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Comparison of different clean-up procedures for the determination of N-methylcarbamate insecticides in vegetable matrices by high-performance liquid chromatography with UV detection

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Abstract

Several clean-up procedures which included the use of glass chromatography columns (silica gel, alumina, Florisil, silanized Celite–charcoal), Sep-Pak cartridges and standard solutions were compared for the determination of the following N-methylcarbamate (NMC) insecticides: aldicarb, carbaryl, carbofuran, methomyl and propoxur. According to recovery results of the compounds after elution in a glass column, the most efficient systems employed 4.6% deactivated alumina and a silanized Celite–charcoal (4:1) as adsorbents, using dichloromethane–methanol (99:1) and toluene–acetonitrile (75:25) mixtures, respectively, as binary eluents. The recoveries of the compounds studied varied from 84 to 120%. Comparable recoveries (75–100%) for Sep-Pak cartridges in normal phase (NH_2, CN) and reversed phase (C_8) were observed. Different temperatures were tested during the concentration step in a rotary evaporator, and we verified a strong influence of this parameter on the stability of some compounds, such as carbofuran and carbaryl. Recovery studies employing the best clean up procedures were performed at the Brazilian agricultural level in potato and carrot samples; validation methodology of the US Food and Drug Administration was adapted for the N-methylcarbamate analysis. Their recoveries ranged between 79 and 93% with coefficients of variation of 2.3–8%. © 1998 Elsevier Science B.V.

Keywords: Sample preparation; Vegetables; Food analysis; Pesticides; Carbamates

1. Introduction

Carbamate pesticides have become increasingly important in recent years due to their broad spectrum of biological activity and are used as insecticides, miticides, fungicides, nematocides, and molluscicides [1]. Among them, the N-methylcarbamate (NMC) insecticides consist of about 15 active compounds that constitute a family of important insecticides which cover a wide range of uses in the treatment of seed, soil and crops.

The determination of carbamate residues is often an intricate problem. Most of the methods developed for determination of these compounds are based on a separation by gas or liquid chromatography [2]. Some of these methods are very sensitive, and have been adopted by regulatory agencies [3]. Selective detection techniques such as fluorescence [3,4] or mass spectrometry [5] minimize the need for clean-up steps because they exclude the co-extractives co-eluting together with NMCs. Therefore, in most

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cases, a further clean-up of the extracts is necessary for subsequent chromatographic measurement. Various clean-up procedures have been previously tested, but most of them are very laborious and time consuming for elution, and require the use of a large quantity of solvents [6–8].

The clean-up techniques most commonly employed for extracts containing residues of NMC pesticides are liquid–liquid partitioning (LLP) or adsorption chromatography, such as column chromatography and solid-phase extraction (SPE). Many methods require a combination of both. The most thorough clean-up method for HPLC determination of NMC pesticides in fruits and vegetable samples was that reported by De Kok et al. [9]. The authors used an aminopropyl-bonded silica SPE column for clean-up, and the detection technique involves the use of postcolumn reaction followed by liquid chromatography [4]. During recent years, postcolumn reaction systems in liquid chromatography have attracted increased interest as a means of converting compounds with unfavorable detection properties into derivatives which show enhanced sensitivity and often a higher selectivity towards such specific detectors as fluorescence and electrochemical detectors. Unfortunately, this technique is not simple because it needs prior laborious optimization of the derivatization reactions that can reduce the final recoveries of some compounds. Moreover more complicate, expensive and non-universal equipment is needed too. On other hand, if ultraviolet or photodiode array systems are used for carbamate detection, a simple protocol for clean-up on an SPE column is not always enough. In many cases, additional partitioning steps are also recommended for interference elimination. Somehow or other, the choice of the analysis method will depend of sample nature and of the number of compounds that are present in.

In view of both the different approaches reported in the literature for carbamate clean-up, and the lack of a suitable method for clean-up of this class of pesticides in vegetable extracts, it was decided to undertake the present work, the aims of which were: (i) to compare several clean-up procedures for extracts containing selected NMCs, using glass columns and SPE cartridges; and (ii) to study the stability of the selected NMCs at different temperatures. Application of the best clean-up procedures to the analysis of selected NMCs in vegetable samples (potato and carrots) is demonstrated. Also, some modifications of extraction and clean-up steps of the collaboratively studied and further validated Krause's method–widely used by regulatory agencies–are proposed for NMC analysis by HPLC with UV detection.

2. Experimental

2.1. Standards, reagents, and elution systems

Toluene (98.9% purity), *n*-hexane (99% purity) and light petroleum (96–97% purity) were obtained from Merck (Augsburg, Germany). Acetone, dichloromethane, methanol and acetonitrile were of 98 to >99% purity (Merck) and were used as received. Water was filtered through a Milli-Q apparatus (Millipore) (Bedford, MA, USA). NaCl (98.8% purity) salt was obtained from Merck. Standards of the N-methylcarbamates were purchased from Dr. Ehrenstorfer (Augsburg, Germany). Stock and work solutions were made up in methanol and were stored, for a maximum of 1 year, in the dark at −20°C.

Four elution systems (ESs) of gradual increased polarity were prepared: (1) acetone–*n*-hexane (15:85); (2) methylene chloride–*n*-hexane (80:20); (3) methylene chloride–methanol (99:1), and (4) toluene–acetonitrile (75:25).

2.2. Cleaning of the glass material

All glass material used is this work was previously washed in current water and, after immersion in a 20% alkaline Extran (Merck) solution, rinsed sequentially with current and distilled water. The cleaned material was then dried at ~130°C, with the exception of the volumetric glass material which was dried at room temperature.

2.3. Adsorbents columns, cartridges and elution procedures

2.3.1. Silica, alumina, and Florisil columns

Silica gel (70–230 mesh ASTM, Merck) was heated at 130°C for 24 h and deactivated with 10%

(w/v) deionized water. Alumina (70–230 mesh ASTM, Merck) and Florisil (60–100 mesh ASTM, Merck) were activated at 600°C for 4 h and deactivated with 4.6 (w/v) and 2%, respectively [10]. The Florisil which had been heated at 600°C for 4 h and kept in an oven at 130°C for 5 days was also tested. All adsorbents were stored in a well-closed flask before use. A glass chromatographic column (200× 20 mm I.D.) was prepared by adding a small plug of glass wool, 10 ml of ES and 2.0 g of an adsorbent. The column was tapped gently, prewashed twice with ES and 1.0 ml of a 8.0-ng/μl NMC standard mixture was transferred to the top of the column. The elution was processed at 25 drops/min. The eluate was collected in a 100-ml round-bottomed flask and evaporated to less than 1.0 ml in a rotary evaporator. The ES was removed under a gentle stream of nitrogen and the residue dissolved in 1.0 ml methanol. The extract was filtered through a 0.45-μm disposable filter before HPLC analysis. Three temperatures (35, 40 and 45°C) were tested when the elution was processed on alumina column at the concentration step.

2.3.2. Silanized Celite–charcoal column

Celite (Nuclear, Sao Paulo, Brazil) was treated with dimethyl-dichlorosilane, and charcoal (Merck) was purified by acid washing according to the method described in the Pesticide Analysis Manual [11]. One part charcoal and four parts Celite were combined by vigorous mixing and stored in a sealed container. Glass and plastic (hypodermic syringe, capacity 10 ml) columns were packed with this mixture, as shown in Fig. 1. In both cases the solutions were eluted under pressure; the elution protocols are described below.

2.3.3. Cartridges

Reversed-phase (C_8, C_{18}, CN) and normal-phase (silica, CN, NH_2) SPE cartridges were provided by the Waters Division (Millipore). All cartridges contained 500 mg adsorbent.

2.3.3.1. Reversed-phase SPE cartridges

Nonpolar C_{18}, C_8, CN cartridges were used. After the bonded phase had been solvated with 15 ml of methanol at a 5.0 ml/min flow-rate, the cartridge was loaded with 0.5 ml standard solution. The NMCs were eluted with 5.0 ml of each ES in decreasing order of polarity (2.0 ml/min flow-rate). The fractions were collected, evaporated to near dryness in a rotary evaporator and concentrated under a stream of anhydrous nitrogen gas. The final residue was then reconstituted with 0.5 ml methanol, filtered and analyzed by HPLC.

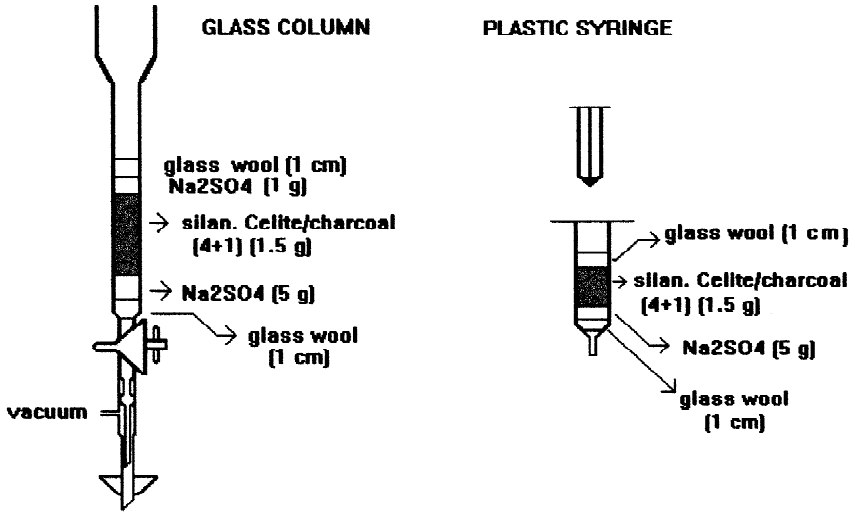

Fig. 1. Silanized Celite–charcoal columns used for clean-up of N-methylcarbamate insecticides.

2.3.3.2. Normal-phase SPE cartridges

Polar silica, CN and NH_2 cartridges were conditioned with *n*-hexane and the clean-up procedures were performed as described above, using 5.0 ml of each ES in gradual increased polar.

2.4. HPLC–UV chromatographic system

The LC system (Waters, Milford, MA, USA) consisted of a Model 501 solvent delivery system, a Model 486 UV variable-wavelength detector, a Model U6K injector and a Model 746 integrator. A LiChrospher 100 RP-18 (125×4 mm I.D., 5 μm) stainless steel column, adapted to a LiChrocart guard column (both from Merck) was employed. The analyses were performed at 195 nm and the mobile phase was acetonitrile–water (30:70) at a flow-rate of 1.0 ml/min. Mobile-phase solvents were degassed by simultaneous filtration and ultrasonic application.

2.5. Carbamate analysis in crops with selected clean-up procedures

As part of the objectives of the Pesticides Residue Analysis Laboratory of the Institute of Chemistry/UNESP, clean-up procedures employing selected adsorbent materials were carried out in order to evaluate the efficiency of these materials in the analysis of the selected NMCs in vegetable samples. Sample extraction and partitioning procedures were based on Krause's method [5], but some modifications were included in order to minimize the number of steps and allow the final determination by HPLC–UV detection. The method proposed in this work for carbamate analysis is summarized in Fig. 2. Considerations with regard to the changes of the original method are presented in Section 3.

2.6. Procedure blanks

Chromatographic analysis consisting of all the reagents and adsorbents used in this work without the pesticides were carried out to check contamination. Recoveries were calculated from the chromatograms of the standard solutions before and after use of the adsorption columns and SPE cartridges.

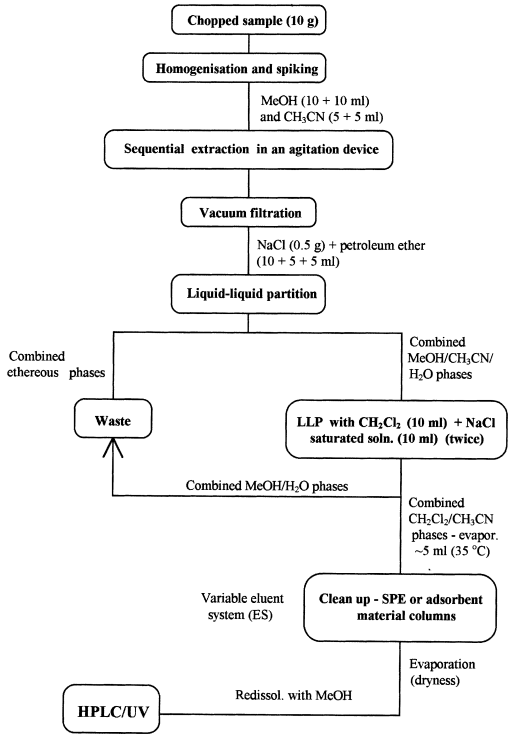

Fig. 2. Scheme of extraction and partitioning procedures before HPLC–UV analysis of the selected N-methylcarbamate insecticides in potato and carrot samples.

3. Results and discussion

3.1. Analytical parameters

Table 1 presents retention times, detectabilities and linear range of the selected NMCs. Retention of compounds may vary a little from column to column; however, separation patterns were reproducible under method conditions stated. Resolutions of compounds were adequate in this isocratic elution; resolution between propoxur and carbofuran was nearly 0.85. The sensitivities of propoxur and carbofuran were such that these compounds could be detected at 0.02 ng. This value is below the tolerated contents of carbamate residues in agriculture products. The linear dynamic range of the detector to the NMCs, at 195 nm, was checked and appeared to be from 0.5 to 50 ng. This is also the practical working range of the selected carbamates.

Table 1
Retention times and sensitivities of selected N-methylcarbamate insecticides[a]

Carbamate	Retention time (min)	Detection limit[b]	Linear range[c]
Methomyl	2.20	5	5–100
Aldicar	5.55	1.0	0.5–50
Propoxur	9.22	0.5	0.5–25
Carbofuran	9.90	0.5	0.5–25
Carbaryl	13.12	7.5	5–50

[a]Chromatographic conditions as described in the text.
[b]Nanograms required to produce a 1-cm peak at maximum sensitivity (0.005 AUFS), 1.0 mV recorder, at retention times shown. These data correspond to limits of the equipment.
[c]Results in nanograms (25-μl volume injected).

3.2. Recovery studies of NMC insecticides after clean-up procedures

Due to the different polarities of the carbamates, the development of a simple and unique clean-up method is very difficult to achieve, especially if more than one compound is simultaneously determined. First, the elution pattern of the carbamates, present in standard solutions, was studied using chromatography columns packed with silica, alumina, Florisil and Celite–charcoal and several binary mixtures as eluent solution. According to the results shown in Table 2, the best ESs and adsorbents were: methylene chloride–methanol (99:1), toluene–acetonitrile (75:25), deactivated alumina (4.6%) and silanized Celite–charcoal (4:1, plastic column), respectively.

Table 2
Recovery of the N-methylcarbamate insecticides after elution on adsorbent columns

Adsorbent material	ES	Recovery (%)				
		Methomyl	Aldicarb	Propoxur	Carbofuran	Carbaryl
10% deactivated silica	1	63 (6.5)	67 (3.2)	66 (2.6)	68 (3.8)	37 (5.5)
	2	94 (4.6)	80 (3.4)	79 (2.3)	85 (3.1)	83 (4.0)
	3	ND	91 (2.7)	79 (3.6)	72 (4.2)	18 (5.0)
	4	80 (12.6)	67 (3.5)	52 (2.7)	59 (4.2)	33 (4.8)
4.6% deactivated alumina	1	81 (4.9)	66 (2.6)	77 (3.2)	91 (4.4)	98 (5.6)
	2	81 (4.0)	69 (3.3)	67 (4.1)	72 (5.3)	44 (4.6)
	3	96 (5.5)	94 (2.7)	89 (3.0)	105 (4.0)	89 (5.2)
	4	69 (6.6)	47 (3.6)	69 (5.3)	70 (5.4)	58 (4.2)
2% deactivated Florisil	1	51 (6.0)	91 (4.0)	67 (3.7)	81 (4.2)	63 (8.0)
	2	65 (6.2)	73 (2.8)	63 (4.0)	75 (3.5)	54 (5.4)
	3	83 (5.0)	108 (2.5)	101 (3.2)	102 (3.7)	95 (2.8)
	4	85 (12.0)	120 (3.3)	104 (2.9)	109 (4.0)	94 (2.8)
Activated Florisil	1	60 (8.0)	79 (2.6)	68 (4.0)	68 (3.6)	48 (3.4)
	2	83 (6.7)	62 (3.0)	75 (3.3)	87 (3.0)	91 (4.0)
	3	99 (7.0)	81 (2.5)	76 (3.0)	87 (4.0)	71 (3.0)
	4	101 (6.5)	90 (3.5)	96 (6.0)	110 (3.5)	108 (4.0)
Silanized Celite–charcoal (syringe)	1	33 (6.2)	85 (2.5)	73 (3.6)	72 (4.0)	40 (3.0)
	2	104 (5.4)	85 (2.6)	60 (2.5)	66 (2.7)	ND
	3	89 (6.0)	92 (2.0)	85 (3.0)	94 (3.2)	97 (2.5)
	4	97 (5.0)	97 (3.5)	86 (5.3)	91 (3.5)	90 (4.6)
Silanized Celite–charcoal (column)	1	8 (4.0)	29 (5.0)	29 (5.0)	39 (5.2)	6 (5.4)
	2	102 (5.5)	98 (2.5)	89 (3.0)	81 (4.5)	21 (6.0)
	3	100 (4.5)	88 (3.2)	87 (4.5)	79 (3.5)	88 (4.3)
	4	105 (3.5)	82 (6.6)	80 (3.5)	92 (2.5)	77 (5.0)

ES, eluent systems: (1) acetone–*n*-hexane (15:85); (2) methylene chloride–*n*-hexane (80:20); (3) methylene chloride–methanol (99:1); (4) toluene–acetonitrile (75:25). R.S.D.s (%) in parentheses ($n=3$); ND, not-detected.

Under these conditions, all the pesticides had total recoveries higher than 85%. ES 1 (acetone–*n*-hexane, 15:85) resulted in poor recoveries due to its lower polarity and insufficient capacity of elution of polar carbamate. Overall recoveries were improved with low deactivated adsorbents. For example, the 2% deactivated Florisil provided higher recoveries than 4, 6 and 10% deactivated alumina and silica, respectively. Such behavior is due the water present in these adsorbents which can hydrolyze the carbamates, as reported by Bertrand et al. [12]. Florisil activated at 600°C was also tested, but the recoveries were much lower. Thus, Florisil is the preferred deactivated material for carbamate clean-up because less OH^- groups are present on the adsorbent surface, which enable the efficient retention of the compounds prior to elution with the methylene chloride–methanol (99:1) mixture. These results agree with the observations of Barceló and co-workers [13] about deactivated adsorbent surfaces. Durand and Barceló [14] studied different clean-up methods for determination of different classes of pesticides–including seven carbamate pesticides–from environmental soil samples. They reached satisfactory results using a deactivated Florisil column combined with a binary acetone–dichloromethane (50:50) mixture. Such an eluent has a polarity similar to the third ES examined in the present study.

The Celite–charcoal mixture was very powerful in retaining the more polar compounds and needed a strong ES, such as toluene–acetonitrile, to elute all the NMCs. Therefore, in extracts where a minimum content of water is present, some emulsion can be formed during elution process. In this case, the third ES (methylene chloride–methanol, 99:1) is recommended for use without considerable losses in pesticide recovery. The advantage of charcoal is to retain efficiently some co-extractives, as for example pigments (xanthophyll, chlorophyll, etc.) [4,5,11]. However, the preparation of this adsorbent mixture is very laborious and time consuming.

After the efficiency of the glass columns was examined, elution on SPE cartridges was studied. Table 3 shows that the elution procedure in normal-phase cartridges resulted in adequate recoveries (71–120%), especially for cyanopropyl- and aminopropyl-bonded cartridges (84–120%) due the similarity of the structures and polarities of these adsorbents and the selected carbamates. The elution protocol proposed in this work was peculiar because it was performed with a small volume (5.0 ml) of each ES in increasing or decreasing polarity in normal- or reversed-phase mode, respectively. In general, the elution mixture is chosen and the elution is performed in one unique action, after column conditioning. Comparable results (75–100%) were obtained with the C_8 cartridge (reversed-phase), but with lowest coefficients of variation. The clean-up procedures employing Sep-Pak cartridges proved to be as efficient in the normal- (NH_2 and CN) as in the reversed (C_8)-phase mode. Direct elution methods use a small volume of each ES and, in addition, these clean-up procedures are extremely fast, efficient and attractive, because they allow a technician to prepare 10–15 samples within one working day.

3.3. Tests in vegetable samples

Clean-up procedures of the vegetable extracts spiked with the selected NMCs were tested. The adsorbent materials were chosen according to the best recovery averages of the compounds and the

Table 3
Recovery of N-methylcarbamate insecticides after elution in SPE cartridges

Sep-Pak cartridges	Recovery (%)				
	Methomyl	Aldicarb	Propoxur	Carbofuran	Carbaryl
Silica (NP)	71 (4.3)	94 (2.5)	88 (2.0)	92 (2.5)	96 (3.5)
CN (NP)	96 (3.8)	92 (2.0)	95 (2.5)	95 (2.8)	94 (3.0)
NH_2 (NP)	120 (3.5)	93 (2.6)	95 (3.0)	89 (4.3)	84 (2.8)
C_{18} (RP)	67 (4.0)	52 (2.4)	62 (2.3)	68 (3.3)	50 (3.5)
C_8 (RP)	98 (5.5)	79 (2.3)	95 (3.0)	100 (3.0)	98 (4.0)
CN (RP)	70 (3.6)	52 (3.5)	59 (4.0)	62 (5.0)	60 (4.0)

NP, normal phase; RP, reversed phase; R.S.D.s (%) in parentheses ($n=3$).

lowest R.S.D. values (see Tables 2 and 3). The methylene chloride–methanol (99:1) mixture was used as eluent in the adsorbent glass columns packed with deactivated alumina and silanized Celite–charcoal—this last into the plastic syringe. For the SPE procedure (performed on a cyanopropyl-bonded cartridge), the normal-phase protocol was carried out again (see Section 2).

The extraction and LLP steps were performed according to the method described by the US Food and Drug Administration (FDA) in the *Pesticide Analytical Manual* [11]; the main adaptations were the mass of the sample, which was considerably reduced, its prior freeze-drying, which was done in order to eliminate interferences that accompany water during the extraction step, and the change of the detection system. As already mentioned, during clean-up on adsorbent columns, the presence of water can sometimes also cause emulsion, making the extract elution as difficult on the adsorbent column as on an SPE cartridge. The determination of the compounds was accomplished using UV detection, which provided a sensitivity of detection at the nanogram level. Obviously, the presence of some co-extractives in the chromatogram may make the quantification of the more polar compounds (for example, methomyl) difficult, but such behavior depends on the matrix complexity. Table 4 shows the recovery rates for selected NMCs in potato and carrot samples after spiking at the maximum recommended residue levels for Brazilian agriculture (0.1, 1.0, 0.5, 0.5 and 0.5 mg/kg for methomyl, aldicarb, propoxur, carbofuran and carbaryl, respectively) [15]. Three different phase materials were tested. In general, lower R.S.D.s were observed for the Celite–charcoal column and the SPE cartridge, due to the almost homogeneous elution process at the adsorbent surface (the flow-rate was the same). Comparing the data in Tables 2–4, we can see that the R.S.D.s were higher after vegetable extract elution than standard solution elution. Methomyl constituted an exception, possibly due the presence of some vegetable substances in the extracts, such as high-molecular mass pigments and others components which possibly have formed an ‘entrapment’ around the adsorbent surface, allowing the removal of the pesticide for the eluent mixture. In other words, the adsorption of the methomyl was strong in the presence of these substances, and the methylene chloride–methanol (99:1) mixture effectively recovered most of the compound.

3.4. Stability of N-methylcarbamate insecticides

Most of these pesticides are thermally labile and have a very low volatility, which prevents direct analysis by GC, therefore LC is ideally suited for carbamate separation employing different detectors [5,16]. A critical point overlooked in these methods, and one that deserves special attention, concerns the NMC degradation temperature. There are many factors that influence the degradation of the carbamate insecticides in the real environment such as, for example, both exposure to the light and elevated temperatures [17] and the presence of the humic acids and salts in the soil and aqueous environments [18]. However, in laboratory work the highest losses in carbamate recovery are due to temperature and the

Table 4
Recovery of the N-methylcarbamate insecticides in potato and carrot samples

Compound	Recovery (%)					
	Potato			Carrot		
	DA	SCC	CN	DA	SCC	CN
Methomyl	92 (5.5)	91 (4.9)	90 (4.5)	—[a]	—[a]	—[a]
Aldicarb	89 (7.0)	90 (2.3)	91 (3.8)	—[a]	—[a]	—[a]
Carbofuran	85 (5.8)	82 (4.5)	90 (5.6)	93 (6.8)	92 (8.0)	91 (3.8)
Propoxur	91 (6.0)	87 (4.0)	92 (4.7)	—[a]	—[a]	—[a]
Carbaryl	79 (4.2)	91 (2.6)	89 (5.4)	80 (4.6)	90 (7.5)	87 (4.3)

DA, deactivated alumina; SCC, silanized Celite–charcoal; CN, CN (NP) cartrdige; NP, normal-phase; R.S.D.s (%) in parentheses ($n=3$).
[a]Not recommended for protection of carrots.

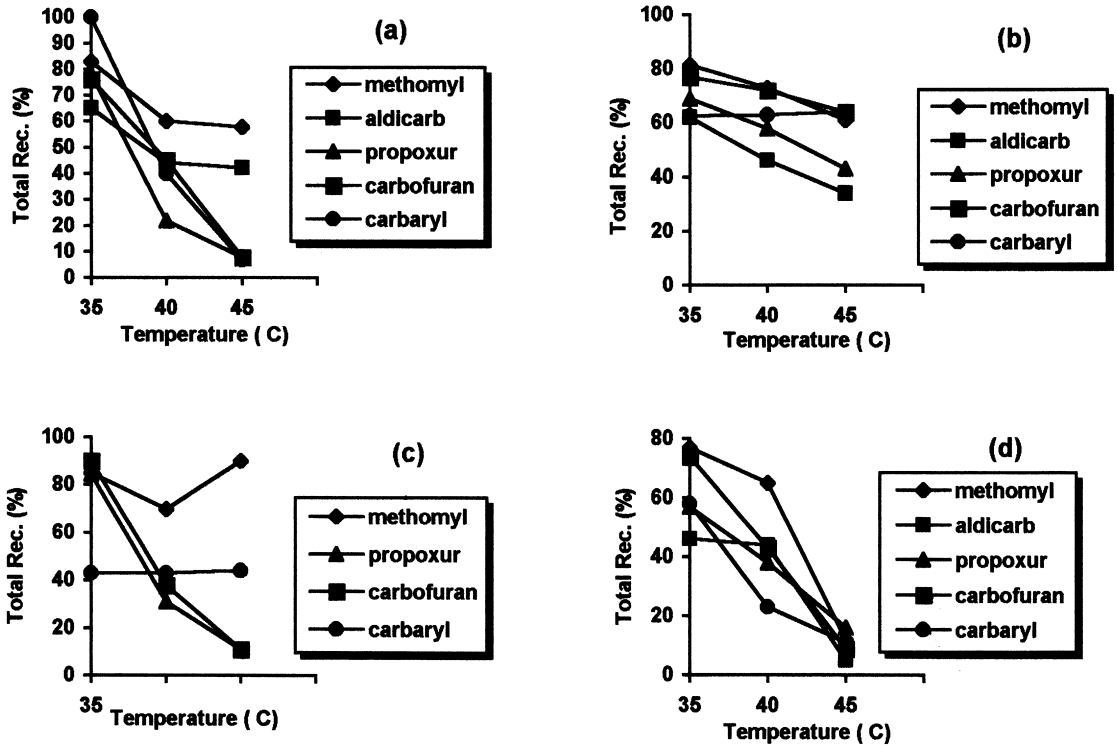

Fig. 3. Effect of temperature during concentration steps in a rotary evaporator on the stability of N-methylcarbamate insecticides. Elution on alumina glass column. ES: (a) acetone–*n*-hexane (15:85); (b) methylene chloride–*n*-hexane (80:20); (c) methylene chloride–methanol (99:1); (d) toluene–acetonitrile (75:25).

period of concentration of the extracts in the rotatory evaporator. As can be seen in Fig. 3, the effect of temperature was stronger for carbaryl and carbofuran. These results agree with other works that made reference to the poor stability of these analytes at higher temperatures of 40–45°C [17,18]. Therefore, during the concentration step in the rotary evaporator, considerable losses can occur at temperatures higher than 35°C. For the fourth ES (Fig. 3d), the losses were more evident because the toluene–acetonitrile mixture demanded a higher duration for extract evaporation.

4. Conclusions

The efficiency of several clean-up procedures for solutions containing parent N-methylcarbamate insecticides were examined by analyzing some parameters.

(1) Time required for clean-up: lower when Sep-Pak cartridges are used; higher for clean-up on adsorption columns (especially for Celite–charcoal columns).

(2) Facility of operation: superior for Sep-Pak cartridges.

(3) Recovery of NMC insecticides (essential parameter): higher than 89% for alumina (ES, methylene chloride–methanol, 99:1) and some cartridges (NH_2 (>84%) and CN (>92%) in normal-phase; C_8 (>79%) in reversed-phase). For Celite–charcoal adsorbent columns (ES, toluene–acetonitrile, 75:25) recoveries from 77 to 105% were founded; alternatively, the ES methylene chloride–methanol (99:1) can be used for elution of NMCs on this adsorbent (79–100% recoveries).

(4) Costs of the procedure: more expensive for SPE cartridges, especially if it is applied to routinely based analyses.

Clean-up methods employing adsorbent columns

and SPE cartridges have been optimized for the analysis of some NMC insecticides commonly used in Brazilian agriculture. A silanized Celite–charcoal syringe column with a cyanopropyl-bonded cartridge, combined with adequate eluent systems, provide an appropriate procedure for determination of selected NMC insecticides in potato and carrot samples. The method has been in operation in the Department of Environmental Chemistry/CSIC for future investigations involving carbamate residue analysis in crops.

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