

Solid-phase micro-extraction–gas chromatography–(tandem) mass spectrometry as a tool for pesticide residue analysis in water samples at high sensitivity and selectivity with confirmation capabilities

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Abstract

Gas chromatography–mass spectrometry (GC–MS) has been widely applied for pesticide monitoring because of its high sensitivity and specificity and for the potential of multi-residue and multi-class analysis. An analytical procedure was developed for the determination of pesticide multi-residues in water samples combining solid-phase micro-extraction (SPME) and gas chromatography–ion trap mass spectrometry. For SPME extraction a poly(dimethylsiloxane)–divinylbenzene coated fibre was selected whereas the mass spectrometer was operated under full scan, selected ion storage (SIS), μ SIS (SIM) and MS–MS and the figures of merit compared. Quantitative and qualitative (confirmatory) capabilities of each operation mode are discussed. Using MS–MS, precision was typically below 10% and limits of detection (LODs) were improved by 1.3 to 20 times (to low- or sub-ppt levels) compared to μ SIS, with the advantage of maintaining identification capabilities. The combination of selective extraction by SPME and highly selective determination by GC–MS–MS made possible ultra-selective and essentially error-free determination of pesticides in complex environmental samples. This aspect will be highlighted in the paper.

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1. Introduction

The contamination of the aquatic environment by organic pollutants, such as pesticides is a matter of great concern world-wide. In addition to effecting human health many pesticides released into the environment can also disrupt the normal endocrine function in a variety of aquatic life and wildlife [1,2].

In the last few decades, pesticides have been used on an increasingly wider scale throughout the world, although lately there is a tendency to slow down, or at least a motivation to use less harmful molecules. Pesticides are characterised by their diversity, their different physical and chemical properties and their low concentrations in real

samples [3]. On account of the large number of active ingredients used, analytical procedures are required for the detection of the greatest number of compounds possible, with the fewest number of extraction and clean-up steps [3–5]. Because of the large-scale dilution these contaminants undergo in aquatic matrices, an enrichment procedure consisting on liquid–liquid extraction (LLE), solid-phase extraction (SPE), or more recently, solid-phase micro-extraction (SPME) is currently employed. SPME is a modern technique that consists on direct extraction of the analytes with the use of a small-diameter fused-silica fibre coated with an adequate polymeric stationary phase [6,7]. In recent years, SPME has gained widespread acceptance for the determination of a wide spectrum of analytes in various fields, such as environmental, forensic, pharmaceutical, food, beverage and flavour chemistry [8–10]. In the present study, a poly(dimethylsiloxane)–divinylbenzene (PDMS–DVB) SPME fibre was used and subsequent analysis was carried

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