Morocco Journal of Chemistry

Extraction of organochlorine pesticides by a matrix of calcium phosphate

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Received 02 May 2014, Revised 29 May 2014, Accepted 06 June 2014.

Abstract

Accumulations of waste pesticides from manufacturing units of pesticides in rivers through drains are sources of environmental pollution. Search for matrices having a large capacity for retention of these pollutants is necessary. We conducted an experimental study on the purification of a mixture of pesticides on a column filled with a matrix based on calcium phosphate (hydroxyapatite). The study provides a satisfactory extraction of organochlorines with a very good performance, organochlorines Landa-cyhalothrin, Délthaméthrine, Beta-endosulfon, Endosulfon-Sulfate, Landa-cyhalothrin, Tertadifon, Delthamethrine, Fenarimol and iprodione have achieved satisfactory recovery percentages.

The results and interpretations were confirmed by physico-chemical analyzes, using appropriate methods of investigation.

***Keywords**: Extraction, CPG, Calcium phosphate, Organochlorine pesticide, Environment.*

1. Introduction

Organochlorine pesticides have adverse effects on living organisms, and they are very persistent in the environment. The analysis of pesticides in laboratory techniques are numerous, but currently the most widely used in the field of trace analysis includes an extraction column chromatography on silica or Florisil step followed by analysis by gas chromatography. There are several methods of purification: florisil column [1-3], column of silica gels [4] or alumina columns [5].

The existence of negative wearer's reaction sites on the surface of hydroxyapatite allows large loads environmental applications [6]. Numerous studies have cited the ability to trap pesticides by calcium phosphate [7-9]. Their adsorption capacity has been exploited in catalysis reactions [10].

2.Materials and methods

2.1 Apparatus CPG

Analysis of pesticide residues is performed using a system of gas chromatography equipped with an Agilent 6890 μECD detector (GC / μECD) and a CP-SIL 8 capillary column filled fused silica CB (25 m × 0.23 mm DB-5 Varian liquid phase. film thickness 0.25 mm). Nitrogen is used as carrier gas and for the "Makeup" for the respective flow rates of 4 to 60 mL / min.

2.2 Chromatographic conditions

The temperatures of the injector and detector were set respectively at 240 ° C and 310 ° C. A sample (1 uL) was injected in splitless mode (0,75 min) and the oven temperature is programmed as follows: 60 ° C (2 min) and increased by 20 ° C / min to 150 ° C , then increased by 10 ° C / min to 200 ° C and maintaining this temperature for 10 min. Then increased to 10 ° C / min to 260 ° C and the latter temperature were maintained for 10 min.

2.3 Preparation of standard solutions

Mixtures of organochlorine pesticides (Tables 1 and 2 mixture N°1 and N°2 mixture) were prepared to be purified on columns filled by Hydroxyapatite.

The two mixtures are analyzed previously by chromatography CPG. They are injected into two columns of different polarity (instrument 1(Column 1: 100 methyl phenyl polysiloxane) and instrument 2 (Column 2: 14 cyanopropyl. 88 dimethyl polysiloxane). The device to record the chromatograms in Figures 1 and 2, and the test results are listed in Tables 3 and 4.

Table 1. Pesticide Mixture N° 1

Active Ingredients	Concentrations	Retention Time (INSTRUMENT 1)	Retention Time 3(INSTRUMENT 2)
Alpha –endosulfon	0,01 ppm	11,68	10,81
Beta –endosulfon	0,01 ppm	13,47	12,35
Endosulfon-Sulfate	0 ,01ppm	14,76	13,96
Landa-cyhalothrin	0,01 ppm	16,53	16,04
Tertadifon	0,01 ppm	18,24	15,559
Chlorothalonil	0,01 ppm	10,39	9,95
Dichlorofluanid	0,01 ppm	10,93	10,42
Delthamethrin	0,02 ppm	42,17	32,019
Fenarimol	0,02 ppm	20,55	17,047
Iprodion	0,02 ppm	15,63	-

Table 2. Pesticide Mixture N° 2

Active Ingredients	Concentrations	Retention Time 1	Retention Time 2
Lindan	0.008	9,52	9,035
Bifenthrin	0,01	14,104	13,184
Landa-cyhalothrin	0,02	16,43	16,57
Délthaméthrin	0,02	41,65	31,75
Azoxystrobin	0,02	34,76	40,47

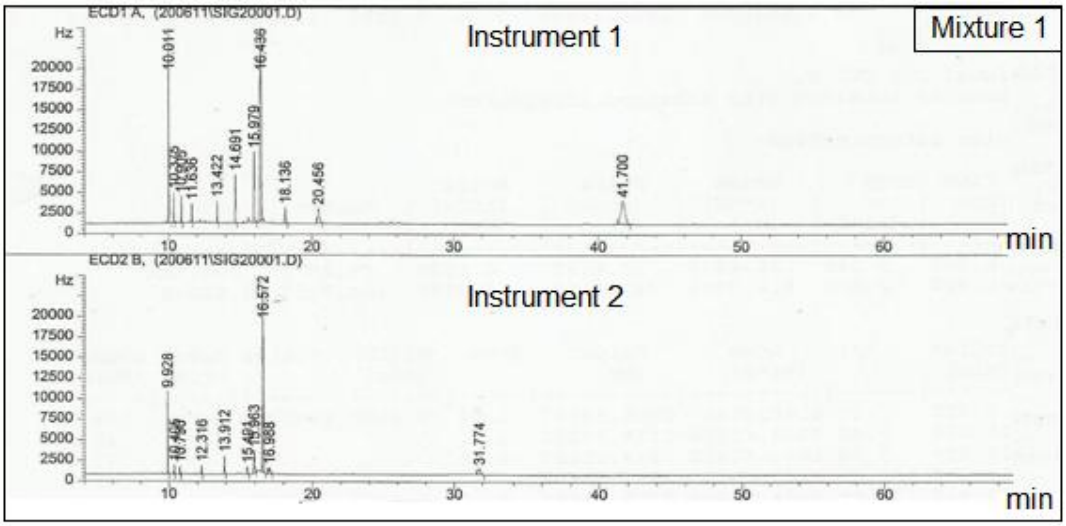

Figure 1. Chromatogram of pesticides mixture N°1

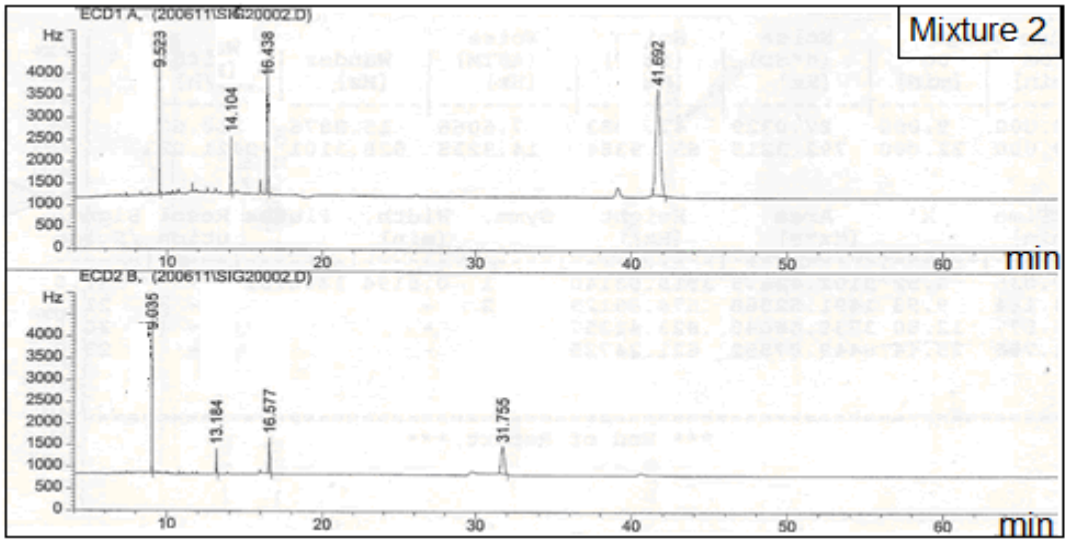

Figure 2. Chromatogram of pesticides mixture N° 2

2.4 Extraction procedure

In a glass column (Figure 3) filled with hydroxyapatite, conditioned with hexane and covered with a layer of Na_2SO_4, both mixtures of pesticides OC is deposited then performs three successive elutions. In a 500 ml flask was recovered three eluates E_1, E_2 and E_3.

E_1: hexane/ methylene chloride (20/ 80), E_2: acetonitril/ hexane/ methylene chloride (0.35/ 49. 65/ 50), E_3: acetonitril/ hexane/ methylene chloride (1.5/ 48.5/ 50).

One proceeds to solvent evaporation under a nitrogen stream and the extraction solutions were analyzed by an apparatus for gas chromatography coupled to an electron capture detector (CPG/ECD) [11]. Recovery rates are calculated from the following equation:

Recovery rate = (area of the sample peak recorded/ area of the peak recorded by standart) * 100

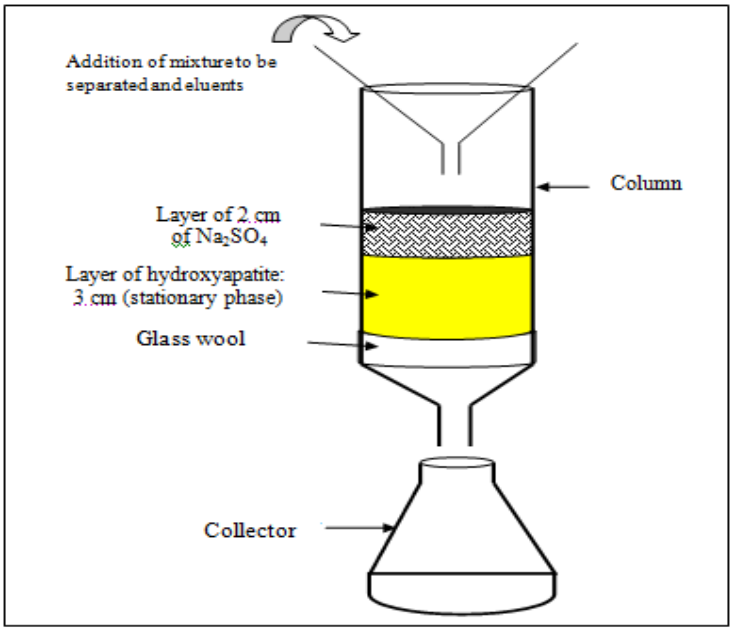

Figure 3. Diagram of elution chromatography column

3. Results and discussion

The apparatus presents the CPG chromatograms Figures 4 and 5. Experimental study on purification by adsorption of traces of pesticides showed a surprising holding capacity with a recovery rate exceeding 80%. Acceptable standards [12] for the rate of recovery are in the area:

$$80 \leq \text{Recovery rate (yield)} \leq 120$$

For two mixtures of organochlorin shows that most of the active materials are recovered by this method, only the compound: azoxystrobin is not recovered (Table N° 4).

We note that for the following active ingredients (Alpha endosulfon, Chlorothalonil, Dichlorofluanid, Bifenthrin), the study allows getting payback percentages that exceed 120% and azoxystrobin (not recovred 0 %). These results demonstrate the chromatographic interference from products.

The Hydroxyapatite leads to repeatable results for most active ingredients whose accuracy is consistent with that required by the standards. We note that our hydroxyapatite and the following

active ingredients (Landa-cyhalothrin, Délthaméthrine, Beta-endosulfon, Endosulfon-Sulfate, Landa-cyhalothrin, Tertadifon, Delthamethrine, Fenarimol, iprodione), allows to obtain satisfactory recovery percentages. In most of the active ingredients mentioned we found a very good performance.

Table 3. Recovery rate for tests 1, 2 and 3 with mixture 1

Active Ingredients	Recovery Rate Test 2	Recovery Rate Test 3	Recovery Rate Test 1	Average Recovery Rate
Alpha –endosulfon	189	250,4	231,48	**223,62**
Beta –endosulfon	84,5	73.4	117,92	91,94
Endosulfon-Sulfat	69,81	85,11	111,62	88,84
Landa-cyhalothrin	98,14	78,12	107,87	94,71
Tertadifon	111,34	112,29	118,57	114,06
Chlorothalonil	300,43	289,4	367,65	**319,16**
Dichlorofluanid	196,15	200,4	251,93	**216,16**
Delthamethrin	102,32	105,2	106,65	104,72
Fenarimol	104,5	98,6	110,64	104,58
Iprodion	128,12	126,31	132 ,09	128,84

Table 4. Recovery rate for trials 1 and 2 with mixture 2

Active Ingredients	Recovery Rate Test 1	Recovery Rate Test 2	Average Recovery Rate
Lindan	128,7	100,79	114,74
Bifenthrin	330,96	233,84	**282,24**
Landa-cyhalothrin	93,4	70,39	81,89
Délthaméthrin	116,47	106,4	111,43
Azoxystrobin	0	29,01	-

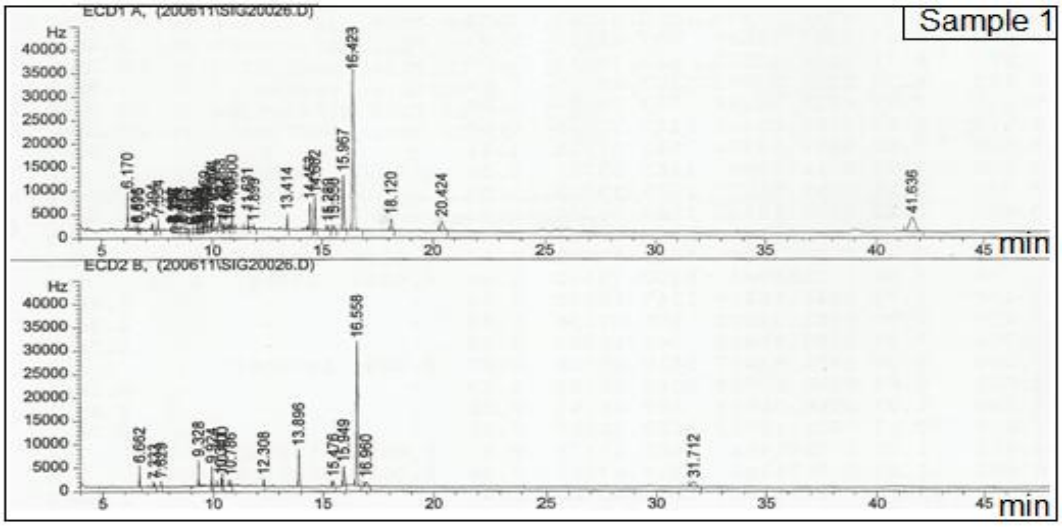

Figure 4. Chromatogram of the sample 1 of pesticides

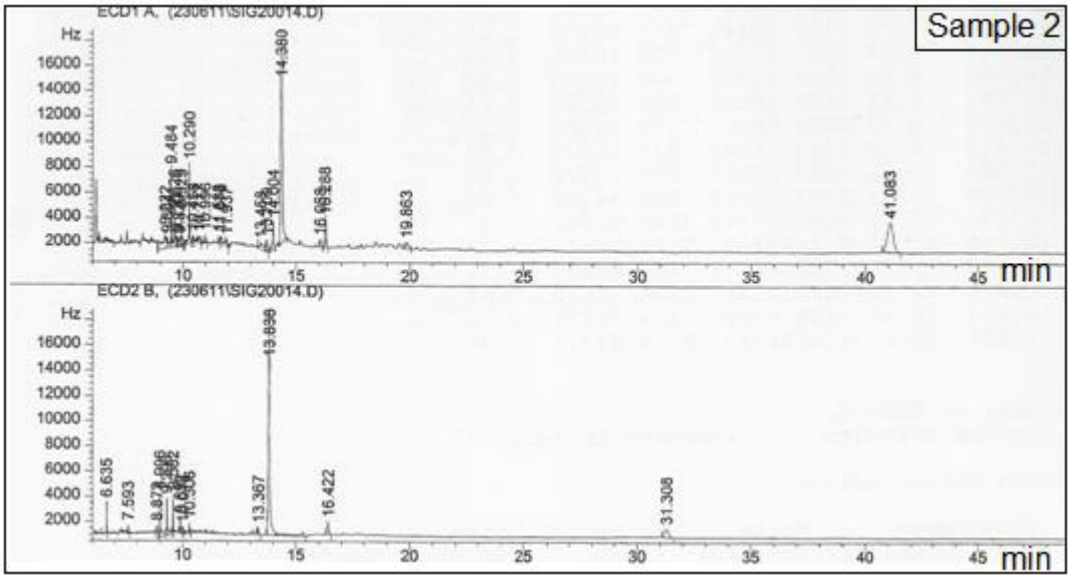

Figure 5. chromatogram of sample 2 of pesticides

4. Conclusion

The study on the extraction of pesticides by calcium phosphate provides a satisfactory extraction of organochlorines with a very good performance. This result contributes to the recovery of phosphate matrices in the decontamination of industrial waste.

The work has highlighted the performance of apatite in the retention of contaminants. The existence of the reaction sites negative charge carriers to the surface of hydroxyapatite, which enables adsorption of pollutants, and allows large areas of industrial and environmental applications.

Acknowledgements

Authors would like to thank autonomous establishment of quality control of food products Berkane, Morocco, for the analyzes carried out by chromatography (GPC)

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