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Short communication

Comparison between accelerated solvent extraction and traditional extraction methods for the analysis of the herbicide diflufenican in soil

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Abstract

In order to reduce time and cost of analysis, a new extractor, ASE 200-Dionex, has been tried out for the extraction of the herbicide diflufenican from soil. This method, which uses a conventional liquid solvent at elevated temperature and pressure, has been developed and compared to traditional extraction with solvent. For each sample the consumption of extraction solvent has been reduced to about a fifth and the time to about a quarter, compared to traditional extraction.

Keywords: Soil; Accelerated solvent extraction; Extraction methods; Environmental analysis; Pesticides; Diflufenican

1. Introduction

Herbicides, used for crop protection, need constant checking for persistence and effects on the environment (air, soil and water). If a very large number of samples must be collected and analysed, the costs are high because large amounts of solvents, glassware and time are needed. Studying herbicide persistence, percolation and accumulation after repeated soil treatments requires sampling at various depths, in various points, and at different times from the beginning of treatment, which means dealing with several hundreds of samples [1–4].

In these studies the more time consuming step is often the extraction. In fact, an active ingredient is extracted from soil by stirring with solvent in a mechanical shaker. Moreover, the solid-phase must be removed from the liquid phase by centrifugation. Often several cycles of the above procedures are requested. This kind of extraction involves a high quantity of waste solvent with several storage and disposal problems [1–4].

The aim of the present paper is to verify the possibility of using, instead of traditional extraction procedures, accelerated solvent extraction (ASE), in order to reduce time, cost of analysis, and waste solvent. This technique uses conventional liquid solvents at elevated temperatures and pressures to achieve quantitative extraction from solid and semi-solid samples in a short time and with a small amount of solvent [5].

Temperature rise increases solubility, diffusion rates and mass transfer, whereas viscosity and surface tension of the solvents are less than at room temperature. Furthermore at elevated temperature the activation energy of desorption is more readily overcome, and the kinetics of desorption and solubilization are also more favorable.

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Pressure allows the extraction cell to be filled faster, helps to force liquid into the pores and to keep the solvent liquid at operating temperatures.

The above mentioned technique was used to extract the herbicide diflufenican from soil; a comparison with the traditional method [6] was made.

All accelerated solvent extractions were performed on ASE-200 Dionex.

2. Materials and methods

Acetonitrile RPE, RS, methanol RS, ammonium acetate RPE-ACS, anhydrous sodium sulfate RPE-ACS and methylene chloride RPE were all from Carlo Erba. Sep-Pak silica cartridge 2 g was purchased from Millipore, Daytimeae Heart-Hydromatrix from Varian, nitrogen for chromatography from Sio and the herbicide standard: diflufenican [N-(2-4-difluorophenyl)-2-(3-trifluoromethylphenoxy)pyry-dine-3-carboxamide], 99.7% from Rhone-Poulenc.

In order to compare the ASE method with traditional extraction, an untreated soil sample was extracted as blank in both techniques; then, the same sample was spiked with diflufenican.

Recovery was tested spiking at 10 g of soil for ASE and at 50 g for traditional extraction, 0.1 mg/kg, 0.2 mg/kg, 0.4 mg/kg of diflufenican dissolved in acetonitrile; furthermore, soil samples were extracted from a treated field.

The characteristics of soil were: pH 7.8; clay 40%; silt 21%; sand 35%; organic matter 2.4%, organic carbon 1.4%; cationic-exchange capacity mequiv./100 g =30.3. The soil was dried and sieved at 2 mm before analyses.

3. ASE extraction

The fundamental parts of the instrument used for accelerated solvent extraction are: (1) high pressure pneumatic pump capable of 3000 p.s.i. at elevated flow-rate (up to 75 ml/min) (1 p.s.i.=6894.76 Pa); (2) extraction solvent pressurised bottle; (3) carousel for 24 extraction cells of 11, 22, 33 ml; (4) carousel for 26 40/60 ml collection vials; (5) microprocessor for storing and editing extraction parameters, such as temperature, time and pressure; (6) IR sensors to detect the arrival of fluid into the collection vial and monitor fluid levels during extract collection.

The extraction process consists of five steps: (1) filling and pressurising cell with solvent at selected pressure; (2) heating cell at selected temperature for temperature equilibration at constant pressure (heat); (3) static extraction at constant pressure and temperature of extraction solvent (static); (4) washing of cell with fresh solvent for total recovery of products, after transfer of extract to sealed vials; the volume of fresh solvent is indicated in % of volume cell (flush); (5) final solvent purging with nitrogen gas (purge).

In this work extraction cells of 11 ml were used and filled with 10 g of soil mixed with diatomeae ground in the ratio of 1:0.1 for improving cell packing which helps acetonitrile filling. All the samples were extracted at 100°C and 2000 p.s.i., the time of heat up, static and purge was respectively 5 min, 4 min, 60 s.

The extraction volume of acetonitrile was about 17 ml. This volume was adjusted to 20 ml and concentrated to small volume by vacuum rotary evaporator with nitrogen purge and redissolved in 2 ml of dichloromethane.

3.1. Traditional extraction

100 ml of acetonitrile were added to 50 g of soil drawn from the same sample extracted with ASE. After stirring for 45 min with a mechanic shaker, the soil was centrifuged at 3000 rpm for 10 min. A portion of 25 ml was collected and treated in the same way than ASE.

3.2. Cleaning up procedure for both techniques of extraction

Sep-Pak silica cartridge 2 g was activated with 40 ml of dichloromethane. 1 ml of extract was deposited on the cartridge and eluted with 20 ml of dichloromethane in 3 min. This solvent was collected, dried, and redissolved with acetonitrile.

3.3. HPLC analytical conditions

A Waters 600E System Controller Millipore pump, a Waters 12 Wisp injector, a UV–Vis Waters 484 tunable adsorbance detector (wavelength: 280 nm)

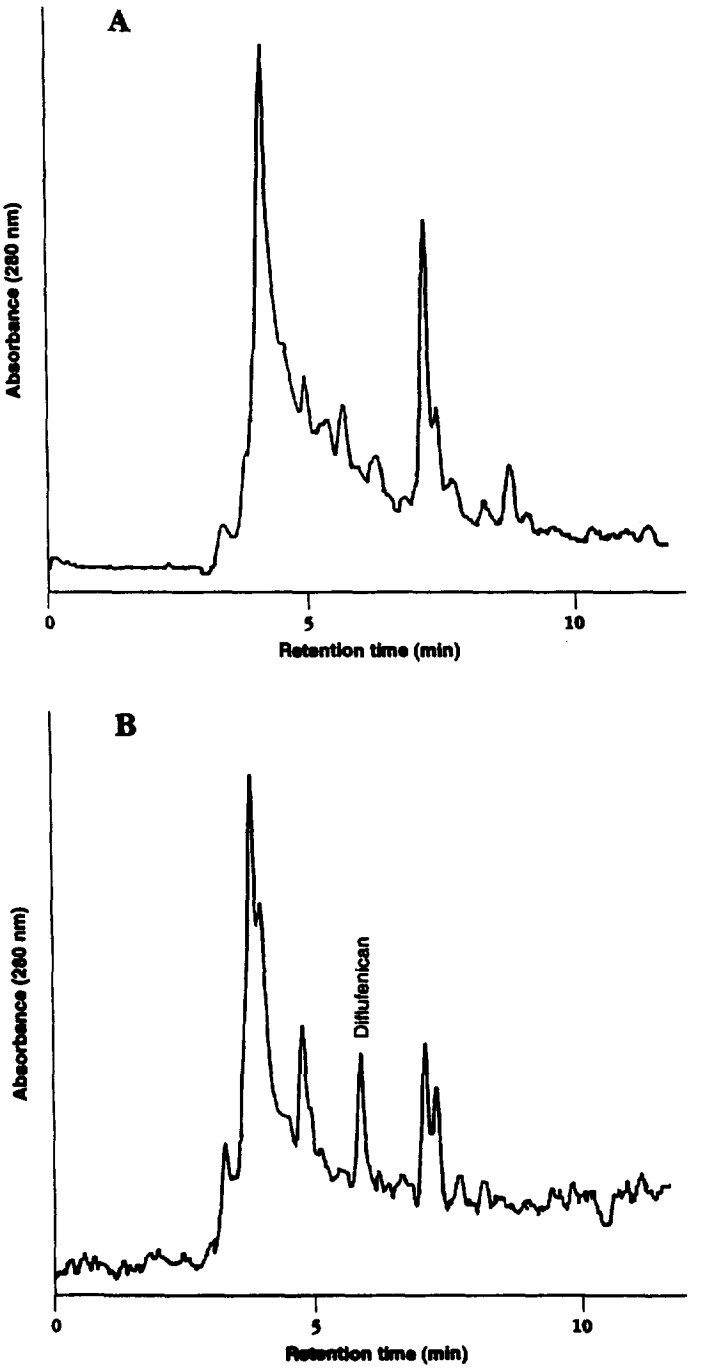

Fig. 1. Chromatograms of ASE extraction. Untreated (A) and sample (B). Reversed-phase liquid chromatographic conditions: mobile phase, methanol–acetonitrile–0.05 *M* ammonium acetate (20:70:10); flow-rate, 1.0 ml/min.

Table 1
Recoveries (each value is the average of four replicates)

Spike mg/kg	ASE recovery (%)	Traditional recovery (%)	R.S.D. ASE (%)	Traditional R.S.D. (%)
0.1	91.5	89.3	5.3	4.6
0.2	96.5	94.5	4.5	4.1
0.4	100.0	98.2	4.2	4.2

were used. The separation column consisted of two columns C_{18} NovaPak Millipore; 300×3.9 mm; 60 Å; 4 μm. The mobile phase was acetonitrile–methanol–0.05 *M* ammonium acetate (70:20:10), at a flow-rate of 1 ml/min.

4. Results and discussion

Table 1 shows recovery results of extraction for the accelerated solvent extraction and traditional method for samples spiked with 0.1 mg/kg, 0.2 mg/kg and 0.4 mg/kg.

The same soil treated in situ with diflufenican was extracted with the two different methods with the following results: ASE extraction 0.089±0.004 mg/kg and traditional extraction 0.076±0.04 mg/kg.

Figs. 1 and 2 show chromatograms of the extract (ASE and traditional) of real sample treated in situ and of a blank extracted with ASE. The comparison of the two methods is shown in Table 2. The accelerated solvent extraction results in an advantage for several reasons: total automation of extraction step allows a complete standardization of procedures, compared with traditional manual techniques; the direct contact between operator and solvent vapour is strongly decreased; the consumption of solvents, the subsequent storage and disposal are limited: volume of used solvent is a fifth of traditional extraction volume; about a quarter of the time is required for the preparation and extraction.

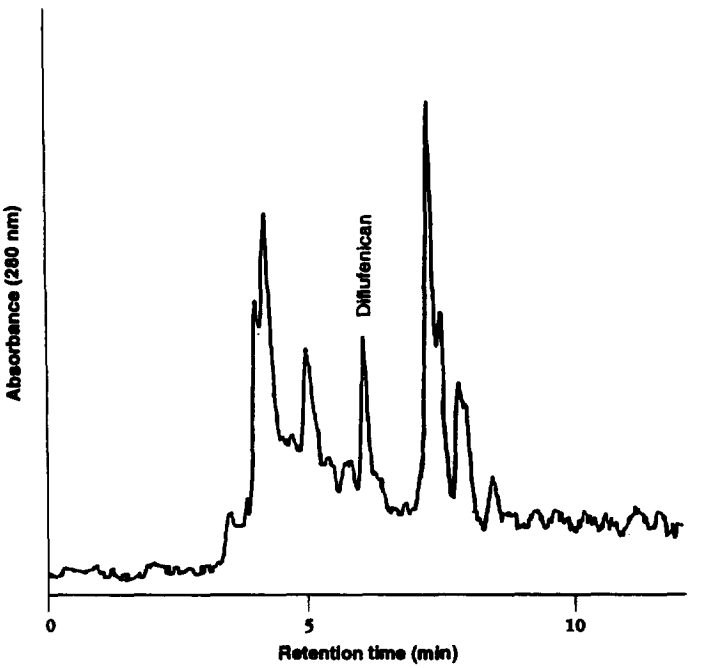

Fig. 2. Chromatogram of traditional extraction. Sample. Reversed-phase liquid chromatographic conditions as in Fig. 1.

Table 2
Comparison between two extraction techniques

	ASE	Traditional
Solvent volume (ml)	20	100
Concentration	15 → 2	25 → 2
Glassware	1 vial	1 funnel, 1 bottles, 1 flask
Preparation and extraction time min	25	70
Average recovery (%)	96±4.6	94±4.3
Lower limit of detection (mg/kg)	0.01	0.01

This technique allowed extraction of about 120 samples in 5 days, working about 6 h/day.

Moreover, the best conditions of extraction were easily recognized because of the limited number of parameters that affect analyte recovery.

The need for rapid production of analytical data about the effect of pesticide use, as continuously requested by the European Union [7–9], greatly increases the amount of work for researchers involved in this task.

This technique could facilitate this research work.

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