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Automatic determination of N-methylcarbamate pesticides by using a liquid–liquid extractor derivatization module coupled on-line to a gas chromatograph equipped with a flame ionization detector

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ABSTRACT

A continuous extraction system for the continuous introduction of carbamate pesticide derivatives into a gas–liquid chromatograph was developed. The hydrolysis products of aryl N-methylcarbamates (phenols) were extracted with or without derivatization in a continuous fashion by using ethyl acetate or acetic anhydride in *n*-hexane, respectively. The acetylated phenolic portion of N-methylcarbamates is highly selective, which was taken advantage of to identify six pesticides (propoxur, carbofuran, carbaryl, aminocarb, benthiocarb and methiocarb). The chromatographic responses obtained were linear between 0.2 and 160 mg/l of the different N-methylcarbamates, and the relative standard deviation was 1.9–3.9%.

INTRODUCTION

Carbamate pesticides have become increasingly important in recent years on account of their broad spectrum of biological activity. Gas–liquid chromatography (GLC) is by far the most commonly used technique for the determination of carbamates [1,2]. Direct GLC causes most N-methylcarbamates to be decomposed into their respective phenols to different extents. However, GLC analysis for carbamate phenols is not a widely accepted practice, because the determination of phenols is hindered by the low sensitivity of flame ionization detectors; nevertheless, on derivatization to their ethers [3] or acetates [4], these substances can be readily determined. Chemical derivatization offers some advantages for the determination of carbamates including improved thermal stability, increased sensitivity and the possibility of implementing multi-residue analysis. There are two general approaches to the determination of derivatized N-methylcarbamates, namely with derivatization of the intact pesticide or of one of its hydrolysis products, which include the volatile methylamine. Methods for the derivatization and extraction of pesticides have been the subject of excellent reviews [5,6]. Reagents such as heptafluorobutyric anhydride [7,8], pentafluoropropionic anhydride [9] and pentafluorobenzyl bromide [10,11] have been employed for this purpose. However, chemical derivatization involves additional steps that result in analyte losses through manipulation. Moreover, many derivatizing reagents are toxic, carcinogenic or explosive. Alternative techniques used for the determination of N-methylcarbamates include spectrophotometry [12], TLC [13] and HPLC [14–17].

Flow-injection analysis (FIA) has also been employed for the determination of carbamates [18]. Various continuous separation systems have been used in combination with chromatographic techniques for this purpose. Thus, one method using a

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continuous-flow extraction system for the determination of organophosphorus pesticides was developed by Farran and co-workers, who used HPLC and UV detection [19] plus MS characterization [20]. Two GC methods for the determination of a variety of phenols in water samples by use of a continuous liquid–liquid extraction–derivatization system were also recently developed; quantification with a flame ionization detector was done with manual injection [21] or via an injection valve allowing 4 μl of vaporized sample to be introduced directly via the instrument's injection port [22]. Also, a continuous gas-diffusion separation system was combined with an electron-capture detection system [23] for the continuous generation and determination of volatile species such as chlorine and sulphur dioxide.

The aim of this work was to reduce human involvement in the determination of N-methylcarbamate pesticides, particularly as regards sample treatment, reaction development and transfer of the treated sample to the detector. This was accomplished by using a continuous liquid–liquid extractor for the simultaneous extraction, with or without derivatization, of various N-methylcarbamates, which was connected on-line to a gas chromatograph. The acetate esters of the hydrolysis products of six N-methylcarbamates were formed by adding acetic anhydride to the *n*-hexane extractants used.

EXPERIMENTAL

Apparatus

The flame ionization detector used was built into a Hewlett-Packard Model 5890 A gas chromatograph. Chromatographic assays were performed on a cross-linked 50% phenyl–50% methylpolysiloxane (film thickness 2.0 μm) fused-silica column (10 m × 0.53 mm I.D.) supplied by Hewlett-Packard (HP-17). Nitrogen was used as the carrier gas at a flow-rate of 35 ml/min. The injector and detector temperatures were kept at 150 and 220°C, respectively, throughout. The temperature programme of the chromatographic oven was either (a) 100°C (held for 2 min), increased at 35°C/min to 175°C (held for 1 min), at 25°C/min to 210°C (held for 1 min) and at 50°C/min to 250°C (held for 3 min) or (b) increased at 8°C/min from 100 to 130°C (held for 3 min), at 15°C/min to 170°C (held for 1 min) and at 30°C/min to 250°C (held for 3 min), to separate the hydrolysis products and their acetates, respectively. Peak areas were measured by using a Hewlett-Packard 3392 A integrator. The flow extraction–derivatization system consisted of a Gilson Minipuls-2 peristaltic pump, a Tecator A-10 T solvent segmenter and a custom-made phase separator furnished with a Fluoropore membrane (1.0 μm pore size, FALP; Millipore) [24]. Poly(vinyl chloride) and Solvaflex pump tubing for aqueous and *n*-hexane solutions, respectively, displacement bottles for pumping ethyl acetate and PTFE tubing for coils were used. A Knauer 6332000 six-port switching valve and a thermostated water-bath were also employed.

Standards and reagents

N-Methylcarbamates were purchased from Dr. Ehrenstorfer (Augsburg), at 97–99% purity. Phenanthrene (internal standard) and all other reagents (acetic anhydride, sodium hydroxide, *n*-hexane and ethyl acetate) were supplied by Merck.

Preparation of test solutions

Stock standard solutions of propoxur, carbofuran and carbaryl (I) or propoxur, benthiocarb, carbofuran, aminocarb, carbaryl and methiocarb (II) for extraction and extraction–derivatization, respectively, were prepared at a concetration of 2 g/l of each pesticide in 99.9% acetone and stored in PTFE bottles at 4°C. Appropriate volumes of these stock solutions were diluted with doubly distilled water to prepare 25 ml of solutions containing between 0.2 and 160 mg/l of each pesticide in $4 \cdot 10^{-3}$ *M* (I) or $1.2 \cdot 10^{-2}$ *M* (II) sodium hydroxide (hydrolysis reagent). Ethyl acetate containing 100 mg/l of phenanthrene (internal standard) for extraction, and *n*-hexane containing the same concentration of phenanthrene plus 8% (v/v) of acetic anhydride (derivatization reagent) for extraction–derivatization, were used as extractants.

Sample introduction system

The system used to introduce the extracted samples into the gas chromatograph is depicted in Fig. 1. The interface between the extraction system and the gas chromatograph has been described elsewhere [22]. The injection interface was constructed by using an injection valve originally designed for

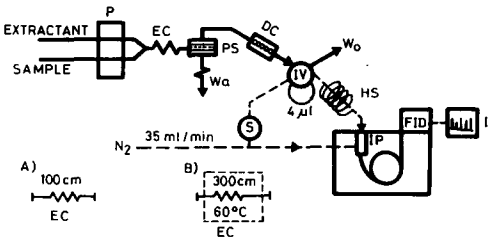

Fig. 1. Flow-injection system for the extraction and extraction–derivatization of N-methylcarbamate pesticides. EC = extraction coil (A for extraction and B for extraction–derivatization); PS = phase separator; DC = desiccating column; IV = injection valve; HS = heating system; S = tube stopcock; IP = injection port; FID, flame ionization detector; I = integrator.

HPLC; the large volume of the valve loop was reduced to 4 µl and a 25-cm stainless-steel tube was fitted to the carrier outlet of the valve. The tube had a stainless-steel needle soldered on one end, which allowed direct fitting of the valve to the injection port of the gas chromatograph by inserting its needle into the septum of the instrument port. This tube linking the valve and the injection port was heated by means of a wire coiled helically around a hollow ceramic tube that could be heated between 25 and 175 °C. The inlet for the carrier gas (nitrogen at 35 ml/min) of the chromatograph was split into two parts that were connected directly to the carrier inlet of the valve (flow-rate 25 ml/min) and the chromatograph injection port (flow-rate 10 ml/min), respectively. The inlet was shut by a stopcock so that the instrument could be used for manual injections by allowing the nitrogen stream to follow its normal pathway through the instrument.

Procedure

Fig. 1 depicts the combined extraction analyser–chromatographic system used. The aqueous sample, containing sodium hydroxide, was continuously mixed with a stream of ethyl acetate (for extraction of the hydrolysis products) or *n*-hexane (for simultaneous extraction–derivatization). The extracts were used to load the loop of the injection valve. The loop contents (4 µl) were transferred to the chromatograph port by the nitrogen carrier gas. The section of the tube valve port was heated at 120 or 125 °C for extraction and extraction–derivatization of the pesticides, respectively, in order to prevent samples from being adsorbed on the tube walls during transfer. A desiccating column (5 cm × 3 mm I.D.) packed with sodium aluminosilicate pellets (pore diameter 4 Å) was used prior to the injection valve to prevent any water from reaching the column.

RESULTS AND DISCUSSION

Four organic solvents (ethyl acetate, toluene, *n*-hexane and dichloromethane) were tried as extractants for the N-methylcarbamates. Ethyl acetate was found to be the most efficient for hydrolysable pesticides (extraction yields ranged between 60 and 80%). On the other hand, simultaneous acylation with acetic anhydride and extraction with *n*-hexane, toluene and dichloromethane was similar in efficiency. Toluene and dichloromethane were discarded as they caused the PTFE membrane of the phase separator to deteriorate rapidly, so *n*-hexane was finally chosen for extraction–derivatization of the hydrolysis products. Extracted underivatized hydrolysis products could not be fully resolved; in fact, the peaks of benthiocarb, aminocarb and methiocarb were markedly overlapped. Conversion of the hydrolysis products into their esters allowed the sequential separation of the above-mentioned pesticides plus carbaryl, carbofuran and propoxur.

Optimization of the extraction unit

The experimental conditions studied included the sodium hydroxide, ethanol and acetic anhydride concentrations, the flow-rates of the aqueous and organic phases, the temperature and the extraction coil length. Thus, a sample solution containing 10 mg/l of each N-methylcarbamate from standard solutions I or II for extraction and extraction–derivatization, respectively, were prepared in doubly distilled water. Table I gives the optimum conditions for the preparation of the samples and extractants and operation of the flow extraction system.

According to the literature, the hydrolysis of N-methylcarbamates is best accomplished in alkaline ethanol media [12]. The influence of the sodium hydroxide concentration was studied over the range $0–2 \cdot 10^{-2}$ *M*. In the absence of alkali, the peaks in the gas chromatogram obtained corresponded to intact N-methylcarbamates and their hydrolysis products because the carbamates were partially

TABLE I

OPTIMUM CONDITIONS FOR THE DETERMINATION OF N-METHYLCARBAMATES

Parameter	Range studied	Optimum range	Selected value
NaOH[a] (*M*)	$0–2 \cdot 10^{-2}$	$2 \cdot 10^{-3}–5 \cdot 10^{-3}$	$4 \cdot 10^{-3}$
NaOH[b] (*M*)	$0–2 \cdot 10^{-2}$	$8 \cdot 10^{-3}–2 \cdot 10^{-2}$	$1.2 \cdot 10^{-2}$
Ethanol[a] (%)	0–4	0–2.4	–
Acetic anhydride[b] (%)	0–12	6–12	8
Reactor temperature[b] (°C)	20–100	50–70	60
Extraction coil length[a] (cm)	20–300	50–300	100
Extraction coil length[b] (cm)	20–500	125–500	300
Flow-rate[a,b] (ml/min):			
aqueous phase	0.4–2.8	1.0–2.8	2.7
organic phase	0.2–1.6	0.3–0.8	0.7
Nitrogen flow-rate[a,b] (ml/min)	15–65	25–50	35
Tube valve port temperature[a] (°C)	25–160	110–125	120
Tube valve port temperature[b] (°C)	25–160	100–150	125

[a] Extraction method.
[b] Extraction–derivatization method.

transformed into their corresponding phenols, which rendered quantitative interpretation of the results difficult. In the presence of sodium hydroxide, however, only the peaks of the hydrolysis products (phenols) were obtained. In order to ensure complete hydrolysis of the pesticides, different amounts of ethanol were added to the samples. Reaction development did not seemingly depend on the ethanol concentration because the N-methylcarbamates were instantaneously hydrolysed to their corresponding phenols by sodium hydroxide alone. The ionic strength, which was adjusted with potassium nitrate, did not affect the signal in the extraction or extraction–derivatization method up to 1.5 *M*. The influence of the acetic anhydride concentration on the yield of acetate derivatives of the hydrolysis products was investigated by using several solutions in *n*-hexane. A 6% solution was found to be adequate for derivatization purposes (Fig. 2); lower concentrations resulted in incomplete derivatization of the phenols and in chromatograms including the peaks of both the underivatized and the derivatized hydrolysis products.

The effect of the extraction coil temperature was studied over the range 15–100°C. This variable affected the extraction yield only when extraction and derivatization were performed simultaneously as a result of ester formation being favoured by heating. Below 50°C, the chromatograms showed the peaks of both the underivatized and the derivatized hydrolysis products. The extraction coil was maintained at room temperature or heated at 60°C for extraction and extraction–derivatization, respectively (Fig. 1).

The flow-rates of the sample and extractant were also optimized. Increasing the sample flow-rate (at a constant organic phase flow-rate) resulted in increased peak areas through increased preconcentration ratios. Obviously, the peak areas also increased with decreasing organic phase flow-rate (at a con-

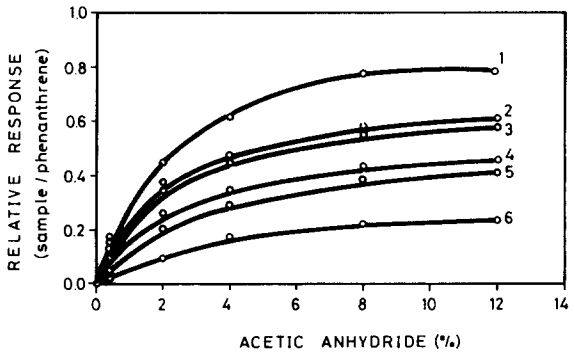

Fig. 2. Effect of the acetic anhydride concentration (%) on the derivatization reaction. 1 = Aminocarb; 2 = methiocarb; 3 = benthiocarb; 4 = carbofuran; 5 = propoxur; 6 = carbaryl. For GC conditions, see text.

stant sample flow-rate) for the same reason. Flow-rates were chosen as a compromise between adequate reproducibility, preconcentration ratio and sampling frequency. Thus, we chose sample and organic phase flow-rates of 2.7 and 0.7 ml/min, respectively. The influence of the residence time was studied at different extraction coil lengths between 20 and 500 cm and the aforementioned sample and extractant flow-rates. The peak area of the underivatized hydrolysis products was not significantly affected by the coil length; however, if the compounds were extracted and derivatized simultaneously, the coil length was somehow influential as esters required some time to form. As shown in Fig. 3, a reaction coil longer than 125 cm was required for the simultaneous extraction–derivatization of all the pesticides. A derivatization–extraction coil length of 300 cm, which resulted in a residence time of 10.5 s, was chosen.

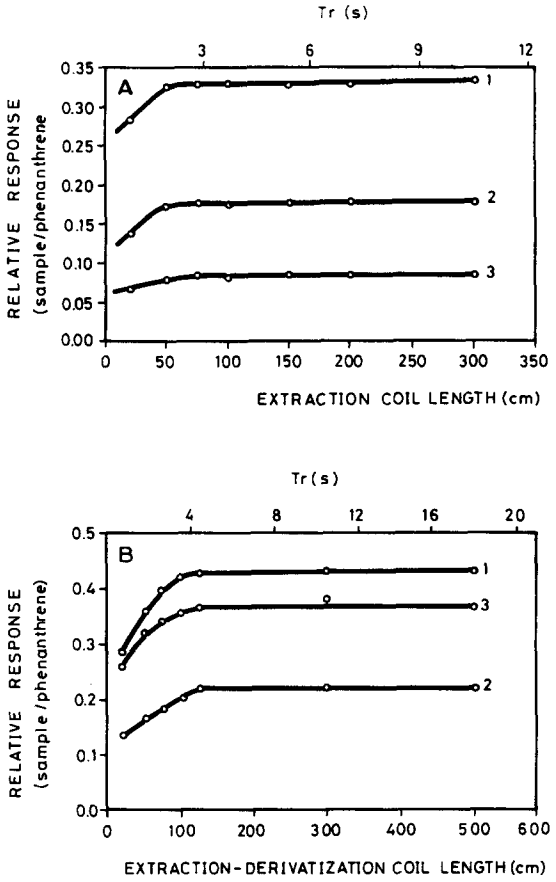

Fig. 3. Effect of the coil length through the residence time (Tr) on (A) the extraction and (B) the extraction–derivatization of (1) propoxur, (2) carbofuran and (3) carbaryl. For GC conditions, see text.

Optimization of the sample introduction device

The extraction unit described above was fitted to the chromatograph via a modified injection valve (see Experimental). Earlier experiments [22] showed that coupling a liquid–liquid extractor to a gas chromatograph required that the carrier gas stream (nitrogen) be split into two: one to be passed through the loop of the injection valve in order to flush the sample into the chromatograph and other to be circulated through the gas inlet of the instrument. Also, the tube linking the valve and the injection port must be heated in order that the sample may reach the chromatograph in vaporized form. The overall flow-rate of carrier gas passed through the valve and the injection port was varied between 15 and 65 ml/min. A flow-rate higher than 25–30 ml/min was required to offset the background signal. An overall gas flow-rate of 35 ml/min (flow-rates through the valve and injection port 25 and 10 ml/min, respectively) was found to be optimum. Higher flow-rates resulted in diminished signals through sample dispersion on the gas side and in the risk of extinction of the detector flame. By using the heating system described under Experimental, the tube valve port was heated at different temperatures (Table I). Fig. 4 shows the chromatograms obtained by injecting extracts of the six derivatized pesticides in *n*-hexane. The first chromatogram (Fig. 4A) was recorded with automatic injection at room temperature and the third (Fig. 4C) with heating at 125 °C. As can be seen, injection at room temperature (Fig. 4A) provided overlapped peaks, so no individual pesticides could be identified. In addition, the background signal was tall owing to adsortion of the pesticides on the walls of the tube valve port, which resulted in sluggish passage through the column and analyte losses. On heating at 125°C (Fig. 4C), the analytes reached the injection port in the vapour phase, so they were readily flushed trough the valve port connecting tube, thereby avoiding clogging the tube and dilution of the analytes in the carrier gas prior to reaching the chromatographic column. Similar results were obtained by extracting the hydrolysis products into ethyl acetate.

TABLE II

FEATURES OF THE CALIBRATION GRAPHS AND DETERMINATION OF HYDROLYSED AND ACETYLATED N-METHYLCARBAMATES

Compound	Regression equation[a]	Correlation coefficient	Linear range (mg/l)	Detection limit (mg/l)	R.S.D. (%)
Propoxur[b]	$y = 8.1 \cdot 10^{-3} + 3.96 \cdot 10^{-2}x$	0.999	0.2–4	0.2	3.80
Carbofuran[b]	$y = -2.4 \cdot 10^{-3} + 4.02 \cdot 10^{-2}x$	0.999	0.2–4	0.2	3.92
Carbaryl[b]	$y = -6.9 \cdot 10^{-3} + 1.23 \cdot 10^{-2}x$	0.997	0.8–4	0.4	3.88
Propoxur[b]	$y = 1.9 \cdot 10^{-2} + 2.97 \cdot 10^{-2}x$	0.999	2–40		2.52
Carbofuran[b]	$y = -1.7 \cdot 10^{-2} + 1.92 \cdot 10^{-2}x$	0.999	2–40		3.00
Carbaryl[b]	$y = 6.3 \cdot 10^{-3} + 7.50 \cdot 10^{-3}x$	0.999	2–40		3.53
Propoxur[c]	$y = 2.3 \cdot 10^{-2} + 4.23 \cdot 10^{-2}x$	0.995	0.2–4	0.2	3.48
Benthiocarb[c]	$y = 3.3 \cdot 10^{-2} + 6.90 \cdot 10^{-2}x$	0.997	0.2–4	0.2	2.97
Carbofuran[c]	$y = 2.8 \cdot 10^{-2} + 3.81 \cdot 10^{-2}x$	0.999	0.4–4	0.2	3.52
Aminocarb[c]	$y = -1.3 \cdot 10^{-2} + 7.20 \cdot 10^{-2}x$	0.997	0.4–4	0.4	2.47
Carbaryl[c]	$y = 2.2 \cdot 10^{-2} + 2.17 \cdot 10^{-2}x$	0.996	0.4–4	0.4	3.00
Methiocarb[c]	$y = 4.5 \cdot 10^{-3} + 4.71 \cdot 10^{-2}x$	0.997	0.4–4	0.4	3.50
Propoxur[c]	$y = -2.8 \cdot 10^{-2} + 4.05 \cdot 10^{-2}x$	0.998	4–40		3.15
Benthiocarb[c]	$y = -3.6 \cdot 10^{-2} + 6.00 \cdot 10^{-2}x$	0.998	4–40		3.20
Carbofuran[c]	$y = -4.2 \cdot 10^{-2} + 4.62 \cdot 10^{-2}x$	0.997	4–40		2.95
Aminocarb[c]	$y = -1.2 \cdot 10^{-2} + 7.86 \cdot 10^{-2}x$	0.998	4–40		2.15
Carbaryl[c]	$y = -1.0 \cdot 10^{-1} + 3.24 \cdot 10^{-2}x$	0.994	4–40		2.15
Methiocarb[c]	$y = -9.0 \cdot 10^{-2} + 6.60 \cdot 10^{-2}x$	0.998	4–40		2.94

[a] y = Analyte peak area/internal standard peak-area ratio; x = concentration (mg/l).
[b] Extraction method.
[c] Extraction–derivatization method.

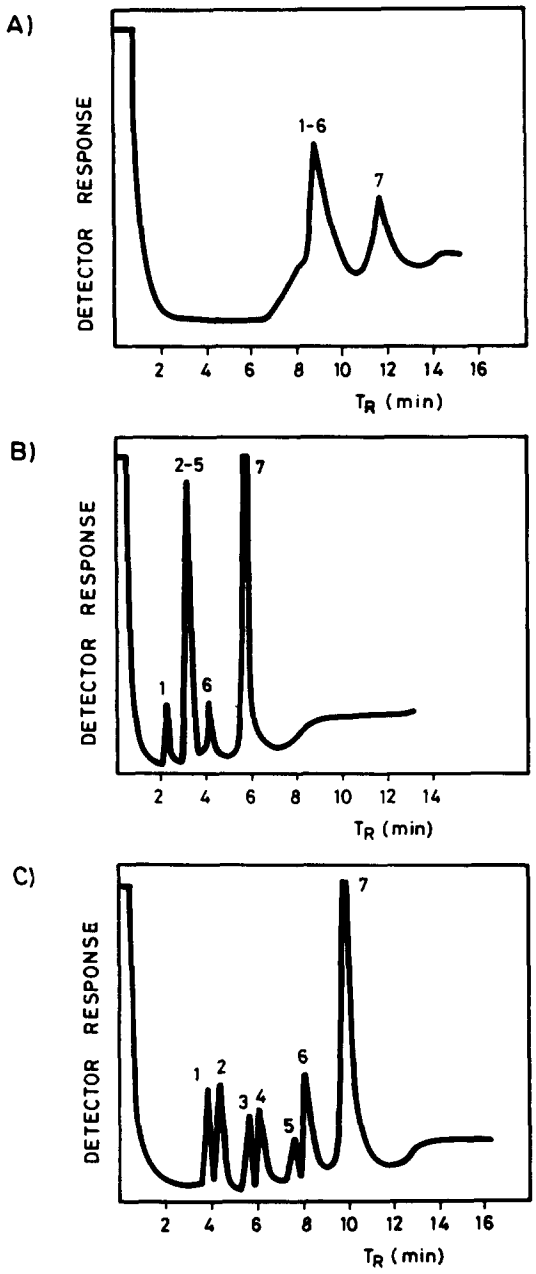

Fig. 4. Gas chromatograms of extracted N-methylcarbamates pesticides. (A) Acetate derivatives without heating the tube valve port. (B) Underivatized hydrolysis products. (C) Acetate derivatives with heating of the tube valve port at 125°C. Concentration of N-methylcarbamates in the aqueous sample, 8 mg/l. Extractants, 6% acetic anhydride in (A,C) *n*-hexane or (B) ethyl acetate. Peaks: 1 = propoxur; 2 = benthiocarb; 3 = carbofuran; 4 = aminocarb; 5 = methiocarb; 6 = carbaryl; 7 = internal standard (phenanthrene).

Determination of N-methylcarbamates

The GC separation of the underivatized and acetylated hydrolysis products (carbamate phenols) is illustrated in Figs. 4B and C, respectively. As can be seen, the peaks of the hydrolysis products of benthiocarb, aminocarb, methiocarb and carbofuran extracted into ethyl acetate were completely overlapped, so derivatization of these pesticides was essential for identification.

The calibration graphs for extracted and extracted–derivatized carbamates were linear throughout the concentration range studied (0.2–160 mg/l). The figures of merit of these graphs at two integrator sensitivities, and those of the analytical procedure, are summarized in Table II. The detection limit was calculated as the concentration yielding the minimum detectable signal in the chromatogram. The relative standard deviation (R.S.D.) was calculated from eleven samples containing intermediate concentrations (1, 20 or 80 mg/l) of each pesticide in the linear range assayed (0.2–4, 2–40 and 40–160, respectively). It ranged between 1.9 and 2.6% for concentrations between 40 and 160 mg/l. Reproducibility was measured by injecting a sample containing also intermediate concentrations of the analytes eleven times; the R.S.D. values thus obtained ranged between 0.4 and 0.7%.

CONCLUSIONS

The two proposed continuous methods for extraction and extraction–derivatization of the phenolic portion of N-methylcarbamates prior to introduction into a gas chomatograph yield better analytical results in terms of precision, throughput and economy than their manual counterparts, which are more laborious (and hence prone to analyte losses) and consume greater amounts of reagents. The sample introduction system used allows the complete introduction of small volumes of low-volatility samples into the instrument injection port, which simplifies on-line coupling of the extractor and the chromatograph without the need to alter the latter in any way.

The sensitivity (slope of the calibration graph) of both methods (extraction and extraction–derivatization) is similar for propoxur and carbofuran. Carbaryl differs in that it results in a low sensitivity when extracted from the phenolic portion (1-naph-

thol). Formation of the carbamate derivative (acetylated 1-naphthol) not only prevents on-column decomposition, but also facilitates detection through increased sensitivity. Excess of acetic anhydride (the derivatizing reagent) causes no disturbance as its peaks overlapped with those of the extractant. Finally, the derivatives of the phenolic portion of the carbamates allow the identification of aminocarb, benthiocarb and methiocarb, which is impossible without derivatization under the chromatographic conditions used.

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