Determination of carbamate and urea pesticide residues in fresh vegetables using microwave-assisted extraction and liquid chromatography

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An analytical multiresidue method for the simultaneous determination of seven pesticides in fresh vegetable samples, namely, courgette (*Cucurbita pepo*), cucumber (*Cucumis sativus*), lettuce (*Lactuca sativa*, Romaine and Iceberg varieties) and peppers (*Capsicum* sp.) is described. The procedure, based on microwave-assisted extraction (MAE) and analysis by liquid chromatography–photodiode array (LC–PDA) detection was applied to four carbamates (carbofuran, carbaryl, chlorpropham and EPTC) and three urea pesticides (monolinuron, metobromuron and linuron). Extraction solvent and the addition of anhydrous sodium sulphate to fresh vegetable homogenate before MAE were the parameters optimised for each commodity. Recovery studies were performed using spiked samples in the range 250–403 $\mu g\,kg^{-1}$ in each pesticide. The pesticide residues were extracted using 20 mL acetonitrile at 60°C, for 10 min. Acceptable recoveries and RSDs were attained (overall average recovery of 77.2% and RSDs are lower than 11%). Detection limits ranged between 5.8 $\mu g\,kg^{-1}$ for carbaryl to 12.3 $\mu g\,kg^{-1}$ for carbofuran. The analytical protocol was applied for quality control of 41 fresh vegetable samples bought in Oporto Metropolitan Area (North Portugal). None of the samples contained any detectable amounts of thestudied compounds.

Keywords: pesticides; carbamates; ureas; microwave-assisted extraction; liquid chromatography; vegetables

1. Introduction

Pesticides comprise a large group of substances with the only common characteristic of being effective against a pest and constituting a challenge to the analyst [1]. In recent decades, significant developments have been achieved in pesticide residue analysis and, in many cases, focus has been put towards sample preparation and analytical detection [2]. This has allowed maximum residue limits (MRLs) to become more and more stringent in food commodities. The European Union (EU) has set new Directives for pesticides in

vegetables in order to meet health concerns (Regulation EC no. 396/2005 that introduces changes to the European Directive 91/414/EEC) [3]. Typically, MRLs range from 0.01– 3 mg kg^{-1} depending on the commodity and the pesticide [4].

Nowadays, most of the extensively used pesticides, such as carbamate and phenylurea pesticides, are polar, low volatile and/or thermolabile compounds that are not directly determinable by GC [1]. Phenylurea compounds are widely used for the protection of different crops with MRLs ranging from 0.02 to 0.1 mg kg^{-1}, within Europe [5], while carbamate pesticides are important pest control agents highly efficient as insecticides, nematocides and herbicides. Although they present low bioaccumulation potentials and relatively low mammalian toxicities, they are considered hazardous to the environment and human health [6].

Analysis of pesticide residues in vegetables and fruits is usually performed by gas chromatography (GC) especially coupled to mass spectrometry (MS) [2,7,8] or MS/MS [9] and by liquid chromatography (LC) coupled to MS [4,10,11], MS/MS [1,12–20] as well as to other less powerful detectors, that are, however, easier to acquire and operate [21,22]. Regarding pesticide residue analysis in food commodities, sample preparation traditionally involves a solid–liquid extraction with an organic solvent. Other extraction methods include matrix solid-phase dispersion [1,10], solid-phase extraction [8], super- critical fluid extraction [11,22], solid-phase microextraction (SPME) [19,23,24], stir bar sorptive extraction [25] and more recently the 'quick, easy, cheap, effective, rugged, and safe' (QuECheRS) method [26].

Numerous papers have reported the successful use of microwave-assisted extraction (MAE) in the analysis of different classes of compounds, from several environmental and food matrices. However, very few of them refer its application to the extraction of pesticide residues from fresh vegetable samples [24,27–30]. Recently, the use of pressurised liquid extraction (PLE) and MAE have been compared for the determination of organochlorine pesticides in several horticultural samples [30]. MAE demonstrated to be cheaper, consuming less time and solvent than PLE while maintaining good performance characteristics, such as recovery or reproducibility [30]. To our knowledge, no study has been presented describing the use of MAE and LC–photodiode array detection (LC–PDA) for the simultaneous analysis of carbamate and urea pesticides in vegetables, although the application of MAE for the extraction of some phenylurea herbicides [31] and carbamate pesticides [32] from soil samples has already been proposed. Moreover, the simultaneous determination of carbamate and phenylurea pesticides in fruit juices, by LC–MS using SPME, has been described [19]. Recoveries ranging from 25 to 82% were obtained with relative standard deviations (RSDs) lower than 17%. The authors of [19] reported the determination of eight different compounds, two of which, carbofuran and monolinuron, are included in the present work.

The purpose of this study was to develop an analytical methodology based on MAE coupled to LC–PDA for the simultaneous determination of four carbamate (carbofuran, carbaryl, chlorpropham and EPTC (*S*-ethyl-*N*,*N*-dipropylthiocarbamate)) and three urea pesticides (monolinuron, metobromuron and linuron) in fresh vegetable samples, namely, courgette (*Cucurbita pepo*), cucumber (*Cucumis sativus*), lettuce (*Lactuca sativa*, Romaine and Iceberg varieties) and peppers (*Capsicum* sp.). Pesticides were selected according to their historical or actual use in vegetable cultures in Portugal while the vegetables were chosen based on their importance to the Portuguese traditional diet.

2. Experimental

2.1 *Reagents and chemicals*

Pesticide analytical standards were purchased from Riedel-de Hae¨ n (Seelze, Germany) and included: carbaryl (99.7%), carbofuran (99.9%), chlorpropham (98%), EPTC (98%), linuron (99.7%), metobromuron (99.9%) and monolinuron (99.9%).

Acetone (Panreac, Barcelona, Spain; purity 99.5%), acetonitrile (Carlo Erba, Rodano, Italy; purity 499.9%), dichloromethane (Panreac, Barcelona, Spain; purity 499.9%), methanol LiChrolsolv (Merck, Darmstadt, Germany) and *n*-hexane Chromasolv (Merck, Darmstadt, Germany) were the solvents used.

A Millipore (Molsheim, France) Milli-Q water purification system was used throughout the study to obtain LC-grade water. Anhydrous sodium sulphate (purity99%) was supplied by Panreac (Barcelona, Spain).

Individual pesticide stock solutions (1000 mg mL^{-1}) were prepared by dissolving a precise amount of compound in acetonitrile in glass stoppered volumetric glassware. Working standard solutions used for sample spiking and LC calibration, containing all thepesticides in study, were prepared by appropriate dilution of the stock solutions using acetonitrile. Stock and working standard solutions were stored in dark amber vials at $-18^{o}C$ and $4^{o}C$, respectively.

2.2 *Sample collection and spiking*

Vegetable samples were obtained from markets located in the Oporto region (North Portugal) and were taken in accordance to the EU guidelines [33]. Different types of markets were considered in this sampling (traditional fairs, small shops, supermarkets and hypermarkets). All recovery studies were performed by using previously analysed pesticide-free samples. For each sample, a total mass of 1 kg was chopped and homogenised. Spiked samples were prepared by adding an appropriate volume of spiking solution to a certain amount of homogenised vegetable. Samples were allowed to stand for 60 min before extraction, protected from light. Recovery studies were performed at least in triplicate.

2.3 *Microwave-assisted extraction*

An aliquot of 0.62–1.00 g of homogenised sample was quantitatively transferred to a glass extraction vessel and 9.00–9.38 g of anhydrous sodium sulphate was added (total mass equal to 10.0 g). Twenty millilitres of the tested MAE solvent (hexane: acetone (1 : 1, v/v); dichloromethane : methanol (9 : 1, v/v) or acetonitrile) was added. Samples were extracted at $60^{o}C$, with constant medium stirring, at 100% magnetron power for 10 min in a MARS-X 1500 W Microwave Accelerated Reaction System for Extraction and Digestion (CEM, Mathews, NC, USA). The maximum vessel pressure cut off was set at 1.38×10^{6} Pa. Extracts were filtered through Whatman GF/C filters using a DINKO D-95 vacuum pump and the solvent was evaporated under vacuum, at $30^{o}C$, in a Bu¨ chi B-940 rotary evaporator (Bu¨ chi, Flawil, Switzerland). Shortlybefore analysis, the residue was re-dissolved using 1000 mL of acetonitrile. The extracts so obtained were filtered through 0.2 mm filters (Chromafil, Macherey-Nagel, Du¨ ren, Germany).

2.4 *Liquid chromatography analysis*

The LC–PDA system used consisted of a Waters 2795 Alliance HT system (Watford, UK) equipped with an automatic injection valve and a 2996 PDA Detector (Waters, Watford, UK). Pesticides separation was achieved on a C_{18} analytical column (Waters Spherisorb® ODS2, 250x4.6mm; 5mm particle size). The column temperature was maintained at 30°C. The mobile phases A and B were pure water and acetonitrile, respectively. A total flow rate of 0.8 mL min^{-1} was used. The initial composition (45% B) was kept for 12 min. Next, a linear gradient to 100% B was programmed in 9 min, with a final hold of 3 min. The initial conditions were reached in 5 min and maintained for 6 min before next run, corresponding to a total time analysis of 35 min. The injection volume used was 40 mL. Absorbance data were acquired in the range 190–400 nm.

The linearity of the detector's response was studied using mixed standard solutions prepared in acetonitrile. Eleven calibration standards, in the range 10.0–500 mg L^{-1}, were used. The integrated peak area data were used to construct the calibration curves. Each analysis was performed at least in triplicate.

3. Results and discussion

3.1 *Chromatographic analysis*

Since no single wavelength is appropriate for monitoring simultaneously all the pesticides, as they exhibit absorbance maxima at different wavelengths in the UV region, each compound was quantified at a different wavelength in order to maximise method's sensitivity (Table 1). Detector response was studied by injecting 11 mixed standard solutions ranging from 10.0 to 500 mg L^{-1} in each compound. A representative chromatogram is shown in Figure 1. Linearity was observed over the entire range of concentrations, with quadratic correlation coefficients (R^2) ranging from 0.9947 for EPTC to 0.9998 for chlorpropham.

Limits of detection (LODs) and limits of quantification (LOQs) were calculated, respectively, as 3 and 10 times the SD estimated for each regression equation ($S_{Y/X}$) dividing by the slope of the calibration equation for each compound [34]. LODs between 5.8 mg kg^{-1} for carbaryl and 12.3 mg kg^{-1} for carbofuran were obtained. The corresponding LOQs were in the range 19.2–41.0 mg kg^{-1}. These values, calculated on a fresh weight basis,

Table 1. Average retention times, optimum wavelengths, calibration data and MRLs for the selected compounds.

Pesticide	t_r (min)	A (nm)	Calibration equation (n ¼ 11)	LOD (mg kg^{-1})	LOQ (mg kg^{-1})	MRL (mg kg^{-1})
Carbofuran	8.6	199.2	y¼425.3x-2421	12.3	41.0	100–300
Carbaryl	9.8	221.4	y¼798.4þ6728	5.8	19.2	50–3000
Monolinuron	11.4	246.5	y¼249.8þ1261	10.1	33.6	n.a.
Metobromuron	12.9	248.5	y¼204.8þ322	8.9	29.8	n.a.
Linuron	18.1	249.7	y¼252.7x-790	7.2	24.0	50–200
Chlorpropham	19.4	240.3	y¼235.9x-2221	6.8	22.8	10000
EPTC	21.3	207.4	y¼114.2x-243	8.2	27.2	50

Notes: y – peak area; x – concentration (mg L^{-1}); n.a. – use not allowed.

are sufficiently low for the method to be used for residue monitoring purposes, considering the MRLs established in the Portuguese legislation [35] (Table 1).

3.2 *Optimisation of MAE procedure*

3.2.1 *Influence of addition of anhydrous sodium sulphate*

As has been pointed out by several authors [31], water plays an important role in MAE, as sample moisture can affect the recovery of target compounds. When analysing fresh vegetable samples, very high moisture contents, usually higher than 90%, are present. Furthermore, for the same vegetable species, there can be a variation in this parameter, from sample to sample. This can lead to a different behaviour during extraction, compromising the reproducibility of this step. Some studies related to the use of MAE for the extraction of pesticides from fresh vegetables, cope with this situation by removing water, for instance, by lyophilising samples before MAE [30]. In order to keep the experimental protocol as simple as possible, the addition of anhydrous sodium sulphate to absorb sample moisture was investigated. This is a common practice in conventional solid– liquid extraction techniques but unusual in MAE. A study was performed in order to determine the appropriate proportion of vegetable to anhydrous sodium sulphate, for which a single liquid phase was observed when the less polar solvent mixture tested in MAE was added (20 mL of dichloromethane : methanol (9 : 1, v/v)). For each vegetable, a set of nine experiments was performed testing different ratios of vegetable sample to anhydrous sodium sulphate, ranging from 0 to 16 times the amount of vegetable used. Average pH and moisture values of the vegetable samples used in this study are presented in Table 2, together with the optimum proportion of vegetable to anhydrous sodium

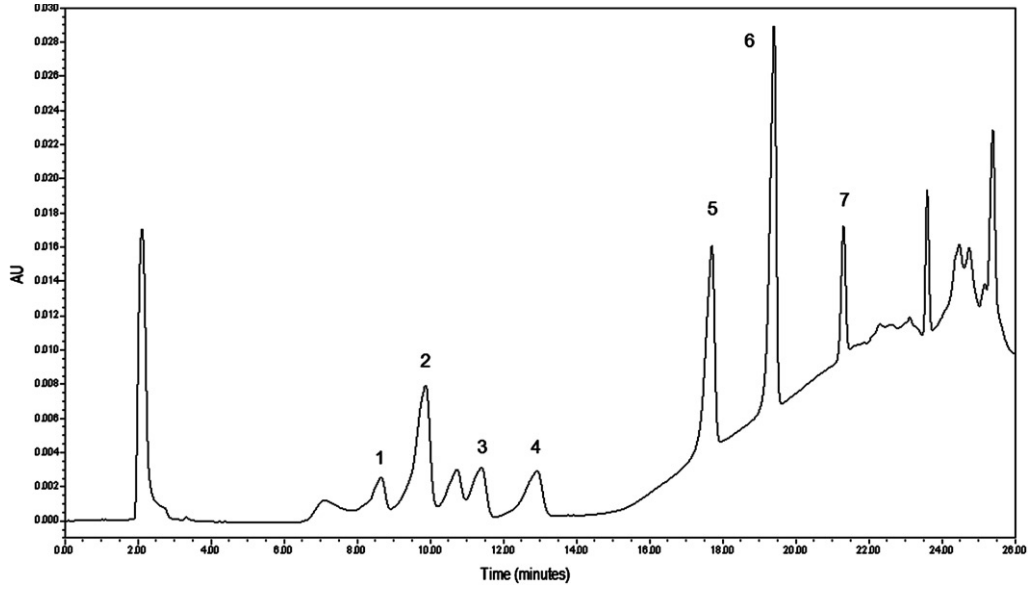

Figure 1. Representative LC–PDA chromatogram (A¼210 nm) obtained for a mixed pesticide standard solution (500 mg L^{-1}). Peaks identification: (1) carbofuran, (2) carbaryl, (3) monolinuron,
(4) metobromuron, (5) linuron, (6) chlorpropham and (7) EPTC.

Table 2. Characteristics of the vegetable samples used in the optimisation of the amount of anhydrous sodium sulphate.

Vegetable	Moisture (%)	pH	Optimum ratio of vegetable: Na_2SO_4 (g/g)
Courgette	94.8	6.0	1 :11.5
Cucumber	95.4	4.9	1 :15.1
Lettuce	91.0	5.5	1 :9.0
Red pepper	94.5	5.9	1 :11.5

sulphate that has to be used in each case. This approach simplifies sample pre-treatment and increases sample throughput.

3.2.2 *Influence of temperature*

Temperature and extraction solvent are also considered to be critical parameters to be controlled during MAE extraction [31]. Furthermore, some ureas and carbamates are thermolabile compounds and for this reason, temperatures higher than $80^{o}C$ are not recommended [32]. In addition, some classical acetone-based extraction procedures used in pesticide residue monitoring programmes, that include the compounds considered in the present study, contain an evaporation step in which water bath temperature may reach 45–$62^{o}C$ [20]. Accordingly, the extraction temperature was set at $60^{o}C$.

3.2.3 *Optimisation of solvent and method validation*

For selection of the optimum MAE solvent, extraction efficiency was evaluated testing hexane : acetone (1 : 1, v/v), dichloromethane : methanol (9 : 1, v/v) and acetonitrile, using spiked samples containing all the pesticides at the same concentration level, namely, 250 $mg\,kg^{-1}$ for lettuce, 313 $mg\,kg^{-1}$ for courgette and red pepper and 403 $mg\,kg^{-1}$ for cucumber. The extraction time was selected as 10 min accordingly with previous related studies [31].

Recovery data obtained are shown in Figure 2. For courgette, recoveries using acetonitrile ranged from 53.6 for carbofuran to 93.3% for metobromuron, with RSDslower than 11% and an overall average recovery of 71.0%. Using the mixture hexane : acetone (1 : 1, v/v) which is the solvent mixture recommended by EPA [36], only three compounds were detected and with low recoveries. Using dichloromethane : metha- nol (9 : 1, v/v) only five of the compounds were extracted, but with lower recovery values, when compared to acetonitrile. A similar pattern was obtained for lettuce samples, for which the lowest recovery results, comparing the four different species tested, were attained. When considering acetonitrile as the extraction solvent, carbofuran recovery was

only 26.1% and the values for chlorpropham and EPTC were 53.4 and 55.6%, respectively. The overall average recovery was 64.6% (RSD57%). The use of hexane : acetone (1 : 1, v/v) and dichloromethane : methanol (9 : 1, v/v) did not allow the extraction of all target compounds.

For cucumber samples, recoveries using acetonitrile ranged between 65.2% for EPTC and 107% for metobromuron. The RSDs were lower than 8% and the average recovery

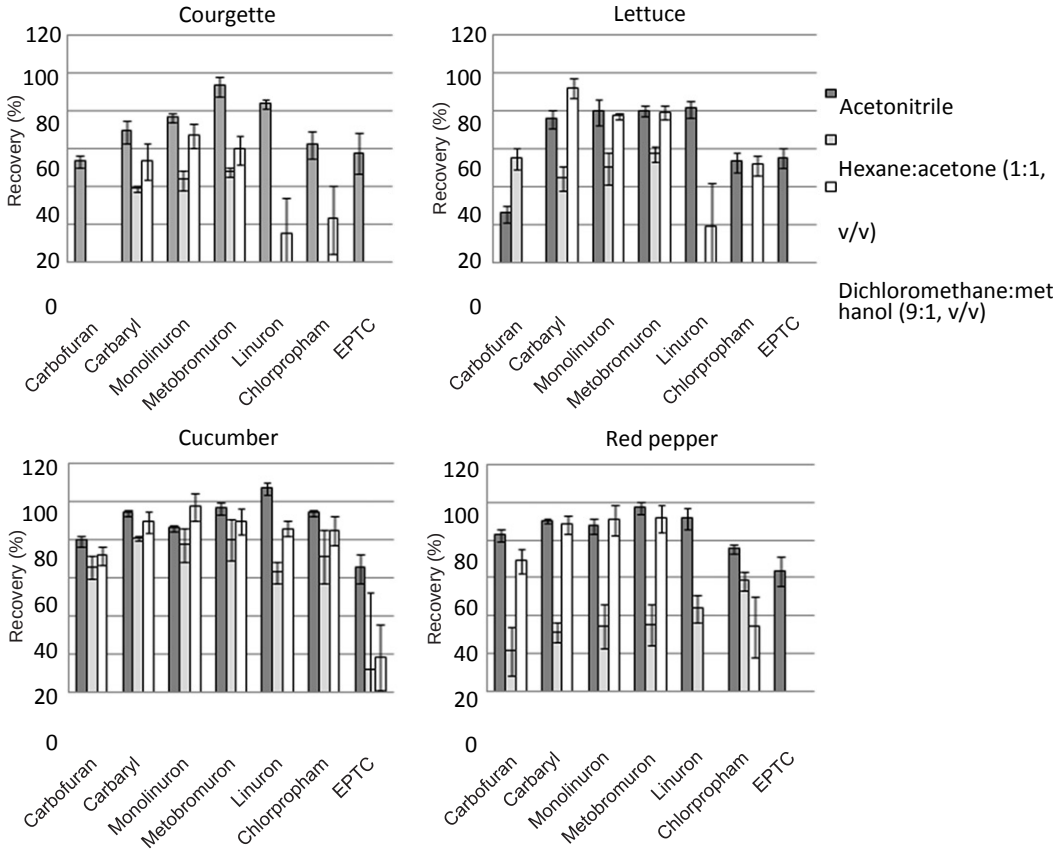

Figure 2. MAE average recovery values (%) and relative SDs, obtained at 60°C, with three different extraction solvents, and using the optimum mass of anhydrous sodium sulphate (n¼4). Spiking levels used (mg kg^{-1}): lettuce: 250; courgette and red pepper: 313; cucumber: 403.

value was 89.1%. In this case, the other two solvent mixtures tested, hexane : acetone (1 : 1, v/v) and dichloromethane : methanol (9 : 1, v/v), also allowed the extraction of all the analytes, although globally with lower recoveries and higher RSD values.

Regarding the results for the red pepper sample, once again acetonitrile was the best extraction solvent, with recoveries between 63.9% for EPTC and 97.2% for metobro- muron. The reproducibility of the method expressed as RSDs was lower than 8% and an average recovery value of 84.2% was obtained. The other two solvent mixtures tested did not permit the extraction of all the pesticides although results are slightly better when dichloromethane : methanol (9 : 1, v/v) is applied instead of hexane : acetone (1 : 1, v/v).

Considering the four vegetables altogether, acetonitrile allows the extraction of all compounds in all the situations tested. The overall average recovery is 77.2% (RSD :s 11%) which can be considered a satisfactory result. Figure 3 shows LC–PDA representative chromatograms of a blank and a spiked lettuce sample at 250 mg kg^{-1} extracted using the optimum conditions described. Although no sample clean-up was used after MAE, most of the co-extractives have retention times different from the ones of the analytes and do not compromise quantification.

After optimising the extraction solvent and in order to assess the performance of the method for different spiking levels, new MAE extractions were performed. Table 3 displays the average recoveries and RSDs attained. Several fortification levels were chosen

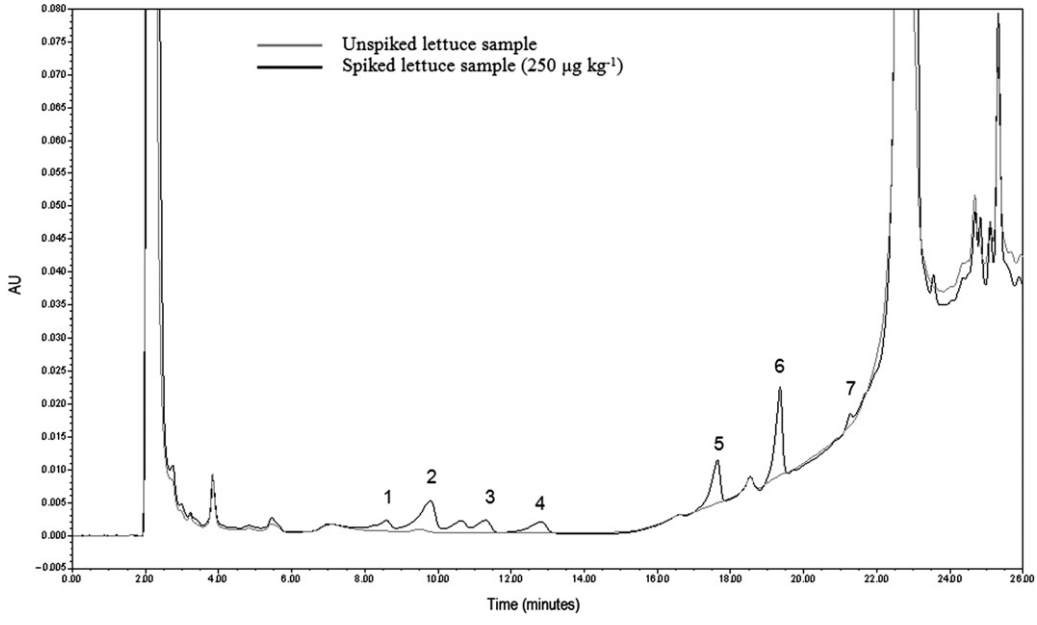

Figure 3. Representative LC–PDA chromatograms (A¼210 nm) obtained for a lettuce sample extract and the corresponding spiked sample at 250 mg kg^{-1}. Peaks identification: (1) carbofuran, (2) carbaryl, (3) monolinuron, (4) metobromuron, (5) linuron, (6) chlorpropham and (7) EPTC.

in order to be lower than or in the interval range of the established MRLs for each compound [35]. Regarding carbofuran, the recoveries for cucumber and red pepper were acceptable and in the range 71.5–83.0% (RSDs56.5%). However, for courgette, recovery values around 50% were obtained while for lettuce no acceptable values were reached.

With respect to the other analytes excepting EPTC, all the spiking levels tested were successfully analysed. For carbaryl, lower average recoveries, close to 70%, were obtained for courgette and lettuce. Better recoveries in the range 82.2–101% were achieved for cucumber and red pepper, for spiking levels higher than 50 mg kg^{-1}. The results obtained for monolinuron were very similar to the ones obtained for carbaryl. For metobromuron, recovery values ranging from 92.6 to 109% were achieved in courgette, cucumber and red pepper for pesticide concentrations 2:50 mg kg^{-1}. Good results were also obtained in the lettuce matrix, especially for spiking levels 2:100 mg kg^{-1} (76.1–83.3%). In these experi- ments, the lowest recoveries were obtained for the last eluting compounds, namely, chlorpropham and EPTC. Nevertheless, regarding the results for chlorpropham in the courgette and lettuce samples, average recovery values of 65 and of 50%, respectively, were attained. For EPTC, recovery values were in the range 48.7–65.2% for all the matrices and spiking levels tested, except for cucumber, at 100 mg kg^{-1}. These results may be explained by the fact that, in some cases, co-extraction of other matrix compounds may occur (Figure 3). The presence of matrix interferences in extracts can adversely affect analyte quantification and identification, thus a clean-up step may be used in order to reduce the detection limits and/or to avoid interferences from the matrix [8]. However, extensive clean-up steps may result in the partial loss of some compounds and in an increase in the time and cost of analysis [37]. Thus, as a compromise situation in the proposed method, no clean-up step was adopted.

Table 3. Mean recoveries (*R*, %) and relative standard deviations (RSDs, %) obtained for the selected carbamates and ureas from fresh spiked vegetable samples (*n* ¼ 3) by using the optimised MAE conditions (20 mL acetonitrile, at 60°C, during 10 min), at different fortification levels.

Compound	Spiking (mg kg^{-1})	Courgette *R* ±RSD	Cucumber *R* ±RSD	Lettuce *R* ±RSD	Red Pepper *R* ±RSD
Carbofuran	200	45.4±2.8	79.7±6.5	n.d.	80.4±1.2
	300[a]	57.5±3.9	71.5±4.6	12.1±9.0	76.9±0.7
	313[b]	53.6±3.2	79.6±2.7	26.1±4.6	83.0±3.4
Carbaryl	30	67.2±5.9	54.2±4.6	32.6±6.9	78.1±8.3
	50	70.8±0.7	51.4±13	43.1±8.1	81.9±2.7
	100	68.7±3.9	98.2±3.7	65.1±5.3	82.2±9.8
	300[a]	72.7±3.5	99.0±4.6	76.0±4.6	101±3.8
	313[b]	69.2±5.9	94.1±1.4	78.0±4.7	90.6±1.1
Monolinuron	50	59.3±5.0	102±3.3	65.9±6.9	51.9±5.7
	100	59.5±3.7	99.1±1.3	72.2±5.2	81.1±5.4
	200	70.5±6.8	95.5±1.3	81.3±4.2	102±1.2
	300[a]	71.4±4.6	97.3±0.0	79.6±6.9	90.3±3.1
	313[b]	76.6±2.5	86.3±1.5	79.0±5.3	87.7±4.0
Metobromuron	30	64.3±10	114±7.6	56.0±9.6	65.1±8.4
	50	92.6±3.9	99.2±8.4	63.0±10	106±3.8
	100	99.9±1.4	109±1.5	76.1±3.8	109±1.5
	200	95.9±4.6	107±3.5	83.3±4.0	102±2.2
	313[c]	93.3±5.2	96.5±3.3	80.2±3.0	97.2±3.1
Linuron	30	41.2±13	109±6.8	72.1±3.7	65.8±6.3
	50	72.6±4.9	116±7.2	79.8±5.8	87.3±4.7
	100	79.6±2.8	115±7.0	81.7±2.8	90.4±5.2
	200	80.8±5.7	106±9.6	78.7±5.0	94.9±3.6
	313[c]	84.2±2.4	107±2.9	81.3±4.4	91.5±5.5
Chlorpropham	30	69.1±5.8	90.2±1.7	23.5±9.8	79.8±2.2
	50	68.4±2.6	82.7±6.3	38.5±11	62.3±6.5
	100	64.7±3.4	85.5±5.9	47.4±13	71.4±8.1
	200	66.4±5.6	93.5±3.1	56.1±9.1	78.6±9.5
	313[c]	62.1±7.3	94.2±1.9	53.4±5.1	75.7±2.5
EPTC	100	62.6±5.7	n.d.	48.7±8.6	58.4±9.8
	200[a]	60.3±6.8	54.8±9.7	55.6±5.4	57.6±8.4
	313[b]	58.0±11	65.2±7.5	52.8±6.1	63.9±7.4

Notes: [a]Spiking level was 250 mg kg^{-1} for lettuce; [b]Spiking level was 403 mg kg^{-1} for cucumber and 300 mg kg^{-1} for lettuce; [c]Spiking level was 403 mg kg^{-1} for cucumber and 250 mg kg^{-1} for lettuce;
n.d. – not detected.

The results obtained by Barriada-Pereira *et al*. [30] for the MAE extraction of organochlorine pesticides from freeze-dried vegetable samples, including lettuce and pepper, show that lower recoveries were obtained for green vegetables, especially the leafy ones, what these authors attributed to presence of an epicuticular wax that could influence the extraction and clean-up processes [30]. These results are in agreement with the ones presented in this study, for which generally lower recoveries were obtained for lettuce samples.

To our knowledge, no study has been presented describing the use of MAE and LC–PDA for the simultaneous determination of carbamate and urea pesticides in fresh vegetable samples. One of the earliest studies regarding the use of MAE and GC–ECD for multiresidue pesticide analysis in vegetables was described by Pylypiw *et al*. [27]. A mixture of 2-propanol and petroleum ether was used as the extraction solvent for seven pesticides, most of them organophosphorus, in five different crops. By comparing MAE and a conventional liquid extraction technique, the authors concluded that MAE extraction data compared favourably with the traditional extraction data, although their results suggested that MAE was more matrix dependent than the conventional blender extraction [27].

Comparing the results presented in this study with those previously reported by Molins *et al*. [31] and Sun and Lee [32] for the use of MAE for the extraction of urea and carbamate residues, respectively, from soils, the proposed methodology provides similar recoveries but, in addition, allows the two classes of pesticides to be extracted simultaneously. The selection of acetonitrile as the extraction solvent may also be considered as an improvement over the MAE-based method reported for the analysis of urea's residues in soils [31]. In the latter MAE was carried out in the presence of dichloromethane–methanol (9 : 1, v/v). The use of dichloromethane and of other halogenated solvents is slowly being phased out from analytical methods, considering the negative impacts they have over the environment.

3.3 *Determination of the studied pesticides in vegetable samples*

The analytical protocol developed was applied for quality control of fresh commercial vegetable samples that were bought in Oporto Metropolitan Area (North Portugal). Different types of markets were considered, such as traditional fairs, supermarkets and hypermarkets. A total number of 41 samples (10 of courgette, 10 of cucumber, 10 of lettuce, 6 of green pepper, 4 of red pepper and 1 of yellow pepper) were analysed. None of the samples contained any detectable amounts of the studied compounds. The sensitivity of the proposed method is sufficient to enable testing of compliance with food regulations and MRLs established in Portugal. However, if necessary, a significant improvement in LOQ can be yield by increasing the total mass of sample to be extracted (maintaining the optimum ratio of vegetable to anhydrous sodium sulphate) or/and redissolving the vegetable residue in a volume $\leq 1000\ \mu L$.

4. Conclusions

In this work, it has been demonstrated the suitability of MAE coupled to LC with PDA detection for the determination of carbamate (carbofuran, carbaryl, chlorpropham and EPTC) and urea (monolinuron, metobromuron, linuron) pesticide residues in fresh vegetable samples.

The extraction method is simple, rapid and efficient. As sample pre-treatment only homogenisation is needed and after MAE no further extract clean-up is necessary. The LOQs attained are sufficiently low for the method to be used for residue monitoring purposes, considering the MRLs established in the Portuguese legislation [35]. The application of the method to a set of 41 commercial samples of vegetables revealed the absence of the target analytes in detectable amounts.

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