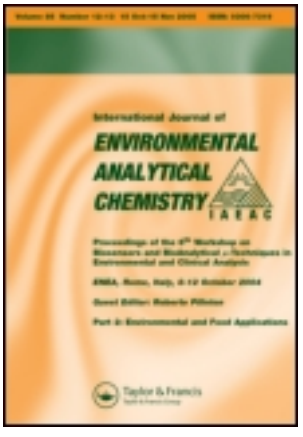

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/geac20

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Available online: 19 Sep 2011

To cite this article: David Moreno-González, José Fernando Huertas-Pérez, Laura Gámiz-Gracia & Ana María García-Campaña (2011): Determination of carbamates at trace levels in water and cucumber by capillary liquid chromatography, International Journal of Environmental Analytical Chemistry, 91:14, 1329-1340

To link to this article: http://dx.doi.org/10.1080/03067319.2010.520127

Intern. J. Environ. Anal. Chem.
Vol. 91, No. 14, December 2011, 1329–1340

Taylor & Francis
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Determination of carbamates at trace levels in water and cucumber by capillary liquid chromatography

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(*Received 22 March 2010; final version received 12 August 2010*)

A sensitive and reliable method using capillary HPLC with UV-diode array detection (DAD) has been developed and validated for trace determination of carbamate pesticides in cucumber and environmental water samples. The analytes, including carbofuran, carbaryl, methiocarb, promecarb, benthiocarb and fenoxycarb, present legal residue levels regulated by the EU Council Directive 98/83/EC on drinking water and by the Regulation (EC) No. 396/2005 on vegetables. A previous off-line solid-phase extraction (SPE) procedure was required for preconcentration and sample clean-up. The separation was achieved using a C_{18} column (150 mm × 0.5 mm I.D, 5 μm particle size) and a mobile phase consisting of ACN : water using gradient mode, with a flow rate of 10 μl min^{-1}. Taking advantages of the characteristics of capillary HPLC, low volume of sample and solvents were required, achieving limits of detection for the studied compounds ranged from 10.0–29.6 ng l^{-1} for water samples and 1.8–5.6 μg kg^{-1} for cucumber, using UV-detection. Recoveries studies for fortified samples, at three different concentration levels, were carried out obtaining recoveries ranging from 70.0 to 111.1% and relative standard deviations (RSDs) lower than 10.6%.

Keywords: carbamates; capillary HPLC; environmental waters; cucumber

1. Introduction

N–methylcarbamates (NMCs) are compounds with chemical structure: R–O–C(O)–$N(CH_3)$–R′, where R is an alcohol, an oxime or a phenol, and R′ is an hydrogen or a methyl group. They are commonly used as broad-spectrum pesticides for control of insects on a wide variety of fruits, vegetables, forage, cotton and other crops including bananas, coffee beans, grapes, potatoes, corn, rice, sugarcane and wheat. They act as reversible inhibitors of the enzyme cholinesterase, being mortal in high dosage [1,2]. Their main characteristics are high toxicity, low stability, and non-accumulation in organic tissues. They are biodegradable, with low soil persistence and can be degraded in water by hydrolysis, biodegradation, oxidation, photolysis, biotransformation and metabolic reactions in living organisms. As minute quantities of these chemicals can affect the human body, trace concentrations of these pesticides in the environment and food need to be controlled. Some of the NMCs, including carbaryl, carbofuran and methiocarb,

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ISSN 0306–7319 print/ISSN 1029–0397 online

http://dx.doi.org/10.1080/03067319.2010.520127
http://www.tandfonline.com

are included in the final list of compounds to be considered for periodic re-evaluations by the Joint FAO/WHO Meeting on Pesticide Residues (JMPR) [3]. In the European Union, the Regulation (EC) No. 396/2005 on maximum residue levels of pesticides in products of plant and animal origin brings together and harmonises in a single act all the limits applicable to the various types of food and feed. It also establishes a maximum residue limit (MRL) of 0.01 mg kg^{-1} as a default value [4].

Chromatographic methods have been usually applied for the determination of carbamates in food and waters, using mainly fluorescence [5–6] and mass spectrometry detection [7–9]. Some reviews concerning the analysis of these compounds in water [10–11] and foods [12–15] can be found in the literature. Post-column hydrolysis of NMCs to methylamine (MA) and subsequent derivatisation with *o*-phtalaldehide (OPA) is the basis of the HPLC-fluorescence method which has been accepted as a standard protocol by several official organisations, including EPA [16]. Chemiluminescence, a less usual detection technique in HPLC, has also been used [17–18].

Capillary HPLC has emerged as an alternative miniaturised technique to conventional HPLC and CE [19]. In this type of chromatography, columns of internal diameter of typically 500 μm and flow rates up to 20 μl min^{-1} are used. Capillary HPLC shows several advantages compared to analytical HPLC, such as better resolution, lower detection limits and lower solvent consumption, being more environmentally friendly than conventional HPLC [20]. It is recommended when sample volume is limited, and especially to gain sensitivity. In this sense, a relatively low sensitive detector as UV/Vis could be used for detecting these compounds, thanks to the higher sensitivity provided by capillary HPLC, as has been shown for different analytes and matrixes [21–22]. Thus, the target of this paper is to show the applicability of this technique for the analysis of trace amounts of carbamates, taking advantage of the higher sensitivity provided by capillary HPLC. With this purpose, we propose the separation and sensitive determination of six NMCs (namely: carbofuran, carbaryl, methiocarb, promecarb, benthiocarb and fenoxycarb, whose structures are shown in Figure 1) in environmental waters and cucumber samples by means of capillary HPLC-DAD. A previous solid phase extraction (SPE) procedure was necessary for preconcentration and clean-up. A rigorous optimisation of the significant variables involved in both extraction and chromatographic separation has been carried out to obtain an adequate separation, peak shape and analysis time. As far as we know, this is the first time that this miniaturised technique has been used for the quantitative analysis of this family of pesticides.

2. Experimental

2.1 *Chemicals*

All the reagents were of analytical reagent grade and solvents were of HPLC grade. Organic solvents (methanol, acetonitrile (ACN) and ethyl acetate), hydrochloric acid and anhydrous sodium sulfate were supplied by Panreac-Química (Madrid, Spain). All solvents used as mobile phase and water samples were filtered under vacuum through 0.45 μm nylon filter (Supelco, Bellefonte, PA, USA). Ultrapure water (18.2 MΩ cm^{-1}, Milli-Q plus system, Millipore, Bedford, MA, USA) was used throughout the work.

Analytical standard of carbofuran, carbaryl, methiocarb, promecarb and benthiocarb were supplied by ChemService Inc. (West Chester, USA) and fenoxycarb was supplied by Riedel-de Haën (Seelze, Germany). Individual stock standard solutions containing

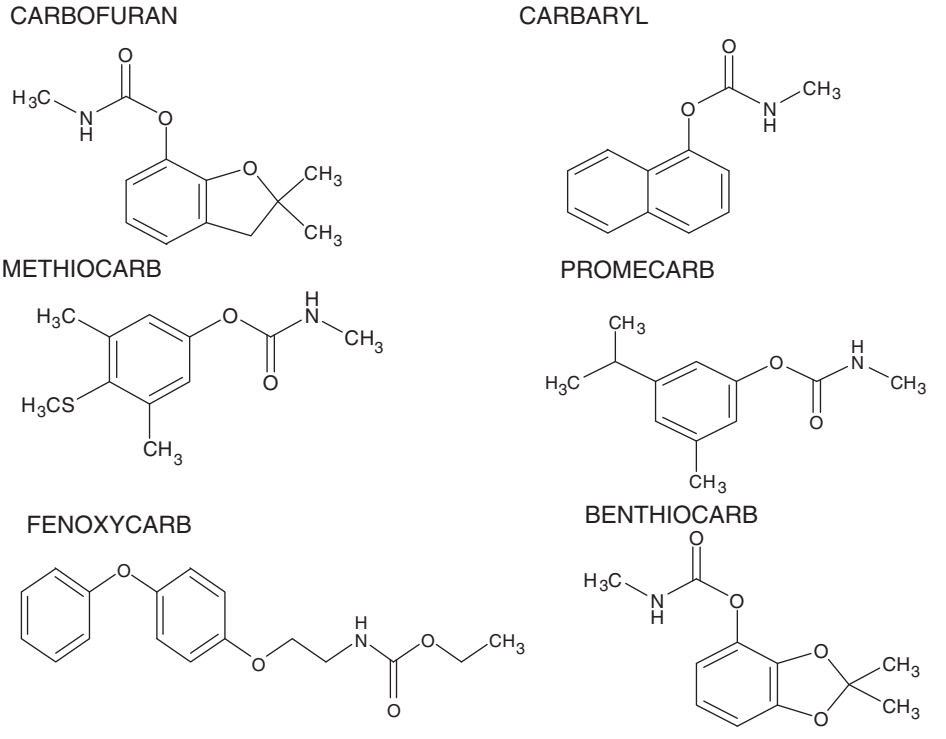

Figure 1. Chemical structures of the studied carbamates.

500 mg l^{-1} of each compound were prepared by dissolving accurately weighed amounts in methanol and stored in the dark at 4°C. They were stable for at least four months. Working standard solutions were freshly prepared by dilution to the desired concentration with methanol.

Extraction cartridges containing a hydrophilic–lipophilic balance (Oasis HLB, 200 mg, 6 ml; Waters, Milford, MA, USA) and Alumina N from Supelco in laboratory-prepared cartridges (1.25 g, 3 ml) were used in the SPE step. Acrodisc 13 mm syringe filters with 0.2 μm nylon membrane (Pall Corp., MI, USA) were used for filtration of cucumber extracts prior to the injection in the chromatographic system.

2.2 *Instruments and equipment*

Chromatographic analyses were performed with an Agilent HP-1200 series capillary HPLC (Agilent Technologies, Waldbronn, Germany) equipped with a binary pump (20 μl min^{-1} maximum flow-rate), online degasser, autosampler (8 μl loop), column thermostat and DAD. ChemStation software (A.10.20 [1757] version) was used for data acquisition and processing. The chromatographic separation was performed on a Luna C_{18} column (150 mm × 0.5 mm I.D., 5 μm particle size) from Phenomenex (supplied by Micrón, Madrid, Spain).

A Preppy vacuum manifold for 12 cartridges from Supelco coupled with a vacuum pump (Büchi model B-169, Flawil, Switzerland), a rotavapor (Büchi RE 121), and a domestic blender from Taurus (Lerida, Spain) were used for sample preparation. For pH measurements, a pH-meter (Crison model pH 2000, Barcelona, Spain) with a resolution of ±0.1 pH unit was used.

2.3 *Chromatographic conditions*

The reverse phase separation was developed in a C_{18} column and the binary mobile phase consisted of ACN : water, using the following gradient elution: 30% ACN (1 min), to 70% ACN (5 min), maintaining these conditions (12 min). The flow rate was 10 µl min^{-1}, the column temperature was kept at 25° C and the injection volume was 0.5 µl. Based on literature the DAD detector wavelength was set at 210 nm [23–24].

2.4 *Sample preparation*

2.4.1 *Water sample preparation*

This procedure was based on a previously reported work, with some modifications [18]. Freshly collected water samples from growing areas susceptible of contamination by NMCs (river water samples from Dilar, Granada, and ground water samples from Santa Fe, Granada) were spiked with proper concentrations of NMCs, filtered to remove suspended particulate matter and pH adjusted to 3.0 with HCl 1M to prevent the potential degradation of the analytes, The samples were stored in the dark at 4°C until analysis. Extraction and preconcentration of the analytes were achieved by SPE using Oasis HLB cartridges (200 mg, 6 ml) preconditioned with 6 ml of ethyl acetate, 6 ml of methanol and 6 ml of ultrapure water, at a flow rate of 3 ml min^{-1}. Then, 500 ml of water sample were loaded on the SPE cartridge at the flow rate of 10 ml min^{-1}. After sample loading, the cartridges were washed with 5 ml of water at a flow rate of 3 ml min^{-1} and air-dried for 15 min. The analytes were eluted with 6 ml of acetone at 3 ml min^{-1}. The eluate was dried under a gentle nitrogen current at 30°C. The dry residue was dissolved in 2 ml of methanol and thoroughly vortexed. A 0.5 µl aliquot was injected into the chromatographic system. Sample throughput was about 12 samples per day.

2.4.2 *Cucumber sample preparation*

Portions of 20 g of cucumber sample collected from an ecological farm (Motril, Granada), were spiked with proper concentrations of NMCs. After equilibration for 1 hour at room temperature, samples were chopped and blended for 5 minutes with 60 ml of ethyl acetate and 60 g of anhydrous sodium sulfate. The mixture was filtered through a paper filter with vacuum and transferred to a round-bottom flask. Fifteen ml of ethyl acetate was used to clean both the filter and the filtering flask, and were also transferred to the round-bottom flask. The obtained solution was concentrated in a rotavapor to ca. 2 ml, using a bath temperature of 30°C. Then, the solution was made up to 5 ml with ethyl acetate and this solution was cleaned up through an alumina cartridge (1.25 g, previously conditioned with 5 ml of water, 5 ml of methanol and 5 ml of ethyl acetate, at a flow rate of 3 ml min^{-1}) at a flow rate of 0.5 ml min^{-1} and the eluate collected in a glass vial. The ethyl acetate was then evaporated at 30°C under nitrogen stream until dryness. The final residue was re-dissolved

with 1 ml of methanol, thoroughly vortexed and injected in the chromatographic system. Sample throughput was about 12 samples per day.

3. Results and discussion

3.1 *Optimisation of the chromatographic separation*

The optimisation of all the parameters involved in the chromatographic separation (such gradient profile, column temperature and injection volume) was performed in a univariate mode. Mixtures of methanol or ACN with water have been widely used for the separation of NMCs on RP C_{18} and C_8 columns [25,26]. Thus, these binary mixtures were tested and ACN : water was selected as the mobile phase since it produces smoother baseline and better peak shapes. The optimised elution program was as follow: 30% (v/v) ACN for 1 min, a linear increase to 70% ACN (5 min), maintaining these conditions (12 min). The flow rate was set at 10 µl min^{-1}. Temperature was studied in a range between 15 and 35°C, selecting 25°C since no significant influence was observed. The injected volume was also tested from 0.10 to 2.00 µl, selecting a final value of 0.50 µl, in order to increase sensivity without losing of resolution. A chromatogram corresponding to a standard mixture of the NMCs is provided (Figure 2).

3.2 *Optimisation of sample treatment for water*

The maximum residue limits (MRLs) of individual NMC pesticides in drinking water allowed by the European Drinking Water Directory is 100.00 ng l^{-1} [27], consequently a preconcentration step prior to HPLC determination is required in order to reach sensitivity levels below these limits, and also to quantify these pesticides in waters, where they are suspected to be at trace levels. Several methodologies have been proposed for preconcentrating these analytes [11]. We have selected off-line SPE for its operational flexibility and simplicity. In some papers Oasis HLB sorbent has been presented as the best option for preconcentrating and cleaning up NMCs in environmental samples [28]. Thus, those cartridges were selected for water samples. Different amount of sorbent (60 mg and 200 mg) were tested and cartridges containing 200 mg (preconditioned with 6 ml of ethyl acetate, 6 ml of methanol and 6 ml of ultrapure water, at a flow rate of 3 ml min^{-1}) were selected since they provided highest retention percentages and allowed to preconcentrate higher amount of sample.

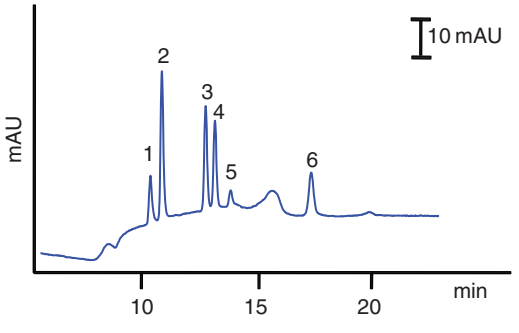

Figure 2. Chromatogran at optimum conditions of the six NMCs (1 mg l^{-1}). Peaks: 1-Carbofuran, 2-Carbaryl, 3-Methiocarb, 4-Promecarb, 5-Fenoxycarb and 6-Benthiocarb.

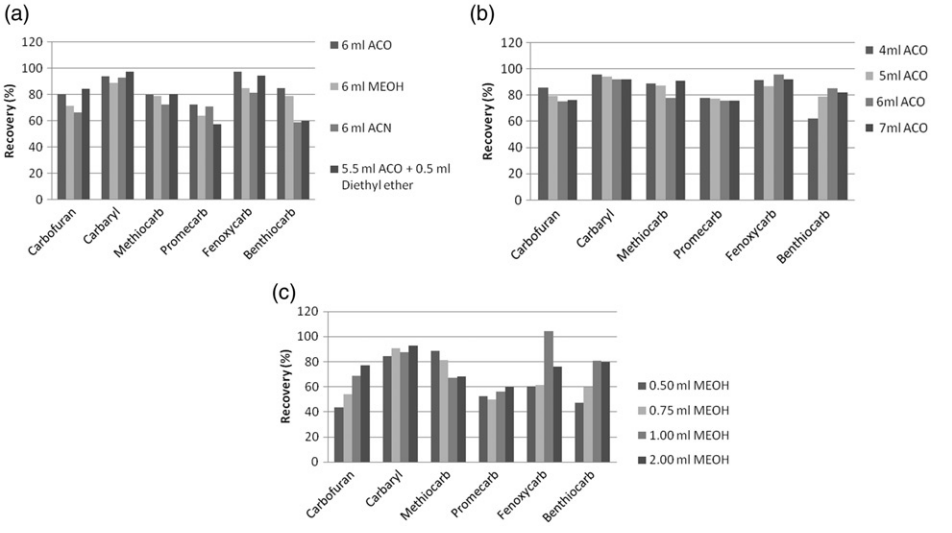

Figure 3. Optimization of variables involved in the water sample treatment. (a) Elution solvents study; (b) Acetone volume; (c) Methanol volume.

Once the sample (500 ml) had been passed through the cartridge, several elution solvents were studied, as mixture acetone-diethyl ether (90 : 10, v/v), ACN, methanol and acetone, with the result that this final solvent was selected. Different volumes of acetone were used to elute the analytes from the cartridges. The best results were obtained by eluting with 6 ml of acetone. In order to avoid losses of the analytes due to thermal degradation the drying temperature of the final extract was set at 30°C as maximum. Different volumes of methanol (0.5, 0.75, 1 and 2 ml) were tested for the reconstitution of the dried extract, and a final value of 2 ml was selected. Thus, considering that sample volumes of 500 ml were used, a preconcentration factor of 250 was achieved. The influence of all of these studied variables on the sample treatment is shown in Figure 3.

3.3 *Optimisation of sample treatment for cucumber*

Extraction and clean-up procedures for the analysis of NMCs in cucumber samples was based in one previously reported [18], slightly modified. The procedure implied a previous solid-liquid extraction with ethyl acetate by means of a blender. Then the extract is concentrated to ca. 2 ml by means of a rotavapor. As can be observed in Figure 4, a degradation of the analytes occurs at temperatures above 40°C [29]; thus, the temperature of the bath was set at 30°C. A subsequent clean-up step by SPE using alumina as sorbent is necessary in order to remove certain interferences from the matrix. Different quantities of alumina were tested (from 0.5 to 1.5 g), and the best results in terms of selectivity (removal of interferences) and recoveries were obtained for 1.25 g. Flow rate of extract through the cartridge was varied in the range from 0.5 to 2 ml min^{-1}, selecting 0.5 ml min^{-1} as optimum. The eluate was evaporated using stream of N_2, at a temperature of 30°C, recomposed in 1 ml of methanol and thoroughly vortexed.

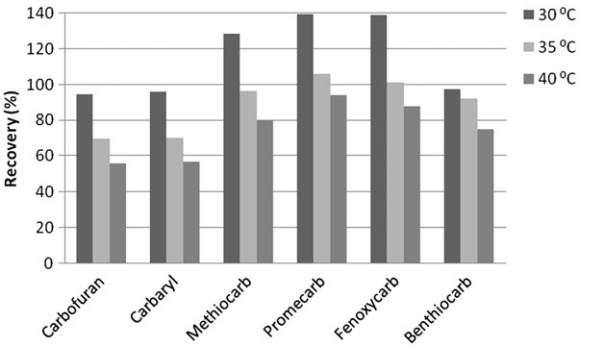

Figure 4. Effect of the temperature of the rotavapor in the cucumber sample treatment.

3.4 *Validation of the method*

The whole method was validated by means of matrix calibration curves, establishment of the performance characteristics of the method (such as limit of detection, limit of quantification, linearity and linear dynamic range), precision study (intraday and interday study) and trueness assessment (recovery study).

3.4.1 *Calibration curves and analytical performance characteristics of the method*

Matrix calibration curves were established using samples free of analytes, previously spiked with different analyte concentrations, processed following the procedures above mentioned (see Section 2.4 above) and considering peak areas as a function of the analyte concentration in the sample. In the case of water samples, matrix calibration curves were obtained using river water spiked with 400, 1000, 2000, 3000 and 4000 ng l^{-1} of each analyte. For cucumber samples, matrix calibration curves were established from samples spiked with concentrations of 12.5, 50, 100, 150 and 200 μg kg^{-1} of carbofuran, carbaryl, methiocarb, fenoxycarb and benthiocarb, and 5, 25, 50, 200 and 250 μg kg^{-1} of promecarb.

Limits of detection (LODs) and quantification (LOQs) were evaluated as the concentration, giving a signal-to-noise (S/N) ratio equal to 3 and 10, respectively. Statistics and performance characteristics of the method for the analysis of NMCs in water and cucumber samples are shown in Tables 1 and 2, respectively. As can be seen, very good LOD were obtained for all the analytes, being lower than the corresponding MRL in those matrices.

3.4.2 *Precision study*

The precision of the method was evaluated in terms of repeatability (intraday precision) and intermediate precision (interday precision). Repeatability was evaluated by application of the proposed SPE and chromatographic method to two different samples (experimental replicates) spiked at two different concentration levels: 1000 and 4000 ng l^{-1} in the case of water samples, and 50 and 150 μg kg^{-1} (except for Promecarb, 25 and 200 μg kg^{-1}), in the case of cucumber samples. The samples were injected by triplicate (instrumental replicates) on the same day, with the same instrument and the same operators. Intermediate precision was evaluated with a similar procedure, but the samples

Table 1. Statistics and performance characteristics of the method for the analysis of water samples.

	Linear dynamic range ($ng\,l^{-1}$)	Intercept (Standard error)	Slope (Standard error (10^{-3}))	R^2	LOD ($ng\,l^{-1}$)	LOQ ($ng\,l^{-1}$)
Carbofuran	98.7–4000.0	−0.2 (0.6)	21.5 (0.3)	0.998	29.6	98.7
Carbaryl	33.3–4000.0	1.4 (1.1)	58.9 (0.4)	0.999	10.0	33.3
Methiocarb	40.0–4000.0	6.2 (1.1)	45.0 (0.4)	0.999	12.0	40.0
Promecarb	98.7–4000.0	−2.6 (0.9)	21.0 (0.4)	0.996	29.6	98.7
Fenoxycarb	50.0–4000.0	26.4 (2.4)	19.9 (0.9)	0.981	15.0	50.0
Benthiocarb	61.5–4000.0	2.0 (0.7)	24.5 (0.3)	0.998	18.5	61.5

Table 2. Statistics and performance characteristics of method for the analysis of cucumber samples.

	Linear dynamic range ($\mu g\,kg^{-1}$)	Intercept (Standard error)	Slope (Standard error)	R^2	LOD ($\mu g\,kg^{-1}$)	LOQ ($\mu g\,kg^{-1}$)	MRL ($\mu g\,kg^{-1}$)
Carbofuran	18.7–200.0	−0.4 (2.8)	1.30 (0.02)	0.996	5.6	18.7	20.0
Carbaryl	4.6–200.0	53.6 (8.2)	3.02 (0.09)	0.997	1.9	4.6	50.0
Methiocarb	7.2–200.0	85.5 (6.0)	2.13 (0.04)	0.996	2.2	7.2	200.0
Promecarb	6.0–250.0	46.5 (1.0)	0.81 (0.01)	0.999	1.8	6.0	10.0
Fenoxycarb	6.7–200.0	23.8 (3.3)	1.34 (0.03)	0.994	2.0	6.7	20.0
Benthiocarb	8.5–200.0	53.6 (5.5)	3.03 (0.04)	0.997	2.6	8.5	50.0

were analysed in three consecutive days. The results, expressed as RSD of the peak areas, are summarised in Tables 3 and 4 for water and cucumber samples, respectively. The results showed good precision, less than 11% in all cases.

3.4.3 *Trueness assessment*

In order to check the trueness of the proposed methodology for the analysis of real samples, recovery experiments were carried out in different types of spiked samples. In all the cases, a sample free of analytes was analysed to check the presence of NMCs, and none of them gave a positive result at the level of detection of the method proposed. In water samples, recovery was estimated for well water and river water, spiked at two different concentration levels (1000 and 4000 ng l^{-1}). The results are shown in Table 5. Very good precision was obtained in most of the cases.

For cucumber samples, recoveries were checked at three different concentration level, which varied depending on the carbamate (see Table 6). Taking into account that in pesticide residue analysis, the acceptable range for recovery is usually between 70 and 120% for routine analysis [30–31], the results obtained with the proposed method can be considered in agreement with current demands.

A typical chromatogram corresponding to a separation of the analytes in cucumber sample under developed conditions is shown in Figure 5.

Table 3. Precision of the method (RSD %) for spiked water samples.

Added (ng l^{-1})	Carbofuran	Carbaryl	Methiocarb	Promecarb	Fenoxycarb	Benthiocarb
Repeatability ($n=6$)						
1000	2.5	1.9	5.8	6.4	9.3	7.5
4000	3.1	3.0	3.1	2.7	4.6	4.6
Intermediate precision ($n=9$)						
1000	6.8	2.1	8.9	7.1	10.6	8.0
4000	2.7	3.6	4.2	4.5	6.5	5.5

Table 4. Precision of the method (RSD %) for spiked cucumber samples.

Added	Carbofuran	Carbaryl	Methiocarb	Promecarb	Fenoxycarb	Benthiocarb
Repeatability ($n=6$)						
a	1.6	3.6	1.8	1.8	5.8	1.5
b	2.4	2.1	1.6	3.3	6.0	5.9
Intermediate precision ($n=9$)						
a	4.4	4.9	4.0	2.3	5.6	9.2
b	4.4	1.9	1.9	3.6	6.4	6.4

a: 50 μg kg^{-1}, except for Promecarb (25 μg kg^{-1}).
b: 150 μg kg^{-1}, except for Promecarb (200 μg kg^{-1}).

Table 5. Recovery study in water samples ($n=6$).

		Carbofuran		Carbaryl		Methiocarb		Promecarb		Fenoxycarb		Benthiocarb	
	Added (ng l^{-1})	R (%)	RSD (%)	R (%)	RSD (%)	R (%)	RSD (%)	R (%)	RSD (%)	R (%)	RSD (%)	R (%)	RSD (%)
River water	1000	94	3	93	94	94	6	83	5	72	13	68	9
	4000	103	3	101	96	96	6	59	5	73	15	92	12
Well water	1000	84	5	95	2	104	11	96	14	105	12	72	11
	4000	93	5	103	2	106	11	101	14	111	14	97	15

4. Conclusion

A sensitive capillary HPLC-DAD method is described for the determination of six NMCs. It can be used for their determination and identification below the established MRLs in drinking water and vegetables. The method has demonstrated its applicability for the analysis of environmental water samples and cucumber, showing very low detection limits, with the advantage of lower solvent consumption. The applied SPE procedure for sample preparation is very adequate for complex matrices such as cucumber and, in the case of natural waters, also allows a preconcentration step which can enhance the sensitivity for

Table 6. Recovery study in cucumber samples ($n = 6$).

Carbofuran			Carbaryl			Methiocarb			Promecarb			Fenoxycarb			Benthiocarb		
Added ($\mu g\ kg^{-1}$)	R (%)	RSD (%)	Added ($\mu g\ kg^{-1}$)	R (%)	RSD (%)	Added ($\mu g\ kg^{-1}$)	R (%)	RSD (%)	Added ($\mu g\ kg^{-1}$)	R (%)	RSD (%)	Added ($\mu g\ kg^{-1}$)	R (%)	RSD (%)	Added ($\mu g\ kg^{-1}$)	R (%)	RSD (%)
20	76	9	10	70	11	10	71	6	5	76	8	12.5	86	6	12.5	90	11
100	70	2	50	71	1	50	72	2	50	71	3	50	71	6	50	80	9
150	80	11	150	80	4	150	84	1	200	90	2	150	87	5	150	84	3

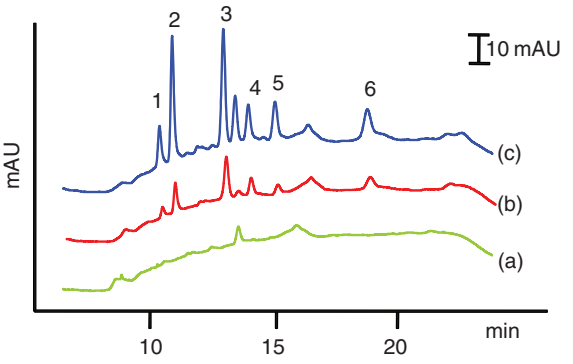

Figure 5. Chromatogram of a cucumber sample applying the proposed capillary HPLC DAD method: (a) sample free of analytes; (b) sample spiked with 50 $\mu g\,kg^{-1}$ for all the analytes, except for Promecarb (25 $\mu g\,kg^{-1}$); (c) sample spiked with 150 $\mu g\,kg^{-1}$ for all the analytes, except for Promecarb (200 $\mu g\,kg^{-1}$); Peaks: 1-Carbofuran, 2-Carbaryl, 3-Methiocarb, 4-Promecarb, 5-Fenoxycarb and 6-Benthiocarb.

the analysis of the low level of residues expected in these samples, and could also be applied for the analysis of NMCs in drinking waters. The developed capillary HPLC-DAD method could be satisfactorily applied as a routine procedure to identify and quantify NMCs in laboratories of food quality and safety control and also for the monitoring of these residues in environmental waters, due to its robustness and feasibility, demonstrating the possibilities of capillary HPLC-DAD in this field.

Acknowledgement

The Ministry of Science and Innovation (Project Ref. CTM2006-06363), EU funds (FEDER) and the Andalusia Government (Excellence Project Ref: P07-AGR-03178) supported this work.

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