Available online at www.sciencedirect.com
ScienceDirect
Talanta 72 (2007) 1833–1841
Talanta
www.elsevier.com/locate/talanta

Determination of organochlorine pesticides in ground water samples using solid-phase microextraction by gas chromatography-electron capture detection

Jorge Luiz Raposo Júnior, Nilva Ré-Poppi *

Departamento de Química, Centro de Ciências Exatas e Tecnologia, UFMS, CP 549, 79070-900 Campo Grande, MS, Brazil

Received 25 October 2006; received in revised form 12 February 2007; accepted 13 February 2007
Available online 22 February 2007

Abstract

A direct immersion solid-phase microextraction coupled with gas chromatography-electron capture detection (SPME-GC-ECD) method was optimized and validated for the quantitative determination of 18 organochlorine pesticides in ground water. Ionic strength, stirring speed, adsorption and desorption time and pH were some of the parameters investigated in order to select the optimum conditions for SPME with a 50/30 DVB/CAR/PDMS fiber coating. The SPME-GC/ECD method showed good linear response below 10 ng L^{-1} with R^2 values in the range of 0.9950–0.9997. The repeatability of the measurements were lower than 10%. Values of relative recoveries located within the acceptable range (80–120%). Limits of quantification (LOQ) from 4.5×10^{-3} to 1.5 ng L^{-1} were obtained. On average 8 organochlorines were found per sample, even so all the 18 organochlorines were quantified among them. Substances such as endrin ketone, γ-BHC and β-BHC were the pesticides determined in larger concentration (0.06–305 ng L^{-1}), while methoxychlor and aldrin in smaller amounts (0.151–1.55 ng L^{-1}). Measured levels of organochlorine pesticides were above the limits established by Brazilian regulations.

Keywords: Solid-phase microextraction; Organochlorine pesticides; Water analysis; GC-ECD; Multivariated analysis

1. Introduction

Organochlorine pesticides are known to be one of the most persistent organic micropollutants present in the environment and tend to accumulate in organisms [1]. The hazardous nature of organochlorine is a result of their toxicity in combination with high chemical and biological stability and a high degree of lipophilicity [2]. These aforementioned characteristics make the organochlorine pesticides prone to bioaccumulation along the food chain involving a wide range of trophic levels [3].

The organochlorine pesticides have been used intensely in agriculture, as a consequence, most of these pesticides have been restricted or even banned in many countries. In Brazil, organochlorines such as aldrin, endrin, heptachlor, lindane and others were the organochlorines most employed from 1950 to 1970. Therefore, the determination of pesticides in water, plants, soils, foodstuff is of major importance for human health protection and environmental control.

Most determinations of organochlorine pesticides were based on chromatographic methods with various detections, such as flame ionization detection (FID) [4], mass spectrometric (MS) detection [5–7] and electron-capture detection (ECD) [8–10]. MS detection currently produces lower limits of detection for many trace compounds, but ECD is still a widely used powerful tool in environmental analysis, especially for screening purposes where most of the samples do not contain these pesticides [9].

Usually, an extraction procedure is performed prior to GC analysis and a solid-phase microextraction (SPME), a solvent-free technique initially reported in the literature [11], has proven to be suitable for environmental trace analysis and a powerful alternative to the classic extraction approaches. The SPME is a novel analytical technique, able to integrate extraction, concentration and sample introduction in a single step [12]. Thus, it has proved to offer a significantly more rapid, simple and easier to automate extraction approach than traditional extraction techniques [13,14]. The SPME technique employs a coated

* Corresponding author. Tel.: +55 67 33453549; fax: +55 67 33453552.
E-mail address: npoppi@nin.ufms.br (N. Ré-Poppi).

0039-9140/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2007.02.024

fiber to extract and concentrate the analytes which are then thermally desorbed by hot injection of a gas chromatograph for analysis.

In the present study, the SPME-GC-ECD method was optimized and applied to determine the 18 organochlorine pesticides concentration in ground water in the district of Culturama (Fátima do Sul, Brazil).

2. Experimental

2.1. Sampling site characteristics

Culturama, rural zone of Fátima do Sul, is located at 22°18′16″S and 54°20′39″W (mid-west of Brazil) and has a population of 3400 inhabitants. The district is at an altitude of 352 m and it is inside in the Fátima do Sul territorial unit [15]. The annual average temperature is 28 °C: the maximum is around 35–36 °C and the minimum is 10–12 °C. The annual pluvial precipitation varies from 1400 to 1600 mm, with water surplus from October to May and deficiency from June to September. The vegetation of Culturama is characterized by low vegetation, known as "Campos de Vacaria" (Vacaria Fields), typical of the Cerrado formed predominantly of herbaceous stratum and some small bush species. Agriculture is the economic activity in the district, characterized mainly by the presence of small rural properties (on average 400,000 m^2), with emphasis on the temporary production of cotton, peanuts, rice, beans, soya and maize. The geographical location of Fátima do Sul is shown in Fig. 1.

2.2. Standards and reagents

Deionized water, produced using a Milli-Q water purification system from Millipore (Bedford, MA, USA), was used to prepare all aqueous solutions. The methanol (chromatography grade) was purchased from Merck (Darmstadt, Germany). The methanol and the deionized water were tested as procedure blanks to verify possible contamination. The analytical standard of the organochlorine pesticide mixture contained aldrin, α-BHC, β-BHC, δ-BHC, γ-BHC, dieldrin, endosulfan I, endosulfan II, endosulfan sulfate, endrin, endrin aldehyde, endrin ketone, heptachlor, heptachlor epoxide, metoxychlor, 4,4′-DDD, 4,4′-DDT and 4,4′-DDE which purchased from Supelco (Bellefonte, PA, USA) with >98% purity. Pentachloronitrobenzene (99%) from Aldrich (Germany) was used as an internal standard (I.S.). A stock solution containing all the analytes (80 mg L^{-1}) was prepared by dissolving 1.0 mL of standard solution (2000 mg L^{-1}) in a 25 mL volumetric flask with methanol and stored at −4 °C. A fresh 100, 10 or 1 ng L^{-1} standard solution containing the 18 pesticides was prepared every 3 weeks and stored at 4 °C. The acetic acid and sodium hidroxide used for pH adjustment were from Merck, as were the sodium chloride and sodium sulfate used for ionic strength.

2.3. SPME fiber

The solid-phase microextraction (SPME) fiber used was 50/30 μm of DVB-CAR-PDMS *StableFlex fiber* for manual extraction with a holder assembly, purchased from Supelco (Bellefonte). Before the first use, the fiber was conditioned as recommended by the manufacturer using the hot injector at 260 °C for 240 min. The column oven and detector were at 200 and 300 °C, respectively. After this time, the fiber was removed from the hot injector and the column oven temperature was elevated to 260 °C (5 °C min^{-1}) to clean it. No additional conditioning was considered for the next analysis, because the results obtained with several desorption blanks did not show carry over.

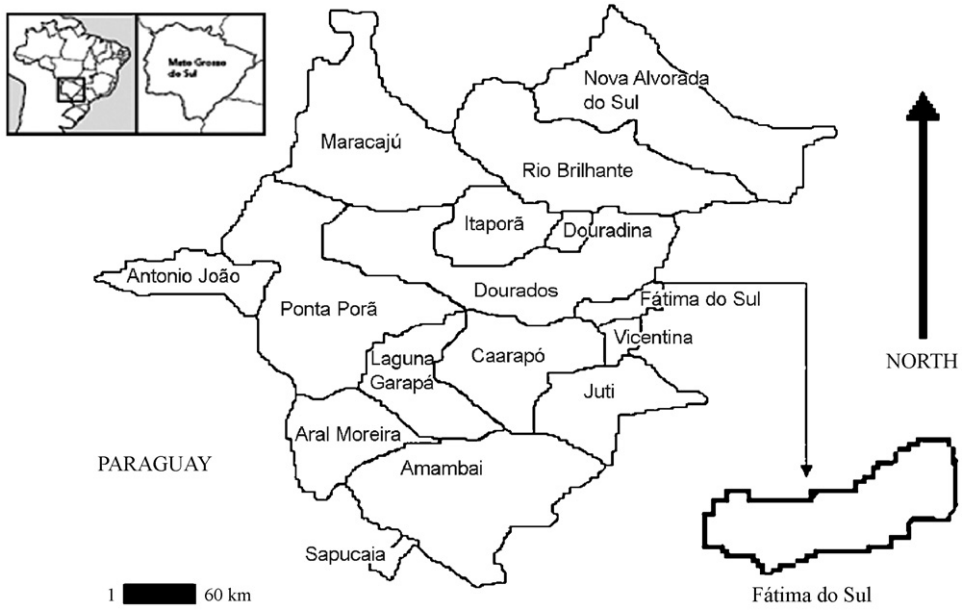

Fig. 1. Geographical location of the municipal district of Fátima do Sul.