

## Determination of dieldrin in river water by solid phase extraction with gas chromatography-electron capture detector

Siti Juliana Drased and Jafariah Jaafar\*

Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 Johor Bahru, Malaysia

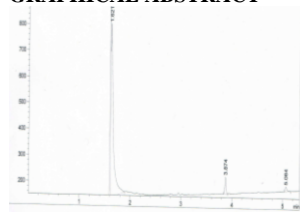
\*Corresponding Author: jafariah@kimia.fs.utm.my

### Article history :

Received 19 May 2017

Accepted 20 June 2017

### GRAPHICAL ABSTRACT



The chromatogram of 8µg/L of standard dieldrin solution when injected into GC-ECD

### ABSTRACT

The usage of pesticides has rose to a wider scale worldwide because of the large number of production and continuous consumption mainly from agriculture fields. Dieldrin is one of the possible pesticides that may contaminates the river water through the leaching or run off process, due to its wide usage as the pest control in controlling the termites and to increase the yield of crops in agriculture. The uses of dieldrin had been banned in some countries due to its persistency and carcinogenic effects. Therefore, human exposure to this compound should be minimized. A sample preparation based on solid phase extraction (SPE) coupled with gas chromatography electron captured detector (GC-ECD) was used for the extraction of dieldrin. Water samples were collected at the Skudai River, Johor Bharu, Malaysia. Water sample was extracted with a SPE cartridge. The elution solvent used was methanol. The concentration of standard dieldrin used for the calibration curve was 2-10µg/L. The limit of detection for dieldrin is 0.1135 µg/L. Meanwhile, the limit of quantification obtained is 0.3441 µg/L. It was found that the concentration of dieldrin was below the detection limit when real water sample was analysed. The advised lifetime drinking water exposure concentration limit by the US EPA for dieldrin was at 0.002 µg/L. The SPE method coupled with GC-ECD proved to be an efficient method and was applied successfully for the determination of dieldrin in the river water sample.

*Keywords:* river water, dieldrin,,organochlorine pesticide, SPE, GC-ECD.

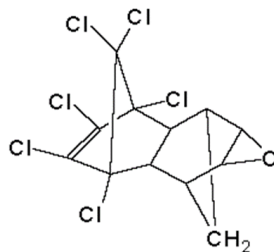
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## 1. INTRODUCTION

The intensive use of pesticides may contaminate soil, sediment, and water. Organochlorine pesticides (OCPs) are persistent in the environment, degraded slowly by natural process and potential to bioaccumulate in aquatic species. Several OCPs were detected in water, human breast milk and foodstuff [1]. One of the organochlorine pesticides is dieldrin.

Dieldrin are highly effective insecticides for soil-dwelling pests and for the protection of wooden structures against termites and wood borers. Dieldrin has also been used against insects of public health importance [2]. Due to its persistence and carcinogenic effect, the uses of dieldrin had been banned for some countries to be used in the agriculture field. In the year 1950s, this pesticide was used intensively in the agriculture field until the year of 1972, where dieldrin was used as the insecticides to kills termites. However, after 15 years, the manufacturers voluntarily stop producing the dieldrin pesticide [3].

Dieldrin is the active compound of Aldrin. Aldrin is not toxic to insects, but it is oxidized in the body of the exposed insect to form dieldrin which is the active compound [4]. Figure 1 shows the structure of dieldrin.



**Figure 1** The structure of dieldrin

Dieldrin is carcinogenic to the human life. World Health Organization (WHO) proposed the guideline value of 0.03 µg/litre [4] while US EPA with respect to the Health Reference Level, based on cancer estimated excess lifetime cancer risks of  $10^{-6}$  only allowed a limit of 0.002 µg/L [5]. Therefore, in order to ensure that the river water is freed from the carcinogenic dieldrin, a study of dieldrin in the river water was done.

This research will emphasize on the extraction of water sample by solid phase extraction (SPE) and further analysed with gas chromatography electron capture detector [6]. The sampling was done at a level below the surface water due to the density of dieldrin which is denser than the water and tends to accumulate at the level below the surface water.

## 2. EXPERIMENTAL

The experiment was divided into 2 parts which were extraction of analyte and analysis with the GC-ECD. For the extraction of dieldrin, a SPE cartridge was used. The conditioning solvents were methanol and ultrapure water. Meanwhile, the elution solvent used was methanol. Ethyl acetate was used to wash the cartridge after sample loading. Ethyl acetate and methanol were purchased from Merck KgaA (Darmstadt, Germany) and were of HPLC grade. Ultrapure water was obtained from Milli-Q water purification system (Darmstadt, Germany). For the SPE method, two samples were prepared to be extracted by the SPE. One sample was spiked with 8 µg/L concentration of standard working solution of dieldrin and another sample was not spiked. The volume of river water samples used were 250 mL. The spiked sample was used to determine the percentage recovery of the SPE technique.

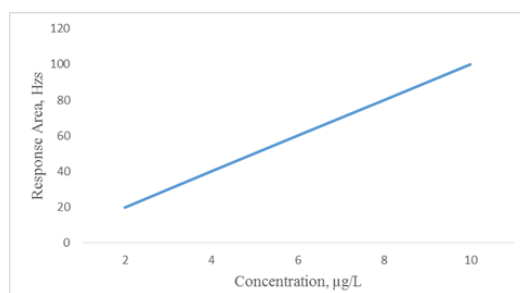
SPE sorbent inside the cartridge was conditioned with 5 mL of methanol and then followed by (2 x 5 mL) ultrapure water. The cartridge must not be dried before the river water sample loading. After loading the sample, the flow rate used was 5 mL/ min under vacuum. The SPE sorbents, SPE cartridges was then washed by using 5 mL of ethyl acetate. Before elution of analyte with 3 mL of methanol, the cartridge was left dry under vacuum for about 2 minutes to remove water molecules. Then after elution, the collected samples in the vials were added with anhydrous sodium sulphate to completely remove the water molecules before being injected into the GC-ECD column.

For the GC analysis of dieldrin, the detector of the gas chromatography used was electron capture detector (ECD). This is due to the sensitivity and selectivity of ECD to halogenated compounds. An Agilent Technologies gas chromatograph 7890 B series (Santa Clara, CA, USA) equipped with an electron capture detector (ECD) was operated at 310 °C, and a HP-5, a (5%-Phenyl)-methylpolysiloxane column (30 m × 0.32 mm × 1.0 µm; J&W Scientific, Folsom, CA, USA) were used for determination of the pesticides. The temperature programmed was used. Initially, the column oven was held at 220 °C held a minute, then increased to 300 °C at 15 °C min<sup>-1</sup>. The injector temperature was set at 300 °C. The detector temperature was set at 310°C. The total run time for each sample was about 5 minutes. Split mode injection with a split ratio of 10:1 was operated for this study.

## 3. RESULTS AND DISCUSSION

Method validation is the process used to confirm that the analytical procedure employed for a specific test is suitable for its intended use. Results that were obtained from method validation can be used to judge the quality, reliability and consistency of analytical results. Several method validation such as accuracy, precision, limit of detection (LOD), limit of quantitation (LOQ), linearity and range are used to report the result of an analytical standard experiment. LOD is defined as the smallest concentration of analyte in the sample that can be reliably be distinguished from the baseline. LOD was obtained at 0.1135 µg/L. LOQ which is the concentration at which quantitative results, typically measured 10 times higher from the baseline was obtained at 0.3441 µg/L.

Calibration curve for the dieldrin working standard solutions had been plotted for five sets of working standard solutions in the range of 2 µg/L to 10 µg/L. A linear relationship was obtained as shown in the Figure 2. It is shown that the working standard solutions displayed a good linear response with correlation coefficient of 0.9984. The data for the calibration graph for dieldrin is shown in Table 1. The percentage relative standard deviation was calculated for each concentration to determine its uncertainty.



**Figure 2** The calibration curve of standard dieldrin at concentration ranges (2-10 µg/L) analysed with GC-ECD. GC conditions: HP5 column (30 m x 0.32 mm x 1.0 µm) Detector temperature: 310°C. Injection temperature: 300 °C, Initial oven temperature: 220 °C and held a minute, ramped 15 °C min<sup>-1</sup> to 300 °C and held a minute.

Reproducibility and repeatability was also calculated to determine its precision. In this study, the concentration of 6 µg/L was kept constant. Results obtained are shown as Table 2 and Table 3. Table 2 shows the repeatability of dieldrin at 6 µg/L which were analysed in triplicate during the same day. The relative standard deviation (%RSD) gave a value of 0.65%. Meanwhile in the Table 4.3, the %RSD obtained for reproducibility was 0.70%. The reproducibility was analysed by injection

of 6 µg/L standard dieldrin into the GC-ECD for three days consecutively. Both repeatability and reproducibility was below than 5% which indicates the high precision.

**Table 1** The concentration of standard dieldrin with range from 2 to 10 µg/L injected into the GC-ECD.

Concentration, µg/L	Mean Response Area	RSD (%)
2	23.0333	0.92
4	43.0667	0.58
6	59.9333	0.63
8	80.2667	0.63
10	101.8333	0.30

**Table 2** The intra-day analysis of 6 µg/L standard dieldrin.

Concentration, µg/L			Mean, µg/L	RSD (%)
1	2	3		
5.84	5.85	5.78	5.82	0.65

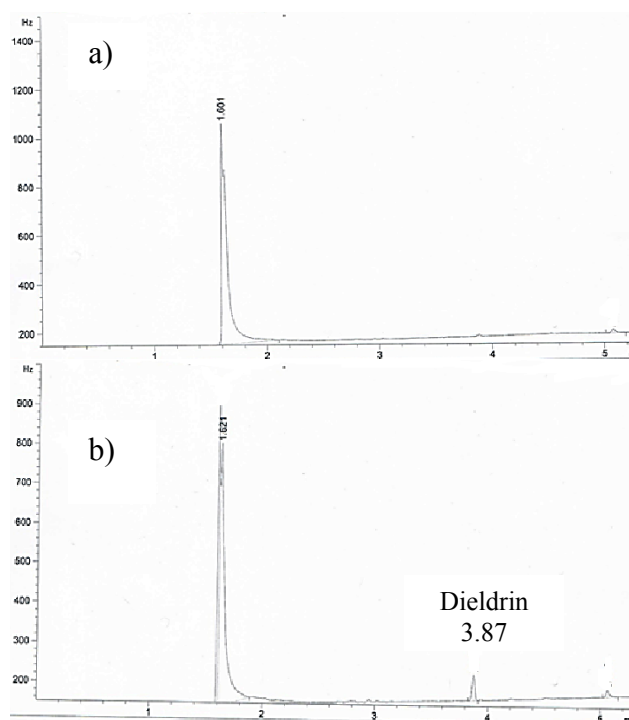
**Table 3:** The inter-day analysis of standard dieldrin at concentration of 6 µg/L for three different days.

Day	Concentration, µg/L			Mean, µg/L	RSD (%)
	1	2	3		
1	5.84	5.85	5.78	5.82	0.65
2	5.82	5.72	5.76	5.76	0.89
3	5.55	5.62	5.55	5.57	0.73
	Average			5.71	0.70

**Table 3** The calculated percentage recovery from the 8 µg/L spiked river water sample.

Analyte	Dieldrin
Spiked (µg/L)	8 µg/L
Recovery (%)	127%
RSD (%)	2.61%

SPE method was applied for the extraction of real sample analysis. The river water collected at Skudai River, Johor Bahru, Malaysia was filtered before being extracted by using the simple and efficient SPE method. The result from extraction of real analysis is shown as in Figure 3. Figure 3(a) shows a river unspiked water sample and no signal was recorded for dieldrin. Figure 3(b) shows the spiked river water sample with 8 µg/L of standard dieldrin and quite an intense peak appeared at 3.87 min, which belong to dieldrin. Accuracy was calculated as the percentage recovery of known amount of target analyte added to the river water sample. The percentage of recovery was calculated and the result is shown in the Table 3.



**Figure 3** GC-ECD chromatograms of real water sample after extraction with SPE. a) Chromatogram of spiked water sample with 8  $\mu\text{g/L}$  of standard dieldrin. b) Chromatogram of an unspiked water sample. GC conditions: HP5 column (30 m x 0.32 mm x 1.0  $\mu\text{m}$ ) Detector temperature: 310°C. Injection temperature: 300°C, Initial oven temperature: 220°C and held a minute, ramped 15°C  $\text{min}^{-1}$  to 300°C and held a minute.

#### 4 CONCLUSION

Solid phase extraction (SPE) combined with the gas chromatography- electron captured detector has been successfully applied to the determination of dieldrin in the river water. SPE was chosen as the extraction method due to the simplicity and effectiveness of the operation, low cost and easy to perform. The calibration curve was plotted by using 5 different concentrations in the range of 2 to 10  $\mu\text{g/L}$ . The linear calibration was plotted with response area against the concentration of the dieldrin standard solutions. The correlation coefficient obtained from the graph is 0.9984. The limit of detection (LOD) obtained was 0.1135  $\mu\text{g/L}$ , while the limit of quantification (LOQ) obtained was 0.3441  $\mu\text{g/L}$ . Repeatability was obtained as 0.65% and reproducibility was obtained as 0.70%. When filtered real water sample was spiked with 8  $\mu\text{g/L}$  of standard dieldrin, the percentage recovery obtained was 127% which indicated that the analysis of dieldrin in river water with SPE had low accuracy. The unspiked sample gave no peak at the retention time of 3.87 min. Therefore, it can be concluded that dieldrin concentration in the river water was below the detection limit.

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