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Simultaneous quantification of insecticides including carbaryl in drinking water by gas chromatography using dual electron-capture and nitrogen–phosphorus detection

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Abstract

A rapid and simple gas chromatographic method for the simultaneous determination of malathion, parathion, fenitrothion, diazinon and carbaryl in drinking water is presented. A fused-silica SE-54 column was used for the separation of the insecticides and was split into two specific detectors; electron-capture and nitrogen–phosphorus detectors by using column switching. A water sample was extracted with methylene chloride. The organic phase was evaporated and the residue was derivatized with pentafluoropropionic acid anhydride. The detection limit was below 0.1 ng/ml and the calibration curves showed good linearity with $r=0.998\sim1.000$. The method was sensitive, reproducible and simple enough to permit the reliable routine analysis of the pesticides in drinking water.

Keywords: Water analysis; Environmental analysis; Pesticides; Carbaryl

1. Introduction

The possible presence of the insecticides carbaryl (1-naphthyl methylcarbamate), malathion [diethyl (dimethoxythiophosphorylthio)succinate], parathion (O,O-diethyl O-4-nitrophenyl phosphorothioate), fenitrothion (O,O-dimethyl O-4-nitro-*m*-tolyl phosphorothioate) and diazinon (O,O-diethyl O-2-isopropyl-6-methylpyrimidin-4-yl phosphorothioate) in drinking water is monitored by regulatory authorities all over the world. The chemical structures of these five insecticides are shown in Fig. 1.

They are used for the control of a wide range of insects in cereals, fruit, vines, hopes vegetables, ornamentals, coffee, cotton, rice, flax, beet, sugar cane and other crops [1].

A large number of analytical methods have been published for the determination of carbaryl. Most analytical methods until now apply high-performance liquid chromatography (HPLC) [2–11]. Reported methods of carbaryl determination by gas chromatography (GC) have encountered problems of thermal degradation. Because of its thermal instability, it has been derivatized prior to analysis [12]. Otherwise malathion, parathion, fenitrothion and diazinon have good thermal stability and have been analyzed by GC without chemical modification [13–15]. Although GC without derivatization has often been used for the analysis of malathion, parathion, fenitrothion and diazinon in drinking water, this is not the

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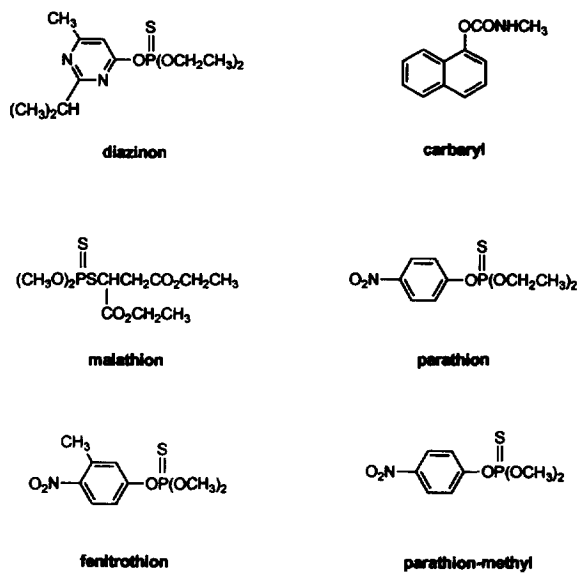

Fig. 1. Structures of insecticides.

case for the simultaneous quantification of insecticides including carbaryl.

We studied here the simultaneous screening and quantification of insecticides including carbaryl using GC–dual nitrogen–phosphorus detection (NPD) and electron-capture detection (ECD).

2. Experimental

2.1. Standards and reagents

Parathion and carbaryl were supplied by Dr. Ehrenstorfer (Germany), fenitrothion and parathion-methyl, which was chosen as an internal standard, were by Riedel-de Häen (Germany) and malathion and diazinon by Wako (Japan). Standard stock solution was prepared as 1000 μg/ml in acetone and stored at 4°C. Working solutions were prepared by sequential dilution of the stock solution with acetone. Methylene chloride, ethyl acetate and acetone (J.T. Baker, USA) were of HPLC grade. Pentafluoropropionic acid anhydride (PFPA) was purchased from Pierce (USA).

2.2. Extraction and derivatization

In a 250 ml separating funnel, 200 ml of the water sample and 20 μl of parathion-methyl (100 μg/ml in acetone) as an internal standard were placed. The sample was extracted with 13 ml of methylene chloride by shaking for 3 min. The two phases were separated by standing the separating funnel for 10 min at room temperature and the organic phase was transferred into a 20 ml glass-stoppered tube, evaporated to dryness in a vacuum evaporator and then under N_2. The dry residue was dissolved in 100 μl of ethyl acetate, and then 100 μl of PFPA was added. The solution was heated for 60 min at 50°C in a heating block. The derivatized reaction mixture was then dried under nitrogen gas and redissolved with 50 μl of ethyl acetate. A 2 μl sample of the solution was injected into GC system.

2.3. Instruments

A Hewlett-Packard 5890 series plus gas chromatograph with NPD and ECD systems was used for the simultaneous determination of insecticides. Samples were injected in injector with the split mode. For the column switching with NPD and ECD, column splitter (Supelco, USA) was used. The GC conditions for the determination of insecticides are shown in Table 1. All mass spectra for the identification of pentafluoropropionyl (PFP) derivatives were obtained with a HP 5890/5972 mass-selective detector.

The ion source was operated in the electron impact (EI) ionization mode (70 eV, 150°C). Full scan mass spectra (m/z 40–450) were recorded for analyte identification.

The same capillary column as described above was also used for GC–MS. The flow-rate of the carrier gas (He) was 0.7 ml/min. The injector temperature was 280°C, oven temperature was programmed from 120°C (held for 2 min) at 20°C/min to 300°C (held for 5 min), and transfer line temperature was 300°C.

2.4. Calibration curve and quantification

The calibration curves for the pesticides were established by adding 0, 5, 10, 50 and 250 μl of standard mixture (10 μg/ml each) and 20 μl of parathion-methyl (I.S., 5 μg/ml) to 200 ml of distilled water and extracting the mixtures according to the method described in Section 2.2. The ratios of

Table 1
Gas chromatographic conditions used for the determination of insecticides in drinking water

Parameter	Conditions
Column	HP-Ultra 2 (25 m×0.2 mm I.D., 0.33 μm film thickness)
Injector temperature	280°C
Detector temperature	300°C
Initial temperature	100°C
Programming rate	10°C/min
Final temperature and time	280°C (0 min)
Carrier gas flow-rate	Nitrogen at 0.5 ml/min
Auxiliary gas flow-rate	Nitrogen at 30 ml/min (for NPD) Nitrogen at 63 ml/min (for ECD)
Hydrogen flow-rate	4.0 ml/min
Air flow-rate	100 ml/min
Splitting ratio	1:10
Septum purge flow-rate	4.5 ml/min
Anode purge flow-rate	Nitrogen at 7.0 ml/min

the peak areas of insecticides to that of parathion-methyl were used to calculate a calibration curve, the slopes of which were used to quantitate the pesticides in samples.

3. Results

3.1. Derivatization of carbaryl with PFPA

Carbaryl was thermolabile and decomposed to 1-naphthol in GC. Fig. 2 shows a total ion chromatogram and mass spectra of the carbaryl standard and its degraded product. The retention times of carbaryl and its degraded product were 12.67 and 5.97 min, respectively. The EI mass spectrum of carbaryl shows a molecular ion at m/z 201 and diagnostic ions at m/z 144, 115 and 89. The ion at m/z 115 may result from the loss of a carbonyl group from 1-naphthol (m/z 144). When carbaryl was reacted with PFPA, PFP-carbaryl was formed and this was not decomposed during analysis by GC. Fig. 3 shows a

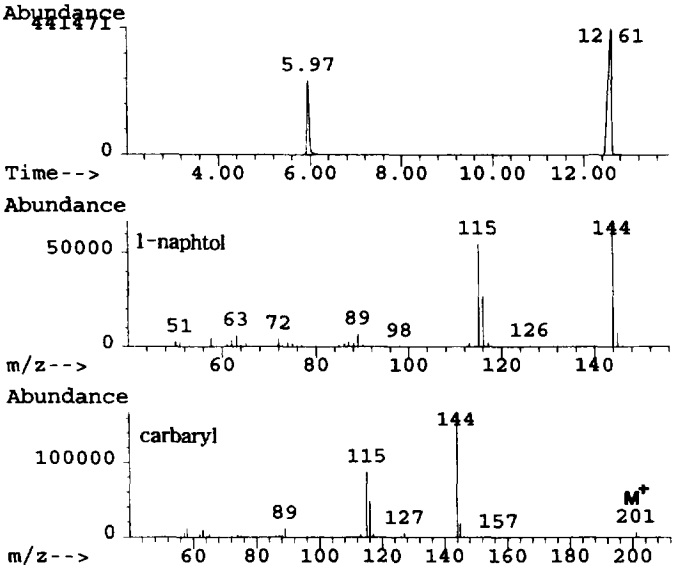

Fig. 2. The gas chromatogram and mass spectra of carbaryl 20 ng (t_R 12.61 min) and its degraded product (t_R 5.97 min).

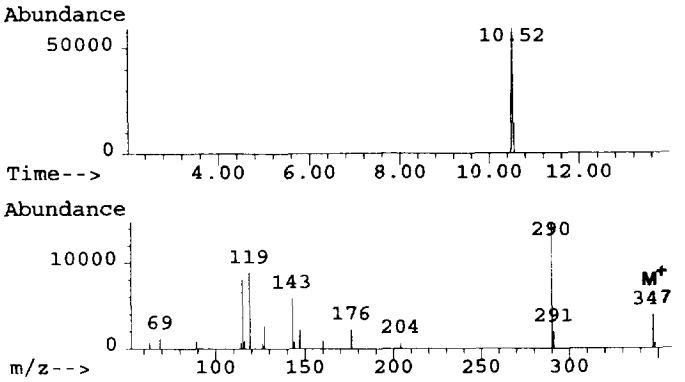

Fig. 3. The gas chromatogram and mass spectrum of carbaryl derivative (about 35 ng).

total ion chromatogram and the mass spectrum of the PFP-carbaryl. The retention time of PFP-carbaryl was 10.52 min, and no 1-naphthol was found. From the spectrum of the synthetic compound, we found the base ion at *m/z* 290, a molecular ion at *m/z* 347 and significant fragment ions at *m/z* 119, 143, 176 and 204.

The derivatization rate depends on time and the temperature of the reaction. Fig. 4 shows a yield percent of PFP-carbaryl from the derivatization with PFPA. The optimum derivatization condition is reaction time 1 h at 50°C.

Otherwise, retention times of malation, parathion, fenitrothion and diazinon before and after derivatization were unchanged. These compounds have no functional groups such as amino, hydroxyl or carboxylic groups to be derivatized by the described derivatization method and are stable under the derivatization condition.

3.2. Detection using dual detectors

In order to increase the sensitivity of pesticides detected in a single run, a dual detector analysis has been used by installing one column in an injector and splitting the column end to NPD and ECD. We combined dual detection and derivatization technique, and compared the responses from the two detectors. Parathion-methyl, whose presence in environmental samples in our country is impossible, was used as an internal in this study, but its choice as

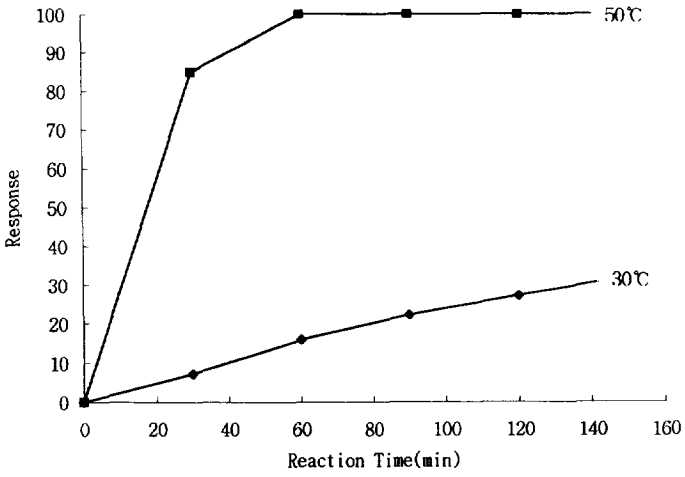

Fig. 4. Time course of the reaction of carbaryl (10 μg) with PFPA.

the internal standard is not recommended for all countries.

The gas chromatogram of the underivatized insecticides obtained from a water sample is shown in Fig. 5, together with that obtained from blank water. No interfering peak in blank water is present near the peaks of five insecticides. Fig. 6 shows the gas chromatogram of the insecticides after the derivatization with PFPA. The underivatized carbaryl at a concentration of 10 ng/ml was not detected with ECD, and had a very low sensitivity with NPD. Otherwise the derivatized carbaryl with PFPA has a good sensitivity not only with NPD but also with ECD at a concentration of 10 ng/ml although ECD was more sensitive. No interfering peaks in blank water are present near the peaks of five insecticides. Diazinon, fenitrothion, malathion and parathion produced single peaks in both the ECD and NPD channel, and they were easily detectable in both channels (although NPD was more sensitive) (Figs. 5 and 6). Here, we found that ECD was preferable for PFA-carbaryl and fenitrothion, and NPD for diazinon and malathion.

3.3. Calibration curves and detection limits

Examination of typical calibration graphs by calculating the regression line of the peak-area ratios of insecticides to the internal standard on concentration using a least-squares fit demonstrated a linear relationship with correlation coefficients consistently higher than 0.998. The line of best fit with ECD was

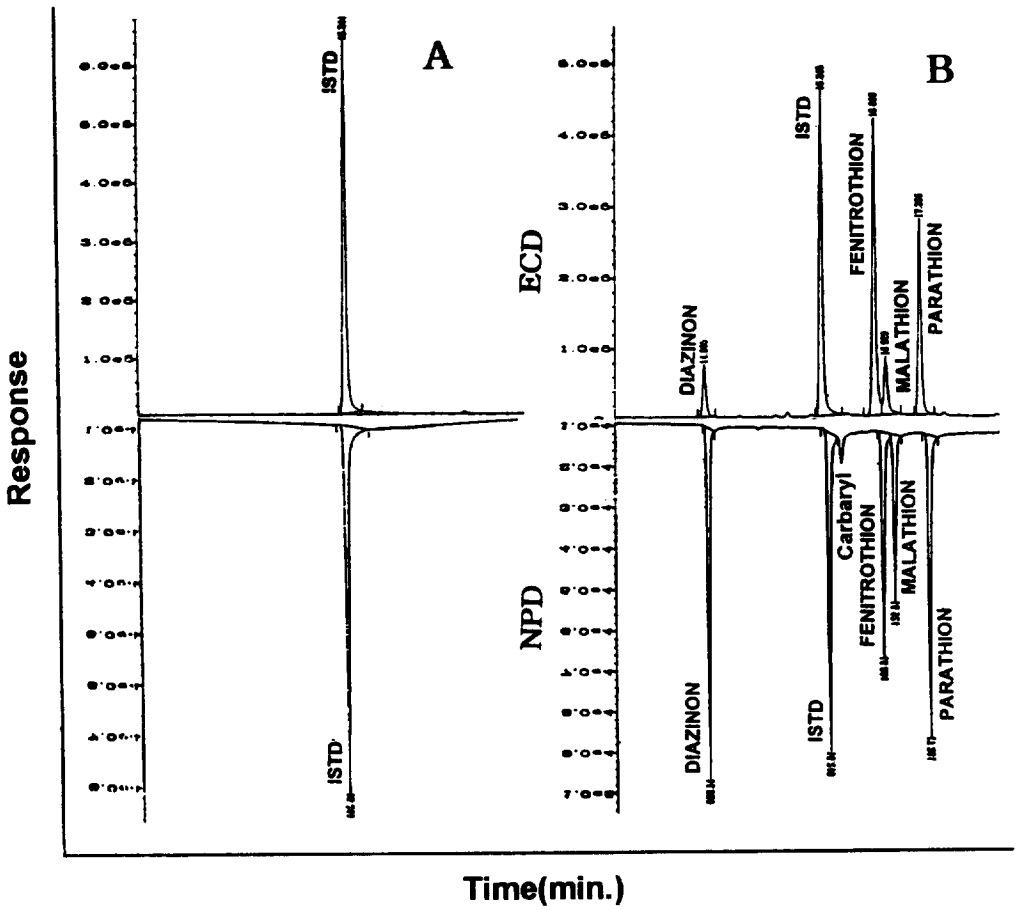

Fig. 5. The gas chromatogram of the underivatized insecticides. (A) Water blank; (B) water sample to which 10 ng/ml of each of the insecticides were added.

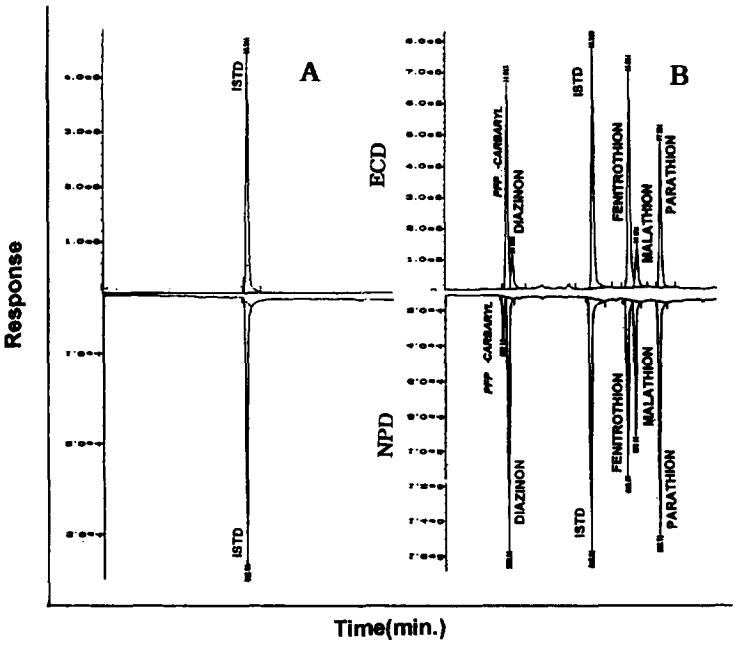

Fig. 6. The gas chromatogram of the insecticides after the derivatization with PFPA. (A) Water blank; (B) water sample to which 10 ng/ml of each of the insecticides were added.

$y=0.0059x+0.0440$ ($r=0.998$) for diazinon, $y=0.0585x+0.0163$ ($r=0.999$) for fenitrothion, $y=0.0182x+0.0051$ ($r=1.000$) for malathion, $y=0.0451x+0.0526$ ($r=0.999$) for parathion, and $y=0.0776x+0.0146$ ($r=0.999$) for PFP-carbaryl, where x is the analyte concentration in range of 0–12.5 ng/ml and y the peak area ratio. A near-zero intercept for this curve indicates that essentially no decomposition of the PFP-carbaryl occurred by GC analysis. The detection limits in drinking water for the PFP-carbaryl and four other insecticides with PFPA were 0.02~0.1 ng/ml with ECD and NPD (Table 2). These limits were defined by a minimal signal-to-noise ratio of 3 and a R.S.D. for replicate determinations of 15% or less.

Table 2
Detection limits (ng/ml) of five insecticides in drinking water

Compounds	ECD	NPD
PFP-Carbaryl	0.02	0.10
Diazinon	0.10	0.02
Fenitrothion	0.02	0.05
Malathion	0.10	0.05
Parathion	0.05	0.05

3.4. Recovery

Several water samples at a concentration of 10 ng/ml were prepared and the recoveries were calculated from the percentage recovered of the insecticides from water samples. The results are reported in Table 3.

3.5. Accuracy and precision

The accuracy and precision calculated by performing the entire procedure was very good, as shown in Table 4. For five independent determinations by

Table 3
Recoveries of five insecticides (10 ng/ml) by the described extraction procedure

Compounds	Mean recovery±R.S.D. (%) ($n=3$)
Carbaryl	79±5.3
Diazinon	76±5.5
Fenitrothion	86±2.0
Malathion	87±1.1
Parathion	86±2.0

Table 4
Accuracy and precision of the determination of insecticide concentration in drinking water

Compounds	Spiked concentration (ng/ml)	Calculated concentration (ng/ml) (n=5), mean±R.S.D. (%)	
		ECD	NPD
Carbaryl	10.00	10.68±2.7	10.21±2.4
	1.00	0.91±4.9	0.93±5.8
Diazinon	10.00	10.69±6.6	9.94±5.6
	1.00	0.97±7.8	0.96±6.3
Fenitrothion	10.00	10.70±1.4	10.11±2.9
	1.00	0.89±4.2	0.90±5.1
Malathion	10.00	10.41±0.4	10.47±2.6
	1.00	1.07±3.6	1.05±4.8
Parathion	10.00	10.71±1.4	9.95±1.9
	1.00	1.04±3.9	0.98±4.5

GC–ECD and –NPD at 10 ng/ml in drinking water, the relative standard deviations were less than 3% except for diazinon, and they were not more than 8% at 1.0 ng/ml.

4. Discussion

The response stability and the precision of quantitative analysis of thermolabile compound carbaryl, were comparable with those of the thermostable insecticides such as malathion, parathion, fenitrothion and diazinon. We used a high injection port and oven temperature to produce a short analysis time. However, this did not alter the precision. The method was developed for a practical purpose. In conclusion, a reliable and sensitive method for the determination of pesticides in drinking water using GC–NPD/ECD was developed and this method should be useful for the routine analysis of insecticides in drinking water.

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