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Automated in-tube solid-phase microextraction–high-performance liquid chromatography for carbamate pesticide analysis

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Abstract

In-tube solid-phase microextraction (SPME) is an automated version of SPME that can be easily coupled to a conventional HPLC autosampler for on-line sample preparation, separation and quantitation. It has been termed ''in-tube'' SPME because the extraction phase is coated inside a section of fused-silica tubing rather than coated on the surface of a fused-silica rod as in the conventional syringe-like SPME device. The new in-tube SPME technique has been demonstrated as a very efficient extraction method for the analysis of polar and thermally labile analytes. The in-tube SPME–HPLC method used with the FAMOS autosampler from LC Packings was developed for detecting polar carbamate pesticides in clean water samples. The main parameters relating to the extraction and desorption processes of in-tube SPME (selection of coatings, aspirate/dispense steps, selection of the desorption solvents, and the efficiency of desorption solvent, etc.) were investigated. The method was evaluated according to the reproducibility, linear range and limit of detection. This method is simple, effective, reproducible and sensitive. The relative standard deviation for all the carbamates investigated was between 1.7 and 5.3%. The method showed good linearity between 5 and 10 000 μg/l with correlation coefficients between 0.9824 and 0.9995. For the carbamates studied, the limits of detection observed are lower than or similar to that of US Environmental Protection Agency or National Pesticide Survey methods. Detection of carbaryl present in clean water samples at 1 μg/l is possible.

Keywords: Solid-phase microextraction, in-tube; Extraction methods; Automation; Interfaces, SPME–HPLC; Pesticides; Carbamates

1. Introduction

Carbamate pesticides have been synthesized and sold commercially since the 1950s. Currently, carbamates are one of the major classes of synthetic organic pesticides and are used annually on a large scale worldwide. Carbamates are mainly used in agriculture, as insecticides, herbicides, fungicides, nematocides, acaracides, molluscicides, or sprout inhibitors. In addition, they are used as biocides for industrial and other applications, and in household products [1]. Most of the carbamates have high melting points and low vapor pressures. They are usually distributed in aqueous environments because of their high solubility in water. Studies have shown that carbamates and their degradation products are potential contaminants of the environment and food resources [2]. There is increasing evidence indicating that carbamates may spread throughout ecosystems by leaching and runoff from soil into ground and surface water [3]. The groundwater ubiquity score (GUS), a simple mathematical modeling technique, identifies carbamates as potential leachers because of

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their high water solubility [4]. They may also enter environmental water from industrial wastes, accidental spillage and dumping. Owing to the environmental impact of pesticides, several priority lists, also called ''red'' or ''black'' lists have been published to protect the quality of drinking and surface waters [5]. Carbamates are on the priority lists released by the US Environmental Protection Agency (EPA) [6]. Their determination in various water sources is therefore of great importance.

Chromatographic methods such as gas chromatography (GC) and high-performance liquid chromatography (HPLC) are widely used for the detection of polar pesticides in the environment. For these applications, they are considered complementary to each other, with neither of these two separation techniques presenting an overall advantage [7]. However, for carbamates and their degradation products, HPLC methods are generally preferred over GC methods, because HPLC is applicable to thermally labile and polar compounds. Other chromatographic techniques, such as supercritical fluid chromatography (SFC) [8], thin-layer chromatography (TLC) [9,10] and micellar electrokinetic capillary chromatography (MEKC) [11,12] are also used for carbamate analysis. Solid-phase extraction (SPE) coupled with MS detection provides an alternate tool for the determination of carbamates [13,14]. Some non-chromatographic techniques, such as UV–Vis or Fourier-transform infrared (FT–IR) spectrophotometry [15–17], immunoassays [18], biosensors [19], and electrochemistry [20] have long been used as well [21].

In general, environmental waters cannot be analyzed without sample pretreatment because they are too diluted or too complex [22]. A sample preparation step is necessary to extract traces of pesticides from the aqueous medium, bring the analytes to a suitable concentration level, and remove them from interference components in the matrix (cleanup) before the chromatographic analysis. The choice of the extraction methodology for various types of pesticides and their transformation products (TPs) from water samples depends on analyte characteristics, such as polarity, ionic character, and stability [23]. Several sample preparation methods have been developed for extraction of carbamate pesticides from water, mainly liquid–liquid extraction (LLE) [24,25] and SPE [26,27]. Solid-phase microextraction (SPME) is a relatively new extraction technique compared to LLE and SPE. The development of the SPME technique has been very promising from both a theoretical and a practical point of view since 1990 when it was first introduced by Arthur and Pawliszyn [28,29]. The driving force behind its rapid development is the desire to explore its solvent-free feature, speed of extraction, convenient automation, and hyphenation with analytical instruments such as GC, HPLC and capillary electrophoresis (CE). SPME has been used in many different applications including analysis of air [30], water [31] and soil [32], for both organic and inorganic compounds. Many of the analytes which can be analyzed by GC can be effectively extracted by SPME. SPME coupled to GC is, however, better suited for the analysis of volatile and semi-volatile organic compounds of low to intermediate polarity. Quite a few semi- or non-volatile, thermally labile, or very polar compounds, e.g. pharmaceutical products, drugs, peptides, proteins, and some polar pesticides such as carbamates and their TPs, are better suited to the HPLC method. Although derivatization [33] in either the extraction step or the final determination can broaden the applications of SPME to non-volatile analytes, the hyphenation of SPME to HPLC is still a natural and important extension in the development of the SPME technique.

Coupling of SPME to HPLC through a specially designed interface was first introduced by Chen and Pawliszyn in 1995 [34]. The heart of the interface is a custom-made desorption chamber used for solvent desorption of the extracted analytes instead of thermal desorption in the GC injector. Polycyclic aromatic hydrocarbons (PARs) [34] and nonylphenol ethoxylated surfactants [35] have been successfully analyzed with this manual interface SPME–HPLC system. In 1996, a commercial SPME–HPLC interface was marketed by Supelco [36]. The SPME–HPLC method opened the analytical window to many new, diverse and exciting applications of the SPME technique. To date, there are four types of SPME fibres available for HPLC analysis: polydimethylsiloxane (PDMS); poly(acrylate)(PA); poly(dimethylsiloxane)–poly(divinylbenzene) (PDMS–DVB); and Carbowax–templated resin (CW–TPR). Coating bleed under harsh solvent conditions can be a concern for the manual interface SPME–HPLC method. PDMS and PA are relatively rugged coatings. For polar pesticide analysis, PA is the most

suitable coating. It was found, however, that the PA coating was damaged after only 10–20 desorptions [37]. The limited selection of commercially available fibre coatings for LC analysis may result in poor selectivity for the analysis of very polar compounds with this method. The inherent disadvantages with the manual operation technique are well understood: lower productivity and reproducibility. Those disadvantages could be overcome by automating the SPME–HPLC method. Manual SPME–HPLC will, however, always be useful for analyzing complex samples because of its great flexibility.

Automation is a necessary step in order to improve the efficiency of an analytical method. A first approach to develop an automated in-tube SPME–HPLC system was successfully demonstrated in our laboratory in early 1997. Phenylurea pesticides as a demonstration mixture of polar thermally labile analytes, were extracted by automated in-tube solid-phase microextraction directly from an aqueous sample and analyzed by HPLC [38]. The automated SPME sample preparation was controlled by a commercial autosampler (FAMOS brand from LC Packings), which was adapted to operate the in-tube SPME. A piece of capillary GC column with a commercially available coating was used for the absorption of the analytes from the aqueous sample. Since there is a larger range of coatings available for the GC capillary columns than for the SPME syringe devices, the in-tube SPME–HPLC system can be used with various coated capillaries for different analytes. In addition, the capillary is thoroughly washed after the desorption step, therefore no carryover is observed. Furthermore, better reproducibility was achieved with the automated SPME–HPLC method than with the corresponding manual methods. Current research is focused on method development of this new technique and its applications to the analysis of carbamate pesticides in water samples.

2. Experimental

2.1. Reagents

The six carbamates under study, barban, carbaryl, chlorpropham. methiocarb, promecarb, and propham were purchased from Chem Service (West Chester, PA, USA). All were of ≥98% purity and were used as received. Acetonitrile, methanol (HPLC-grade quality) and hexane (glass distilled) were ordered from EM Science (Gibbstown, NJ, USA). 1-Propanol and 1-butanol (certified A.C.S.) were purchased from Fisher Chemical/Fisher Scientific. 2-Propanol, diethyl ether, and cyclohexane (analytical reagent) were obtained from BSH (Toronto, Canada). Tetrahydrofuran (reagent) was purchased from Caledon Labs. (Georgetown, Canada). Water was obtained from a Barnstead/Thermodyne NANO-pure ultrapure water system (Dubuque, IA, USA).

Single standards with concentrations of 1 mg/ml were prepared for each compound using methanol (HPLC grade) as a solvent. A standard mixture using methanol (HPLC grade) as solvent was prepared containing the organic compounds at a concentration of 0.1 mg/ml, each. Aqueous samples with concentrations of 2 mg/l were prepared by spiking this standard into nano-pure water for our studies. Degradation was observed for a few carbamates, especially carbaryl. Therefore, fresh aqueous samples were prepared before each experiment. The aqueous samples for limit of detection, and linearity tests were nano-pure water spiked with the methanolic standard stock mixture or diluted standard mixtures reducing the concentration to suitable levels.

2.2. HPLC conditions

A Nova-Pak C_{18} 100×8 mm (4 μm) HPLC column (Waters, Milford, MA, USA) was used. An acetonitrile–water (50:50, v/v) mixture was used as the mobile phase under isocratic elution. The HPLC cartridge was contained in a Waters RCM 100×8 mm cartridge holder. A TSK-6010 HPLC pump was used. The flow-rate was set at 1.4 ml/min. A UV detector (Toso-Haas, Philadelphia, PA, USA) was used. The wavelength chosen for detection was 220 nm. Data acquisition and processing were performed using Star 4.5 software (Varian, Palo Alto, CA).

2.3. In-tube SPME technique

A FAMOS autosampler (LC Packings, Amsterdam, Netherlands) was used to control the in-tube SPME. A section of coated GC capillary (typically 60 cm long) was mounted in the autosampler in place of the non-coated silica capillary (retention gap

capillary) which is installed in that position in the conventional configuration. A stainless steel needle protects the end of the capillary when it pierces through the septum of the vial containing the spiked aqueous sample. Sample vials (2 ml) were placed on the commercial autosampler tray, followed in the tray by their respective 2 ml solvent vials. The HPLC injection loop was a 56 cm long poly(ether ether ketone) (PEEK) tubing (300 μm I.D.) which has a total volume of 40 μl. The autosampler software can be manually programmed to control the SPME extraction and the desorption processes. The instrumental set up for the in-tube SPME–HPLC system and a detailed schematic of the in-tube SPME capillary were published previously [38].

The first step in this method consists of rinsing the GC capillary with methanol; methanol remains inside the capillary before the extraction. In the extraction step, a sample volume of 25 μl, which is the total volume of the syringe used in this study, is aspirated from the sample vial. Then the same sample volume is dispensed back into the vial. These aspirate/dispense steps are repeated several times. After the extraction step, the six-port valve is switched to the ''LOAD'' position. Then, 38 μl of methanol is aspirated from the respective solvent vial for desorbing the extracted analytes from the capillary coating and transferring them into the injection loop. After the desorption step, the six-port valve is switched to the ''INJECT'' position while a trigger signal is sent to the personal computer to start the data acquisition. The sample is sent from the loop to the analytical column by the mobile phase.

3. Results and discussion

Similar to the conventional SPME technique, method development for the in-tube SPME addresses primarily two important processes: extraction and desorption. The extraction process is achieved by moving sample in and out of the extracting capillary by repeated aspirate and dispense steps. During sample aspiration steps, the sample moves into the capillary and thus comes into contact with the extraction phase, and the partitioning of analytes between the coating and matrix starts. After extraction, the needle containing the SPME capillary is programmed to draw a certain amount of solvent from the appropriate solvent vial to desorb the analytes from the capillary and transfer them into the injection loop. Extraction and desorption were studied separately during the optimisation of the in-tube SPME procedure.

The selection of a suitable coating, based on the chemical nature of analytes, is the key step in the development of the extraction methods includes the in-tube SPME. A large range of coatings are available for GC capillaries, and so the use of GC capillaries in the in-tube SPME method affords the higher levels of selectivity and sensitivity required for the polar carbamates. Five different types of GC open tubular capillary columns with variable polarities (SPB-1, SPB-5, PTE-5, Supelcowax, Omegawax 250) and retention gap capillary (deactivated fused-silica, without coating) were evaluated. A complete calibration was performed, using eight concentrations (1, 2, 5, 10, 25, 50 and 80 100 ng/μl). The linearity was good with correlation coefficients between 0.9976 and 0.9999. The detector response was calibrated with three replicate 5 μl standard injections of each of the above samples. The masses extracted with the different SPME capillaries were calculated and the results are presented in Table 1. Fig. 1 shows the comparison of the extraction efficiencies with the different capillaries. It was observed that the most polar coating, Omegawax 250, offers the highest extraction efficiency for the carbamates studied. It was therefore selected for further studies.

Equilibration time is a critical parameter in SPME experiments. It is defined as the time after which the amount of extracted analyte remains constant and corresponds, within experimental error, to the amount extracted at infinite extraction time [29]. It is determined from the extraction time profile, which is produced by plotting the extraction time against the amount (mass) of an analyte extracted. In the in-tube SPME method, the extraction of analytes is achieved by moving the sample in and out of the extraction capillary at specific speeds (63 μl/min was used in our studies). The extraction time profile can be easily obtained by plotting the number of aspirate/dispense steps versus the amounts of analytes (mass) extracted. The number of aspirate/dispense steps correlate to the extraction time. Based on the aspirate/

Table 1
Amounts extracted with different capillaries (ng) after 25 aspirate/dispense (a/d) steps of 25 μl volume at a flow-rate of 63 μl/min, $n=6$; the concentration of the aqueous sample was 2000 μg/l for each compound

GC capillary	Carbaryl	Propham	Methiocarb	Promecarb	Chlorpropham	Barban
Fused silica	13±1	24±1	29±2	20±1	29±1	43±1
SPB-1	6±1	46±1	55±1	42±1	126±3	125±3
PTE-5	21±1	42±1	57±3	35±1	112±5	197±6
SPB-5	15±1	72±3	71±4	56±5	202±6	199±6
Supelcowax	35±3	32±3	61±3	22±3	94±6	271±5
Omegawax 250	173±5	159±9	248±6	114±5	323±8	468±9

dispense profile (see Fig. 2), we can conclude that five of the carbamates: methiocarb, chlorpropham. propham, promecarb, and carbaryl, achieved equilibrium extraction after 25 steps (roughly 25 min). Barban did not achieve equilibrium extraction, even after 50 steps. A total of 25 aspirate/dispense steps was selected for further studies.

In a pure matrix, the distribution constant K_{fs} defines the sensitivity of the method [29]. Under equilibrium conditions, K_{fs} can be calculated from Eq. (1):

$$K_{fs} = \frac{n_f^{\infty} V_s}{V_f (C_o V_s - n_f^{\infty})} \quad (1)$$

where C_o is the initial sample concentration (2000 μg/l), n_f^{∞} is the mass of analytes extracted by the capillary at equilibrium. and V_s is the sample volume

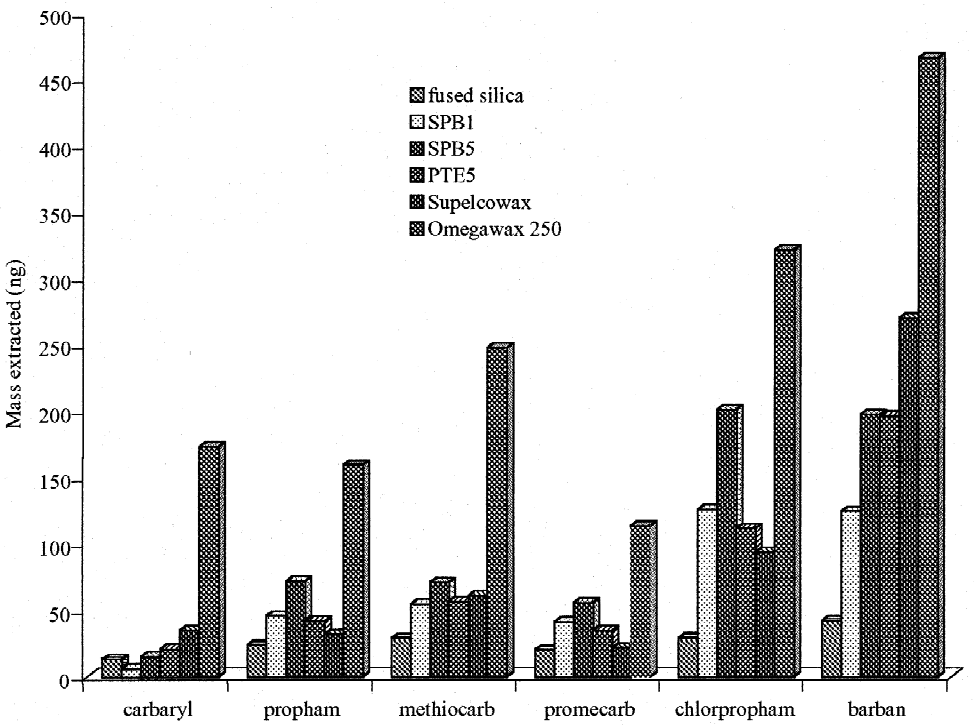

Fig. 1. Comparison of the extraction efficiencies with the different capillaries. Sample concentration: 2000 μg/l, 25 aspirate/dispense (a/d) steps, six replicates for each capillary.

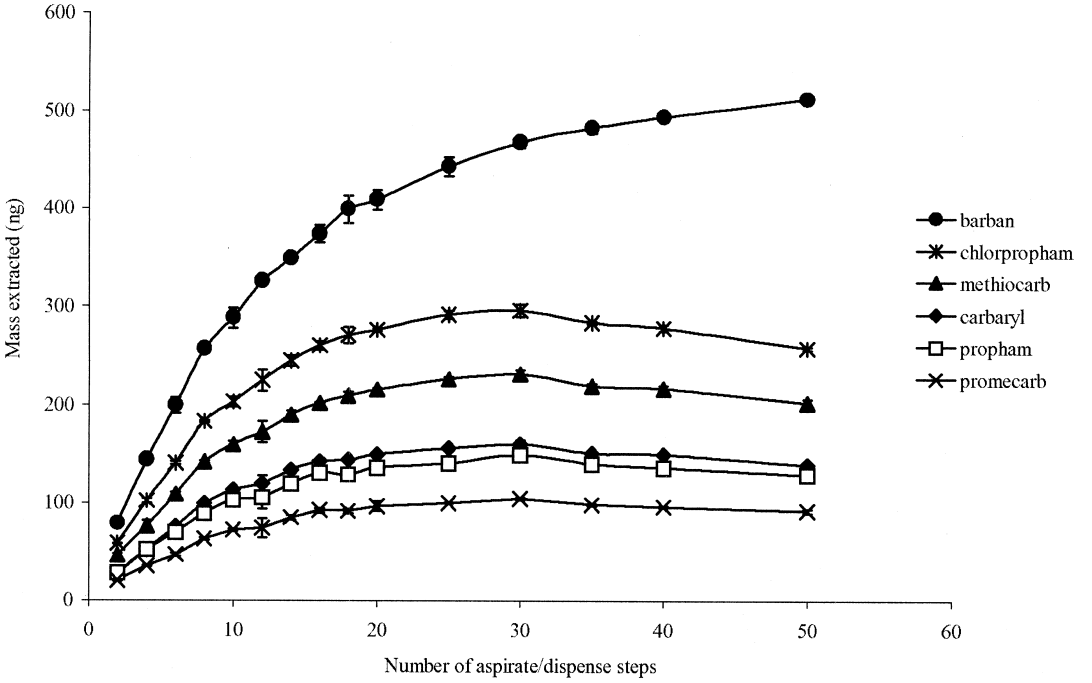

Fig. 2. Extraction profiles (number of aspirate/dispense steps) for six carbamates using a Omegawax 250 capillary. Duplicate aqueous samples were extracted using 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 25, 30, 35, 40 and 50 aspirate/dispense steps.

(1 ml), V_f. is the volume of coating inside the capillary. For our experiments, as only 25 μl of sample was aspirated/dispensed inside the capillary, the effective coating volume of the capillary used was only 100 nl rather than 118 nl which is the total coating volume of the 60 cm long capillary. The estimated K_{fs} values for the six carbamates studied are shown in Table 2. The K_{fs} of barban was 3054 under 25 aspirate/dispense steps conditions; the true value is expected to be larger than this value. Barban had the largest K_{fs} value among the six compounds. The larger the K_{fs} value is, the longer the equilibrium time. That is why barban hadn't reached equilibrium even after 50 aspirate/dispense steps.

For the desorption solvent screening experiments, nine solvents from four solvent groups (nitriles, alkanes, alkyl alcohols and alkyl ethers) were evaluated. Their respective UV cutoffs were less than 220 nm (which is the UV wavelength used for our studies) in order to avoid interference with the target analytes. The solvents studied included: acetonitrile, methanol, tetrahydrofuran, 1-propanol, 2-propanol, 1-butanol, diethyl ether, cyclohexane and hexane. Fig. 3 shows the desorption efficiencies of the solvents compared to methanol. Experimental results show the following: (1) Non-polar solvents, such as cyclohexane and hexane were less efficient than the other solvents. For example, compared to methanol, the desorption efficiency of hexane and cyclohexane for carbaryl was 87 and 86%, respectively, while for barban, it was of only 69 and 68%, respectively. (2) For propham, methiocarb, chlorpropham and barban, ethyl ether desorbed analytes more efficiently than the other solvents. The advantage relative to metha-

Table 2
Estimated K_{fs} values for six carbamates

Carbaryl	Propham	Methiocarb	Promecarb	Chlorpropham	Barban
949	867	1417	603	1923	>3054

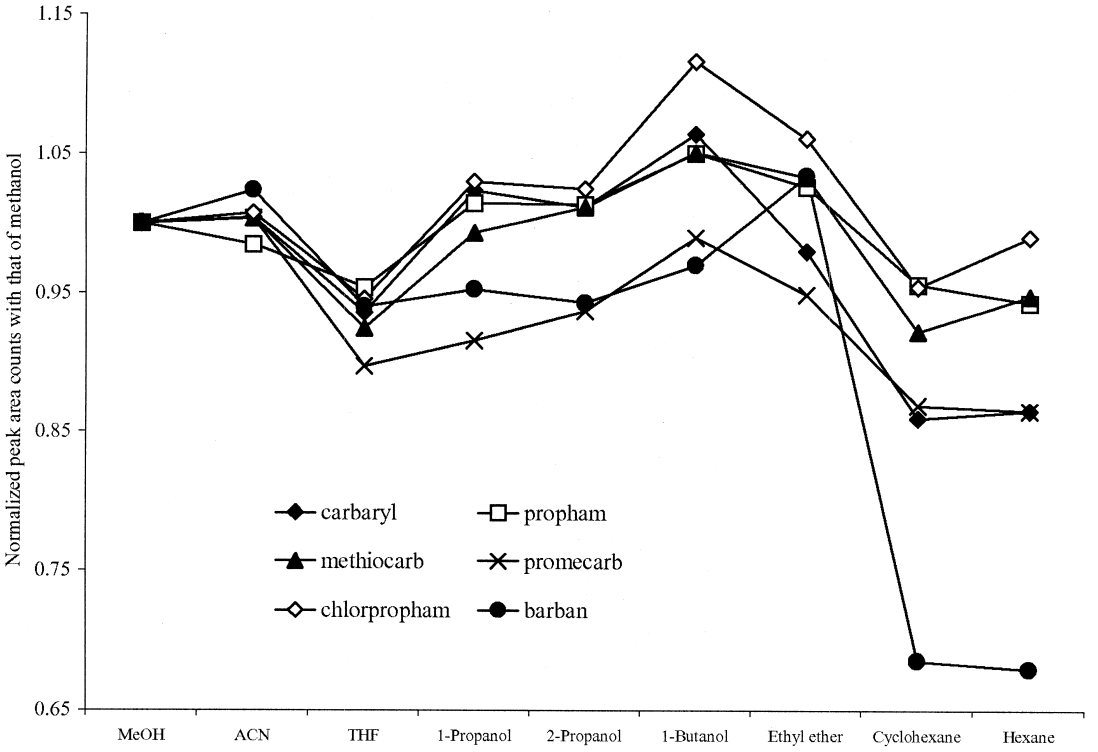

Fig. 3. Comparison of the desorption efficiencies of the solvents studied to that of methanol. Sample concentration: 2000 μg/l, 25 a/d steps, six replicates for each solvent.

nol, however, is only within the 5% experimental error. In general, the ethers such as tetrahydrofuran (THF) and diethyl ether are not considered the best choice as desorption solvents because of the impurities that exist in those solvents. (3) The desorption power of acetonitrile is very similar to that of methanol. (4) Among the alcohol solvents, butanol desorbed some carbamates better than methanol, but again the advantage mainly remained within the 5% experimental error. Considering the toxicity and cost of the solvents tested, methanol is still considered the best choice as desorption solvent.

The solvent volume used in the desorption step can be programmed with the FAMOS autosampler. The desorption efficiency (peak area counts) varies with the different desorption volumes. The optimal desorption volume can be determined based on desorption curves. Fig. 4 shows the desorption curves of the carbamates studied. Considering a 5% experimental error, nearly full recovery was achieved when a desorption volume of 35 μl was used. The desorption efficiency was constant between 35~60 μl. Beyond 60 μl the efficiency dramatically decreased. This indicated a loss of sample. Almost no analytes could be contained in the injection loop when 100 μl methanol was drawn. Since the void volume of the injection loop is about 40 μl, a value of 38 μl was arbitrarily selected as the optimal desorption volume in order to avoid the loss of sample.

The injection loop, injection needle, SPME capillary and the buffer tubing were normally washed with 250 μl methanol after each injection. Using this procedure, no carryover was detected. However, it is still very important to determine the absolute desorption efficiency and hence potential for carryover when 38 μl methanol was used as the desorption solvent. In the carryover study, a chromatogram was obtained using 38 μl of methanol as the desorption solvent (see Fig. 5(a)), followed by a second chromatogram after flushing with another 38 μl of methanol (see Fig. 5(b)) and, finally, a third chro-

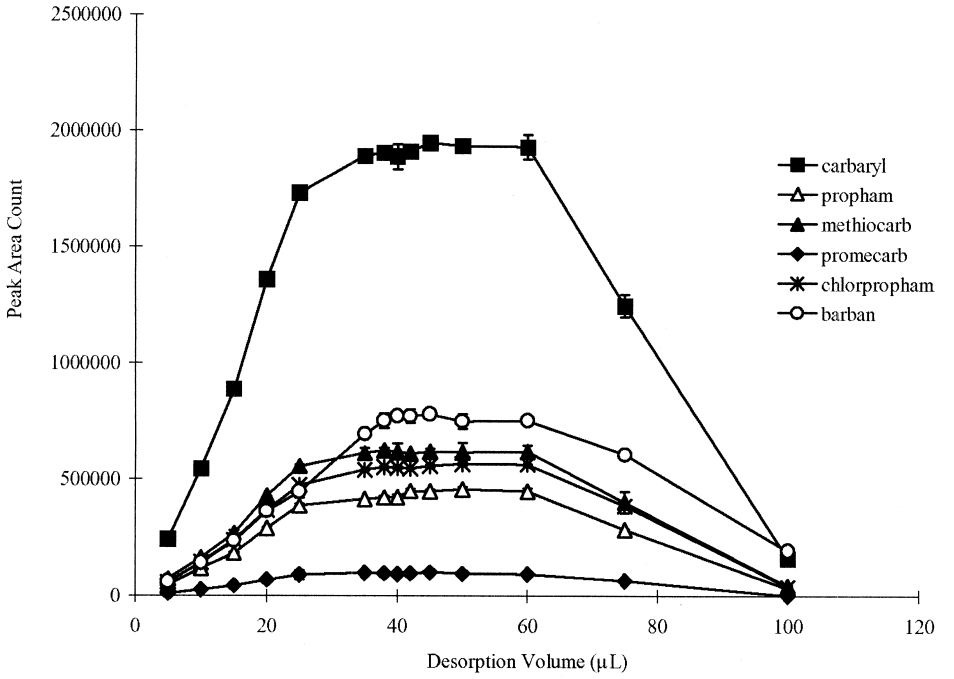

Fig. 4. Desorption curves for the carbamates studied. Sample concentration: 2000 μg/l, 25 a/d steps, $n=2$. Error bars indicate the standard deviation (SD) to the mean. The absence of error bars indicates that the SD is smaller than the symbol size.

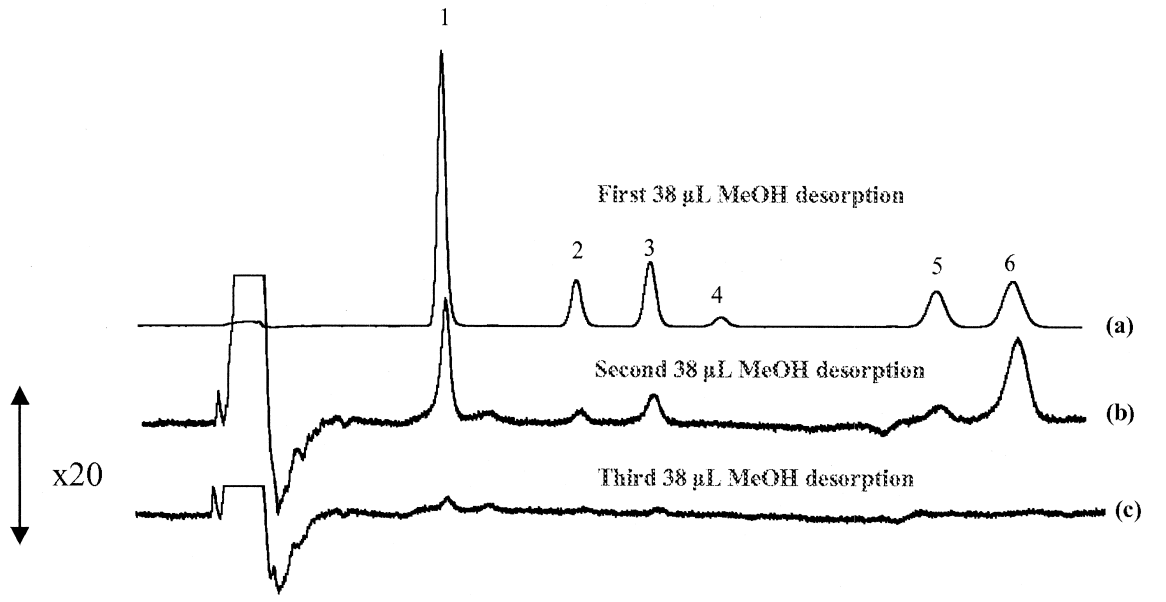

Fig. 5. Carryover study. (a) In-tube SPME–HPLC of six carbamates using 25 aspirate/dispense steps with desorption solvent of methanol 38 μl; (b) trace resulting after a second 38 μl methanol desorption; (c) trace resulting after a third 38 μl methanol desorption. Note the *y*-axis in the case of (b) and (c) is expanded 20 times. Peak identifications: (1) carbaryl; (2) propham; (3) methiocarb; (4) promecarb; (5) chlorpropham; (6) barban.

Table 3
Recovery of the carbamates studied with 38 μl methanol used as desorption solvent, $n=3$

Recovery (%)					
Carbaryl	Propham	Methiocarb	Promecarb	Chlorpropham	Barban
99.1	99. 8	99.2	100.0	100.0	97.3

matogram with an additional 38 μl of methanol (see Fig. 5(c)). We can see from the chromatograms that only trace amounts of carbaryl, propham, methiocarb and barban could be detected after the second flushing of methanol, and that no peaks could be detected after the third injection. The total recovery can be calculated based on the peak area counts. Table 3 lists the recovery for each of the carbamates studied when 38 μl methanol was used as the desorption solvent, three replicate samples were run for this study. Excellent recoveries for the carbamates studied were achieved. These results are in good agreement with the desorption curve.

The method was evaluated for the reproducibility, linear range and limit of detection. The reproducibility of the method, using the optimal experimental conditions, was determined by analyzing six replicate samples (see Table 4). The method was reproducible with precision between 1.7 and 5.3% RSD for the carbamates studied. The good method precision achieved is probably due to both the agitation conditions (flow in and out) and, most importantly, to the automation process. Linearity was determined over a concentration range of 5 to 10 000 μg/l. The method was linear for all the carbamates studied with correlation coefficients (R^2) between 0.9824 and 0.9995. Fig. 6 shows the chromatograms of six carbamates analyzed at different concentrations. The limits of detection (LODs) for the six carbamates were determined using a 10 μg/l sample concentration with duplicate analysis. The calculation method for the LOD test was a signal-to-noise ratio of three. The number of aspirate/dispense steps used was 15. Table 4 lists the LODs of the six carbamates studied with the in-tube SPME–HPLC method. These ranged between 1 and 15 ppb, which was quite reasonable using a UV detector. The LOD is expected to be lower as the aspirate/dispense steps increase. For the purpose of comparison, the LODs of the carbamates achieved by EPA and NPS (Na-

Table 4
Precision and limit of detection (LOD) of the in-tube SPME–HPLC–UV for six carbamates

No.	Compound	Chemical formula	M_r [a]	Log P_{ow} [b]	t_R (min)[c]	Precision (%RSD)		LOD (μg/l)	
						t_R (min)	Area counts	In-tube SPME–HPLC[d]	EPA/NPS method
1	Carbaryl	$C_{12}H_{11}NO_2$	201	236	445	0.05	2.7	1.0	2[e]
2	Propham	$C_{10}H_{13}NO_2$	179	2.60	6.44	0.07	5.3	5.1	11[f]
3	Methiocarb	$C_{11}H_{15}NO_2S$	225	2.92	7.52	0.06	2.1	4.0	4[e]
4	Promecarb	$C_{12}H_{17}NO_2$	207	3.10	8.55	0.04	3.7	15.0	N/A
5	Chlorpropham	$C_{10}H_{11}ClNO_2$,	214	–	11.71	0.08	2.2	8.5	0.5[g]
6	Barban	$C_{11}H_9NO_2Cl_2$	258	–	12.81	0.10	1.7	7.5	3.8[f]

[a] M_r, molecular mass.
[b] Log P_{ow}, octanol–water partition coefficients, from Ref. [40].
[c] Average retention time.
[d] Signal-to-noise ratio of three.
[e] EPA 531.1, direct aqueous injection into HPLC with postcolumn derivatization. After elution, hydrolysis with 0.05 *M* NaOH at 95°C, reaction with *o*-phthalaldehyde (OPA) and 2-mercaptoethanol to form a highly fluorescent derivative.
[f] NPS method 4, dichloromethane extraction, LC–UV method.
[g] EPA 507, dichloromethane extraction, GC–NPD method.

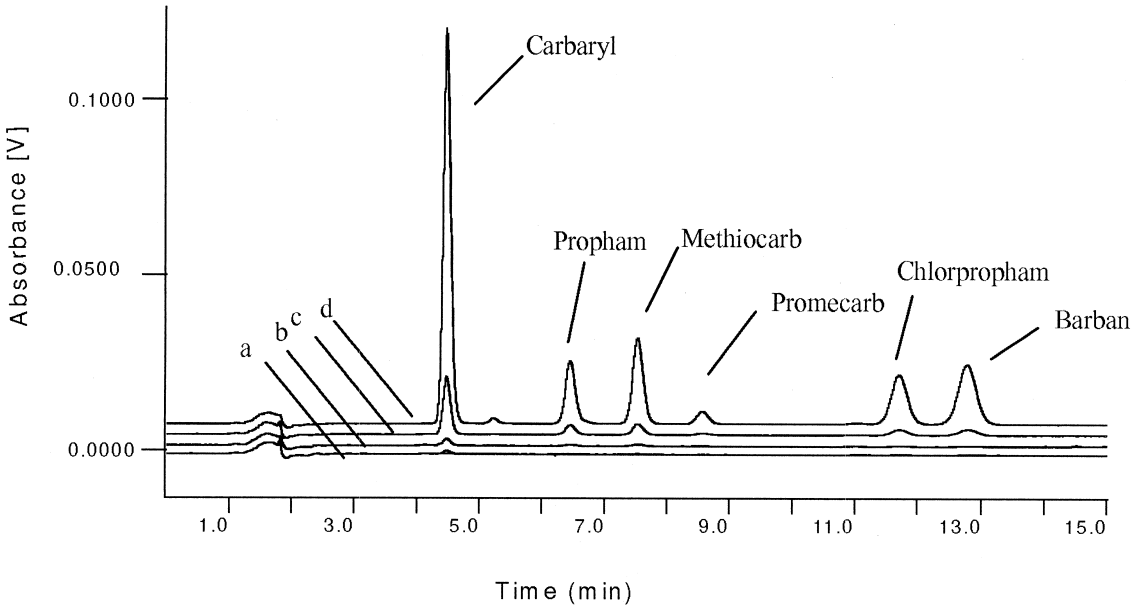

Fig. 6. Chromatograms of extraction and analysis of six carbamates using the in-tube SPME–HPLC method with four concentrations: (a) 5, (b) 10, (c) 100, and (d) 1000 μg/l, a/d steps=15.

tional Pesticides Survey) methods are also listed in Table 4.

EPA method 531.1 is considered to be the most sensitive and selective method for the analysis of carbamates. This method uses a RP-HPLC reversed-phase HPLC with postcolumn fluorogenic derivatization. Obviously, this method has to use complicated devices for on-line derivatization and consumes considerable amounts of reagents.

Compared to EPA 531.1, the LOD value for carbaryl with the in-tube SPME–HPLC method was significantly lower. For methiocarb, a comparable LOD was achieved with the in-tube SPME–HPLC method. EPA method 507 for chlorpropham has a lower detection limit since GC–NPD (nitrogen–phosphorous detection) was used. NPS method 4 is a LC–UV method using dichloromethane extraction. For propham, the LOD is two times lower with the in-tube SPME–LC method compared to the NPS method. The LOD for barban was lower with NPS method 4, possibly because of the high hydrophobicity of this compound, which makes it easier to extract in dichloromethane. There are no data available for promecarb with either EPA or NPS methods. Promecarb is no longer marketed because it is considered highly hazardous to the environment [39].

4. Conclusions

In-tube SPME was easily coupled to a FAMOS HPLC autosampler from LC Packings. The interface could be readily attached without further modification to the autosampler itself. It provided a very efficient and simple preparation method that was automatically controlled by the autosampler software. This system was successfully used to analyze the above mentioned carbamates. All the main parameters relating to both the extraction and the desorption processes of the in-tube SPME were investigated. The new in-tube SPME method presents the following advantages over manual SPME–HPLC. (1) It is a fully automated method, requiring no sample manipulation between the extraction and the HPLC analysis, therefore offering a very high operating efficiency and precision. (2) It also affords a high selectivity, as the range of coatings available for GC capillaries is wider than is currently available

for SPME fibres. (3) It does not present any carryover problems. This method has a reasonably low LOD for UV analysis of the carbamates studied, and is lower or similar to those obtained by EPA or NPS methods.

Acknowledgements

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