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Microwave-assisted extraction through an aqueous medium and simultaneous cleanup by partition on hexane for determining pesticides in agricultural soils by gas chromatography: A critical study

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Abstract

A simple microwave-assisted extraction and partitioning method (MAEP) using water–acetonitrile and *n*-hexane for desorption and simultaneous partitioning, respectively, together with gas chromatography (GC) was studied to determine representative pesticides (trifluralin, metolachlor, chlorpyriphos and triadimefon) with a broad range of physico-chemical properties in agricultural soils. Three points were considered crucial in this study: instrumental and sample-associated factors affecting extraction of the target compounds were studied through experimental design; the spiking procedure at trace levels was carried out to reproduce the solute-soil sorption taking place in the environment as closely as possible; and results were analyzed taking into account the adsorption behaviour of the compounds on different kinds of soils. The complete analytical procedure proposed consisted of the MAEP of pesticides from 1.0 g of soil with 1 mL of 1:1 water/acetonitrile mixture, and 5 mL of hexane for trapping. The microwave heating program applied was 2 min at 250 W and 10 min at 900 W, and 130 °C maximum temperature. After extraction, the hexane layer was evaporated to dryness; the residue was re-dissolved and directly analyzed by gas chromatography electron capture detection (GC-ECD). Clean chromatograms were obtained without any additional cleanup step. Besides the four pesticides used to optimise MAEP, the method was applied to determine an additional group of pesticides (triallate, acetochlor, alachlor, endosulphan I and II, endrin, methoxychlor and tetradifon) in different soils. Most of the compounds studied were recovered in good yields with relative standard deviations (R.S.D.s) below 9% and detection limits ranged from 0.004 to 0.036 $\mu g\,g^{-1}$. The described method is efficient and fast to determine hydrophobic pesticides at $ng\,g^{-1}$ level in soil with different clay-to-organic matter ratios.

Keywords: Microwave-assisted extraction; Water–hexane partition; Pesticides; Soils

1. Introduction

The ubiquitous presence of pesticides as environmental contaminants has created concern about their fate and transport in natural waters, sediments and soils. Soils function as chemical and biological filters that diminish the environmental impact of pesticides introduced into the biosphere by design or accident. Thus, monitoring of these compounds in soils with intensive agriculture is clearly necessary. However, because of the lipophilic properties of some compounds and the complexity of this kind of matrix, analytical procedures to determine pesticides in soils are usually tedious and time-consuming, especially at the extraction stage.

For solid samples, Soxhlet extraction (SE) followed by cleanup of the extracts by solid phase extraction is a common analytical method and has reached official status in many countries (AOAC) [1]. This extraction technique requires refluxing large volumes of solvent through the sample for several hours. Newer extraction techniques developed for environmental analysis of organic contaminants are mainly instrumental and include supercritical fluid extraction (SFE), sub-critical water extraction (SBWE), pressurised liquid extraction (PLE) and microwave-assisted extraction (MAE) [2–4]. SFE and SBWE are selective and not solvent-consuming techniques; however,

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for SFE, a relatively complex and expensive system is needed. On the other hand, PLE and MAE require a small amount of solvent, short extraction time and, pressurised MAE, permitting the simultaneous extraction of several samples. Nevertheless, because of its low selectivity, the main drawback of this extraction technique is the need of a cleanup procedure to determine pesticides in the final extracts. The use of non-polar solvents reduces the co-extraction effect, allowing the determination of a large number of pesticides by gas chromatography coupled with different detection systems. However, according to the principles of microwave energy transfer, the solvent must possess a dipole; thus, non-polar solvents would not be the most suitable for microwave extraction. To overcome this disadvantage in MAE, water could be used as the extracting solvent, since at high-pressure and temperature its dielectric constant, viscosity, and surface tension become reduced, these facts making it effective to extract organic compounds having a broad spectrum of polarities from solid samples. On comparing water, methanol, acetone–hexane and dichloromethane, water has turned out to be as efficient as organic solvents to extract triazines from soil samples in MAE at 600 W [5]. Water capability to extract polar and medium polar compounds under pressure and high temperature has been applied in PLE on aged spiked soils through hot phosphate buffered water [6]. Sub-critical water extraction in a hot-water percolation setup has been proposed for the extraction of six selected pesticides from forest soils; recoveries ranged from 44% to 95% depending on the compound solubility in water [7]. Although water is a good alternative in MAE and PLE, the necessary cleanup procedure to eliminate co-extracted polar interferences from soils, the non-compatibility of extract with GC techniques, and the low extraction efficiency in the case of less hydrophilic compounds are the principal limitations.

To overcome these limitations we propose MAE of low water-soluble pesticides (trifluralin, chlorpyriphos, triadimefon and metolachlor) from agricultural soils using an aqueous phase containing an organic modifier (acetonitrile) for desorption and *n*-hexane for simultaneous partitioning and cleanup (MAEP method). Factors affecting extraction of the target compounds from soils were studied and optimised by using experimental designs. Moreover, in order to reproduce the solute-soil adsorption occurring in the environment as closely as possible, special attention was paid to the spiking procedure used in the recovery studies. Thus, soils samples were contaminated through a batch equilibrium method with aqueous solution to ensure a whole pesticide sorption process. Fortified soil samples with different physico-chemical properties were used to verify the applicability of the method to different types of soils. Ageing effects in the sorption process were also considered of particular concern. The developed MAEP and GC-ECD method was applied to determine a wide range of pesticides in agricultural soils and compared with an ultrasound-based extraction method using ethyl acetate as extracting solvent. The MAEP method has the advantages resulting from the use of a low volume of organic solvent – an unnecessary cleanup step – and good efficiency to extract pesticides actually adsorbed on different soils at residual levels.

2. Experimental

2.1. Chemicals and reagents

The pesticides used had purity $\geq$99% (Pestanal®, Riedel de Häen and ChemService). All the solvents used were residue analysis grade (Fisher). Water was purified with a NANOPure system (Barnstead Thermolyne). Pentachloronitrobenzene (PCNB Aldrich) was used as internal standard for GC determinations. Stock solutions were prepared in acetone at $1\,\mathrm{g\,L^{-1}}$, except for PCNB, which was prepared in hexane. Working standard solutions for GC analysis were diluted with hexane and with water for spiking purposes.

2.2. Equipment and experimental GC conditions

For MAEP, a Milestone MLS 1200 MEGA high-pressure microwave oven extraction system was used, equipped with pressure and temperature sensors and an exhaust module EM-45/A.

GC-ECD. A Hewlett Packard 5890 Series II gas chromatograph equipped with split/splitless injector, an ECD and HP 3395 integrator were employed. An HP-5 capillary column (30 m × 0.32 mm i.d., 0.25 μm film thickness) was used. Helium and nitrogen were selected as carrier and auxiliary gas, respectively. Halogenated pesticides were separated and determined under the following conditions: injector temperature, 250 °C; detector temperature, 300 °C; column temperature program, 170 °C, held for 1 min, increased at $2.5^\circ\,\mathrm{min^{-1}}$ up to 210 °C, and increased at $15^\circ\,\mathrm{min^{-1}}$ up to 260 °C, held for 5 min. A 1 μL volume of the extract was injected in the split mode in ECD (split ratio 1:30). The carrier gas flow in the column was $1.3\,\mathrm{mL\,min^{-1}}$. Under these conditions, the mixture of 12 pesticides (those used for MAEP optimisation and a group of eight additional halogenated pesticides) and the internal standard was well resolved in 25 min using the oven temperature program.

2.3. Soil samples for sorption

Recovery and optimisation studies were carried out using sieved samples (2 mm mesh) of six soils with diverse physico-chemical properties, collected (0–20 cm depth) in different agricultural zones in Chile: three non-allophanic soils, two from the Aconcagua Valley (V Region of Chile), Pocuro (PCR) and Quillota (QTA) and one from an apple orchard in the Cachapoal Valley (VI Region of Chile), Rancagua (RGA) and three allophanic soils from the Araucanía Region (IX Region of Chile), Vilcún (VLC), Temuco (TEM) and Galvarino (GLV). Some of the most relevant physical and chemical properties of these soils are given in Table 1.

2.4. Preparation of spiked soil samples

In the preliminary studies performed to evaluate time and temperature effects and the presence of acetonitrile in the aqueous phase on MAEP efficiency, freshly spiked QTA soil was used owing to its medium content of organic matter. For this