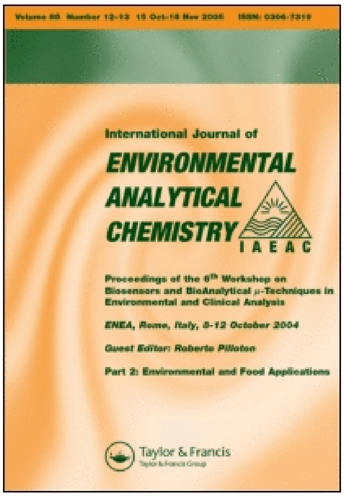

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Evaluation of Combined Flow Injection–High Performance Liquid Chromatography for the Determination of Three Organophosphorus Pesticides in Liquid Wastes

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The separation and analysis of a mixture of diazinon, azinphos-methyl and fenthion have been studied using HPLC with UV detector. In order to carry out this analysis in a simple and rapid way a system of flow injection (FIA) has been connected to the HPLC apparatus. This combined technique has shown great possibilities in the analysis of pesticides.

The removal of pesticides from liquid wastes has been studied by means of adsorption on activated carbon using this technique.

KEY WORDS: HPLC, FIA, organophosphorous pesticides, activated carbon, adsorption.

INTRODUCTION

A recent study[1] concerning pesticide factories in Spain has indicated that the analysis and treatment of waste water from these factories is

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not carried out very often. In this context, analysis and removal of organophosphorus pesticides from waste water are of great importance.

In this study three organophosphorus pesticides widely used in Spain:[1] diazinon, azinphos methyl and fenthion have been chosen.

One analytical technique especially suited to pesticide analysis is high performance liquid chromatography (HPLC) with UV absorbance detector.[2,3] In order to analyze these pesticides in a simple and rapid way a system of flow injection (FIA)[4] has been connected to the HPLC apparatus. Different FIA methods have been developed to solve analytical problems. In this work two operation modes have been tested: (i) normal FIA, where a carrier is used to transport the sample to the HPLC injector and (ii) completely continuous, where the sample solution is transported directly to the HPLC injector.[5]

The normal FIA method has been used to study the removal of pesticides from waste water by means of adsorption through activated carbon. A great variety of solutions containing phenols, chlorinated hydrocarbon and organophosphorus pesticides have been treated by carbon adsorption in the last years. This system appears to be the most effective and least expensive for removal of pesticides.[6-8]

In the present work, we try to confirm these observations and to prove that the FIA–HPLC is a suitable technique for the analysis of pesticides.

EXPERIMENTAL

Materials

Organophosphorus pesticides (azinphos methyl, diazinon and fenthion) were obtained from Bayer. Standard solutions were prepared by accurately weighing each pesticides into a 100 ml volumetric flask and diluting to volume with methanol.

Solvents were HPLC grade (Scharlau) and distilled water was microfiltered by Millipore filters (0.45 μm).

F-400 granular activated carbon (Panreac) with a particle size between 0.5 and 1 mm was used as the adsorbent in this study.

Instrumentation

High performance liquid chromatography The HPLC system consisted of a Spectra-Physics Model SP-8700 solvent delivery unit, an injection valve (Rheodyne) with a 10 μl sample loop, an UV–Vis detector (SP-8440), an integrator (SP-4270) and a Knauer Nucleosil-C18 column (120 × 4 mm i.d.). The wavelength used was 220 nm. The mobile phase was 60:40 acetonitrile/water. The flow rate was set at 1 ml/min. Quantitative analyses were made using peak areas.

Under these conditions, the retention time of each pesticide was: diazinon (1.3 min), azinphos methyl (3.0 min) and fenthion (5.0 min).

Flow injection analysis The FIA system consisted of a Watson-Marlow (202 U/AA4) peristaltic pump and an Omnifit 100 μl injection valve. Teflon tubing (0.5 mm i.d.) was used to connect the FIA to the HPLC. Silicone tubing (1.5–1.65 mm i.d.) was used as a column for the activated carbon.

FIA techniques

1) Completely continuous In this technique (Figure 1A) the main carrier is the standard solution. The injection valve of the FIA is not used. The solution is pumped and flows continuously through the injection valve of the HPLC apparatus and it can be injected at any time. The pesticide concentration can be determined without interruption.

2) Normal FIA In this technique (Figure 1B) the carrier is distilled water and flows continuously through the HPLC apparatus. The standard solution is also pumped to the FIA injector. A well-defined volume of this standard solution is injected into the carrier stream at any time. The sample solution takes a certain time from FIA to HPLC injector. This time is a function of teflon tube length and FIA flow rate and should be perfectly determined in order to always inject the same amount of the sample through the HPLC column. Tube length has been kept constant (122 × 0.5 mm i.d.) and the time has been calculated for several flow rates.

This operation mode can be used to analyze samples which have been treated before being injected into the carrier. One possibility is

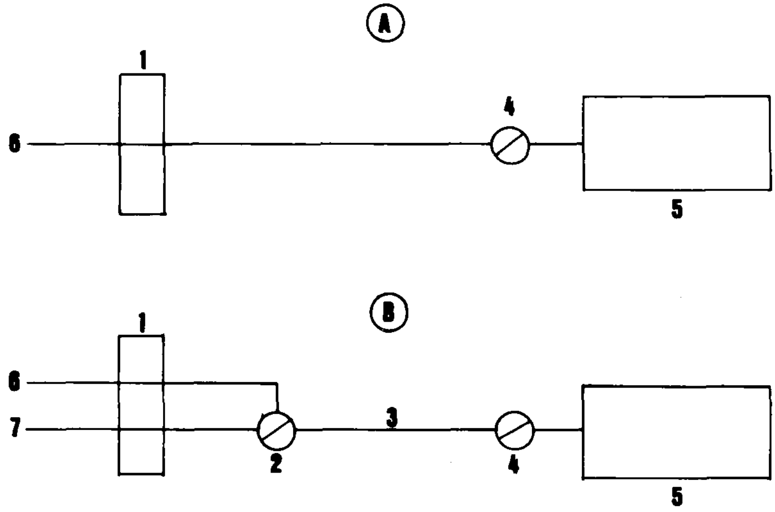

Figure 1 Manifolds for the determination of pesticides. (A) continuous, (B) normal. (1) peristaltic pump, (2) FIA injector, (3) teflon tube, (4) HPLC injector, (5) HPLC-UV detector, (6) sample, (7) carrier, W: waste.

to recirculate this sample through an ion exchange or an adsorption column. Figure 2 shows this recirculation mode. In this work, this mode has been used to study the removal of pesticides from water by adsorption on activated carbon. Measured amounts of the three pesticides are poured into a flask containing distilled water. This standard solution is pumped to the FIA injector in load position, thus this solution circulates through the activated carbon column and returns to the reservoir. The initial concentration in the reservoir was 10 mg/L for each pesticide. The relationship between mass of activated carbon and sample volume was 10 mg/mL. The pesticide concentration at any time can be obtained by injecting the sample into the carrier and observing the HPLC chromatograms.

RESULTS AND DISCUSSIONS

The detection limit was 0.5 mg/L in all cases.

Figure 3 shows some chromatograms of the same standard solution obtained with the completely continuous mode. It can be observed that the reproducibility of this mode is really good. Thus it can be useful for routine control of pesticides in industrial waste waters.

Figure 4 shows the chromatograms obtained by using the normal FIA mode for three different FIA flow rates. It can be observed that there are no response differences, so it is possible to select any of these conditions. In order to reduce consumption of standard solution the flow rate was restricted to 0.62 ml/min.

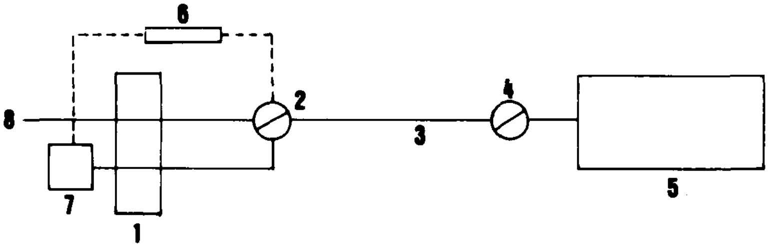

Figure 2 Manifold showing the recirculation mode. (1) peristaltic pump, (2) FIA injector, (3) teflon tube, (4) HPLC injector, (5) HPLC–UV detector, (6) Activated carbon column, (7) flask containing pesticide solution, (8) carrier, W: waste.

The chromatograms of both figures show narrow and symmetrical peaks. This means that there is no sample dispersion,[9] thus the FIA–HPLC technique allows to analyze these pesticides with the same sensibility as in conventional HPLC, but with an easier sample handling.

Figure 5 shows the decrease of pesticide concentration as a function of time. It can be observed that the adsorption percentage is different for each pesticide (diazinon 55%, azinphos methyl 60% and fenthion more than 90%). This can be related to the polarity of these compounds and thus their solubility in water (diazinon 40 mg/L, azinphos methyl 33 mg/L and fenthion 2 mg/L)[10] as there is a competition between adsorption and solubility, i.e. a higher solubility involves a lower adsorption.

Kobylinsky *et al.*[7] define the efficiency of the activated carbon column by means of an efficiency factor (k) by using a mass balance of the system.

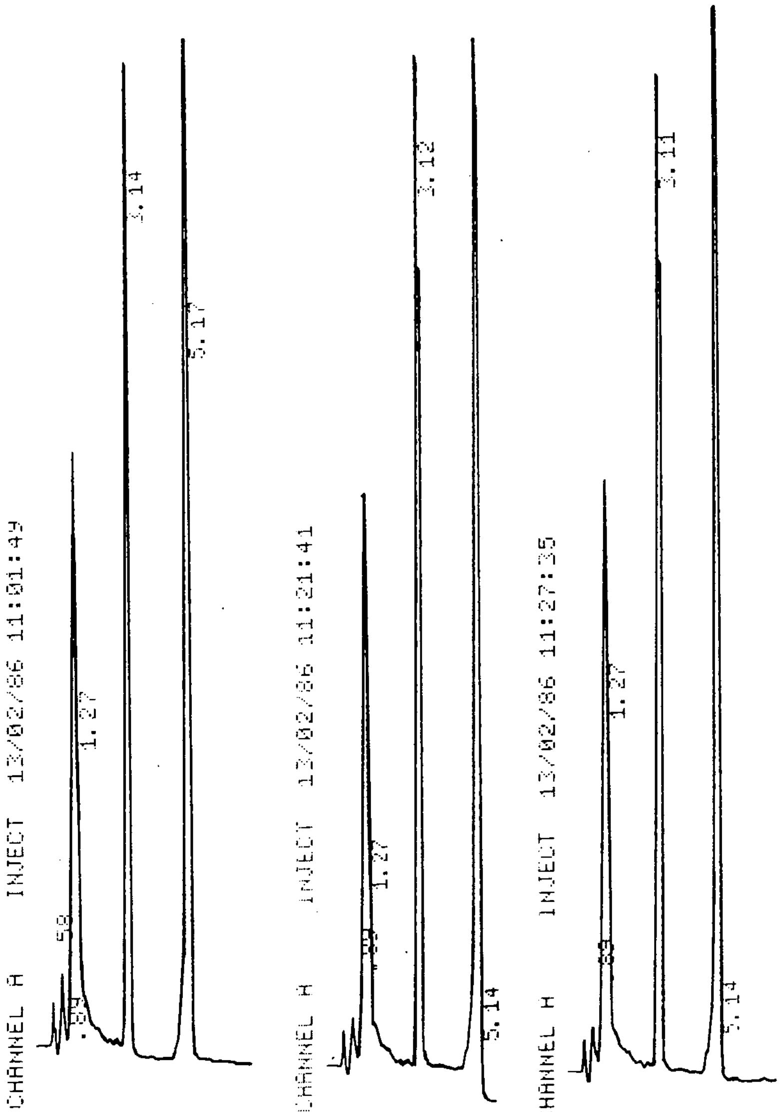

Figure 3 Chromatograms obtained by using completely continuous FIA.

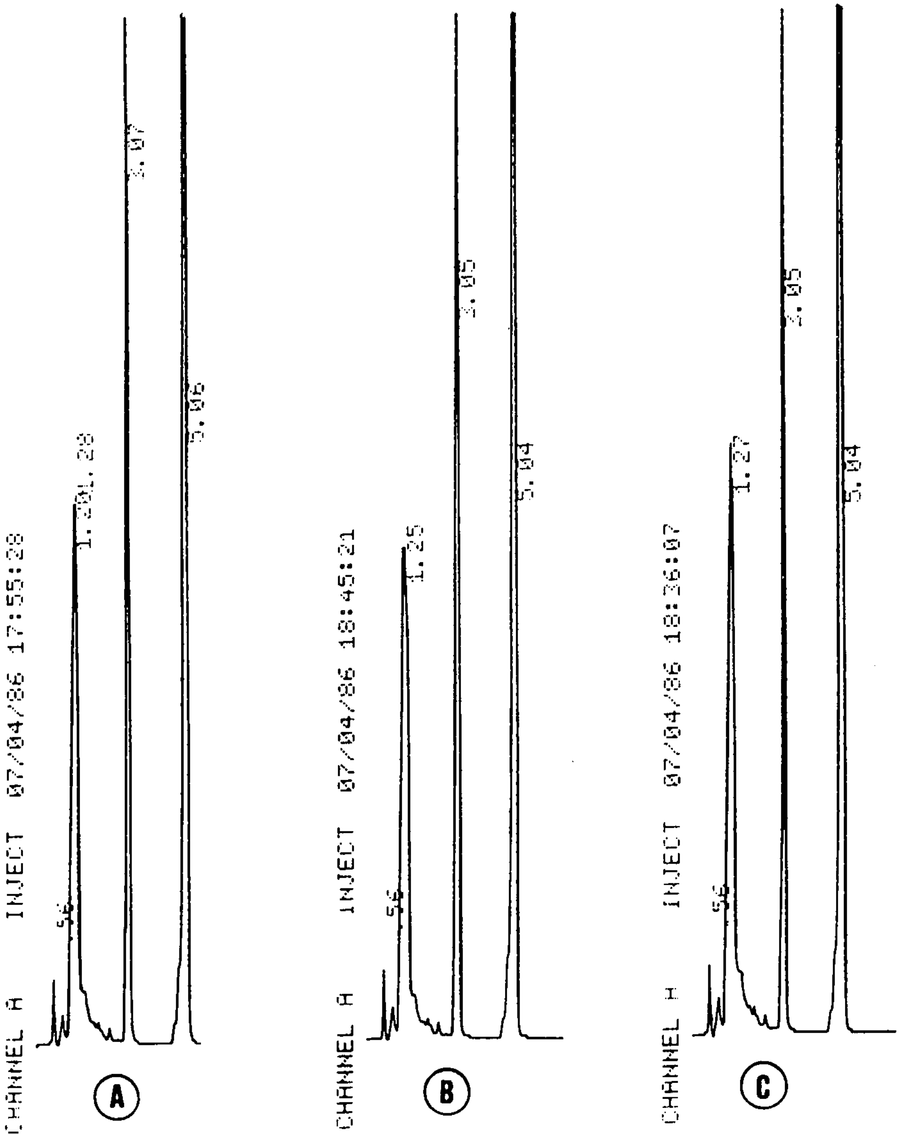

Figure 4 Chromatograms obtained by using normal FIA at different flow rates. (A) 0.62, (B) 1.3 and (C) 2 ml min^{-1}.

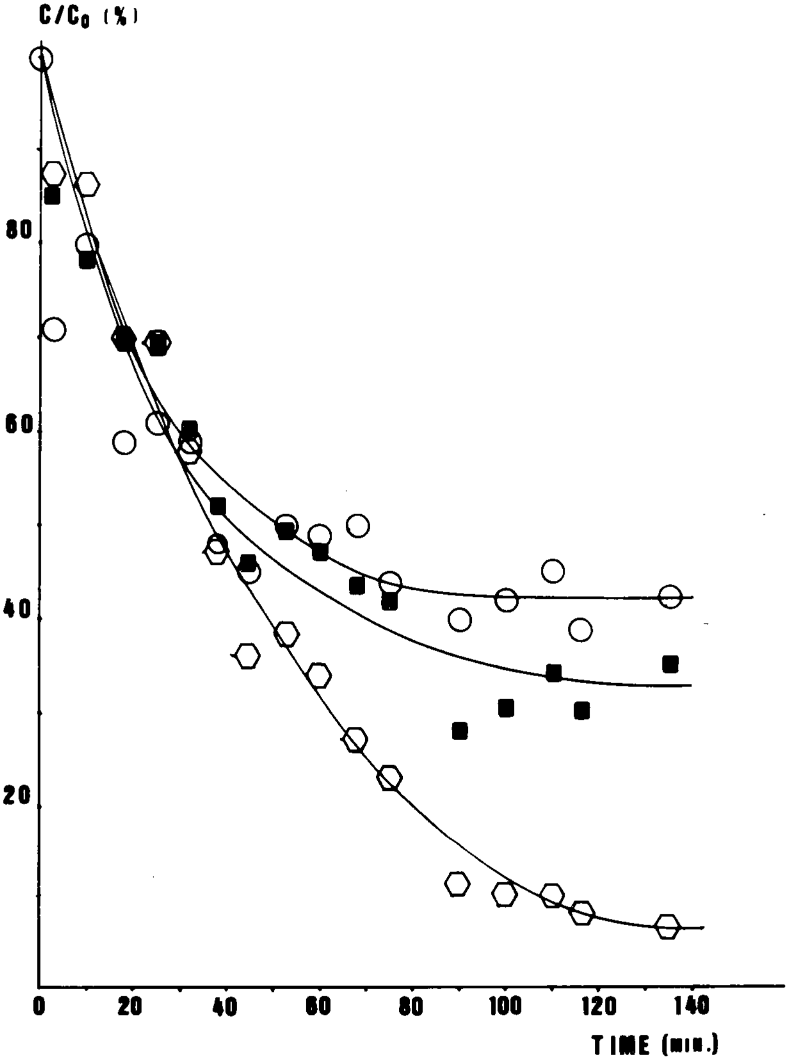

Figure 5 Concentration percentage *vs* time.

Diazinon ○
Azinphos-Me ■
Fenthion ⬡

According to the following equation:

$$\log C/C_0 = -[kq/2.303\,V]t$$

Where q: FIA flow rate (ml min^{-1})
V: sample volume (ml)
C: concentration at any time (mg/L)
C_0: initial concentration (mg/L)
t: time (min)

Plotting $\log C/C_0$ *vs* t, the efficiency factor can be obtained as the slope of the straight lines above the saturated time as shown in Figure 6. The k-values are: diazinon 0.24, azinphos methyl 0.20 and fenthion 0.35.

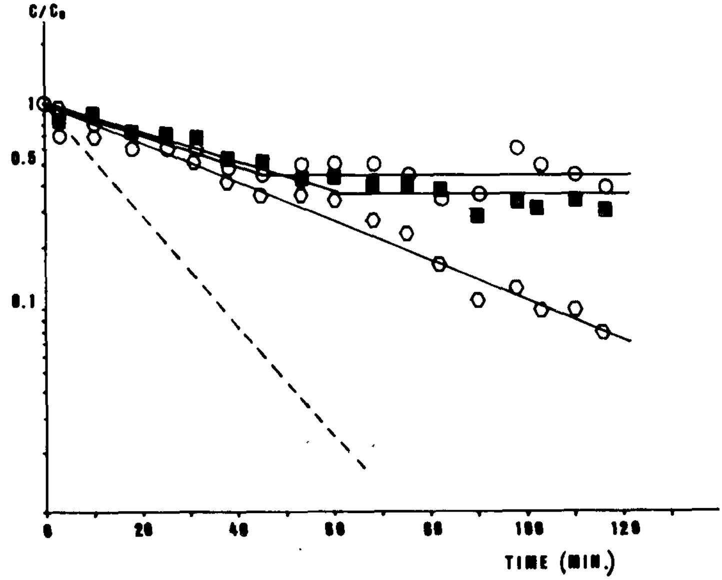

Figure 6 Semilogarithmic plot of the pesticide concentration *vs* time. Dashed line corresponds to $k = 1$.
Diazinon ○
Azinphos-Me ■
Fenthion ○

The efficiency factor can be improved by changing different parameters such as flow rate, relationship between volume and carbon mass, etc. These influences are being studied at the moment.

In this work, it has been proved that the combined FIA–HPLC is a simple and versatile technique because it facilitates the sample handling and can be used in routine analysis, as well as to study pesticide reactivity e.g. adsorption on activated carbon in this case.

Acknowledgement

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