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Monitoring of *N*-methyl carbamate pesticide residues in water using hollow fibre supported liquid membrane and solid phase extraction

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ABSTRACT

The aim of this work was to develop a method for the determination of N-methyl carbamates in water involving hollow fibre supported liquid membrane (HFSLM) and solid phase extraction (SPE) as sample preparation methods. Four *N*-methyl carbamate pesticides, aldicarb, carbaryl, carbofuran and methiocarb sulfoxide, were simultaneously extracted and analysed by a liquid chromatograph with a diode array detector (LC-UV/DAD) and a liquid chromatograph coupled to a ion trap quadrupole mass spectrometer (LC–ESI–MS). The high performance liquid chromatography (HPLC) separation of carabamate extracts was performed on a C_{18} column with water–acetonitrile as the mobile phase. The mass spectrometry analyses were carried out in the positive mode, operating under both the selected ion monitoring (SIM) and full scan modes. The solid phase recoveries of the extracts ranged between 8% and 98%, with aldicarb having the highest recoveries, followed by carbaryl, carbofuran and methiocarb had the lowest recovery. The HFSLM recovery ranged between 8% and 58% and the order of recovery was similar to the SPE trend. Factors controlling the efficiency of the HFSLM extraction such as sample pH, stripping phase pH, enrichment time, stirring speed as well as organic solvent used for entrapment of analytes, were optimised to achieve the highest enrichment factors.

1. Introduction

N-methyl carbamates are a class of compounds with a characteristic methyl and nitrogen groups and are derivatives of carbamic acid. The compounds like other carbamates are used as insecticides or fungicides (Selim et al., 2011) and have an advantage of having a broad range of activity (Ni et al., 2005). Toxicologically these compounds are known to be inhibitors of acetylcholinesterase, preventing the breakdown of acetylcholine in the synapse in human and animals (Ni et al., 2005; Joseph and Raj, 2011). The ester compounds of N-methylcarbamates have been reported to cause a reversible carbamylation of acetylcholinesterase thus resulting in the accumulation of acetylcholine (Ecobichon, 1996; Rotenberg and Almog, 1995).

However, there has been a health concern of these compounds because of the fact that their water solubility is high and can easily enter the water streams and affect the health status of consumers (Goto et al., 2006). The solubility of aldicarb in water for instance is 4930 mg/L implying that it can easily be transported by water from the region of pollution to another environmental compartment (Makihata et al., 2003). The European Union has stipulated the maximum permissible concentration of an individual N-methyl carabamate pesticide of 0.1 μg/L and not exceeding a total concentration of 0.5 μg/L (Rawn et al., 2004).

Due to this legal limit the development of highly sensitive and selective analytical methods for the determination of both the parent compounds and their metabolites in water samples is needed (Ni et al., 2005). Normally the analytical procedures for the determination of chemical molecules begin with sample preparation procedures. Sample preparation is one of the most important steps in any analytical process as it enables the removal of other nontarget compounds that may interfere with the detection system (Smith, 2003; Hercegová and Dömötörová, 2007). Sample preparation also allows for enrichment/pre-concentration of the analyte of interest where low detection limits are required or in cases of dilute samples (Makihata et al., 2003).

Many sample preparation methods have been reported for the extraction of N-methyl carbamates in water. Liquid–liquid extraction (LLE), has been reported numerously. Rawn et al. (2004) for instance have reported the use of solvent extraction in the analysis of N-methyl carbamates in apples and grape juices where maximum levels of carbaryl, methomyl and oxamyl were found to be 93, 6.7 and 4.6 ng mL^{-1}, respectively. The main disadvantage of LLE is the large quantities of solvent used and the multiple steps required before analysis and therefore not economical and may not be very environmentally friendly as most of the solvents will end up being disposed to the environment and will harm the ecosystem (Sagratini et al., 2007). Solid phase extraction (SPE) is another extraction technique that has been used for N-methyl carbamates to purify samples before analysis. Arraez-Roman et al. (2004) have reported

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the use of SPE in the extraction of aldicarb, carbofuran and some of their main metabolites in groundwater. The detection limits obtained in this SPE method with a subsequent evaporation step were in the range 2–7.4 μg L^{-1}. Another SPE method was reported by Atrache and Sabbah (2003), who analysed phenyl-*N*-methylcarbamates and their hydrolysis products in water. Limits of detection (LODs) and limits of quantitation (LOQs) reported ranged, from 1 to 4 μg/L and from 4 to 10 μg/L for the compounds they analysed. Microwave assisted extraction (MAE) technique has recently been reported for the extraction of samples containing carbamates with other pesticides (El-Saeid et al., 2010). However, MAE demands skilled personnel; it is expensive and uses relatively large volumes of solvents (Sun and Lee, 2003).

In this work we report also the use of HFSLM extraction of N-methyl carbamates. The technique is a simple, time efficient and cost effective for the selective extraction of the target analyte molecules. In liquid membrane extraction, the analyte molecule diffuses across the hydrophobic porous membrane coated with organic solvent (Msagati et al., 2008a,b). The detection method of choice for this work is high performance liquid chromatography with UV-DAD and a liquid chromatograph coupled to a mass spectrometer (LC–ESI–MS). LC–ESI–MS has become an alternative to gas chromatography–mass spectrometry (GC–MS) as sample pretreatment is more tedious with GC–FID or GC–MS as it does not require the samples to be volatile (Berhanu et al., 2006; Chimuka et al., 2004). Carbamates are polar and thermally unstable so gas chromatographic methods are not appropriate (Abdi et al., 2006). Many carbamate pesticides can be detected by high performance liquid chromatography (HPLC) with fluorescence detection but this does not provide specificity and derivatisation is required. To solve this problem LC–ESI–MS is therefore the method of choice as the analysis can be performed directly and easily, without the need for derivatisation (Ni et al., 2005; Makihata et al., 2003).

The objectives of this work was to develop a simple, greener and cost effective extraction method for N-methyl carbamate compounds which is based on the use of hollow fibre supported liquid membrane and validate it by comparing with the mostly used extraction method based on solid phase extraction.

2. Materials and methods

Aldicarb, carbofuran, carbaryl and methiocarb sulfoxide were purchased from Merck Chemicals (Darmstadt, Germany) (Fig. 1). HPLC grade acetonitrile and methanol was obtained from Sigma Aldrich (Steinheim, Germany). The organic solvent isooctane was purchased from Merck and trioctylphosphine oxide (TOPO) used was from Eastman Organic Chemicals. The hydrochloric acid (32%) used in the preparation of buffers were purchased from Associated Chemical Enterprises (Glenvista, South Africa). Potassium chloride, which was also used in the preparation of the buffers, was purchased from Capital Lab Suppliers (Pinetown, Durban). The hollow fibre tubing used in the extractions were Q3/2 Accurel polypropylene (200 μm wall thickness, 600 μm inner diameter, 0.2 μm pore size) and obtained from Membran (Wuppertal, Germany). An Agilent Technologies 10 μL microsyringe was used in the Hollow fibre supported liquid membrane (HFSLM) extraction. Solid phase extraction (SPE) manifold with vacuum and Isolute SPE cartridges (500 mg, 6 mL) were used for SPE.

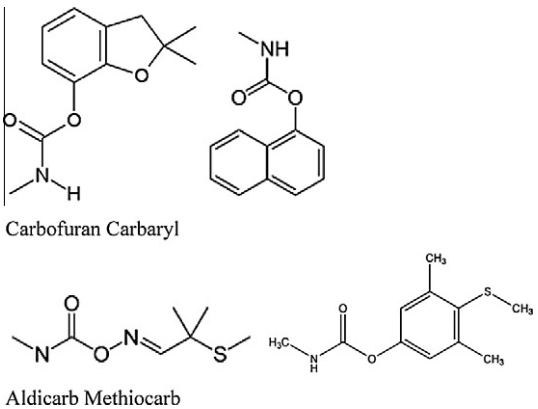

Fig. 1. Chemical structures of the pesticides tested in this study.

2.1. Instrumentation

High performance liquid chromatography used was an Agilent HP 1200 HPLC, equipped with an UV-diode array detector an autosampler and a thermostated column compartment. The column used was an HP Agilent XDB C18 column (1.8 μm, 4.6 × 50 mm). The LC–MS used was a HP Agilent 1100 Series with LC/MSD trap with electrospray ionisation (ESI) source and quadrupole ion trap mass analyser. The mobile phases consisted of acetonitrile (60%) and water (40%) modified with 1% formic acid and this mobile phase was filtered through 0.45 μm Millipore filters.

3. Experimental procedures

3.1. Preparation of individual pesticide standards

Stock solutions of 100 mg L^{-1} of each individual pesticide standard, aldicarb, carbofuran, carbaryl and methiocarb sulfoxide was prepared and from this stock, working solutions of 10 mg L^{-1} were prepared by adding 10 mL into 100 mL volumetric flasks and making it to the mark with distilled water. The calibration standards of 0.5, 1.0, 1.5 and 2.0 mg/L solutions were then prepared from the 10-mg/L solutions in 50-mL volumetric flasks. The solutions were then stored in the refrigerator at 4 °C.

3.2. Hollow fibre supported liquid membrane (HFSLM) extraction

The stripping buffer solutions at the desired pHs were prepared using 0.1 M HCl and 0.1 M KCl solutions according to the standard methods. The hollow fibre was cut into 4 cm pieces and cleaned by soaking in acetone for about 15 min, thereafter sealed at one end by using heat. The open end was used to fill the lumen of the fibre with the stripping buffer solution using 100 μL HPLC syringe. The fibre pieces were then rolled in isooctane solution containing 5% tri-n-octyl phosphine oxide (TOPO) for a about 10 s and then immersed into the sample solution for extraction and enrichment for 30 min. The set up was stirred at an optimum speed of 300 rpm to encourage mass transfer from the bulky solution (Fig. 2). After 30 min extraction time, the hollow fibre piece was removed from the sample solution, opened the sealed end and the extract was bled into an 100 μL Teflon insert placed inside the HPLC auto sampler vial (Fig. 2) ready for HPLC and LC–MS analyses.

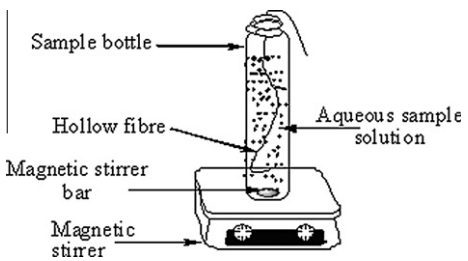

Fig. 2. Diagrammatic representation of the HFSLM extraction procedure.