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Journal of Chromatography A, 972 (2002) 231–239

JOURNAL OF CHROMATOGRAPHY A

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Determination of propamocarb in vegetables using polymer-based high-performance liquid chromatography coupled with electrospray mass spectrometry

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Received 8 July 2002; accepted 19 July 2002

Abstract

A method for the determination of propamocarb in vegetables with liquid chromatography–electrospray ionisation mass spectrometry (LC–ESI-MS) was developed. The performance of a polymer-based analytical LC column for the separation was investigated. Residues of propamocarb were extracted from the matrix with methanol. Subsequently, the extract was directly injected into the LC–MS system, without any additional concentration or cleanup procedures. Separation of propamocarb from the matrix components was achieved on a polymethacrylate-based analytical column. Propamocarb was concurrently detected with electrospray ionisation mass spectrometry in the selected ion monitoring mode and two-stage full scan MS application. Quantitation was done with matrix-matched calibration standards of propamocarb. Unambiguous confirmation was achieved by comparison of the full scan product ion mass spectrum of the chromatographic peak in the sample with the spectrum of a standard solution of propamocarb at the same retention time. The analytical performance of the method was validated for five relevant matrices, spiking propamocarb at fortification levels from 0.05 to 15.0 mg kg^{-1}. This covers the range of maximum residue limits in agricultural commodities, stated in the Dutch national legislation. The mean recovery of propamocarb was better than 90% with a precision of less than 10% in both scanning applications. As could be concluded from the calibration curve and matrix background levels, observed in blank control samples, the estimated limit of detection was 25 μg kg^{-1} for the two-stage full scan MS application. The method has been applied in a survey of 285 samples of lettuce, radish, leek, and cabbage for the presence of residues of propamocarb. In 50% of the samples analysed, a residue of propamocarb was detected.
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Keywords: Vegetables; Food analysis; Propamocarb; Pesticides

1. Introduction

Propamocarb hydrochloride [propyl 3-(dimethylamino)propylcarbamate hydrochoride, Fig. 1], a systemic fungicide with protective action against phycomycetous diseases (*Phythium*, *Phytophthora* spp.), is used on a wide variety of mainly greenhouse vegetables [1], and is registered in The Netherlands for application on many agricultural products, such as lettuce, radish, leek, potato, cabbage and fruiting

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PII: S0021-9673(02)01089-0

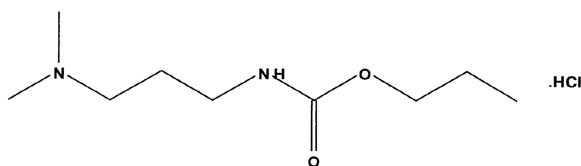

Fig. 1. Chemical structure of propamocarb hydrochloride.

vegetables. Maximum residue limits (MRLs) have been set for these commodities in the National Pesticide Act. In order to enforce these MRLs and in view of the extensive use of the fungicide in The Netherlands, there was an urgent need to develop a simple and fast analytical method for propamocarb in agricultural products.

Few publications on the determination of propamocarb in agricultural products have appeared in the literature [2,3]. One analytical method utilizing gas chromatography (GC) was employed for the quantitative determination of propamocarb in agricultural commodities. The analyte was extracted with acetone–water and cleaned up by liquid–liquid partition into diethyl ether. Recoveries of propamocarb, fortified at 0.1 mg kg^{-1}, were greater than 75%, except for samples of lettuce (41%). In general, the use of GC methods for the analysis of polar, non-volatile pesticides results in poor reproducibilities, due to erratic degradation of the analyte in the GC injector, which makes GC not a very suitable technique for these analytes. Hence liquid chromatography (LC) has acquired a role of growing importance in the analysis of polar, thermolabile and non-volatile pesticides as is attested by the wide variety of applications reported in recent years. Using conventional LC detection methods [UV, diode array detection (DAD)], detection of propamocarb at low levels ($\mu g\ kg^{-1}$) in vegetables is almost impossible, due to the absence of a chromophore in the molecule.

Over the last few years, liquid chromatography coupled with atmospheric pressure ionisation interfaces to mass spectrometry (LC–API-MS) has gained in popularity for the analysis of polar and/or ionic pesticides. This promising technique combines the advantages of LC and MS for the separation and unequivocal identification of pesticides at low $\mu g\ kg^{-1}$ levels in real matrices, such as food and environmental samples.

Recently, several authors have reported LC–API-MS methods for the determination of ionic pesticides, e.g., quaternary ammonium compounds, in different matrices [4–7]. Ion-exchange, ion-pair and reversed-phase chromatography have been evaluated for the separation of these ionic pesticides. Often reported drawbacks of these separation techniques are asymmetrical peak shapes, unreproducible retention times after prolonged use of the LC column and limited column life, drastically affecting the robustness of the analytical method. Since a decennium [8], we have good experiences in our laboratory, using a polymer-based polymethacrylate LC column for the separation of ionizable pesticides, such as the benzimidazole fungicides, thiabendazole and carbendazim. Recently [9], we have successfully applied this LC column for the separation of chlormequat and subsequent detection with mass spectrometry. The method comprehends an extraction with methanol and direct injection of the methanolic extract, without prior clean up, onto the polymer-based analytical column. Chlormequat showed good separation from the matrix compounds (pear, cereals) with a methanol–ammonium acetate mobile phase composition, resulting in a fast, simple and robust analytical LC–MS method. This method was used as a starting point for the development of a similar method for the analysis of propamocarb.

The aim of this study was to develop a quantitative and specific analytical method for the determination of propamocarb down to low $\mu g\ kg^{-1}$ detection levels in a variety of food commodities, and to apply the method in a survey for the presence of propamocarb in various domestically grown vegetables.

2. Experimental

2.1. Chemicals

Methanol (HPLC grade) and ammonium acetate (analytical-reagent grade) were obtained from Merck, Darmstadt, Germany. HPLC-grade water was obtained by purifying demineralized water in a Milli-Q-Plus ultra-pure water system (Millipore, Molsheim, France). Propamocarb free base was purchased from Dr. Ehrenstorfer (Augsburg, Germany) and stored at

−18 °C in a freezer. A standard stock solution of 1 mg ml^{-1} was prepared in methanol, and working standard solutions of 100, 10 and 1 μg ml^{-1} were prepared by dilution in methanol and stored at 4 °C in a refrigerator. Organically-grown head lettuce, leek, radish, cabbage, potato and cucumber were used as blank control matrices in recovery experiments and for the preparation of matrix-matched calibration solutions. They were shown not to contain any detectable residues of propamocarb.

2.2. Sample preparation

Samples (lettuce, radish, leek and cabbage) were randomly collected at wholesalers and auctions as part of the Dutch National Pesticide Monitoring Program in the period of March to October 2000. Normally five to ten units, with a minimum mass of the laboratory sample of 1 kg, were collected for the survey. Before analysis, samples were chopped and homogenised in a food cutter (Stephan, Hameln, Germany). A 25 g analytical portion of the homogenate was extracted with 50 ml methanol in a polytetrafluorethylene centrifuge tube (250 ml) using a Polytron, Model PT 6000, homogenizer (Kinematica, Luzern, Switzerland) at 20 000 rpm for 60 s. The homogenate was centrifuged at 3600 rpm for 5 min. Subsequently, 1 ml of the methanolic extract was filtered into an autosampler vial using a 0.45 μm membrane filter (Spartan 30/0.45 RC, Schleicher and Schuell, Dassel, Germany). An aliquot of 20 μl was injected into the LC–MS system. Samples found to contain concentrations of propamocarb higher than 500 ng ml^{-1} were diluted with blank matrix extract and re-analysed.

2.3. Instrumentation

The LC–MS system consisted of a LCQ Classic (ThermoFinnigan, San Jose, CA, USA) ion trap mass spectrometer coupled to a HP 1050 (Hewlett-Packard, Waldbronn, Germany) quaternary LC pump with vacuum degasser, a Gilson (Villiers le Bel, France) 231 XL autosampler and a Surveyor photodiode-array detection system, equipped with 5 cm pipe-line flowcell (ThermoFinnigan). The injection loop volume of the autosampler was 20 μl. A two-position valve actuator (Valco Instruments, Houston, TX, USA), was installed between the LC column and the MS system. The effluent from the LC system was switched to waste during the initial time (9 min) of the analysis.

Chromatographic separation was performed using a 150×6 mm Shodex RSpak DE-613 column (Waters, Etten-Leur, The Netherlands), packed with a polymethacrylate gel (6 μm). Isocratic elution of propamocarb was achieved with a mobile phase of methanol–25 m*M* aqueous ammonium acetate (pH 6.8) (1:1, v/v). The flow-rate was 0.75 ml min^{-1}. Before starting the analysis, the LC column was conditioned with mobile phase for half an hour.

The mass spectrometer, equipped with a pneumatically-assisted electrospray (ESI) interface, was operated in the positive ionisation mode with a voltage of 4.5 kV on the electrospray needle. By infusing a solution of propamocarb into the ion source with the aid of a syringe pump, optimum instrument operating conditions were achieved. Typical settings of the instrument were as follows: capillary voltage 35 V; sheath gas flow: 80 arbitrary units (1.2 l min^{-1} N_2); auxillary gas flow: 20 arbitrary units (6 l min^{-1} N_2); and capillary temperature: 270 °C.

Two-stage full scan MS application (collisionally induced dissociation) was performed by increasing the resonance ejection radiofrequency (RF) voltage to the endcap electrodes of the ion trap detector. The relative collision energy (35%) was set at 1.75 V for maximum yield of the product ions *m/z* 102 and *m/z* 144 of propamocarb. The maximum ionisation time was 200 ms. Data acquisition was concurrently acquired in the selected ion monitoring (SIM; *m/z* 189) and two-stage full scan MS (*m/z* 50–200) application.

2.4. Quantitation

Calibration curves were established using matrix-matched calibration solutions. The calibration solutions were prepared by dilution of the working standard solutions with extracts of blank control samples to give final concentrations of propamocarb between 10 and 500 ng ml^{-1}. This working range is equivalent to residue concentrations of propamocarb of between 0.026 and 1.3 mg kg^{-1}. MS acquisition

data were processed using Xcalibur version 1.2 software (ThermoFinnigan).

Quantitation of propamocarb was done using the response (area) of the precursor ion at m/z 189 in the SIM application, and by summing the product ions m/z 102 and m/z 144 in the two-stage full scan MS application, respectively. Non-weighted linear calibration curves were composed using data from the calibration standard solutions (five levels), bracketing each set of samples. The extraction solvent volume was corrected for the natural water content of the commodities and contraction of water with methanol during the extraction process. As an average extraction solvent volume, 65 ml was used for the calculation of the propamocarb concentration in the sample.

3. Results and discussion

3.1. Liquid chromatography

Modern polymeric stationary phases have high sample loading capabilities, no silanol activity and are unaffected by the pH of the mobile phase. These properties are typically advantageous for basic, polar and ionizable compounds.

As mentioned before, the plant growth regulator, chlormequat was separated on the polymethacrylate-based LC column, Shodex RSpak DE-613, with methanol–25 mM ammonium acetate (pH 6.8) (1:1, v/v) in approximately 9 min. According to the manufacturer, the Shodex RSpak DE-613 column exhibits a mid-range hydrophobicity index equivalent to a C_8 bonded silica phase. Under the LC conditions obtained with the separation of chlormequat, propamocarb eluted from the analytical column in 10.1 min. From initial experiments, it appeared that the retention time of propamocarb was dependent on the concentration of ammonium acetate in the mobile phase. The concentration was varied and optimised to obtain an effective separation of propamocarb from the matrix components in sample extracts. Matrix-matched standard solutions of propamocarb were injected onto the LC column with a mobile phase consisting of 50% (v/v) methanol in 0, 25, 50, and 100 mM of aqueous ammonium acetate, respectively. The capacity factor (k') of propamocarb (pK_a 9.5) decreased with increasing concentrations of ammonium acetate in the mobile phase. Ammonium acetate concentrations less than 25 mM prolonged the analytical run time unnecessarily. With an ammonium acetate concentration of 25 mM in the mobile phase, sufficient separation efficiency was achieved between the UV absorbing matrix components and propamocarb, as could be monitored with the DAD system. Besides hydrophobic interaction, the polymethacrylate column seems to exhibit weak cation-exchange properties. This retention mechanism could possibly be caused by residuals of methacrylic acid, which are still present in the polymer gel. Furthermore, propamocarb showed good symmetrical peak profiles and reproducible retention times, demonstrating the excellent performance of this polymer phase.

One significant drawback of electrospray mass spectrometry is that the ionisation process in the ion source is highly susceptible to ion formation suppression due to matrix effects. The effect of the LC effluent on the mass spectrometry signal response of propamocarb, after injecting the extraction solvent (methanol) and blank samples extracts, was investigated. The efficiency of the LC separation on reducing signal suppression by matrix components was visualized by a technique involving post-column infusion of a standard propamocarb solution [10]. As an example, Fig. 2 shows the detector response of propamocarb, continuously introduced post-column, during injection of the extraction solvent (methanol) and a blank sample extract of lettuce. The selected ion chromatogram obtained from m/z 189, showed drastic decrease in response during the early eluting times of the analysis. The response was completely restored after approximately 15 to 20 min. There was no significant difference in ion suppression observed between the six matrices tested. It was decided that an ammonium acetate concentration of 25 mM in the mobile phase was chosen as optimum with respect to the separation efficiency, total analysis time and observed degree of matrix effect.

Earlier extraction experiments revealed that methanol appeared to be a more favourable extraction solvent compared to water, because no precipitation of the matrix components occurred, especially with fatty food products like cereals. Loop injections up to 100 μl of propamocarb in 100%

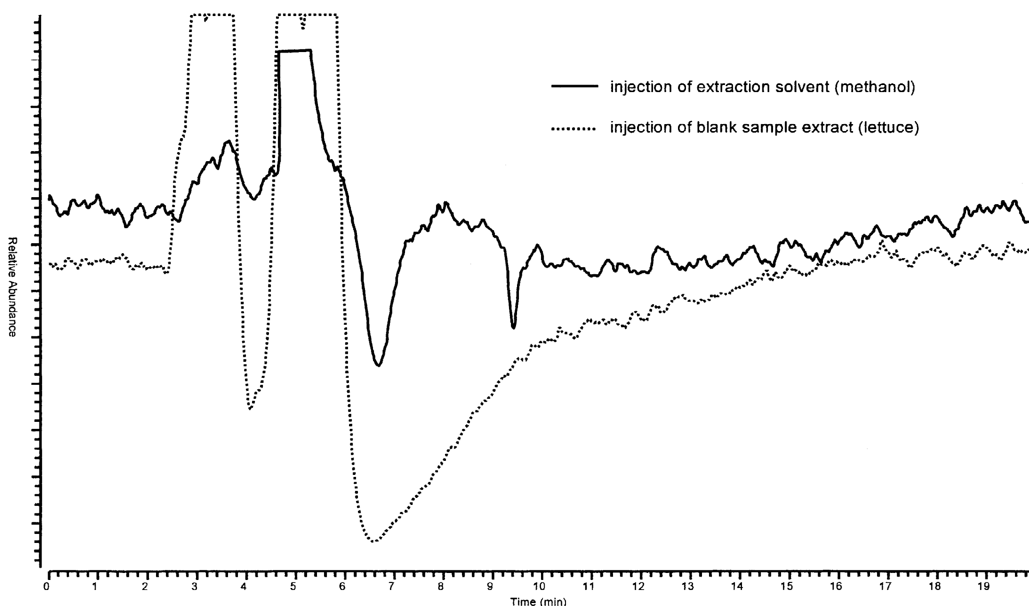

Fig. 2. Effect of the LC effluent on the MS detector response (m/z 189) of post-column infused propamocarb after injection (20 μl) of extraction solvent (methanol) and blank sample extract of lettuce.

methanol could be made without loss of separation efficiency or extra bandbroadening compared to water as an injection solvent. In this way a good sensitivity of the method could be maintained, because the methanolic extracts did not have to be diluted with water before injection. Maintaining this injection volume, a detection limit of 5 μg kg^{-1} in vegetables is feasible. From the calibration data, it was concluded that an injection volume of 20 μl yielded enough sensitivity to obtain the targeted reporting limit (0.05 mg kg^{-1}) of the survey. Using a fivefold lower injection volume reduces the need for cleaning of the ion source, correspondingly.

The polymer-based Shodex RSpak DE-613 column has already been in use for more than 6 years in our laboratory, being loaded with hundreds of uncleaned agricultural samples for the analysis of chlormequat and propamocarb, without loss of separation efficiency, proving the reliability and robustness of this LC column.

3.2. Mass spectrometry

Propamocarb was characterised executing MS and MS–MS experiments in the positive ion mode during infusion of a 1 μg ml^{-1} standard solution. As propamocarb is already charged in solution, it is easily amenable to the electrospray ionisation mode. Running the automatic ''tuning'' software of the LCQ, optimum electrospray ionisation parameters and collision energy for propamocarb were achieved. The positive ion ESI mass spectrum of propamocarb was predominantly characterised by the protonated molecule $(M+H)^+$ of propamocarb (m/z 189). The product ion mass spectrum obtained upon dissociation of the precursor ion of propamocarb was dominated by the product ions at m/z 102 and m/z 144, respectively. These two product ions, corresponding to $[CH_2CH_2CH_2NHCO_2(CH_2)_2CH_3]^+$ (m/z 144), and $[CH_2CH_2CH_2NHCO_2H]^+$ (m/z 102) were formed by the neutral loss of dimethylamine and propene, respectively. Representative reconstructed ion chromatograms of a head lettuce sample, field incurred with propamocarb, are shown in Fig. 3. A comparison of ion chromatograms on the LCQ (ion trap) obtained with selected reaction monitoring (SRM) and two-stage full scan MS experiments on a sample lettuce, fortified with 0.05 mg kg^{-1}, demonstrated that SRM and two-stage full scan MS application are comparable as to the signal-to-noise ratio

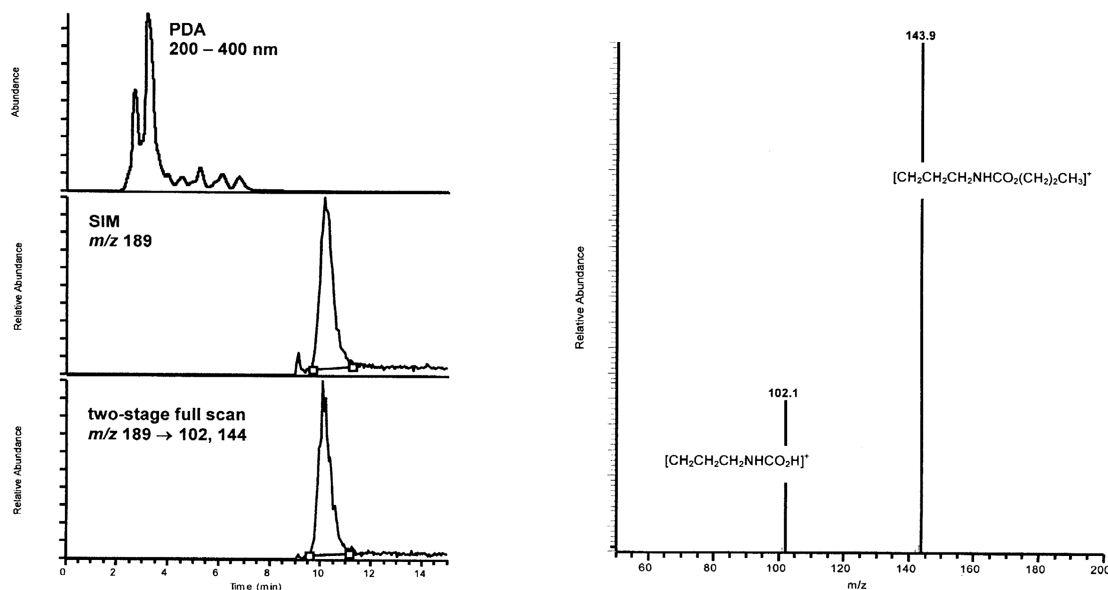

Fig. 3. Chromatograms (unsmoothed) and full scan product ion spectrum (m/z 50–200) from the analysis of a lettuce sample, field incurred with 0.12 mg kg^{-1} of propamocarb. Channels are (top to bottom), DAD: spectrum maximum 200–400 nm, SIM: m/z 189, and two-stage full scan MS: m/z 189→102, 144.

(S/N). It is well-known that an ion trap mass spectrometer permits quantitative assays by two-stage full scan MS without loss of sensitivity relative to an SRM assay. Furthermore, two-stage full scan MS permits greater flexibility than an SRM assay, because the ion(s) to be monitored may be selected at any time after the run has been performed. Therefore, it was decided that MS–MS experiments were run in the full scan mode.

Most of the matrices tested produced potentially interfering peaks at m/z 189, although these were mainly significant for the detection of relatively low concentrations of propamocarb. The selectivity could be improved by applying two-stage MS. For the blank control samples tested, no signal-to-noise ratio greater than 3:1 was observed for the product ions from the precursor ion (m/z 189) at the retention time of propamocarb. After optimisation of the MS–MS conditions, two-stage full scan MS experiments (m/z 50–200) afforded sufficient sensitivity at 10 ng ml^{-1} (20 μl injection volume) by summing the responses of both product ions m/z 102 and m/z 144.

Monitoring the photodiode-array detector signal, direct injections of the methanolic sample extracts showed that the main interferences of the matrices eluted in the initial part of the DAD chromatogram (Fig. 3). The LCQ built-in two-position valve actuator, controlled by the Xcalibur software, enabled us to direct the LC flow to waste during the initial part (9 min) of a run. Before the expected elution of the analyte, the valve actuator was switched to the MS system. In this way, loss of sensitivity due to contamination of the ion source was prevented, which resulted in an improvement of the robustness of the analytical method. Not using the valve actuator, resulted frequently in blockage of the sampling capillary and precipitation in the ion source region of the instrument, especially for samples containing high contents of sugar and/or fat. This device reduced the down-time of the LC–MS system significantly. Maintenance on the ion source region usually had to be performed after approximately 100 injections (24 h). Omitting a sample clean up, reduces the total analysis time of the method drastically.

3.3. Calibration and analytical performance

The method was validated for six different agricultural commodities (head lettuce, leek, potato,

cucumber, radish and cabbage) relevant to the intended use of propamocarb by studying the linearity of the calibration curve, the instrument and method detection limit, the accuracy and the precision. Calibration curves were constructed preparing calibration solutions at seven different concentrations in both solvent and blank matrix extract solutions. Each calibration level was injected five times. The slope of the linear calibration curves was diminished when matrix solutions were used instead of solvent-based solutions, indicating a matrix effect (ion suppression), as was discussed earlier. Between the matrices tested, no significant difference for slope sensitivity was observed. Thus in routine analysis, for matrix matched calibration, only one representative matrix has to be selected for all matrices analysed in the same batch of samples. Linear calibration curves in matrix were obtained from 10 to 500 ng ml^{-1}, in all cases with correlation coefficients greater than 0.995. At higher concentration levels non-linear response (curvature) became evident, giving a decrease in the slope with increasing concentration. Routinely, extracts of samples found to contain more than 500 ng ml^{-1} propamocarb were re-injected after dilution in blank extract to improve the accuracy of quantitation.

The instrument limit of detection was estimated to be 200 pg, which is equivalent to a method limit of detection of 25 μg kg^{-1} in the matrix, for acquisition in two-stage full scan MS application. The calculation is based on a signal-to-noise ratio of 3:1 in blank control samples and is valid for all agricultural commodities tested. The limit of confirmation, based on the less intense product ion (m/z 102), was 60 μg kg^{-1}. The method limit of detection for the SIM application was at least two times higher and greatly dependent on the matrix analysed.

Accuracy and precision were determined via conducting recovery experiments (five replicates). The recoveries were determined in fortification studies in which defined amounts of propamocarb, ranging from 0.05 to 15 mg kg^{-1}, were added to blank samples prior to extraction. The lowest fortification level corresponded to the estimated method limit of determination, namely 0.05 mg kg^{-1}. All samples were analysed using SIM (m/z 189) and two-stage full scan MS (m/z 189→102, 144) within the same run. The recoveries were calculated using a matrix-matched standard solution at a concentration level corresponding with a recovery of 100%. The recovery data are summarised in Table 1. The table shows the mean values calculated per matrix and fortification level ($n=5$), as well as the mean value per matrix ($n=10$, 15), including the relative standard deviations (RSDs).

For the SIM (m/z 189) application, the mean recovery values of propamocarb for the individual commodities ranged from 94 to 97% with a RSD from 4.7 to 7.7%. For the two-stage full scan MS (m/z 189→102, 144) application, the mean recovery values of propamocarb for the individual commodities ranged from 90 to 102% with RSDs from 3.7 to 10.3%. Based on the accuracy and precision data obtained at the lowest fortification level, the method limit of determination was confirmed to be 0.05 mg kg^{-1}. It is evident that the two-stage MS application is more specific, but the analytical performance of both scanning techniques is clearly within the same order of magnitude and is sufficient for the determination of propamocarb at low μg kg^{-1} levels in all agricultural matrices investigated. This was also demonstrated by the excellent correlation ($r^2=0.9959$) between the results obtained from a survey using both scanning techniques. From the limit of determination, all residues of propamocarb detected via the SIM (m/z 189) application could be confirmed by the two-stage full scan MS application, demonstrating the sufficient selectivity of the SIM application.

3.4. Survey of propamocarb in agricultural products

Monitoring of foods is necessary in order to enforce MRLs, to provide information on intake of pesticides by consumers, and will give impetus to further toxicological studies if occurrences of pesticides becomes a concern.

Under regulatory monitoring, the Dutch Inspectorate for Health Protection samples lots of domestically grown and imported crops for analysis of pesticide residues. Within the framework of this survey, a limited number of lettuce, leek, cabbage and radish samples were analysed for residues of propamocarb. The samples, mainly of domestic origin, were randomly collected at auctions, wholesalers and dis-

Table 1
Analytical performance of the LC–MS method for propamocarb

Commodity	Fortification level (mg kg^{-1})	SIM application, m/z 189		Two-stage MS application, m/z 189→102, 144	
		Mean recovery (%)	RSD (%)	Mean recovery (%)	RSD (%)
Lettuce	0.05	96	7.1	100	5.7
	1.0	96	2.8	96	3.0
	15	96	4.4	98	5.8
	Ø[a]	96	4.7	98	4.9
Leek	0.05	95	7.9	88	3.7
	1.0	92	4.1	92	2.9
	Ø	94	6.3	90	3.7
Radish	0.05	97	7.4	109	5.2
	1.0	96	3.8	95	1.2
	Ø	96	5.6	102	8.2
Cabbage	0.05	96	7.8	108	8.5
	1.0	96	1.6	93	1.9
	Ø	96	5.3	101	9.8
Potato	0.05	100	7.9	111	2.8
	1.0	93	2.7	93	3.6
	Ø	97	6.5	102	10.3
Cucumber	0.05	99	9.2	95	5.7
	1.0	92	4.1	92	1.7
	Ø	95	7.7	93	4.3

[a] Mean recovery value per matrix.

tribution centers of supermarkets by field inspectors. The results of the survey are presented in Table 2. The reporting limit for this survey was set at 0.05 mg kg^{-1}. It can be seen that most of the samples analysed, particularly lettuce, contained detectable residues of propamocarb. Of the 195 lettuce samples analysed, 114 samples (60%) contained a residue of propamocarb greater than the detection limit. The concentration of propamocarb detected ranged from <0.05 to 18 mg kg^{-1}. However, all propamocarb residue levels were well below the maximum residue limit of 15 mg kg^{-1}, stated by national legislation, except for one lettuce sample. This lettuce sample contained a residue level of 18 mg kg^{-1}. Furthermore, in 11 (45%) of 24 leek samples, and in 13 (80%) of 16 radish samples, residues of propamocarb were detected. Residue concentrations ranged from <0.05 to 0.51 mg kg^{-1}, and <0.05 to 1.9 mg kg^{-1} in leek and radish samples, respectively. In case of one sample of radish with a residue

Table 2
Survey data for the presence of residues of propamocarb in vegetables from March to October 2000

Commodity	Number of samples with residue concentrations in classes up to and including (mg kg^{-1})								
	Total number of samples	Not detected	<0.05*	0.1	1	10	>10	Dutch (CODEX) maximum residue limits	Number of samples with residues exceeding the Dutch MRL
Lettuce	195	81	7	21	37	45	4	15 (10)	1
Leek	24	13	6	1	4			3 (5)	
Radish	16	3	4	1	7	1		1	1
Cabbage	50	50						0.2 (0.1)	
Total	285	147	17	23	48	46	4		2

*<0.05 represents a residue concentration with a signal-to-noise ratio greater than 3: 1, but below the reporting limit of the survey.

level of 1.9 mg kg^{-1}, the maximum residue limit (1 mg kg^{-1}) was exceeded. In 50 samples of cabbage, no residues of propamocarb were detected.

4. Conclusions

We have developed and validated a sensitive, quantitative analytical method for the detection of propamocarb at low μg kg^{-1} levels in vegetables. The method yields satisfactory results in terms of linearity, accuracy, precision and sensitivity. Two-stage full scan MS application provides unambiguous confirmation of propamocarb in all matrices and can be used to rule out ‘‘false positive’’ results. Compared to established methods, the rapid extraction and redundancy of a clean-up makes the method highly suitable for routine control of residues of propamocarb. In contrast to existing analytical methods, it is potentially applicable to a wide variety of agricultural commodities. The Shodex DE-613 analytical HPLC column greatly improves the robustness of the analytical method, due to the stability and inertness of the polymeric phase. The specificity of the LC–MS method is demonstrated by the comparable quantitative results obtained with both scanning techniques.

A survey has revealed that propamocarb is heavily applied in the agricultural sector in The Netherlands. Despite the high concentrations of propamocarb detected, no negative health effects can be anticipated, because MRLs are rarely exceeded. The frequency of residue findings, however, suggests that periodical monitoring of propamocarb residues in agricultural samples for human consumption is recommended.

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