

EVALUATION OF AN SPME AND GC-MS METHOD FOR ANALYSIS OF FLUAZIFOP IN WATER

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SUMMARY

Combination of solid-phase microextraction with gas chromatography enables rapid, repeated analysis of organic compounds in water. Fluazifop-p-butyl (FPB) (propanoic acid 2-[4-[[5-(trifluoromethyl)-2-pyridinyl]oxy]phenoxy] butyl ester) is the active substance in the herbicide Fusilade. Samples of distilled water were spiked with FPB in the laboratory and the analyte was isolated from the water by solid-phase microextraction on a polydimethylsiloxane fibre. Optimum conditions (time, temperature, stirring, pH) were found for extraction of FPB from the water matrix. Limit of detection, standard curve calibration, and range of concentration in which detector response was linear were determined. Suitable conditions for chromatographic analysis were also determined.

INTRODUCTION

Pesticides are dangerous pollutants in the environment. The source of pesticides are manufacture, transport, handling, and application to crops. Although liquid-liquid extraction and, more recently, solid-phase extraction have been used for isolation of pesticides from water samples [1], there remains a need for reliable methods to measure their concentrations in natural waters. Isolation of the analytes is an important stage in the process of determination.

Solid-phase microextraction (SPME) is an extraction technique recently proposed for analysis of trace amounts of organic substances [2-8] which has advantages over more conventional extraction techniques [9]. Because it is a solvent-free sample-preparation procedure it minimizes the cost of high-purity solvents, which are often toxic and flammable. It is also rapid and easy to use, and very small sample volumes (1-5 mL) are sufficient for analysis. SPME can significantly reduce field analysis time

by combining sampling, extraction, concentration, and injection in a single process. This process has two steps—partitioning of the analytes between the sample matrix and a stationary phase, which is coated on a fused-silica fibre, and desorption of the trapped analytes into the analytical instrument. Choice of the right fibre with appropriate polarity and stereoselectivity depends on the physicochemical properties of the analyte(s). The time required to achieve partition equilibrium and active diffusion of molecules at the phase boundary has crucial importance in the selection of conditions for adsorption of analytes from the matrix.

The first application of SPME was in the field of water analysis [10] – combination of solid-phase microextraction (SPME) with gas chromatography–mass spectrometry (GC–MS) enabled identification and quantification of many organic compounds in water, including rapid, repeated analysis of pesticides. The work discussed in this paper was a preliminary investigation of the analysis of fluazifop (FPB; Fig. 1) in water samples. Successive stages of the analysis are described, including separation of the compound from water by SPME on to a solid-phase and qualitative and quantitative determination using gas chromatography joined with mass spectrometric detection.

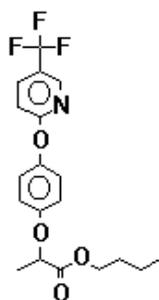


Fig. 1

Structure of fluazifop-p-butyl (FPB) (propanoic acid, 2-[4-[[5-(trifluoromethyl)-2-pyridinyl]oxy]phenoxy]butyl ester)

EXPERIMENTAL

Preparation of Standard and Sample Solutions

The herbicide Fusilade 125 EC (propanoic acid 2-[4-[[5-(trifluoromethyl)-2-pyridinyl]oxy]phenoxy] butyl ester; Zeneca) was 95% pure. A

working standard solution of FPB was prepared by dissolving 11.66 mg Fusilade in triple-distilled water in a 1000-mL flask. Standard solutions were prepared in 10-mL flasks by diluting the working standard solution 10^5 -, 10^4 -, 10^3 -, 10^2 -, 10 -, and 2-fold with water.

Microextraction Conditions

SPME was performed with a system from Supelco. Samples (3 mL) of standard or sample solutions were placed in 4-mL vials and pH was adjusted to 2, 5, or 8 before extraction with a 100- μ m polydimethylsiloxane fibre for 10–150 min at 28–75°C while stirring at 50–1000 rev min⁻¹.

Chromatographic Conditions

GC–MS was performed with a GC-17A gas chromatograph and QP5050 mass spectrometric detector (both from Shimadzu). The SPME fibre was desorbed for 5 min at 260°C, splitless, and desorbed compounds were separated on a 30 m \times 0.25 mm capillary column coated with a 0.25 μ m film of BPX5 (Phenomenex). Helium, pressure 55 kPa, was used as carrier gas (total flow 72 mL min⁻¹, column flow 0.8 mL min⁻¹). The column temperature was maintained at 80°C for 5 min during desorption then programmed at 10° min⁻¹ to 280°C, which was held for 10 min. The detector temperature was 300°C. The MS was operated in full-scan and selected ion monitoring modes (TIC or SIM at m/z 383, 282, and 254) with electron-impact ionization. The instrumentation was controlled by software Class 5000 with the NIST 107 and 21 library of mass spectra. A chromatogram obtained under these conditions, and the mass spectrum obtained for FPB, are depicted in Fig. 2. The calibration plot obtained is shown in Fig. 3.

RESULTS AND DISCUSSION

As a result of this research optimum conditions were established for isolation of FPB from water (volume of sample, type of vial) including adsorption conditions (time, temperature, pH, stirring). The range of concentrations of FPB for which linear detection response was obtained was also established. Optimum conditions for thermal desorption in the chromatograph injector, capillary gas chromatographic analysis, and identification of FPB by use of the library of mass spectra to achieve the lowest limits of detection were also established.

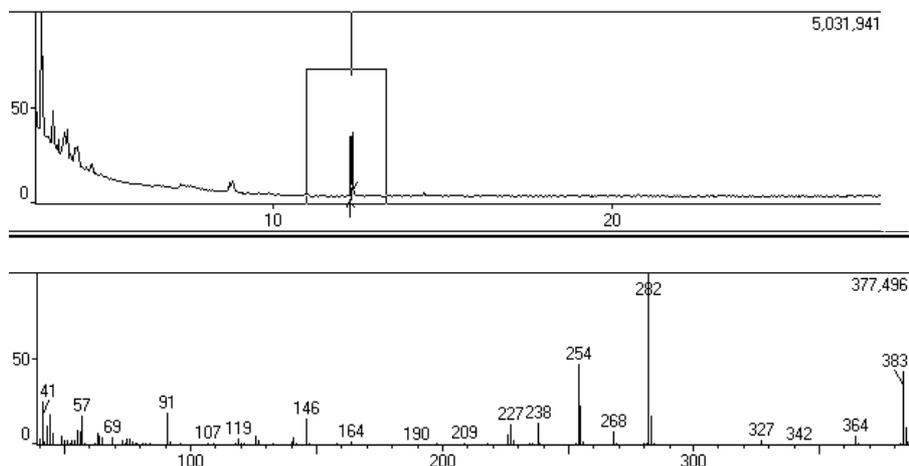


Fig. 2

Typical chromatogram, and mass spectrum of fluazifop-p-butyl

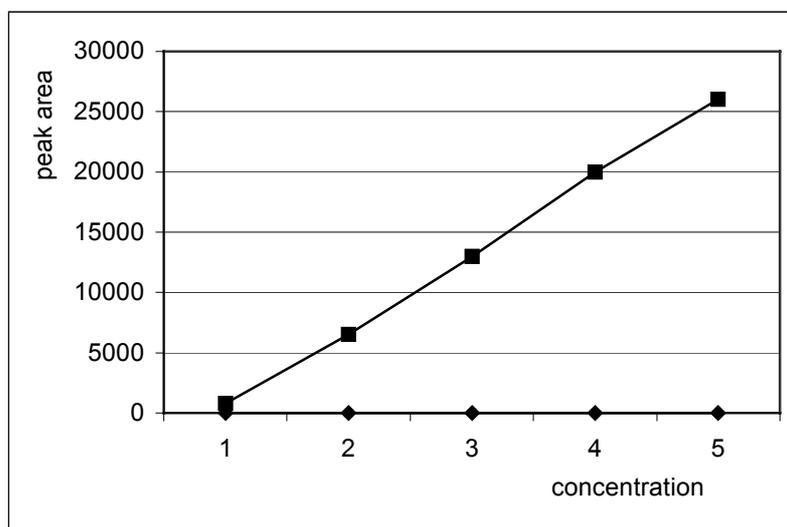


Fig. 3

Calibration curve obtained for the fluazifop-p-butyl. The regression equation was $y = 0.7276x + 0.0159$ (correlation coefficient, $R^2 = 0.9887$)

Extraction was best performed for 45 min at pH 5, with stirring at 500 rev min⁻¹. As an example, the effect of extraction time on the amount of FPB adsorbed is illustrated in Fig. 4. Desorption was performed splitless for 5 min at an injector temperature of 260°C. Linear detector response was obtained for concentrations from 0.5 to 58 µg L⁻¹. Under these conditions detection limits for TIC and SIM response were 10 ng L⁻¹ and 1 ng L⁻¹, respectively. The relative standard deviation calculated for *n* = 5 and a concentration of 0.5 µg L⁻¹ was <25%.

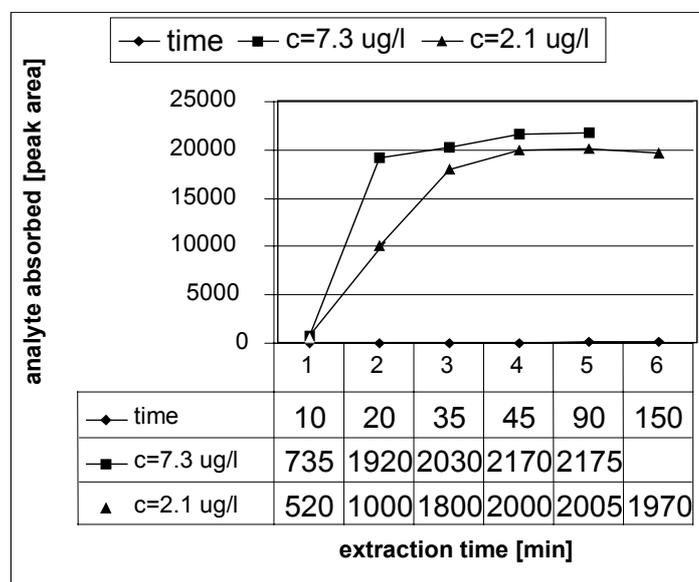


Fig. 4

Effect of extraction time on the amount of FPB absorbed by SPME sampling

CONCLUSION

Use of GC–MS with SPME enabled rapid and efficient identification, separation, and quantitative determination of fluazifop. The amount of analyte adsorbed by the coating at equilibrium was directly related to the concentration of the analyte in the sample. In SPME neither complete extraction of analytes nor full equilibrium is necessary, but sampling time, temperature, speed of stirring, addition of an electrolyte to the sample, and adjustment of pH can be critical.

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