ORGANOCHLORINE AND ORGANOPHOSPHOROUS PESTICIDE TRACES DETERMINATION IN WATER.

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Ukrainian approved analytical methods in use often suffer from the lack of precision relating to identification and quantification. In particular, this is defined by preliminary sample preparation step. Thus, trace enrichment of semipolar and polar contaminants such as chlorinated and phosphorous pesticide compounds from aqueous solutions is difficult due to low analyte recoveries in liquid-liquid extraction or early analyte breakthrough on commercially available in Ukraine styrene-divinylbenzene- based or Polysorb sorbents.
The purpose of this study was to elaborate a more efficient and rapid pre-concentration procedure to determine μg/l concentrations of chlorinated and phosphorous pesticides (for example, lindane, methoxychlor, and chlorpyrifos) by following GC/ECD. The used VAB-TGM sorbents present a porous polymeric material which exhibits a higher affinity to above mentioned compounds resulting in higher recovery of the analytes.
Results of the study show that the characteristics of VAB-TGM sorbents exceed the Ukrainian requirements as well as the characteristics of traditional sorbents. It has been determined that the recovery data obtained by means of VAB-TGM sorbents were as following: for lindane up to 98%, for chlorpyrifos up to 96%, and for methoxychlor up to 97%.
Reduction in the extraction time and relatively small quantity of water samples, and reuse means are also advantages.
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INTRODUCTION

Drinking water quality and safety is of paramount importance to life and existing of healthy world society. According to the data presented by the World Health Organization (WHO) nearly 1.5 billion people lack safe drinking water and at least 5 million deaths per year can be attributed to waterborne diseases (1). A long-distance migration of anthropogenic pollutants via atmosphere or world ocean has already become an international problem.

The heavy use of synthetic pesticides (WHO estimates a global consumption of pesticide chemicals per year about 2,5 million metric tons) in agricultural applications over the past half century has led to their detection in drinking water. Therefore, rigorous analytical control of drinking water supplies is among the special priorities of environmental policy of any state in a world community.
In Europe, Ukraine possesses 18,9 % of agricultural lands and 26,9 % of sown areas (2). For decades, pesticides have not been used properly and safely. The most common route of pesticide exposure leading to environmental contamination appears due to carelessness and misuse. Besides, as many as about 22 thousand metric tons of unusable pesticides are stored in the unequipped storage sites. As a result, significant concentrations of pesticides remain in soil and water sources.

Organochlorine and phosphorous pesticides have been included on the European Community and US EPA Lists of Priority Pollutants because of their utmost stability and widespread persistence in the environment (3). They are highly toxic compounds even in minute concentrations (disrupt function of nervous system, mainly brain, build up in fatty tissues affecting a person's reproduction system, and may cause cancer, genetic mutations, or death and other dangerous diseases).
Current World and European Commission water acts and regulations set the maximum residue limits (MRLs) of chlorinated and phosphorous pesticides in drinking water of 0.1 μg/l for separate compound and 0.5 μg/l for their sum and require a regular monitoring of drinking water supplies pesticides traces presence (4,5).

One of the most widely used and applicable methods for chlorinated and phosphorous pesticides analysis involves the use of Gas Chromatography (GC). Before the water sample to be analyzed, the

targets must be separated from the aqueous matrix and pre-concentrated. In modern practice, the most acceptable pre-concentration method is based on solid-phase extraction (SPE) of analytes using small cartridges filled with sorbents of small particle sizes (6).
In trace-level analyses, the most commonly employed SPE sorbing material to extract pesticides from water samples are represented by chemically bonded silica-based materials such as Octylsilane (C8) or Octadecylsilane (C18) (7).

Ukrainian standard approach currently used for pesticides traces determination in water involves liquid-liquid extraction as the pre-concentration. Classical liquid-liquid extraction is a time consuming method requiring large volumes of toxic and expensive solvents. The latter entails creating a problem of wastes disposal. An additional evaporation step is necessary due to large volume of the obtained extracts. In common, that all leads to unavoidable losses of the target compounds and to the decrease in analysis accuracy.
Lack of the effective and low cost SPE sorbents for analytical application in Ukraine has prompted this research. The presently available Ukrainian sorbents such as Polysorb and Styrene-divinylbenzene (St-DVB) demonstrated low recovery rates because of early analyte breakthrough effect.

The purpose of this study has been elaboration of the method determination of trace-level amounts of chlorinated and phosphorous pesticides in water samples based on rapid and effective pre-concentration of the target analytes onto novel VAB-TGM polymer sorbents followed by gas chromatography/ electron-capture detector (GC/ECD) quantification.

METHODOLOGY

We have obtained novel polymer sorbents via radical suspension co-polymerization of esteracrylate-based olygomer (TGM) and polyfunctional hydroperoxide co-polymer (VAB_{244}) in the presence of different porogenic agents (8). Assumed scheme of the polymer matrix is presented in the **Fig 1**.

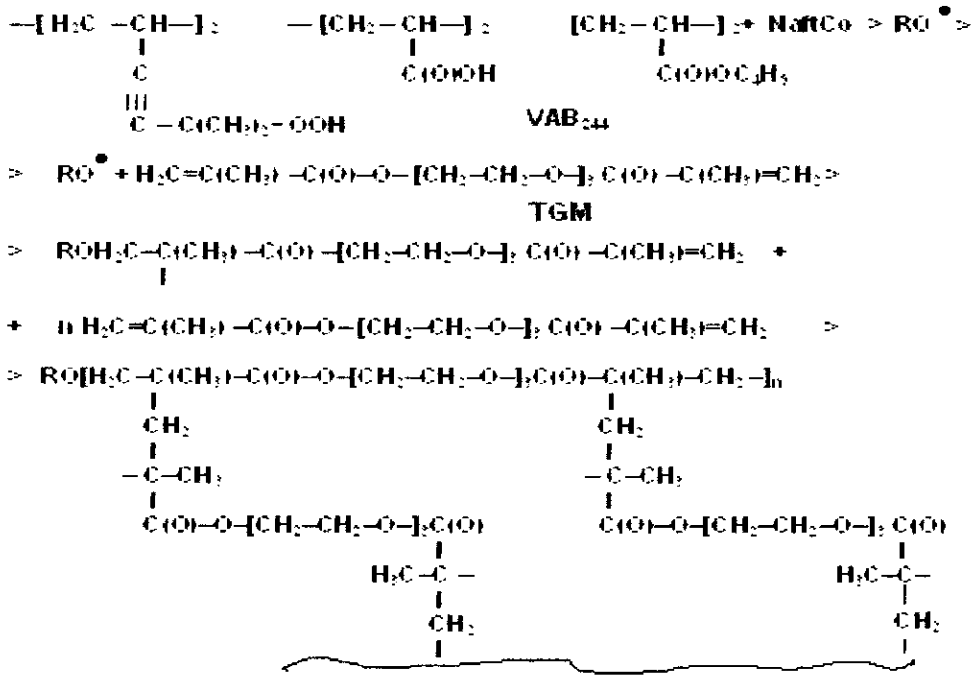


Fig.1 Assumed scheme of the VAB-TGM polymer matrix

The pesticide compounds, namely lindane, methoxychlor, and chlorpyrifos, have been choosen for this study.
Water samples were prepared by fortifying 250 ml of purified water with measured amounts of standard spiking solutions to obtain levels of individual pesticide compound in mixture ranged from 5 µg/l up to 10 mg/l. High spiked concentrations were interesting for additional confirmation of good sorption capability of the novel sorbents with no obvious reaching a breakthrough.
SPE experiment has been carried out in accordance with the standard dynamic method. Two commercial units of the "Baker 10™ SPE System Vacuum Manifolder" have been combined with

commercially available polypropylene 6 ml "Bakerbond" cartridges pre-packed with 0.5 g of the Octylsilane (C8) and novel VAB-TGM sorbents selected. The recovery data have been processed for 16 polymer sorbent samples. Prior to application, all the sorbents were conditioned thoroughly with MeOH in order to obtain the hydrophilic properties of the solid phase surface.
It has taken approximately 20-25 min for water drawn to completely elute 250 ml of fortified water samples through the polymer sorbents, whereas the Octylsilane (C8) samples required over 1 hour for complete elution under the conditions maintained (vacuum).
To collect the extracted pesticides, three portions of 1 ml of acetone (as a middle polar solvent) or acetonitrile (as a more polar solvent) were used for elution of the retained analytes from the sorbents.
Gas chromatography has been performed on Hewlett-Packard (HP) 5890 A GC equipped with an electron-capture detector, HP autosampler, and split-splitless injection port and HP Chem Station.
To achieve the satisfactory separation of the target compounds, the GC experiment was performed under the temperature programmed conditions (see Fig 3.).
Quantification of the recovery values for extracts was performed in relation to the standards. The recovery data were determined by comparing the ratios of peak areas for each pesticide extracted from the fortified water samples with those found for the mixture of pesticides of known concentration.
Additionally, it has been carried out the experiment on the reuse of some sorbents after a simple regeneration procedure : acetone flushing and air drying under the vacuum maintained by water aspiration.

RESULTS

VAB-TGM polymer sorbents synthesis presents an one-stage and enough short in time procedure (up to 1 hour) providing a high yield (~95%) of a final product. Obtained sorbents are polydispersed particles of spherical shape having particle sizes ranged from 50 to 200 μm and surface areas ranged from 5-40 m^2/g . The micrographs of the selected polymer and standard Octylsilane (C8) sorbents are presented in the Fig. 2.

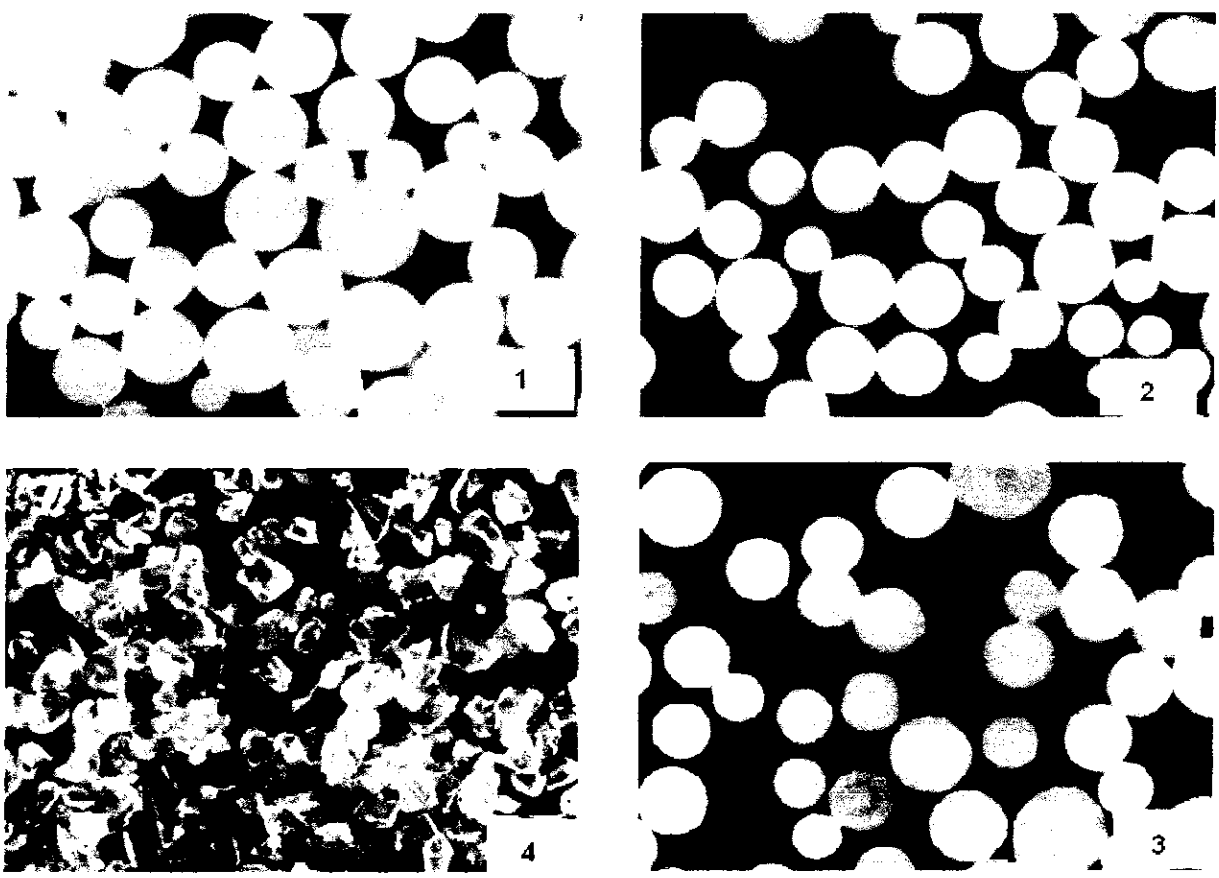
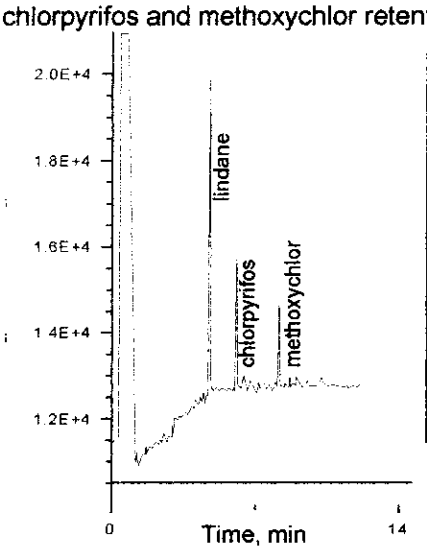


Fig. 2. Micrographs of the selected polymer sorbents: **1 - # 125, 2 - # 98, 3 - # 96, 4** -Octylsilane (C8)

Particles exhibited no swelling in water and organic solvents (such as acetone, hexane, and acetonitrile). The VAB-TGM sorbents differed mainly by the nature and amount of the diluents used during the co-polymerization process.

Typical chromatogram showing the retention times and peak heights of the extracted pesticides and GC conditions is presented in Fig.3. Lindane elutes first, retention time is 4,727 ± 0.001 min. For chlorpyrifos and methoxychlor retention times are 5.993 ± 0.002, and 8.171 ± 0.002 min respectively.



Sample:	5 µg/l of each pesticide in water
GC:	HP 5890 Series II
Column:	HP-1(Restec Inc.), 8 m x 0.20 mm x 0.33 µm
Carrier gas:	Helium, ml/min, 11.2 psi
Make up gas:	N_2 ,30-60 ml/min,
Injection:	Splitless, 1 µl, inlet 250 ° C
Purge off time:	1.0 min
Oven:	100° C/ 0.5 min, 280° C/ 20° C/min /5 min
Detector:	ECD, det.temp. 250 ° C
Total run time:	14.5 min
The detector signals were stored, and results were analyzed by the Hewlett-Packard Chem Station software.	

Fig.3. Typical chromatogram of pesticides mixture separation and gas chromatography conditions

The average recovery values of the high level (10 mg/l) spiked compounds have found ranged from 84% up to 97% for lindane, from 88% up to 99 % for chlorpyrifos, and from 87% up to 95% for methoxychlor. For Octylsilane (C8) sorbents these values were 86-88%, 62-65% and 62-72% respectively.

At the low spiking level (5 µg/l) recovery results ranged from 88% up to 98% for lindane, from 86% up to 96% for chlorpyrifos, and from 87% up to 97% for methoxychlor. For Octylsilane (C8) sorbents these meanings were 68-77%, 69-72%, and 70-72% respectively (under the conditions maintained).

The recovery values of the selected pesticides obtained by adsorption onto VAB-TGM polymer sorbents in comparison to standard Octylsilane (C8) sorbents are shown in Table.1.

SAMPLE	10 mg/l		5 µg/l		SAMPLE	10 mg/l		5 µg/l	
	% REC	% RSD	% REC	% RSD		% REC	% RSD	% REC	% RSD
	Lindane					**Chlorpyrifos**			
#125	97.0	3.5	98.1	4.9	#96	99.2	3.2	96.2	5.1
reuse	96.3	4.3	97.7	4.2	reuse	97.5	3.8	95.3	4.6
#93	94.1	3.9	95.1	3.7	#124	96.7	4.3	93.6	5.4
Octyl C8	88.2	4.5	76.6	5.7	Octyl C8	65.4	4.1	72.0	3.8
reuse	71.8	3.1	67.3	4.7	reuse	52.3	4.9	59.4	4.7
	Methoxychlor								
#98	94.8	3.6	97.0	4.3					
reuse	94.0	4.3	96.7	4.8					
# 109	93.2	4.2	94.7	6.1					
Octyl C8	72.3	5.7	70.1	4.7					
reuse	50.4	5.2	47.4	5.2					

Table 1. Recovery values of the selected pesticides

The effect of two different solvents on the recovery values of extracted pesticides has also been investigated. Better results were obtained for VAB-TGM sorbents those from which extracted analytes were eluted with acetone.

CONCLUSIONS

- We report the development of the efficient, fast and reliable method determination of selected organochlorine and organophosphorous pesticide compounds
- In this research we focused on the application of novel SPE VAB-TGM polymer sorbents for pre-concentration (extraction and recovery) of the selected pesticides from fortified water solutions followed by the GC/ECD determination.(9)
- Synthesis of the VAB-TGM sorbents differs in simplicity, sufficient speed and high yield of a final product (~95%).
- Sorption ability of the VAB-TGM sorbents standed the comparison with the established Octylsilane (C8) sorbents. Obtained recovery values confirmed good sorption properties of the VAB-TGM sorbents towards such pesticides as lindane, methoxychlor, and chlorpyrifos. In some cases, the SPE onto of novel sorbents have achieved higher recovery yields under the conditions maintained.
- Usage of the different type and amount of diluents allowed to change and to control the sorption properties of obtained sorbents.
- Novel VAB-TGM sorbents can be used without additional fractionating and easily regenerated with no loss in sorption properties and reused for pre-concentration of the pesticide compounds from water.

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