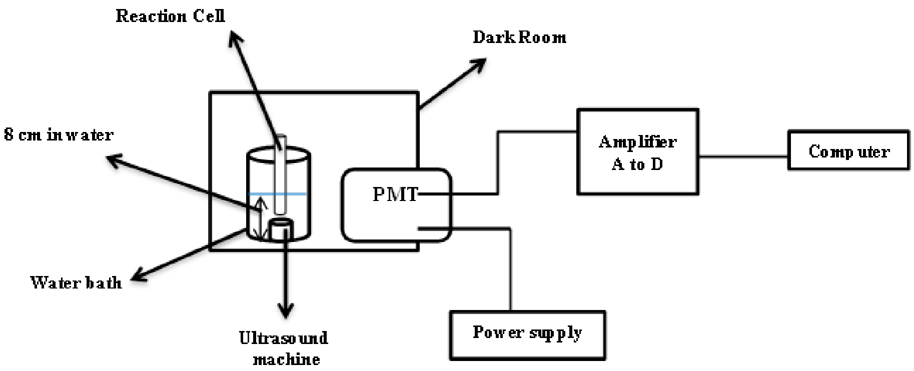

Figure 2. Block diagram of Sonochemiluminescence instrument

2.4 Analytical Procedure

First, 3 mL of Luminol solution was transferred into the reaction cell using a calibrated micropipett. Then, the cell was placed at its location in the darkroom in front of photomultiplier tube (PMT). Analytical signal obtaind by appling pulsed voltages on piezoelectric device and injecting four 250 µL aliquots of solvent (blank signal) or pesicide solution with 1 min intervals using a micropipett. The time profile of SCL emission was recorded by a computer. The data information was collected automatically into an Excel file.

Result and Discussion

Effect of different pesticedes on SCL signal of luminol

SCL originates from reaction between OH radicals and luminol molecules. Radical scavengers can react with OH radical and SCL emission will be inhibited in presense of antioxidand chemicals. Some pesticides can react with OH radicals like an antioxidat reagent and inhibit SCL of luminol. In table 1, effect of ome pesticides is shown on the SCL of luminol.

Table1. Impact of pesticides 10^{-3} concentration

Pesticides	S_{Blank}	S_{Sample}	S_{Blank} - S_{Sample}	$\frac{S_{Blank} - S_{Sample}}{S_{Blank}}$
penconazole	25552	16796	8783	0.344
Malathion	46557	42068	4489	0.096
Imidaclopride	53799	52707	1092	0.020
Bentazon	55054	53984	1070	0.019
Cyperconazole	9767	11289	-1522	0.156-
Diazinon	37801	42248	-4447	-0.118

Effect of ultrasonic time on the alalytical signal of penconazole

In this study, the effect of ultrasonic appling time on the SCL signal of penconazole was studied. Various ultrasonic appling times between 500 and 2000 ms was investigated on the SCL signal. As can be seen in figure 3, the greatest difference between SCL of blank and sample solutions was obtained on 1500 ms.

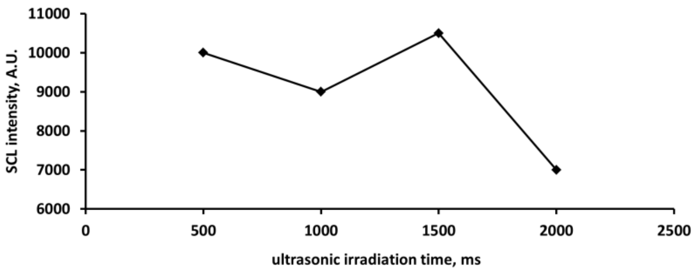

Figure 3. effect of ultrasonic irradiation time on the SCL response of penconazole

Figure 4 shows the effect of penconazole pesticide on the SCL of luminol at optimum conditions.

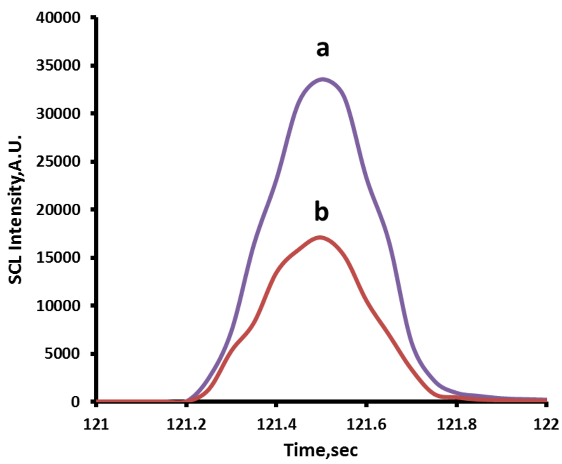

Figure 4. Effect of penconazole on SCL of luminol. a: Blank. b: Penconazole 1.0×10^{-3}

Conclusions

SCL is a new and very attractive analytical technique, mostly due to instrument simplicity and wide detection ability. Nowadays, only a few number of researches based on SCL technique have been reported for analysis purposes. Therefore it is interesting to develop new SCL strategies for analytical chemistry applications. Pasticids like penconazole can be determined using this method in enviromental waters.

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