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DETERMINATION OF PERSISTENT ORGANOCHLORINE PESTICIDES IN DRINKING WATER USING LLE AND GC/ECD

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Abstract

Pesticide pollution is a subject of global concern and, although many countries have now banned the use of persistent organochlorine polluting pesticides, they linger in the environment and can contaminate water sources. The analysis of organochlorine pesticides in water has proved a challenging matrix to implement, to meet the data requirements of end users.

This investigation/method development was to establish extraction method using dichloromethane (DCM) analyzed of gas chromatographic from Agilent Technologies, in capillary column and ECD detector, EPA 508 method.

In this study, we investigated concentration of 7 organochlorine pesticides in drinking water that was sample from 4 points along city water supply network. These were accomplished by optimizing a Liquid Liquid Extraction (LLE) method. A measured volume of sample (1 L) is solvent extracted with DCM by shaking in a separatory funnel. The DCM extract is isolated, dried and concentrated to a volume of 1 ml with hexane. The concentration values were in different range as min $8.0543 \cdot 10^{-4}$ µg/ml of DDT pesticides and max $1.355 \cdot 10^{-2}$ µg/ml endosulfan another among were compatibility.

Dichloromethane as the extraction solvent for the determination of selected persistent organic polluting pesticides in aqueous samples ranging from the low µg/ml ppb range, with a minimum of organic solvent consumption, also conforming to the European Union standards.

Key words: *Pesticides, gas-chromatography analysis, drinking water.*

1. Introduction

Pesticides constitute an important component in agriculture development and protection of public health. Pesticide is a general classification as insecticides, rodenticides, fungicides, herbicides and fumigants. Although pesticides may be selectively toxic to these forms of life, they may still be toxic to humans if food contaminated by them is ingested. Pesticides are known to be toxic to humans, (Ademoroti [1]). Since for example, DDT in particular can block potassium influx across the membranes of nerve fibers and causes increase negative after-potentials (Ademoroti [1]). DDT also induces the mixed function oxidize system thereby altering the metabolism of xenobiotics and steroid hormones. Some of the symptoms of pesticides poisoning include irritation, dizziness, tremor, tonic and chronic convulsion (Winter [2]).

Pesticide pollution is a subject of global concern and, although many countries have now banned the use of persistent organic polluting pesticides, they linger in the environment and can contaminate water sources (Bulut [7]). Organochlorine pesticides (OCPs) are categorized as a group of Persistent organic pollutants (POPs), which most of these compounds have been prohibited from use due to their toxic effects, (Vasilescu [3]). Due to their lipophilic nature, hydrophobic characteristics, and low chemical and biological degradation rates, organochlorine pesticides (OCPs) have led to their accumulation in the biological tissues and subsequent magnification of concentrations in the organisms due to the progression up the food chain. The analysis of pesticides in water has proved a challenging matrix to implement, to meet the data requirements of end users. The organochlorine pesticides group includes DDT (dichlorodiphenyl trichloroethane), methoxychlor, aldrin, dieldrin, chlordane, toxaphene, endrin, heptachlor, and lindane (gamma isomer of benzene hexachloride (BHC). These are trade names for closely related hydrocarbon compounds to which several chlorine atoms have been joined (Hung and Thieman [4]).

This investigation/method development was to establish extraction method using dichloromethane (DCM) analyzed of gas chromatographic from Agilent Technologies, in capillary column and ECD detector, EPA 508 method. In this study, we investigated concentration of 7 (seven) organochlorine pesticides in drinking water that was sampled from 4 points along city water supply network. This was accomplished by optimizing a Liquid Liquid Extraction (LLE) method. A measured volume of sample (1 L) is solvent extracted with DCM by shaking in a separatory funnel (Irani *et al.* [5]).

The results show that dichloromethane (DCM) as the extraction solvent yielded high recoveries on the primary column along with the confirmation column with runtimes of 10 minutes on the GC/ECD (Table 1). Using dichloromethane (DCM) as the extraction solvent was more convenient and met the European Union's requirements as well. This study performed using automated phase extraction with Liquid Liquid Extraction (LLE) method achieves high recoveries of persistent organic polluting pesticides in water samples. The methylene chloride extract is isolated, dried and concentrated to a volume of 5 mL after solvent substitution with methyl tert-butyl ether (MTBE). Chromatographic conditions are described which permit the separation and measurement of the analytes in the extract by capillary column GC with an electron capture detector (ECD). In total, samples were extracted, concentrated, cleaned and analyzed within 2 hours. In this study were examinated Organochlorine pesticides (OCPs) such as: lindan, heptachlor, aldrin, endosulfanI, dieldrin, endrin and pp'DDT.

The aim of this paper is to determine the concentrations of persistent organochlorine pesticides in drinking water taken from four places in our city. Obtained results from extraction method using dichloromethane (DCM) analyzed of gas chromatographic in capillary column and ECD detector, EPA 508 method, confirm that DCM is good extraction agent for determining organochlorine pesticides and can be used for analyses to other OCPs in different samples (Munch [6]).

From obtained results to conclude that drinking water in our city is according with regular world prescription, apropos determined concentration of seven OCPs in drinking water that are under maximum permissive limit.

2. Materials and Methods

Samples of drinking water taken from 4 points along city water supply network have presented the material for this research. Instruments and materials used in this study were: Automated Extraction Method, EPA 508 method, of gas chromatographic from Agilent 6890 GC Technologies, in capillary column and electron capture detector, ECD detector. This is a gas chromatographic (GC) method applicable to the determination of certain chlorinated pesticides in groundwater and finished drinking water. A measured volume of sample of approximately 1 L is solvent extracted with methylene chloride by shaking in a separatory funnel or mechanical tumbling in a bottle. The methylene chloride extract is isolated, dried and concentrated to a volume of 5 mL after solvent substitution with methyl tert-butyl ether (MTBE). This method was generated using the automated extraction procedure with the mechanical tumbler. Adjusted the sample to pH 7 add NaOH or H_2SO_4 and by adding 50 mL of phosphate buffer. Checked pH, add 100 g NaCl to the sample, seal, and shake to dissolve salt, add 300 mL methylene chloride to the sample bottle, seal, and shake 30 seconds to rinse the inner walls. Transfer the solvent to the sample contained in the separatory funnel or tumbler bottle, seal, and shake for 10 seconds. Shake or tumble the sample for one hour. Complete mixing of the organic and aqueous phases should be observed within about two minutes after starting the mixing device. If the tumbler is used, pour contents of tumbler bottle into a 2 L separatory funnel. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration through glass wool, centrifugation, or other physical methods. Collect the methylene chloride extract in a 500 mL Erlenmeyer flask.

Determine the original sample volume by refilling the sample bottle to the mark and transferring the water to a 1000 mL graduated cylinder. Record the sample volume to the nearest 5 mL.

Extract concentration devices or techniques may be used in place of the K-D concentrator

Extract is dried by pouring it through a solvent-rinsed drying column containing about 10 cm of anhydrous sodium sulfate. Methylene chloride extract is decanted the into the K-D concentrator. The remaining sodium sulfate is rinsed with two 25 mL portions of methylene chloride and the rinses are decanted into the K-D concentrator. K-D apparatus is placed on a hot water bath, 65-70 °C, so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. When the apparent volume of liquid reaches 2 mL, K-D apparatus is removed and we allow it to drain and cool for at least 10 minutes. The Snyder column is removed and flask rinsed and its lower joint into the concentrator tube with 1-2 mL of MTBE. Than 5-10 mL of MTBE is added. Vertical position of the apparatus is adjusting and the water temperature as required to complete concentration in five to 10 minutes. When the apparent volume of liquid reaches 2 mL, we remove the micro K-D from the bath and allow it to drain and cool. 5-10 mL MTBE is added to the micro K-D and it's reconcentrated to 2 mL. We removed the micro K-D from the bath and allow it to drain and cool. Than the micro Snyder column is removed, and we rinsed the walls of the concentrator tube while adjusting the volume to 5.0 mL with MTBE.

The concentrate was analyzed with GC/ECD. (Following GC Conditions)

The system was calibrated to inject 2 μL of the sample extract. Record the resulting peak size in area units responsible for the peak exceeds the working range of the system diluted the extract and reanalyze. Internal standard calibration have used, add an appropriate amount of additional internal standard to maintain the concentration of 0.1 μg/mL.

Identification of Analytes

Sample component are identified by comparison of its retention time to the retention time of a reference chromatogram. If the retention time of an unknown compound corresponds, within limits, to the retention time of a standard compound.

Calculation with external standard calibration procedure was used, and calculates the amount of material injected from the peak response using the calibration curve or calibration factor. The concentration (C) in the sample is calculated from the following equation:

$$C\ (\mu g/mL) = \frac{(A)(Vt)}{(Vi)(Vs)}$$

where: A = Amount of material injected (ng); Vi = Volume of extract injected (μL); Vt = Volume of total extract (μL); Vs = Volume of water extracted (mL).

Statistical arrange results was done of variation - statistical methods using Microsoft Office Excel, calculate average, standard deviation and yielded conclusion of descriptive statistics.

3. Results and Discussion

Identification and quantitative determination of persistent organochlorine pesticides in examination samples drinking water was done with extraction agent, dichloromethane (DCM) and concentrate with GC/ECD. Obtained values on OCPsreadings from 4 place, points along city water supply network for 3 months (January, February, and March) is shown in Table 1.

Table 1. Values on OCPs (10^{-3} μg/ml) from 4 place, drinking water for 3 months

Month	Place	Organochlorne pesticides OCPs (10^{-3} μg/ml)						
		Lindan	**Heptachlor**	**Aldrin**	**Endosulfanl**	**Dieldrin**	**Endrin**	**pp'DDT**
January	1	7.29125	5.64547	3.08389	1.80977	0	0	1.64364
	2	3.22378	5.16482	1.49252	1.355	0	7.88885	8.0543
	3	6.85777	6.06838	1.93483	1.74012	0	1.9242	2.21149
	4	2.46881	1.37547	1.60842	4.11887	0	2.94782	3.88405
average		*4.960403*	*4.563535*	*2.029915*	*2.25594*	*0*	*3.190218*	*3.94837*
st. dev		*2.466897*	*2.157193*	*0.727176*	*1.257953*	*0*	*3.36235*	*2.897777*
February	1	2.26661	2.38281	2.16303	3.82504	4.28662	3.00802	1.00302
	2	5.29373	6.99305	1.60842	4.11887	0	2.94782	3.88405
	3	1.88785	4.8412	3.08225	1.04356	2.70912	0	1.06495
	4	3.00333	1.82158	3.84155	2.51806	1.45626	3.12056	4.87829
average		*3.11288*	*4.00966*	*2.673813*	*2.876383*	*2.113*	*2.2691*	*2.707578*
st. dev		*1.525885*	*2.382324*	*0.987656*	*1.406101*	*1.823555*	*1.514426*	*1.974827*
March	1	1.24567	2.97845	0	1.54567	0	1.44733	2.94567
	2	2.98456	1.71228	7.77328	7.23901	0	1.23768	6.18944
	3	7.65782	5.78921	1.02993	0	2.31267	2.31	2.88421
	4	1.28934	1.92345	3.23489	4.32812	0	1.34789	3.97856
average		*3.294348*	*3.100848*	*3.009525*	*3.2782*	*0.578168*	*1.585725*	*3.99947*
st. dev		*3.019547*	*1.875869*	*3.450613*	*3.190538*	*1.156335*	*0.490384*	*1.543881*

According average of concentration values that show organocholrine pesticides on percentage from different place three month with different present (Figure 1).

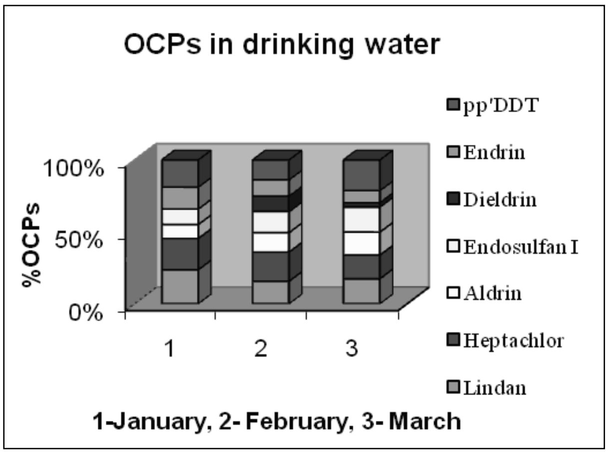

Figure 1. OCPs residues in drinking water

4. Conclusions

- This study is showing that solvent extraction with DCM is an accurate and reliable method for OCP residue analyses in drinking water. It also shows that present of persistent each OCPs in samples in per three month equable and confirming to the European Union standards.
- The levels of OCPs residues were same similarly that obtained in the water samples from four different places. Because this thesis is serious need for the monitoring of these pesticide residues in water, food and the environment, as this will go a long way towards preventing various environmental and public health hazards.

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