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Optimization of supercritical fluid extraction of pesticide residues in soil by means of central composite design and analysis by gas chromatography–tandem mass spectrometry

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Abstract

An environmentally friendly methodology is proposed for the analysis of pesticides in soil samples based on supercritical fluid extraction (SFE) and analysis at high selectivity and sensitivity, by gas chromatography–tandem mass spectrometry (GC–MS–MS). The pesticides investigated are among the most commonly used in intensive horticulture activities comprising organochlorine and organophosphorous insecticides, triazine and acetanilide herbicides, amongst others. An experimental design approach was used for modelling SFE and optimised extraction conditions were derived for the total pesticides extraction or for specific sub-groups of interest. Pesticide residues could be detected in soils in the sub-ppb range (0.1–3.7 $\mu g\,kg^{-1}$), with quite good precision (4.2–15.7%) and extraction efficiency (80.4–106.5%). The analysis of soil samples from an intensive horticulture area in Póvoa de Varzim, north of Portugal, revealed the presence of persistent pesticides, parent compounds and degradation products among the following: endosulfan, endosulfan sulfate, dieldrin, 4,4′-DDE, 4,4′-DDD, atrazine, alachlor, metolachlor, chlorpyrifos, pendimethalin and lindane. The important features to point out are the easy interpretation of chromatograms and straightforward confirmation of analytes that greatly facilitates the analyst judgement on the contamination of the sample.

Keywords: Soil; Pesticides; SFE; Central composite design; Intensive horticulture; Tandem-MS

1. Introduction

A supercritical fluid can be defined as a physical state, in which a substance is compressible, behaves like a gas, has a density of a liquid, fills and assumes the shape of its container [1]. Supercritical fluids are macroscopically homogeneous but microscopically inhomogeneous consisting of solvent clusters and free volumes which result in unusual properties attributed to local density effects [2]. As general properties, they possess high diffusive power, low viscosity, good penetration capabilities and adjustable density to fit any particular needs [3].

A trend towards more time-effective and environmentally friendly processes has boosted the interest in supercritical fluid extraction (SFE) [2,4–6]. Unanimously recognized advantages of SFE have been discussed in the literature which are worth mentioning: rapidity, simplicity, great analyte selectivity [7], good extraction efficiency, no need of clean-up step, suitability for thermally labile compounds, automation, solventless or near solvent free character and reduced environmental hazard [3,5,7–12]. Despite evident advantages, SFE is not widely adopted in official methods and several analytical protocols for pesticide analysis in soils still rely on liquid–solid extraction, e.g. the DFG S19 multimethod [9,13]. Several research papers have demonstrated the suitability of SFE to replace the conventional solvent extraction methods [14–17]. A good assortment of SFE-based analytical protocols have been developed for a wide range of matrix types [8,10,18] and specific category of pollutants such as: polycyclic aromatic hydrocarbons (PAHs) [12,19], organochlorine pesticides (OCPs) [14], triazines [20,21], organophosphorus pesticides (OPPs) [22] and carbamates [4]. Nevertheless, a few approaches have dealt with multiresidue analysis of pesticides in soils [9], which presents

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