DETERMINATION OF PESTICIDE RESIDUES OF NATURAL WATERS IN SAKON NAKHON PROVINCE BY USING PIEZOELECTRIC SENSORS

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ABSTRACT

A piezoelectric sensor has been used for the detection of small mass changed which caused by the selective absorption of pesticide residues. Instrumentation is relatively inexpened and easily used in the field. Analysis is nondestructive and requires very little time. In this project we propose a new device for detection of pesticide residues by using piezoelectric biosensor in the natural waters of Sakon Nakhon province, Thailand: water supply, Pla hangs creek, Nongharn lagoon, Nam Oon dam and Nam pung dam. It was found that the amounts of pesticide residues in natural waters are higher than the US EPA standard, all the tested samples. The Nam Oon dam is the highest mass of pesticide exceeds the standard in the 3.26 times and the Nongharn lagoon is the lowest mass of pesticide exceeds the standard in the 1.27 times, respectively.

KEYWORDS: *Sensor, Piezoelectric, Natural waters, Pesticide, Mass loading effect*

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INTRODUCTION

Environmental pollution of natural waters by pesticide residues is of very anxious these days [1]. Water pollution by pesticides can affect many biological systems; it may take very long time to clear and pose danger of bioaccumulation [2]. Pesticides are divided into many classes, of which the most important are organochlorine and organophosphorus compounds. Organochlorine pesticides are known to resist biodegradation and therefore they can be recycled through food chains and produce an expanded significantly of the original concentration at the end of the chain [3]. Organophosphorus pesticides on the other hand are known to degrade rapidly depending on their formulation, method of application, climate and the growing stage of the plant [4].

Organophosphorus are commonly esters, amides or thiol derivatives of phosphoric, phosphonic, or phosphinic acids, which have general structural formula is shown in Figure 1 where R_1 and R_2 are alkyl-, alkoxy, alkylthio-, or amido-groups. R_3 is the acyl residue (labile fluorine-, cyano-, substituted or branched aliphatic, aromatic, or heterocyclic groups) [5].

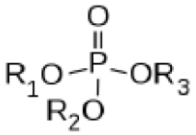

Fig. 1. Chemical structure of Organophosphorus compound

Normally used organophosphorus pesticides consist parathion, malathion, methyl parathion, chlorpyrifos, diazinon, dichlorvos, phosmet, fenitrothion, tetrachlorvinphos and azinphos methyl [6]. Pesticide residues from agriculture areas can reach the aquatic environment through direct run off, cleanse, careless disposal of empty containers, equipment washings, etc. [7]. Recently, various inhibition and non-inhibition biosensor systems based on the immobilization of acetylcholinesterase (AChE) or organophosphorus hydrolase onto various electrochemical, piezoelectric or optical transducers, have been used to detect organic phosphorous residue [8]. Quartz crystal sensor has a feature that it oscillates

resonance frequencies stably with thickness shear vibration. When a substance put on the electrode and adsorbed on the electrode plate of the crystal sensor, the frequency of the vibration is decreased corresponding to the weight. This is known as mass loading effect [9]. Quartz crystal piezoelectric device is shown in the figure 2.

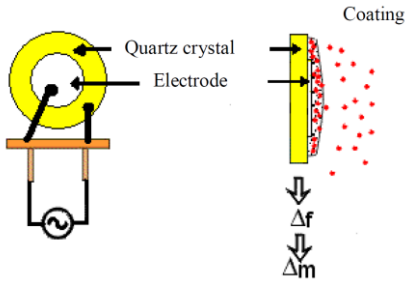

Fig. 2. Quartz crystal piezoelectric sensor device

In this paper, we propose a new device for detection of pesticide residues by using piezoelectric biosensor in the natural waters of Sakon Nakhon province and then compare it with the standard of toxins not harmful to humans.

MATERIALS AND METHODS

Step 1, water samples were collected in 2.5 liters glass bottles, between March 2015 and May 2015 from the following natural waters in Sakon nakhorn province: water supply, Pla hang creek, Nongharn lagoon, Nam Oon dam and Nam pung dam. Samples put in glass bottles, and covered tightly, then stored at room temperature.

Step 2, experimental setup was shown in figure 3 consist of quartz crystal piezoelectric, function generator Model 8110 for a frequency generator to crystalline quartz and frequency counter for measuring frequencies between coated with the load.

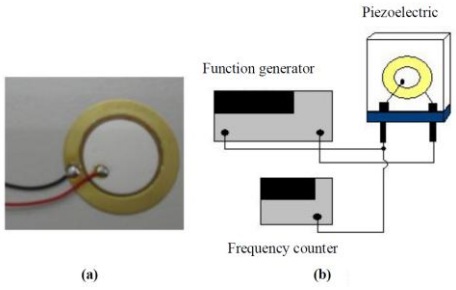

Fig. 3. shown the quartz crystal piezoelectric (a) and the experimental setup (b)

Step 3, determinations of pesticide residues by bring 1 cc for each sample from step 1 to coated on the surface of quartz crystal piezoelectric then recorded the change of frequency by read from frequency counter to calculated the mass of pesticide by used relationship between mass deposited or adsorbed on the crystal surface and the resonant frequency variations. This relationship is expressed by Sauerbrey's equation [10]:

$$\Delta f = -2.3\times10^{6}\,\frac{f^{2}\Delta m}{A} \qquad (1)$$

where Δf is the change of frequency (Hz) due to coating was calculated by $\Delta f = f_2 - f_1$, where f_1 and f_2 represents the frequency before and after the absorption of pesticide, respectively, f is the fundamental frequency of the quartz crystal (9 MHz), Δm is mass (g) of pesticide and A is the coated area of the crystal (1.328 cm^2)

RESULTS AND DISCUSSION

The relation between frequency shift (MHz) and time (min.) from the following natural waters in Sakon nakhorn province: Water supply, Pla hangs creek, Nongharn lagoon, Nam Oon dam and Nam Pung dam were shown in the figure 4.

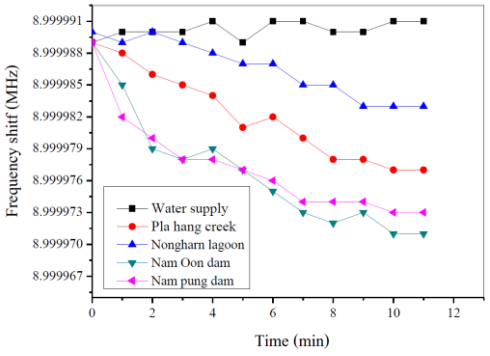

Fig. 4. The relation between frequency shift and time for natural waters in Sakon Nakhon province

The results of the analysis to the mass change on the surface of quartz crystal piezoelectric are loaded on the natural waters in Sakon Nakhon province are shown in the Table 1. It was found that the amounts of pesticide residues in natural waters are higher than standard of the United States Environmental Protection Agency (US EPA) [11], all the tested species. The Nam Oon dam is the highest mass of pesticide exceeds the standard in the 3.26 times and the Nongharn lagoon is the lowest mass of pesticide exceeds the standard in the 1.27 times, respectively.

Natural waters	Frequency change (Hz)	Mass change (μg/l)	Standard of the US EPA (US EPA, 1992) (μg/l)	Results
water supply	2	14.4	40	Do not exceed standard
Pla hang creek	12	86.9	40	exceeds standard
Nongharn lagoon	7	50.7	40	exceed standard
Nam Oon dam	18	130.3	40	exceed standard
Nam pung dam	16	115.8	40	exceed standard

CONCLUSION

We propose a new device for detection of pesticide residues by using piezoelectric biosensor in the natural waters of Sakon nakhon province: water supply, Pla hang creek, Nongharn lagoon, Nam Oon dam and Nam pung dam, Thailand. It was found that the amounts of pesticide residues in natural waters are higher than the US EPA standard, all the tested species. The Nam Oon dam is the highest mass of pesticide exceeds the standard in the 3.26 times and the Nongharn lagoon is the lowest mass of pesticide exceeds the standard in the 1.27 times, respectively .

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