Influence of helium and nitrogen as carrier gases during capillary GC analysis

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Helium is normally used as a carrier gas for capillary gas chromatography (GC) in Japan. However, helium faces the possibility of decreasing supply because of difficulties at helium plants in the USA and the rapidly increasing demand of helium for technical and medical uses, especially in developing countries. Helium and hydrogen are recommended as carrier gases by CIPAC (Collaborative International Pesticide Analytical Council Limited), which is the international organization that publishes guidelines for developing analysis methods for pesticides used in agriculture and public health. Because hydrogen is explosive, many laboratories in Japan do not use it as a carrier gas for GC. Since nitrogen is not explosive and is stable and inexpensive, the suitability of nitrogen as an alternative gas to helium was studied herein.

Keywords: pesticides, GC, carrier gas, helium, nitrogen

Introduction

Inert gases such as helium, hydrogen, and nitrogen are routinely used as carrier gases in capillary GC. In particular, helium and hydrogen are used for capillary GC because they have a high resolution at high line velocity, leading to short analysis times.

Although the supply of helium has become unstable in recent years, it is mainly used as a carrier gas for capillary GC analytical work at FAMIC (Food and Agricultural Materials Inspection Center). In the event of helium shortfall, works such as the analysis of pesticide samples submitted by applicants for registration and formulations that are taken for on-site inspection from manufacturers risk being suspended. To avoid such suspension of work, an alternative of helium is needed.

At CIPAC (Collaborative International Pesticide Analytical Council Limited), helium and hydrogen are recommended as carrier gases for capillary GC [1]. However, hydrogen is an explosive gas. Therefore, nitrogen was studied as an alternative to helium because nitrogen is inert like helium and hydrogen, is not explosive, and is easy to obtain. However, nitrogen has a lower resolution at high line velocity than helium [2]. During the analysis of a formulation, a few peaks of the a.i. (active ingredient), IS (internal standard), and some impurities are obtained, and therefore, high resolution is not needed for formulation analysis unlike residue analysis. Hence, nitrogen was suggested. The influence on the analysis by the difference in carrier gas (between helium and nitrogen) was studied using some pesticides and columns.

The linearity, limit of detection, HETP (height equivalent of one theoretical plate), and contents of a.i. were measured using several columns with various polarities of liquid phase, inner diameters, and film thicknesses. A polar column for bioallethrin and a non-polar column for etofenprox and procymidone were used.

Materials and methods

1. Chemicals and reagents

Bioallethrin (97.1% purity) and procymidone (99.9% purity) were purchased from Hayashi Pure Chemical. Etofenprox (99.3% purity) was purchased from Wako Pure Chemical Industries.

Dibutyl sebacate (97% purity) and dicyclohexyl phthalate (99% purity) were purchased from Wako Pure Chemical Industries; *m*-terphenyl (99% purity) was purchased from Sigma-Aldrich Japan.

Acetone (JIS (Japanese industrial standards) guaranteed reagent) and methanol (HPLC grade) were purchased from Wako Pure Chemical Industries.

2. Preparation of standard solutions

The standard solutions of pesticides were prepared by the CIPAC method [3-5].

2.1 Bioallethrin

About 1.2 g of *m*-terphenyl was dissolved in acetone (100 mL), and this solution was called IS_b (internal standard solution for bioallethrin). About 100 mg of bioallethrin was weighed into a 100 mL volumetric flask (to the nearest 0.1 mg); IS_b (5.0 mL) was added by pipette and dissolved completely. The flask was filled up to volume with acetone and mixed well. This solution was prepared in duplicate and the solutions were called $C_{b100(1)}$ and $C_{b100(2)}$. $C_{b100(1)}$ was further diluted with acetone 100 and 10 times and these solutions

were called $C_{b100(1)/100}$ and $C_{b100(1)/10}$, respectively.

About 50 mg of bioallethrin was weighed into a 100 mL volumetric flask (to the nearest 0.1 mg); IS_b (5.0 mL) was added by pipette and dissolved completely. Then, it was filled up to volume with acetone and mixed well. This solution was called C_{b50}, and it was diluted with acetone 100 and 10 times and the resulting solutions were called $C_{b50/100}$ and $C_{b50/10}$, respectively.

About 200 mg of bioallethrin was weighed into a 100 mL volumetric flask (to the nearest 0.1 mg); IS_b (5.0 mL) was added by pipette and dissolved completely. Then, it was filled up to volume with acetone and mixed well. This solution was called C_{b200}; it was diluted with acetone 100 and 10 times and these solutions were called $C_{b200/100}$ and $C_{b200/10}$, respectively.

2.2 Procymidone

About 1.6 g of dibutyl sebacate was dissolved in acetone (200 mL) and the resulting solution was called IS_p (internal standard solution for procymidone). Next, about 50 mg of procymidone was weighed into a 50 mL volumetric flask (to the nearest 0.1 mg); IS_p (5.0 mL) was added by pipette and dissolved completely. Then, it was filled up to volume with acetone and mixed well. The solution obtained was prepared in duplicate and called $C_{p100(1)}$ and $C_{p100(2)}$. $C_{p100(1)}$ was diluted with acetone 100 and 10 times and these solutions were called $C_{p100(1)/100}$ and $C_{p100(1)/10}$, respectively.

About 25 mg of procymidone was weighed into a 50 mL volumetric flask (to the nearest 0.1 mg); IS_p (5.0 mL) was added by pipette and dissolved completely. Then, it was filled up to volume with acetone and mixed well. The solution was called C_{p50}, which was diluted with acetone 100 and 10 times. The resulting solutions were called $C_{p50/100}$ and $C_{p50/10}$, respectively.

About 100 mg of procymidone was weighed into a 50 mL volumetric flask (to the nearest 0.1 mg); IS_p (5.0 mL) was added by pipette and dissolved completely. Then, it was filled up to volume with acetone and mixed well. This solution was called C_{p200}; it was diluted with acetone 100 and 10 times and these solutions were called $C_{p200/100}$ and $C_{p200/10}$, respectively.

2.3 Etofenprox

About 1.0 g of dicyclohexyl phthalate was dissolved in acetone (100 mL) and this solution was called IS_e (Internal Standard Solution for etofenprox). About 30 mg of etofenprox was weighed into a 25 mL volumetric flask (to the nearest 0.1 mg); IS_e (2.5 mL) and methanol (0.5 mL) were added by pipette and dissolved completely. Then, it was filled up to volume with acetone and mixed well. This solution was prepared in duplicate, called $C_{e100(1)}$ and $C_{e100(2)}$. $Ce_{100(1)}$ was diluted with acetone 100 and 10 times and the solutions obtained were called $C_{e100(1)/100}$ and $C_{e100(1)/10}$, respectively.

About 15 mg of etofenprox was weighed into a 25 mL volumetric flask (to the nearest 0.1 mg); IS_e (2.5 mL) and methanol (0.5 mL) were added by pipette and dissolved completely. Then, it was filled up to volume with acetone and mixed well. This solution was called C_{e50}. The solution was diluted by acetone 100 and 10 times and these solutions were called $C_{e50/100}$ and $C_{e50/10}$, respectively.

About 60 mg of etofenprox was weighed into a 25 mL volumetric flask (to the nearest 0.1 mg); IS_e (2.5 mL) and methanol (0.5 mL) were added by and dissolved completely. Then, it was filled up to volume with acetone and mixed well. This solution was called C_{e200}. It was diluted with acetone 100 and 10 times and these solutions were called $C_{e200/100}$ and $C_{e200/10}$, respectively.

3. Preparation of sample solutions

The formulation of bioallethrin could not be obtained because bioallethrin is not registered in Japan. The sample solutions of procymidone [6] and etofenprox [7] were prepared based on the CIPAC method.

3.1 Procymidone

Here, 50% wettable powder of procymidone was used and called 50WP.

About 200 mg of 50WP was weighed into a 20 mL volumetric flask (to the nearest 0.1 mg) and 10 mL of IS_p was added by pipette. This operation was repeated in quintuplicate. Then, the solutions were shaken mechanically for 10 min and the supernatants were filtered through 0.45 μm PTFE (polytetrafluoroethylene) filters (SYRINGE FILTER, Whatman). Next, 1.0 mL of filtrate solutions were pipetted into 20 mL volumetric flasks and 9 mL acetone was added by a measuring cylinder. These solutions were called S_{p1}, S_{p2}, S_{p3}, S_{p4}, and S_{p5}.

3.2 Etofenprox

Here, 20% emulsifiable concentrate of etofenprox was chosen and this sample was called 20EC.

About 300 mg of 20EC was weighed into a 50 mL volumetric flask, and then, 1 mL of methanol and 5 mL of IS_e were added by pipette. This operation was repeated in quintuplicate. Then, the resulting solutions were filled to the mark with acetone and mixed well, and were called S_{e1}, S_{e2}, S_{e3}, S_{e4}, and S_{e5}.

4. GC conditions

An Agilent 6890N gas chromatograph with FID (flame ionization detector) was used.

Gas chromatographic conditions for bioallethrin, procymidone, and etofenprox are shown in Table 1 (1)-(3), respectively.

DB-FFAP for bioallethrin is a highly polar column and the DB-1 column for procymidone and etofenprox is a non-polar column. These columns were purchased from

Agilent Technologies.

5. Linearity

The C_{50}, $C_{100(1)}$, and C_{200} solutions of bioallethrin, procymidone and etofenprox (1 μL) were injected in duplicate and the correlation coefficient (r) was calculated.

6. Limits of detection

The $C_{50/100}$, $C_{100(1)/100}$, $C_{200/100}$, $C_{50/10}$, $C_{100(1)/10}$, $C_{200/10}$, C_{50}, $C_{100(1)}$, and C_{200} solutions of bioallethrin, procymidone, and etofenprox (1 μL) were injected in duplicate. The correction coefficient calculated by the results of $C_{50/100}$, $C_{100(1)/100}$, and $C_{200/100}$ was called $r_{/100}$; that calculated based on the results of $C_{50/10}$, $C_{100(1)/10}$, and $C_{200/10}$ was called $r_{/10}$; and the one calculated by the results of C_{50}, $C_{100(1)}$, and C_{200} was called $r_{/1}$. The limit of detection was determined as the lowest value in the measurement range, which had good linearity ($r > 0.99$).

7. Influence of line velocity

C_1 (1 μL) was injected at line velocities ranging from low (20 cm/s) to high (60 cm/s) at steps of 5 cm/s and the HETP was calculated at each line velocity. However, the line velocity for procymidone could not be set over 50 cm/s using nitrogen with some columns because the total flow exceeded 200 mL/min.

HETP was calculated as follows[2]:

$$HETP = L / N$$

where L: column length [mm], N: theoretical plate number, calculated as follows:

$$N = 5.545 \times (t_r / W_{1/2})^2$$

where t_r: retention time of the peak [min], $W_{1/2}$: half width of the peak [min].

8. Sample analysis

All samples except for bioallethrin were determined by the bracketing method[8].

Then, 1 μL each of the $C_{100(1)}$, $C_{100(2)}$ standard solutions and S_1-S_5 sample solutions was injected as follows:

$C_{100(1)}$, S_1, S_1, $C_{100(2)}$, S_2, S_2, $C_{100(1)}$, …, S_5, S_5, $C_{100(2)}$

The concentrations of S_1-S_5 were determined, and the average and coefficient of variation (CV %) of the results were calculated.

Table 1. GC conditions

(1) bioallethrin

DB-FFAP column [inner diameter / length / thickness]		0.25 mm / 30 m / 0.25 μm		0.32 mm / 30 m / 0.25 μm		0.32 mm / 30 m / 1.00 μm		0.53 mm / 30 m / 0.25 μm	
carrier gas		He	N_2	He	N_2	He	N_2	He	N_2
column	oven temperature [℃]	240	240	240	240	240	240	240	240
	line velocity [cm/sec]	35	35	35	35	35	35	35	35
injection port	temperature [℃]	250	250	250	250	250	250	250	250
	split ratio	30/1	30/1	30/1	30/1	30/1	30/1	30/1	30/1
	volume [μl]	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
detection port	detector	FID	FID	FID	FID	FID	FID	FID	FID
	temperature [℃]	250	250	250	250	250	250	250	250
	hydrogen flow [ml/min]	40	40	40	40	40	40	40	40
	air flow [ml/min]	450	450	450	450	450	450	450	450
	make up flow (N_2) [ml/min]	15	15	15	15	15	15	15	15

Table 1. GC conditions

(2) procymidone

DB-1 column [inner diameter / length / thickness]		0.25 mm / 30 m / 1.00 μm		0.32 mm / 30 m / 1.00 μm		0.32 mm / 30 m / 0.25 μm		0.53 mm / 30 m / 1.00 μm	
carrier gas		He	N_2	He	N_2	He	N_2	He	N_2
column	oven temperature [℃]	240	240	240	240	240	240	240	240
	line velocity [cm/sec]	35	35	35	35	35	35	35	35
injection port	temperature [℃]	250	250	250	250	250	250	250	250
	split	70.9/1	70.9/1	70.9/1	70.9/1	70.9/1	70.9/1	70.9/1	30.6/1
	volume [μl]	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
detection port	detector	FID	FID	FID	FID	FID	FID	FID	FID
	temperature [℃]	300	300	300	300	300	300	300	300
	hydrogen flow [ml/min]	40	40	40	40	40	40	40	40
	air flow [ml/min]	450	450	450	450	450	450	450	450
	make up flow (N_2) [ml/min]	15	15	15	15	15	15	15	15

(3) etofenprox

DB-1 column [inner diameter / length / thickness]		0.25 mm / 30 m / 1.00 μm		0.32 mm / 30 m / 1.00 μm		0.32 mm / 30 m / 0.25 μm		0.53 mm / 30 m / 1.00 μm	
carrier gas		He	N_2	He	N_2	He	N_2	He	N_2
column	oven temperature [℃]	260(40 min) →10/min→ 300(3 min)	260(33min) →10/min→ 300(3min)	260(23min) →10/min→ 300(3min)	260(23min) →10/min→ 300(3min)	260(15min) →10/min→ 300(3min)	260(12min) →10/min→ 300(3min)	260(15min) →10/min→ 300(11min)	260(15min) →13/min→ 300(2min)
	line velocity [cm/sec]	45	45	45	45	45	45	45	45
injection part	temperature [℃]	300	300	300	300	300	300	300	300
	split	30/1	30/1	30/1	30/1	30/1	30/1	30/1	30/1
	volume [μl]	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
detection part	detector	FID	FID	FID	FID	FID	FID	FID	FID
	temperature [℃]	300	300	300	300	300	300	300	300
	hydrogen flow [ml/min]	40	40	40	40	40	40	40	40
	air flow [ml/min]	450	450	450	450	450	450	450	450
	make up flow (N_2) [ml/min]	15	15	15	15	15	15	15	15

Results and discussions

1. Linearity

The correction coefficients are shown in Table 2.

Correction coefficients using helium as carrier gas were between 0.9997 and 1.0000, while that obtained using nitrogen as a carrier gas were between 0.9999 and 1.0000.

The difference between carrier gas, inner diameter, liquid phase, and thickness of the column had no effect on the linearity.

Table 2. Results of correction coefficients for linearity

bioallethrin								
DB-FFAP column [inner diameter / length / thickness]	0.25 mm / 30 m / 0.25 µm		0.32 mm / 30 m / 0.25 µm		0.32 mm / 30 m / 1.00 µm		0.53 mm / 30 m / 0.25 µm	
carrier gas	He	N_2	He	N_2	He	N_2	He	N_2
correction coefficient (r_b)	1.0000	1.0000	1.0000	0.9999	1.0000	1.0000	1.0000	1.0000
procymidone								
DB-1 column [inner diameter / length / thickness]	0.25 mm / 30 m / 1.00 µm		0.32 mm / 30 m / 0.25 µm		0.32 mm / 30 m / 1.00 µm		0.53 mm / 30 m / 1.00 µm	
carrier gas	He	N_2	He	N_2	He	N_2	He	N_2
correction coefficient (r_p)	1.0000	1.0000	1.0000	0.9999	1.0000	1.0000	0.9997	1.0000
etofenprox								
DB-1 column [inner diameter / length / thickness]	0.25 mm / 30 m / 1.00 µm		0.32 mm / 30 m / 0.25 µm		0.32 mm / 30 m / 1.00 µm		0.53 mm / 30 m / 1.00 µm	
carrier gas	He	N_2	He	N_2	He	N_2	He	N_2
correction coefficient (r_e)	0.9999	0.9999	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000

2. Limits of detection

The correlation coefficients and the limits of detection are shown in Table 3 (1)-(3), and the typical chromatographs are shown in Fig. 1-3.

The retention times of the peaks did not change when helium is replaced by nitrogen.

The limits of detection of bioallethrin and procymidone using helium were 5 ng/mL, while those obtained using nitrogen were 5-50 ng/mL.

The limits of detection of etofenprox using helium and nitrogen were 6 ng/mL.

The limits of detection of etofenprox using helium and nitrogen were the same, but those of bioallethrin and procymidone using helium and nitrogen were the same or lower. It was considered that the peak became too wide when nitrogen is used.

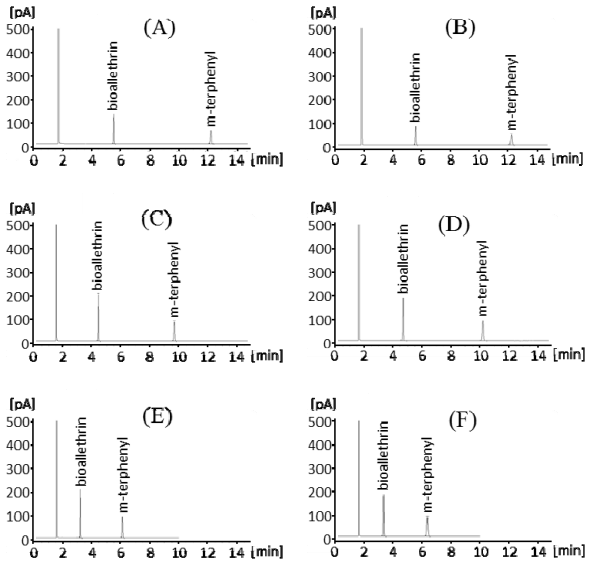

Fig. 1. Chromatograms of bioallethrin and IS_b by varying carrier gas and inner diameter of the DB-FFAP column.

The column length and thickness are 30 m and 0.25 µm. The carrier gas and the column inner diameter are:

(A) He, 0.25 mm, (B) N_2, 0.25 mm, (C) He, 0.32 mm

(D) N_2, 0.32 mm, (E) He, 0.53 mm, (F) N_2, 0.53 mm

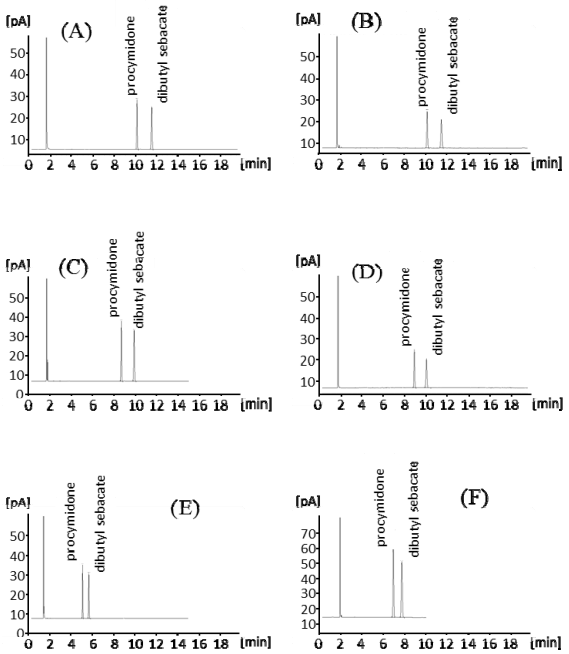

Fig. 2. Chromatograms of procymidone and IS_p by varying the carrier gas and inner diameter of DB-1 column.

The column length and thickness are 30 m and 1.00 μm; the carrier gas and the column inner diameter are:

(A) He, 0.25 mm, (B) N_2, 0.25 mm, (C) He, 0.32 mm,

(D) N_2, 0.32 mm, (E) He, 0.53 mm, (F) N_2, 0.53 mm

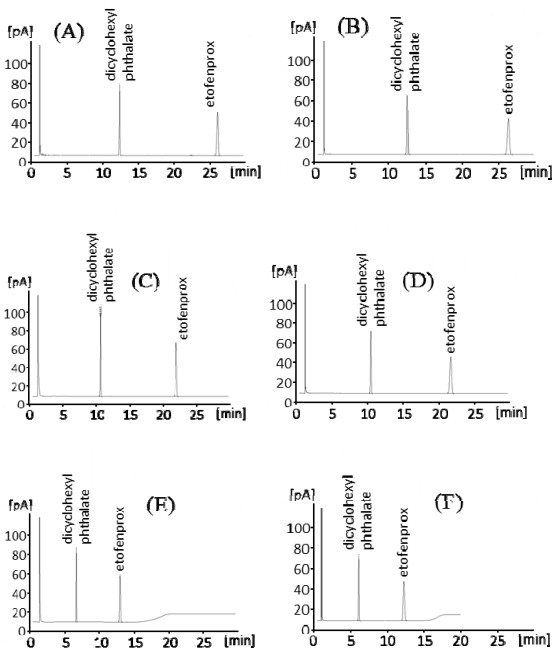

Fig. 3. Chromatograms of etofenprox and IS_e by varying the carrier gas and inner diameter of DB-1 column.

The column length and thickness are 30 m and 1.00 μm; the carrier gas and the column inner diameter are:

(A) He, 0.25 mm, (B) N_2, 0.25 mm, (C) He, 0.32 mm,

(D) N_2, 0.32 mm, (E) He, 0.53 mm, (F) N_2, 0.53 mm

3. Influence of line velocity

It was observed that the HETP using nitrogen ($HETP_{N2}$) was equal to or smaller than that obtained using helium gas ($HETP_{He}$) at a low line velocity (20-30 cm/s). In contrast, at higher line velocity, $HETP_{N2}$ was larger than $HETP_{He}$ (Fig. 4-6). There were no differences with the column and sample.

Nitrogen provides the best efficiency when the line velocity is low. In brief, a low line velocity using nitrogen is needed to obtain the same HETP using helium. As a result, because a longer time of analysis is needed, the use of nitrogen is not recommended. Therefore, it was considered that helium is superior to nitrogen as the carrier gas at high line velocities.

4. Sample analysis

The contents of a.i. are shown in Table 4 (1) and (2).

The concentrations of procymidone in 50WP were between 496.7 and 498.6 g/kg, and their CV% values were between 0.08% and 0.70% using helium. Using nitrogen, the concentrations of procymidone in 50WP were between 496.0 and 499.7 g/kg, and their CV% values were between 0.11% and 0.30%.

The concentrations of etofenprox in 20EC were between 201.9 and 208.4 g/kg, and their CV% values were between 0.45% and 0.86% using helium. Using nitrogen, the concentrations of etofenprox in 20EC were between 200.7 and 208.5 g/kg, and their CV% values were between 0.11% and 0.30%.

Differences of column polarity, inner diameter of column, thickness, and carrier gases had no effect on the analysis of 50WP and 20EC. Therefore, it was considered that when analyzing pesticide formulations, nitrogen can be used as an alternative carrier gas to helium.

Table 3. Limits of detection

(1) bioallethrin

DB-FFAP column [inner diameter / length / thickness]			0.25 mm / 30 m / 0.25 μm		0.32 mm / 30 m / 0.25 μm		0.32 mm / 30 m / 1.00 μm		0.53 mm / 30 m / 0.25 μm	
carrier gas			He	N_2	He	N_2	He	N_2	He	N_2
correction coefficient	5 – 20 [ng/ml]	$r_{/100}$	0.9994	0.9988	0.9996	0.9981	0.9989	0.9820	0.9994	0.9998
	50 – 200 [ng/ml]	$r_{/10}$	1.0000	1.0000	0.9999	1.0000	0.9999	0.9995	0.9999	1.0000
	500 – 2000 [ng/ml]	$r_{/1}$	1.0000	1.0000	1.0000	1.0000	1.0000	0.9999	1.0000	1.0000
limit of detection [ng/ml]			5	5	5	5	5	50	5	5

(2) procymidone

DB-1 column [inner diameter / length / thickness]			0.25 mm / 30 m / 1.00 μm		0.32 mm / 30 m / 0.25 μm		0.32 mm / 30 m / 1.00 μm		0.53 mm / 30 m / 1.00 μm	
carrier gas			He	N_2	He	N_2	He	N_2	He	N_2
correction coefficient	5 – 20 [ng/ml]	$r_{/100}$	0.9923	0.9780	0.9961	—	0.9997	0.9398	0.9984	0.9910
	50 – 200 [ng/ml]	$r_{/10}$	1.0000	1.0000	1.0000	0.9968	1.0000	1.0000	1.0000	0.9999
	500 – 2000 [ng/ml]	$r_{/1}$	1.0000	0.9999	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
limit of detection [ng/ml]			5	50	5	50	5	50	5	5

(3) etofenprox

DB-1 column [inner diameter / length / thickness]			0.25 mm / 30 m / 1.00 μm		0.32 mm / 30 m / 0.25 μm		0.32 mm / 30 m / 1.00 μm		0.53 mm / 30 m / 1.00 μm	
carrier gas			He	N_2	He	N_2	He	N_2	He	N_2
correction coefficient	6 – 24 [ng/ml]	$r_{/100}$	0.9978	0.9953	0.9937	0.9969	0.9989	0.9991	0.9991	0.9979
	60 – 240 [ng/ml]	$r_{/10}$	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	0.9999	1.0000
	600 – 2400 [ng/ml]	$r_{/1}$	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	0.9998	0.9999
limit of detection [ng/ml]			6	6	6	6	6	6	6	6

Table 4. Results of analysis

(1) procymidone 50WP

DB-1 column [inner diameter / length / thickness]		0.25 mm / 30 m / 1.00 µm		0.32 mm / 30 m / 0.25 µm		0.32 mm / 30 m / 1.00 µm		0.53 mm / 30 m / 1.00 µm	
carrier gas		He	N_2	He	N_2	He	N_2	He	N_2
concentration [g/kg]	S_{p1}	500.0	499.9	498.1	494.1	495.7	497.8	491.9	496.2
	S_{p2}	498.7	498.8	497.9	496.1	496.0	498.0	499.9	497.5
	S_{p3}	498.3	499.2	498.9	497.5	497.8	499.2	499.3	498.4
	S_{p4}	498.2	499.2	497.9	494.8	496.9	498.3	494.4	497.6
	S_{p5}	498.9	501.6	498.3	497.3	497.1	498.5	498.5	498.5
	Average	498.6	499.7	498.2	496.0	496.7	498.4	496.8	497.6
coefficient of variation (CV %)		0.17	0.22	0.08	0.30	0.17	0.11	0.70	0.18

(2) etofenprox 20EC

DB-1 column [inner diameter / length / thickness]		0.25 mm / 30 m / 1.00 µm		0.32 mm / 30 m / 0.25 µm		0.32 mm / 30 m / 1.00 µm		0.53 mm / 30 m / 1.00 µm	
carrier gas		He	N_2	He	N_2	He	N_2	He	N_2
concentration [g/kg]	S_{e1}	207.6	207.9	208.3	207.4	207.7	207.9	200.9	202.7
	S_{e2}	207.7	208.5	208.3	208.3	208.1	207.9	200.5	200.3
	S_{e3}	206.9	207.7	207.6	208.0	207.8	207.6	202.4	203.1
	S_{e4}	208.0	208.1	207.9	207.7	208.0	207.9	200.9	197.6
	S_{e5}	209.7	210.4	210.0	210.3	210.5	210.7	204.7	199.7
	Average	208.0	208.5	208.4	208.3	208.4	208.4	201.9	200.7
coefficient of variation (CV %)		0.50	0.52	0.45	0.55	0.56	0.62	0.86	1.13

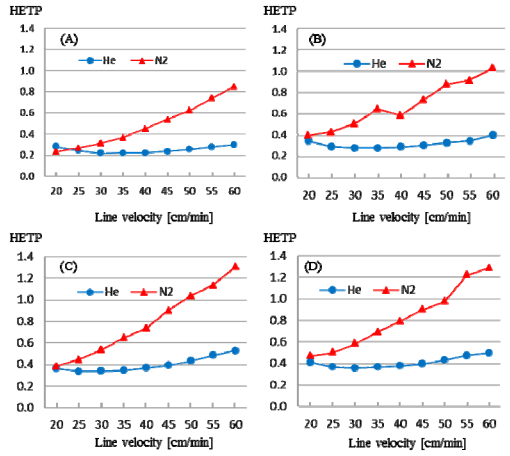

Fig. 4. HETP by difference of line velocities for bioallethrin using a DB-FFAP column.

The length, inner diameter, and thickness of the column are:

(A) 30 m / 0.25 mm / 0.25 µm, (B) 30 m / 0.32 mm / 0.25 µm,

(C) 30 m / 0.32 mm / 1.00 µm, (D) 30 m / 0.53 mm / 0.25 µm

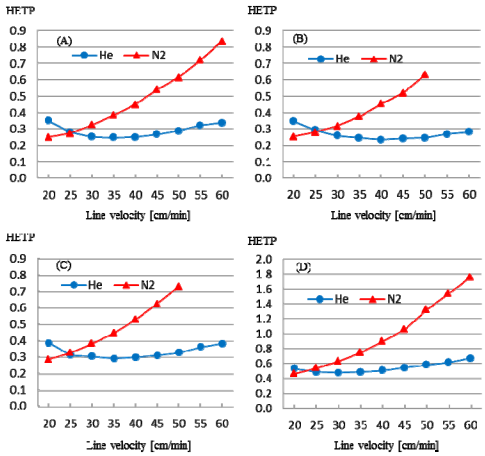

Fig. 5. HETP by difference of line velocities for procymidone using DB-1 column.

The length, inner diameter, and thickness of the column are:

(A) 30 m / 0.25 mm / 1.00 µm, (B) 30 m / 0.32 mm / 0.25 µm,

(C) 30 m / 0.32 mm / 1.00 µm, (D) 30 m / 0.53 mm / 1.00 µm

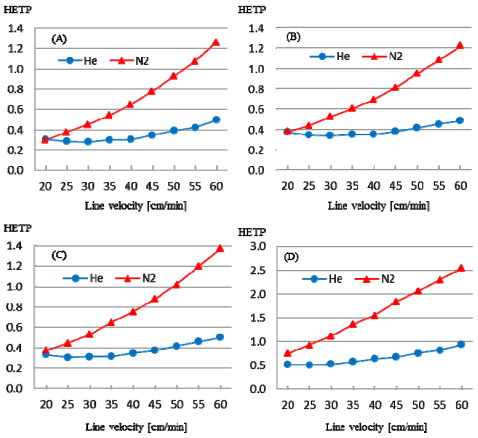

Fig. 6. HETP by difference of line velocities for etofenprox using a DB-1 column.

The length, inner diameter, and thickness of the column are: (A) 30 m / 0.25 mm / 1.00 µm, (B) 30 m / 0.32 mm / 0.25 µm, (C) 30 m / 0.32 mm / 1.00 µm, (D) 30 m / 0.53 mm / 1.00 µm

Conclusions

When the carrier gas was changed from helium to nitrogen, the HETP increased, peaks became broader, and the limit of detection became higher. However, no differences were observed in the analytical results of pesticide formulation between nitrogen and helium when pesticides were analyzed under different column conditions such as polarity of liquid phase, film thickness, length, and inner diameter. Hence, based on the analysis of a.i. in formulation and after checking the separation of a.i., IS, and impurities, it is concluded that nitrogen is a potential alternative carrier gas to helium.

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