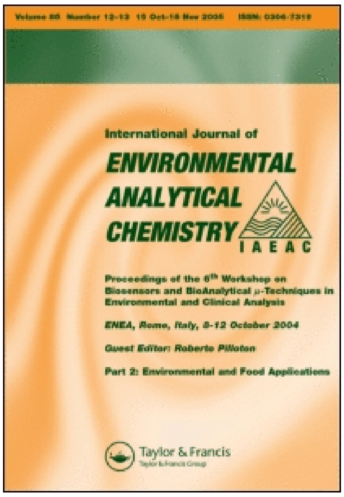

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DETERMINATION OF ORGANOCHLORINE PESTICIDES DISSOLVED IN WATER: A COMPARISON BETWEEN SOLID PHASE AND SOLVENT EXTRACTION

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Sixteen organochlorine pesticides (EPA priority) were spiked into water at a concentration range of 20 ng/L to 20,000 ng/L and then extracted by utilizing solid phase techniques and the method 608 of EPA.

The solid phases XAD-2 and C-18 were studied. The reverse phase C-18 presented a recovery of about 85%, except for heptachlor and aldrin. The solvent extraction showed better recovery in concentrations higher or equal to 200ng/L for about all pesticides.

We concluded that both methods showed good recoveries. Nevertheless, the solvent extraction is time consuming, the apparatus is cumbersome and large volumes of solvents are required while the solid phase extraction (SPE) is quick, low solvent consuming and sometimes achieving higher sensitivity than solvent extraction.

Both methods were used and compared to determine organochlorine pesticides in a river from the state of São Paulo, Brazil.

KEY WORDS: Solid phase extraction, solvent extraction, organochlorine pesticides.

INTRODUCTION

The use of solid adsorbents to extract chemical species, particularly those of environmental relevance, is receiving increased attention as evidenced by a special topical symposium during a recent meeting of the American Chemical Society in San Francisco[1]. A variety of procedures aimed at the determination of low concentration levels of chlorinated organic compounds have been documented in the literature. Several of them make use of solid phase adsorbents (e.g. charcoal[2], macroreticular resins[3-6] and Tenax[7]). Solid collectors offer distinctive advantages over liquid-liquid solvent extraction procedures[8-10], particularly with the possibility of chemical derivatization of silica-based surfaces[11].

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In this paper we compare liquid-liquid solvent extraction of a series of pesticides containing organochlorine compounds with removal of the same species by use of two solid adsorbents (the macroreticular resins XAD-2 and a C-18 silica gel reversed phase). The advantages and disadvantages of both approaches are discussed with regard to the analysis of water samples taken from the Capivara River in the State of São Paulo, Brazil.

EXPERIMENTAL

Reagents and standards

All solvents were of analytical grade (Merck, Rio de Janeiro, RJ, Brazil) submitted to chemical treatment[13] and distilled prior to use. The pesticide standards were obtained from Supelco (Supelco, Bellefonte, PA, USA). They were: α-BHC, β-BHC, γ-BHC, heptachlor, δ-BHC, aldrin, heptachlor epoxide, endosulfan-I, 4,4'DDE, dieldrin, endrin, 4,4'DDD, endosulfan-II, 4,4'DDT, endrin aldehyde, endosulfan sulfate.

The water free of organic matter, used to prepare standard solutions, was purified by filtration through a Millipore system, distilled in presence of $KMnO_4$/KOH, and eluted through a microcolumn with C-18 packing. The C-18 bonded reversed phase on porous silica was obtained from Sigma Chemical Company (St. Louis, MO, USA) and purified by Soxhlet extraction using the following solvent sequence: hexane, ethyl acetate and finally methanol. Each solvent was refluxed for 10 cycles. The XAD-2 macroreticular resin (Merck) was purified using the procedure described for the C-18 bonded phase. Blanks were tested by GC.

Two standard solutions were used to spike the water for test purposes containing, respectively, 2 and 200ng of each compound/mL of hexane. Aliquots of the stock solution were measured by using a 100μL syringe (type 701 RN, Hamilton Co., Reno, NV, USA).

Apparatus

All experiments were performed using a high resolution gas chromatograph (Hewlett Packard, model 5890, Palo Alto, CA, USA) equipped with a nickel-63 electron capture detector (ECD). The output of the ECD was connected to an integrator (Hewlett Packard, model 3393). A fused silica capillary column with 20% diphenyl and 80% dimethyl polysiloxane phase (SBP-35, Supelco Inc, 30-m long × 0.25mm i.d. and with a film thickness of 0.25μm) was used with a split/splitless injector.

Solid phase extraction (SPE) procedure

The influence of the solvent volume on recovery was studied with a 100mL of an aqueous solution of pesticides and at a concentration level of 20 μg/L. This solution was forced through the micro column loaded with 200mg of the solid phase (C-18 or XAD-2). Then, the adsorbed pesticides were eluted with 0.5mL portions of ethyl acetate when utilizing the C-18 solid phase and with 0.5mL portions of hexane when the solid phase was the XAD-2 resin. The recovery was calculated in relation to the total amount of adsorbed pesticides on the solid phase and the desorbed amount after solvent elution.

The influence of the amount of solid phase on recoveries of pesticides was studied in the range of 100mg to 400mg, and using 2mL of ethyl acetate as elution solvent for the C-18 solid phase and 5mL of hexane for XAD-2.

A microcolumn containing 230mg of C-18 and another containing 230mg of XAD-2 were washed with 5mL of ethyl acetate, followed by 1mL of methanol. Four pesticide solutions in 100mL of water were prepared with a concentration range of 20ng/L to 20,000 ng/L. These solutions were then forced through each microcolumn, using a 50mL glass syringe, at a flow rate about 15mL/min. The stationary phase of each column was then dried by drawing room air through the column from a water aspirator. The adsorbed pesticides were eluted by gravity flow of the eluent.

The capacity factor (CF) for the solid phases was determined by constraining 100 mL of a 1.0 mg/L pesticide solution through of 170 mg of C-18 or 470 mg of XAD-2. The capacity factor (CF) was determined as follows: CF = (amount of adsorbed pesticides)/(initial pesticide amount in aqueous solution).

Liquid-liquid extraction procedure

1,000mL of free organic water and spiked with the reference mixture of pesticides mentioned above were extracted with dichloromethane[13]. The final extract was in rotary evaporated and dissolved in 10mL of hexane.

Water sample extraction

The water sample was collected and submitted to both extraction methods described above. When using SPE the solid phase utilized was the C-18.

Analysis of eluates and extracts

A volume of 1μL of each eluate was injected onto the SBP-35 gas chromatographic column under the following conditions: temperature injector: 270°C; temperature detector: 290°C; initial column temperature: 180°C held constant for 2 min and programmed at 5°C/min to 280°C. The carrier gas was hydrogen at an average linear velocity of 45 cm/s. The split rate was 1:30 and the make up gas was nitrogen at 60mL/min.

The standard deviations of repeated injections (n = 5) were ±0.05μL.

Table 1 Recovery (%) on solid phase XAD-2 by using increasing volumes of hexane.

COMPOUND	*0.50mL (%)*	*1.50mL (%)*	*3.50mL (%)*
α-BHC	59.0±2.9	26.0±1.3	15.0±0.7
γ-BHC	60.0±3.0	31.0±1.5	9.0±0.8
β-BHC	66.0±3.3	29.0±1.4	6.0±0.3
Heptachlor	73.0±3.6	10.0±0.9	8.0±0.4
δ-BHC	46.0±2.3	23.0±1.1	31.0±1.5
Aldrin	52.4±2.6	18.0±0.9	30.0±1.5
Heptachlor epoxide	70.0±3.5	27.2±1.3	9.2±0.5
Endosulfan I	68.6±3.4	25.9±1.3	7.3±0.4
4,4'DDE	66.5±3.3	26.8±1.4	7.5±0.4
Endrin	63.0±3.1	31.6±1.6	5.4±0.3
4,4'DDD	70.6±3.5	16.8±0.8	12.6±0.6
Endosulfan II	54.0±2.7	18.7±0.9	27.3±1.3
4,4'DDT	60.4±3.0	24.6±1.2	15.0±0.7
Endrin aldehyde	74.5±3.7	19.5±0.9	6.0±0.3
Endosulfan sulfate	43.7±2.2	16.3±0.8	40.0±2.0
Dieldrin	40.0±2.0	28.3±1.4	31.7±1.6

Calibration plots

Standard pesticide solutions were prepared at five different concentration levels and determined by chromatography. A calibration plot was automatically constructed by the integrator software utilizing the aldrin peak as internal standard.

Table 2 Recovery (%) on solid phase C-18 by using increasing volumes of ethyl acetate.

COMPOUND	*0.50mL (%)*	*1.00mL (%)*	*2.00mL (%)*
α-BHC	96.2±4.8	3.8±0.2	—
γ-BHC	96.3±4.5	2.7±0.1	—
β-BHC	93.7±4.7	6.3±0.3	—
Heptachlor	95.8±4.8	4.2±0.2	—
δ-BHC	95.3±4.8	4.7±0.2	—
Aldrin	93.4±4.7	6.6±0.3	—
Heptachlor epoxide	93.5±4.7	6.5±0.3	—
Endosulfan I	94.2±4.6	5.8±0.2	—
4,4'DDE	90.9±4.8	4.5±0.2	—
Endrin	96.5±4.8	—	4.6±0.2
4,4'DDD	97.3±4.9	2.7±0.1	3.5±0.2
Endosulfan II	100.0±5.9	—	—
4,4'DDT	97.0±4.8	—	—
Endrin aldehyde	100.0±5.0	—	3.0±0.1
Endosulfan sulfate	95.4±4.8	4.6±0.2	—
Dieldrin	96.6±4.8	3.4±0.2	—

Table 3 Dependency between the recovery and the amount of solid phase XAD-2 used.

COMPOUND	*0.10g (%)*	*0.23g (%)*	*0.40g (%)*
α-BHC	55.5±2.0	91.2±4.6	92.3±4.4
γ-BHC	59.2±3.0	99.1±4.9	101.3±5.1
β-BHC	38.9±1.9	68.4±3.4	73.1±3.6
Heptachlor	21.2±1.1	46.4±3.3	55.9±2.8
δ-BHC	35.5±1.8	44.2±2.2	56.8±2.8
Aldrin	22.1±1.1	33.7±1.7	47.8±2.4
Heptachlor epoxide	51.4±2.6	102.6±5.1	101.1±5.1
Endosulfan I	57.0±2.9	92.9±4.6	94.6±4.7
4,4'DDE	28.3±1.9	67.9±3.4	74.0±3.7
Endrin	58.3±2.9	91.1±4.6	95.6±4.8
4,4'DDD	61.7±3.1	97.9±4.9	98.4±4.9
Endosulfan II	39.4±2.0	83.8±4.2	85.8±4.3
4,4'DDT	53.7±2.7	97.7±4.9	99.7±4.9
Endrin aldehyde	53.3±2.6	67.1±3.4	69.7±3.5
Endosulfan sulfate	36.1±1.8	91.0±4.6	93.0±4.7
Dieldrin	24.1±1.2	83.1±4.1	84.9±4.2

RESULTS AND DISCUSSION

The results described in Tables 1 and 2 show the recovery of the pesticides by using the solid phases XAD-2 and C-18. With the C-18 phase the recovery of all pesticides is near to quantitative with 1mL of ethyl acetate. It was, therefore, decided to use this solvent. For the XAD-2 resin, the best solvent elution was hexane[14], but the desorption process is lower and requires an equilibrium time of at least 15 min.

The results given in Tables 3 and 4 show the dependence between the recovery and the amount of solid phase used. The elution was carried out with 2mL of ethyl acetate for reverse

Table 4 Dependency between the recovery and the amount of solid phase C-18 used.

COMPOUND	*0.10g (%)*	*0.23g (%)*	*0.40g (%)*
α-BHC	82.8±4.1	75.7±3.8	73.1±3.6
γ-BHC	98.5±4.9	88.4±4.4	78.0±3.9
β-BHC	84.3±4.2	92.7±4.6	88.0±4.4
Heptachlor	39.3±2.0	33.8±1.7	41.6±2.0
δ-BHC	94.0±4.7	92.5±4.6	96.8±4.8
Aldrin	28.5±1.4	27.8±1.4	32.7±1.6
Heptachlor epoxide	79.0±3.9	78.9±3.9	82.3±4.1
Endosulfan I	80.0±4.0	82.2±4.1	80.2±4.0
4,4'DDE	77.0±3.8	100.0±5.0	99.7±4.9
Endrin	78.0±3.9	77.3±3.8	83.2±4.1
4,4'DDD	91.0±4.4	83.7±4.2	86.9±4.3
Endosulfan II	79.0±3.9	78.0±3.9	79.0±3.9
4,4'DDT	82.4±4.1	77.4±3.8	79.5±4.0
Endrin aldehyde	82.9±4.1	83.0±4.1	82.9±4.1
Endosulfan sulfate	81.2±4.0	89.3±4.5	91.1±4.6
Dieldrin	79.8±3.9	80.5±4.0	79.8±4.0

phase C-18 and with 5mL of hexane for XAD-2 resin. The amount of solid phase used for recovery is more remarkable in the case of XAD-2 resin, that has less active sites for unit surface area than the C-18 phase. The capacity factor for retention of organochlorine pesticides was 0.47mg/g for XAD-2 resin and 1.70mg/g for reverse phase C-18.

By comparing results obtained with both solid phases, it can be seen that there are some advantages when using the C-18 reversed phase. These advantages are: high recoveries for lower amount of phase, elution of organochlorine pesticides in a narrow band and no necessity of an equilibrium time. The stability of the C-18 toward elution solvents is better than for XAD-2 which after a long period in contact with an organic solvent looses its properties. On the other hand, the C-18 phase can be used repeatedly several times. For all these reasons, the C-18 solid phase is recommended for the routine use.

Tables 5 and 6 present the results obtained for recovery of pesticides in water by using both methodologies (solvent extraction and solid phase extraction). In both, the recoveries were higher than 70% for all the concentration range studied, except for heptachlor and aldrin. Aldrin gives lower recovery in concentrations smaller than 200ng/L when solvent extraction was used and heptachlor was just not recovered in both cases. This fact suggests the low affinity of the C-18 phase for them.

At 20ng/L concentration level the extraction with the C-18 phase is more adequate than solvent extraction, except for 4,4'DDD, endosulfan II, 4,4'DDT and endrin aldehyde which present best recoveries using solvent extraction. The loss of recovery on solvent extraction is probably due to the adsorption of pesticides in the walls of the glass extractor apparatus, to non-quantitative extract transfer steps, or to losses during solvent evaporation. Consequently, solid solvent extraction of the organochloride pesticides represents a useful alternative to the traditional solvent extraction-based methods[15].

Figure 1 shows the chromatograms of extracts from river water using solvent extraction and SPE with C-18 phase. It can be seen that the latter procedure provides chromatograms

Table 5 Recovery (%) of pesticides in water with solid phase C-18.

	CONCENTRATION OF PESTICIDES IN WATER (ng/L)			
COMPOUND	*20*	*200*	*2,000*	*20,000*
α-BHC	72.0±3.6	74.0±3.7	76.0±3.8	78.0±3.9
γ-BHC	88.0±4.4	91.0±4.2	77.0±3.9	77.0±3.8
β-BHC	84.0±4.2	78.0±3.9	72.0±3.7	75.0±3.7
Heptachlor	—	42.0±4.1	56.0±2.8	62.0±3.1
δ-BHC	85.0±4.3	77.0±3.8	74.0±3.7	81.0±4.0
Aldrin	38.0±1.9	47.0±4.3	73.0±3.6	83.0±4.1
Heptachlor epoxide	59.0±2.9	96.0±4.3	88.0±4.4	89.0±4.4
Endosulfan I	76.0±3.8	100.0±5.0	100.0±5.0	93.0±4.6
4,4'DDE	78.0±3.9	100.0±5.0	92.0±4.6	95.0±4.7
Endrin	73.0±3.8	100.0±5.0	90.0±4.5	92.0±4.6
4,4'DDD	86.0±4.3	100.0±5.0	96.0±4.3	96.0±4.8
Endosulfan II	91.0±4.5	100.0±5.0	102.0±5.1	105.0±5.2
4,4'DDT	87.0±4.4	100.0±5.0	96.0±4.8	107.0±5.3
Endrin aldeyde	98.0±4.9	101.0±5.0	101.0±5.1	103.0±5.1
Endosulfan sulfate	88.0±4.4	93.0±4.7	91.0±4.6	97.0±4.3
Diendrin	81.0±4.0	100.0±5.0	88.0±4.4	92.0±4.1

Table 6 Recovery (%) of pesticides in water with solvent extraction (dichloromethane).

	CONCENTRATION OF PESTICIDES IN WATER (ng/L)			
COMPOUND	*20*	*200*	*2,000*	*20,000*
α-BHC	82.0±4.1	76.0±3.8	76.0±3.8	69.0±3.4
γ-BHC	91.0±4.6	89.0±4.4	88.0±4.4	73.0±3.6
β-BHC	89.0±4.4	87.0±4.3	92.0±4.6	82.0±4.1
Heptachlor	—	—	34.0±1.7	45.0±2.2
δ-BHC	94.0±4.7	92.0±4.6	93.0±4.6	82.0±4.1
Aldrin	—	—	28.0±1.4	42.0±2.1
Heptachlor epoxide	84.0±4.2	76.0±3.8	79.0±3.8	65.0±3.3
Endosulfan I	86.0±4.3	79.0±3.9	82.0±4.1	70.0±3.5
4,4'DDE	100.0±5.0	99.0±5.0	100.0±5.0	73.0±3.6
Endrin	79.0±3.9	74.0±3.7	77.0±3.8	62.0±3.1
4,4'DDD	80.0±4.0	82.0±4.1	83.0±4.1	71.0±3.5
Endosulfan II	79.0±3.9	76.0±3.8	78.0±3.9	69.0±3.4
4,4'DDT	72.0±3.6	66.0±3.3	77.0±3.8	71.0±3.5
Endrin aldeyde	87.0±4.3	84.0±4.2	83.0±4.1	78.0±3.6
Endosulfan sulfate	93.0±4.2	88.0±4.4	89.0±4.4	79.0±3.9
Dieldrin	84.0±4.1	83.0±4.1	80.0±4.0	76.0±3.8

with less background or interfering peaks. Comparing the relative retention times for the peaks with respect to aldrin, we can identify three BHC isomers: α-BHC, β-BHC and γ-BHC, in concentrations lower than 50ng/L.

CONCLUSIONS

Both extraction methods present high recovery for organochlorine pesticides. They can determine a concentration range of about 2ng/L, except for heptachlor and aldrin.

The advantages of using SPE with C-18 phase are: the use of inexpensive devices, short extraction time (about 15 min), less solvent used thereby cutting costs and decreasing waste accumulation. No solvent removal steps are necessary, thus saving considerable time and further increasing safety.

The method using C-18 phase is more adequate for extraction at trace levels in tap and drinking waters where the amount of other solutes is lower. However, the method of solvent extraction is more adequate for extraction in waste water or water with high levels of organic matter.

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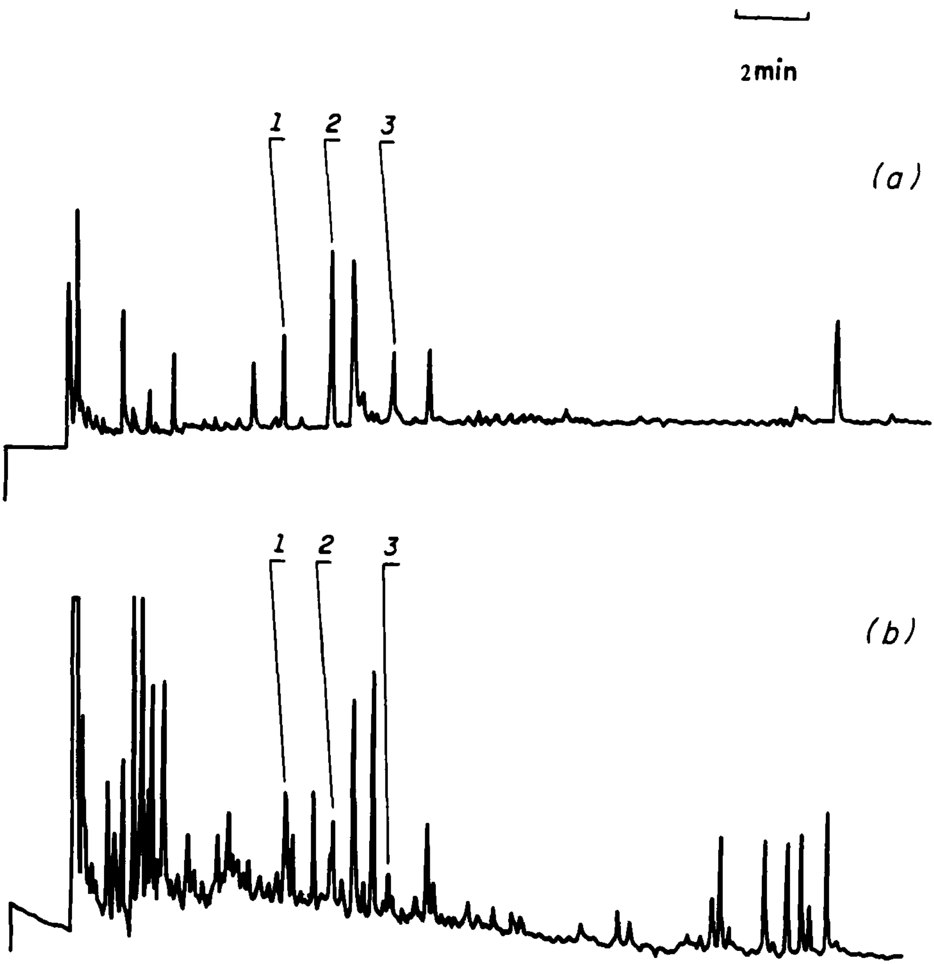

Figure 1 Chromatograms of a river water extract, (a) solid phase C-18 extraction and (b) solvent extraction. Identified peaks: 1. α-BHC, 2. β-BHC and 3. δ-BHC.

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