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Application of liquid-phase microextraction and on-column derivatization combined with gas chromatography–mass spectrometry to the determination of carbamate pesticides

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Abstract

A method has been established for the determination of five carbamate pesticides in water samples using liquid-phase microextraction (LPME) followed by on-column derivatization and gas chromatography–mass spectrometric (GC–MS) determination. Trimethylphenylammonium hydroxide (TMPAH) and trimethylsulfonium hydroxide (TMSH) were used as derivatization reagent for extracts prior to GC–MS analysis as carbamate pesticides are thermally labile compounds. Parameters that affect the extraction efficiency (selection of organic solvent and extraction time) and derivatization efficiency (choice of derivatization reagent and concentration of derivatization reagent) were investigated. The proposed method provided good enrichment factors up to 224, with reproducibility ranging from 4.86 to 7.81%, and good linearity from 1 to 400 μg/L. The limits of detection (LODs) ranged between 0.2 and 0.8 μg/L (S/N = 3) using GC–MS with selective ion monitoring. This method was applied to the determination of carbamate pesticides in tap water and waste water.

Keywords: Liquid-phase microextraction; Carbamate pesticides; On-column derivatization

1. Introduction

Carbamate pesticides, a class of highly effective commercial pesticides, are used worldwide against insects, fungi and weeds. They are increasingly used instead of organochlorine and organophosphorous pesticides due to their lower environmental persistence. However, since they are acetylcholinesterase inhibitors, carbamate pesticides are suspected carcinogens and mutagens [1]. Thus, the increasing use of carbamate pesticides poses a risk to aquatic systems and further becomes a potential hazard to human environment. Carbamate pesticides have been on the priority blacklist released by the US Environmental Protection Agency (EPA).

Common techniques for determining carbamate pesticides include high-performance liquid chromatography (HPLC) with UV detection [2–4], fluorescence detection [5–8] and MS detection [9–11]. GC–MS is another powerful analytical tool for these analytes [12–14], as it provides good selectivity and sensitivity. Because carbamate pesticides are thermally labile compounds, direct GC analysis of carbamate pesticides often leads to their breakdown to the corresponding phenols and amines in the injection port or in the column during the analysis. Therefore, for this reason, derivatization of carbamate is desirable before GC analysis.

Different derivatization reactions including acetylation [15], silylation [16], alkylation [17,18] and perfluorination [18] have been applied to carbamate analysis by GC. Among these techniques, on-column derivatization [19,20] has a distinct advantage as a simple and rapid one-step derivatization approach.

Different sample preparation methods coupled with derivatization have been applied to the determination of carbamate pesticides, such as liquid–liquid extraction (LLE) [21,22], solid-phase extraction (SPE) [13,17] and supercritical fluid extraction (SFE) [17,23]. LLE is a very tedious procedure, and use substantial amounts of toxic organic solvent. SPE is more moderate in organic solvent usage, but it is still in the milliliter range. SFE is a generally organic solvent-free

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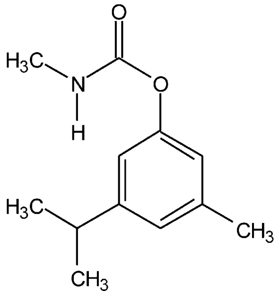
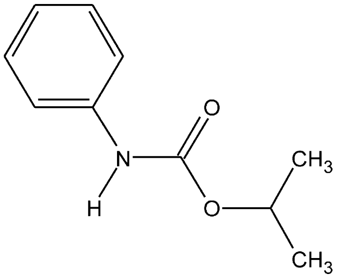
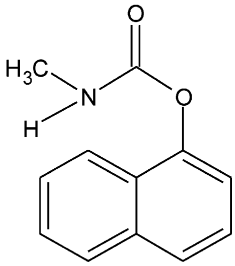
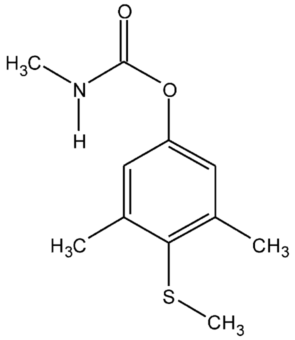
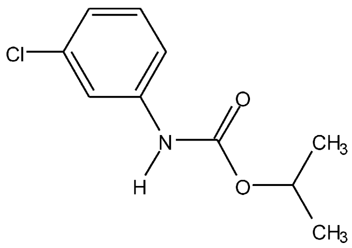
sample preparation method, but it requires high purity supercritical fluids and a relatively expensive fluid delivery system.

In the past few years, liquid-phase microextraction (LPME) has emerged as an organic solvent-minimized sample approach to sample preparation. Solvent requirements are in the microlitre range. Many reports have appeared that highlighted LPME as a simple, fast and effective extraction and preconcentration method [24,25]. LPME has been applied to the determination of many organic compounds in various matrices [26–30].

Table 1
Chemical structure and physical properties of target analytes[a]

Chemical	Structure	CAS	log K_{ow}	Water solubility (mg/L)
Promecarb		2631-65-7	3.10	92.0
Propham		122-42-9	2.60	32.0
Carbaryl		63-25-2	2.36	82.6
Methiocarb		2032-65-7	2.92	104.0
Chlorpropham		101-21-3	3.51	89.0

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[a] Values taken from ref. [33].