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In-tube solid-phase microextraction-capillary liquid chromatography as a solution for the screening analysis of organophosphorus pesticides in untreated environmental water samples

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Abstract

This paper describes a method for the selective screening of organophosphorus pesticides in water. In-tube solid-phase microextraction (SPME) in an open capillary column coupled to capillary liquid chromatography (LC) with UV detection has been used to effect preconcentration, separation and detection of the analytes in the same assembly. For in-tube SPME two capillary columns of the same length and different internal diameters and coating thicknesses have been tested and compared, a 30 cm × 0.25 mm I.D., 0.25 μm thickness coating column, and a 30 cm × 0.1 mm I.D., 0.1 μm of coating thickness column. In both columns the coating was 95% dimethylpolysiloxane (PDMS)-5% diphenylpolysiloxane. The proposed methodology provided limits of detections (LODs) for the tested organophosphorus pesticides in the 0.1–10 μg/L range, whereas the direct injection of the samples onto the capillary LC system provided LODs in the 50–1000 μg/L range. The sensitivity of the proposed in-tube SPME-capillary LC method is adequate to monitorize the analyte levels in drinking water. Several triazines, polycyclic aromatic hydrocarbons (PAHs), nonylphenol, organochloride pesticides or polybrominated diphenyl ethers (PBDEs) have been evaluated as possible interferents. The reliability of the described method is demonstrated by analysing different real water samples.

Keywords: In-tube solid-phase microextraction; Capillary liquid chromatography; Screening analysis; Organophosphorous; Water samples

1. Introduction

Over the past decades the analysis of compounds used in agriculture to increase crop production such as organophosphorus pesticides has become an important topic because, owing to their persistence and water solubility, they constitute an important source of environmental contamination [1]. There is a real need for developing analytical methods to detect these compounds at low concentration levels, as they are included in the list of priority pollutants.

Most analytical methods for pesticide analysis are based on gas chromatography (GC) [2] and on liquid chromatography (LC) [3]. In the former case, detection typically entails nitrogen-phosphorous detection [4], electron-capture detection [5], mass spectrometry (MS) [6] or flame photometric detection [7]. In LC-based methods detection is usually accomplished by UV [8], UV-diode-array [9], electrochemical [10] or fluorescence [11] detection. Regardless of the separation and detection methods, analyte preconcentration and cleanup using some kind of extraction is necessary to achieve adequate sensitivity and selectivity. The type of extraction depends on the complexity of the matrix and on the characteristics of the target compounds. Off-line procedures, such as liquid–liquid extraction (LLE) [12], solid-phase extraction (SPE) [13] or ion exchange [14] are time consuming, labour-intensive, and require large volumes of sample and organic solvents. Nowadays, the general tendency is to simplify the sample preparation. In the last years, solid-phase microextraction (SPME) has emerged as a very attractive alternative because it is a solvent-free technique in which extraction and preconcentration can be carried out simultaneously and directly from aqueous samples [15], or from the headspace above them [16]. Other recent efforts have been focused on the miniaturisation of LLE, or on the development of alternatives such as the single-drop microextraction (SDME) [17] and the micro solid–liquid extraction with focused ultrasound (μFUSLE) [18].

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On-line extraction techniques with sorbents are very useful because the whole extracted analytes can be transferred to the analytical instrument [19]. In this sense, in-tube SPME appears as one of the most useful approaches for sample preparation. In-tube SPME is a mode of SPME which typically uses a GC capillary column with a proper coating on the internal surface to extract the analytes [20–22]. There are two fundamental approaches to perform in-tube SPME, passive or static and active or dynamic. In the former mode the capillary is immersed into the sample, the analytes are extracted into the coating by diffusion, and then desorbed by introducing a moving stream of mobile phase or static desorption solvent [23,24]. In the dynamic method the analytes are extracted by flushing the samples through the capillary. This can be easily done by programming an autosampler to pass the sample in and out of the extraction capillary until the equilibrium or until a suitable extraction level is reached [25,26]. Alternatively, samples can be manually injected using the extraction capillary as an injection loop [27,28]. In such a way, the sample preparation can be effected on-line, and the sample size as well as the consumption of solvents can be substantially reduced.

Another potential advantage of in-tube SPME is that it can be easily coupled to miniaturized chromatographic systems thus enhancing the sensitivity. This has been illustrated for triazines in a recent paper [28]. The limits of detections (LODs) obtained for such pesticides were about 250–500 times lower than those achieved by using on-fibre SPME combined with conventional LC. In spite of its inherent advantages the application of in-tube SPME is still limited. To date, according to the Web of Science database the in-tube SPME based method amount about 2% of the total papers on SPME, and only in a few of such applications in-tube SPME is coupled to capillary LC [29,30].

In the present study, a method has been developed for the determination of organophosphorus pesticides in water based on the employment of in-tube SPME coupled to a capillary chromatographic LC system. The reliability of the method is demonstrated through the analysis of several real water samples. These water samples were obtained from an area with great agricultural activity, the mean crops being citrus, and thus organophosphorus compounds are commonly used.

2. Experimental

2.1. Apparatus and chromatographic conditions

The capillary chromatographic system used consisted of a LC capillary pump (Agilent 1100 Series, Waldbronn, Germany) equipped with a high-pressure six-port injection valve (Rheodyne model 7725), a GC capillary column which was used as an injection loop. Capillary connections were facilitated by the use of a 2.5 cm sleeve of 1/16 in. polyether ether ketone (PEEK) tubing at each end of the GC capillary. 1/16 in. PEEK nuts and ferrules were used to complete the connections. Another injection valve with an internal loop of 2 μL was used for direct injection of compounds. A UV detector (Hewlett-Packard, 1046 Series) equipped with a 1 μL micro flow cell was used. Details of the analytical column and mobile phases used are given in the following. In some assays a fluorescence detector (Agilent, 1100 Series) equipped with a 8 μL flow cell was connected in series with the UV detector. All the components of the system were linked with fused silica tubing (550 mm × 50 μm I.D., supplied by Agilent). The UV detector operated at 230 nm, whereas the fluorescence detector was programmed to collect the signal at variable excitation and emission wavelengths (Table 1). The detectors were coupled to a data system (Agilent, HPLC ChemStation) for data acquisition and calculation.

Table 1
Programme of excitation and emission wavelengths for the fluorescence detector

Time (min)	Excitation wavelength (nm)	Emission wavelength (nm)
0	275	300
15	280	330
25	250	375
29	280	420
35	290	430
42	300	500
47	290	410

2.2. Reagents and solutions

All the reagents were of analytical grade. Parathion, fenitrothion, chlorfenvinphos, fenthion, chlorpyriphos, trifluraline and simazine, atrazine, propazine, ametryn, prometryn, terbutryn, were obtained from Sigma (St. Louis, MO, USA). Fensulfothion, fenamiphos, fonofos, malathion, nonylphenol, naphthalene, anthracene, fluoranthrene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indene[1,2,3-cd]pyrene and benzo[ghi]perylene, endosulfan, dieldrin, DDD, alachlor, hexachlorobenzene, DDT, isodrin, DDE, lindane, aldrin, BDE-47, BDE-100 and BDE-99 were obtained from Dr. Ehrenstorfer (Augsburg, Germany). Acetonitrile and methanol were of HPLC grade (Scharlau, Barcelona, Spain).

Stock standard solutions of organophosphorus pesticides (1 μg/mL each), triazines (10 μg/mL each), polycyclic aromatic hydrocarbons (PAHs) (1 μg/mL each prepared from a 10 μg/mL stock solution in acetonitrile), organochloride pesticides (1 μg/mL each), polybrominated diphenyl ethers (PBDEs) (1 μg/mL each) and nonylphenol (1 μg/mL) were prepared in water. Working solutions of these compounds were prepared by dilution of the stock solutions with water. Water was deionised and filtered through 0.45 μm nylon membranes (Teknokroma, Barcelona, Spain). All solutions were stored in the dark at 2 °C.

2.3. Columns and mobile phases

A Zorbax SB C_{18} (150 mm × 0.5 mm I.D., 5 μm particle diameter) column (Agilent) was used for the separation of the analytes. The mobile-phase was a mixture of acetonitrile–water in gradient elution mode at a flow rate of 10 μL/min. The eluent was 100% water during the 0–0.5 min time interval. Then, the acetonitrile content was increased up to 50% at min 2. This per-