Determination of Organophosphorus Pesticides in Water, Vegetables and Grain by Automated SPE and MEKC

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Received: 17 December 2004 / Revised: 15 February 2005 / Accepted: 1 March 2005
Online publication: 27 April 2005

Abstract
A sensitive method for the multi-residue analysis of organophosphorus pesticides in environmental samples has been developed. It involves an automated solid phase extraction procedure using a Gilson ASPEC XLi and capillary electrophoresis analysis with UV detection. Acephate, methamidophos, dichlorvos, dicrotophos and malathion could be separated by micellar electrokinetic capillary chromatography using an electrophoretic electrolyte containing 20 mM phosphate buffer (pH 7.5) and 75 mM sodium dodecyl sulphate. A linear relationship between concentration and peak area was obtained within the range 0.2–450 g mL\(^{-1}\) with correlation coefficients greater than 0.996 and detection limits between 7 and 150 ng mL\(^{-1}\). Intra- and inter-day precision values of about 0.8–2.3% RSD (n=11) and 0.9–3.0% RSD (n=15), respectively were obtained. When the preconcentration step was used, an enrichment factor of 250 was easily achieved in the analysis of water samples, making it possible to determine pesticide residues at concentration levels as low as 0.04 ng mL\(^{-1}\). In analyses of vegetables and grains, the sensitivity levels were about 0.03 g kg\(^{-1}\).

Keywords
Micellar electrokinetic capillary chromatography
Automated solid phase extraction
Organophosphorus pesticide residues
Environmental samples

Introduction
Organophosphorus pesticides (OPs) are one of the most common pesticides used in industrialized countries and represent an important source of environmental contamination due to their universal application in agriculture. High-level exposure to these neurotoxins results in acetylcholine accumulation, which interferes with muscular responses, leading to the possibility of death. For this reason, the level of these compounds needs to be monitored so that appropriate measures can be taken. Several studies have been reported on the analysis of OPs in aqueous human body fluid samples using chromatographic techniques. Gas chromatography (GC) with atomic emission detection [1], nitrogen-phosphorus detection [2], flame ionization detection [3], mass spectrometry [4, 5] and flame photometric detection [6] has traditionally been the method of choice for the analysis of OPs. One disadvantage with GC is that some OPs are difficult to analyse because of their lack of volatility. High performance liquid chromatography (HPLC) has offered an alternative to the analysis of non-volatile and thermally unstable OPs. HPLC with tandem mass spectrometry [7, 8], UV absorbance [9], chemiluminescence [10] or amperometric [11] detection systems has been proposed for the analysis of thermally labile and/or very polar OPs.

Capillary electrophoresis (CE) has developed rapidly since its introduction in the mid 1980s, and adds a separation tool of greater efficiency to the more conventional chromatographic methods [12]. CE has been applied to a number of biological separation problems, but only a few articles report applications to pesticides or environmental samples [13]. CE has been successfully applied to the separation of phenoxy acids [14], bipyridium salts [15–17], sulfonylureas [18], chloroanilines [19], fiaimidides [20] and s-triazines [21, 22] herbicides.

The separation of OPs has rarely been carried out by CE [13]. The quantitative determination of glyphosate and amidomethylphosphoric acid in water [23] and a commercial herbicide [24] was accomplished by capillary zone electrophoresis (CZE) with indirect photometric detection. The usefulness of micellar electrokinetic capillary chromatography (MEKC) has been checked in the separation of the three phosphorus containing...
water samples.

Automated Extraction of OPs

StrataX cartridges (200 mg with a 3-mL reservoir) were conditioned with 2 mL of acetone followed with 2 mL of ultrapure water, with 0.5 mL air, in between prior to application of the sample. The water samples were pumped through the cartridge at a flow rate of 5 mL min⁻¹ using a Gilson 306 pump, which was controlled by the software of the ASPEC. The washing of the cartridge was performed with 1 mL ultrapure water and 0.5 mL air. The retained OPs were eluted at 1 mL min⁻¹ with 2 mL of acetone followed with 3 mL air. The eluate was evaporated to near dryness at 45 °C by passing a stream of air for 1 min. The residue was dissolved with 1 mL of ultrapure water and transferred by the ASPEC into the sample vial of the CE system. The CE system and the SPE worked simultaneously.

Sample Preparation Procedures

Water Samples

Other than ultrapure water, tap and surface runoff waters were used as environmental samples. Samples were stored at 4°C but analysed within two days of collection. Pesticides were added to water samples by placing 10 mL of a pesticide mixture solution (containing between 2 and 320 μg of each OPs) in a volumetric flask and making up to 1 L with the water sample. Tap and surface runoff water were filtered through a 0.45 μm membrane filter (Millipore) and then degassed by sonication and evacuation.