

Optimisation and validation of a solid-phase microextraction method for simultaneous determination of different types of pesticides in water by gas chromatography–mass spectrometry

E. Beceiro-González^{a,*}, E. Concha-Graña^a, A. Guimaraes^b, C. Gonçalves^{b,c},
S. Muniategui-Lorenzo^a, M.F. Alpendurada^{b,c}

^a Department of Analytical Chemistry, University of A Coruña, Campus da Zapateira s/n, 15071 A Coruña, Spain

^b IAREN, Water Institute of the Northern Region, Rua Dr. Eduardo Torres, 229/4450-113 Matosinhos, Portugal

^c Laboratory of Hydrology, Faculty of Pharmacy, University of Porto, Rua Aníbal Cunha, 164/4050-047 Porto, Portugal

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Abstract

A solid-phase microextraction (SPME) method for the simultaneous determination of a large number of pesticides (46) with a wide range of polarities and chemical structures (organochlorine, organophosphorous, triazines, pyrethroids and others) in water samples by GC–MS has been developed. Three different fibres and parameters that influence the extraction and desorption efficiency were studied. The selected conditions were: a 60 μm polydimethylsiloxane/divinylbenzene (PDMS/DVB) fibre, 45 min of extraction time, sample agitation and temperature control at 60 °C; neither pH adjustment nor ionic strength correction were applied. Good detection limits, linearity and repeatability were obtained with this method for the 46 pesticides studied. The method was validated for 29 pesticides following the recommendations of the international norm ISO/IEC 17025 including the calculation of the uncertainties. The detection limits ranged from 4 to 17 ng l^{-1} . Furthermore, repeatability (6.9–20.5%) and intermediate precision (4.5–19.7%) were shown to be satisfactory. To validate matrix effects for drinking and surface water analytical recoveries were calculated for these matrices. The accuracy of the method was also evaluated by participating in a proficiency inter-laboratory test.

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1. Introduction

Pesticides contamination of surface and ground water due to agricultural activities has been of concern for a long time. Organochlorine pesticides (OCPs) are characterised by their toxicity and persistence in the environment; and common pesticides, such as organophosphorous pesticides (OPPs) by their misuse and runoffs [1,2]. For this reason, presence of pesticides in waters for human consumption is regulated by the European Directive 98/83/EC [3] that establishes the maximum concentration of each pesticide at 0.1 $\mu\text{g l}^{-1}$ and the total amount of pesticides at 0.5 $\mu\text{g l}^{-1}$. The maximum individual concentration is even lower for aldrin, dieldrin, heptachlor and heptachlor epoxide (0.03 $\mu\text{g l}^{-1}$). Thus, simple, fast, highly sensitive and

low cost analytical methods are required to detect and quantify these pollutants in water.

In a routine analytical laboratory it is necessary to obtain analytical results from a large number of samples in a short period of time. For this reason, the introduction of solid-phase microextraction (SPME), as a rapid, inexpensive and quantitative analytical technique, by Arthur and Pawliszyn [4], and the novel stir bar sorptive extraction (SBSE) by Baltussen et al. [5] have gained acceptance for the determination of a wide spectrum of analytes in the recent years. Both techniques are essentially solvent free, which is a highly convenient feature. The main disadvantage of SBSE with respect to the SPME technique resides in the fact that a whole automation of the extraction and analysis is not possible nowadays.

SPME has been employed as a sample preparation method for the analysis of pesticides in different matrices [6–13]. The most widely used SPME coating for the analysis of non-polar pesticides has been the 100 μm thickness polydimethylsiloxane

* Corresponding author. Tel.: +34 981167000.

E-mail address: elisa@udc.es (E. Beceiro-González).