

Optimization of a technique of solid-phase micro-extraction and capillary gas chromatography with electron capture detection for the determination of nine organochlorine pesticides in drinking water

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Summary — Nine organochlorine pesticides have been extracted from aqueous samples by SPME using a 7 μm fibre of polydimethylsiloxane. The method was evaluated with respect to the time of fibre exposure, limit of detection (LOD) and linearity and precision. The limits of detection depend on the compounds and vary between 0.04 and 0.22 $\mu\text{g.L}^{-1}$ for the concentration range studied between 0.05 and 1 $\mu\text{g.L}^{-1}$, with a coefficient of correlation usually > 0.97 . For the organochlorine pesticides at a concentration of 0.3 $\mu\text{g.L}^{-1}$, the standard deviation varies from 4 to 23% depending on the compound. The recoveries obtained were 90–105%.

Résumé — Optimisation d'une technique de micro-extraction en phase solide et de chromatographie capillaire en phase gazeuse avec détection de capture électronique pour la détermination de neuf pesticides dans l'eau potable. Neuf pesticides organochlorés ont été extraits des échantillons aqueux par SPME en utilisant des fibres de 7 μm de diamètre en polydiméthylsiloxane. La méthode a été évaluée en tenant compte du temps d'exposition, de la limite de détection, de la linéarité et de la précision. Les limites de détection dépendent des composés et varient entre 0,04 et 0,22 $\mu\text{g.L}^{-1}$ pour un intervalle de concentrations étudiées comprises entre 0,05 et 1 $\mu\text{g.L}^{-1}$, avec des coefficients de corrélation généralement > 0.97 . Pour les pesticides organochlorés dont la concentration est de 0,3 $\mu\text{g.L}^{-1}$, l'écart-type varie de 4 à 23 % suivant les composés. Les taux de récupération obtenus étaient de 90 à 105 %.

solid-phase micro extraction (SPME) / organochlorine pesticides (OCPs) / capillary gas chromatography (CGC)

Introduction

Pesticides may lead to an extensive pollution of surface and ground water as well as soil. As a result of the low biological activity in ground water, these compounds may persist for several years. Organochlorine pesticides (OCPs) have relatively low solubilities in water, are fat soluble and resistant to metabolism, thus posing a threat to the environment because of their persistence and capacity to bioaccumulate [1]. The organochlorine pesticides constitute a serious problem because of their toxicity revealed in mammals. When absorbed by an organism, some of them are not immediately metabolized but are stored in fat tissue [2]. They have also been found in human milk and human blood, where they are a risk factor [3]. It is difficult to predict the risks from the presence of micro quantities of these compounds in drinking water and also to establish their influence on the incidence of cancer in man. The carcinogenic action of some of these compounds has been observed in animals, but we must be careful when transposing these results to man. In the 1960s the tendency for bioaccumulation of these compounds was observed. The researchers found higher levels of organochlorine pesticides in predators than in their preys [2]. They are easily spread in the aquatic environment from superficial to ground water [4]. The European Community Directive set a maximum permissible level of 0.1 $\mu\text{g.L}^{-1}$ per pesticide [5, 6]. The sample was extracted with a fused silica fibre coated with an immobilized stationary phase of polydimethylsiloxane. After the extraction the fibre was transferred into the hot injector of the gas chromatograph where the organic compounds were thermally desorbed from the stationary phase. The method is discussed in detail in the *Materials and methods*. SPME is very simple, inexpensive and can be automated [7, 8]. It requires only a small amount of sample and no organic solvent. This method presents a great sensitivity and reproducibility [9, 10]. Indeed, SPME retains the advantages of SPE in terms of its simplicity, low cost, easy

automation and on-line sampling, whilst eliminating its disadvantages, such as plugging and the use of organic solvents. Special devices are not necessary for desorption, and it is also not necessary to make changes in the chromatographic system. With this method, the extraction and concentration during sample preparation are joined together in a simple process step. The total amount of extract obtained is used for the determination by CGC with ECD, in contrast to the conventional extraction methods [11–13]. The objectives of this work were to compare the advantages of this new solid-phase extraction method, such as simplicity, low cost, small sample volume, speed, good precision and sensitivity to routine analysis in environmental laboratories [14–16] with conventional methods. We have also tried for the first time to use this method for the determination of hexachlorobutadiene (HCB) and isodrine. SPME is a completely solvent-free technique that is harmless to the environment. Also, small sample volume is required (approximately 1–2 mL), which constitutes an important feature since it simplifies the collection protocol, avoiding large volume manipulation of water, therefore making transportation easier. The same fibre can be used for the extraction of a large number of drinking water samples (about 100) without any change in its performance, thereby allowing low cost analysis.

Materials and methods

Chemicals

Hexachlorobutadiene, hexachlorobenzene, lindane, aldrine, 4,4'-DDE, dieldrine, 4,4'-DDD and 4,4'-DDT were purchased from Supelco, Bellefonte, USA. Isodrine was purchased from Greyhound, Birkenhead, UK. They were mostly of $> 98\%$ purity and used as received; *n*-hexane and methanol were from Merck, Darmstadt, Germany, and were of trace analysis quality. The water was of HPLC grade.

Water type and composition

Several water samples were used for this study. All of them were taken from the Porto Municipality. The main characteristics were: pH 7.3;

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