Original Article

Determination of nitenpyram and its metabolites in agricultural products by using hydrophilic interaction liquid chromatography-tandem mass spectrometry

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A simple and rapid method for the measurement of a neonicotinoid pesticide, nitenpyram, and its metabolites, CPMA and CPMF, was investigated. The three compounds were determined individually and simultaneously by simple ultrasonic extraction followed by hydrophilic interaction liquid chromatography-tandem mass spectrometry (HILIC-MS/MS). Good chromatograms were obtained using a non-modified silica gel column. The calibration curves were straight ($R^2 > 0.999$) for each compound; they were 0.002–2 mg/kg for 5 g of agricultural product sample with limits of detection ($S/N=3$) of 0.24–0.36 $\mu\text{g/kg}$ (nitenpyram), 0.12–0.19 $\mu\text{g/kg}$ (CPMA), and 0.13–0.18 $\mu\text{g/kg}$ (CPMF). Good recoveries were obtained for sweet pepper, mandarin orange, onion, and brown rice (93.0–106.6% in recovery). For contaminated samples, data by the presented method agreed well with nitenpyram data by HPLC-UV and the total of CPMA and CPMF by derivatization followed by gas chromatography-flame thermionic detection.

Keywords: nitenpyram, 2-[N-(6-chloro-3-pyridylmethyl)-N-ethyl]amino-2-methyliminoacetic acid (CPMA), N-(6-chloro-3-pyridylmethyl)-N-ethyl-N'-methylformamidine (CPMF), hydrophilic interaction liquid chromatography, tandem mass spectrometry.

Introduction

Some pesticides have high activity even after metabolizing; thus, both the pesticides and their metabolites must be analyzed. The Japanese Ministry of Health, Labor, and Welfare determined as a food standard that the nitenpyram content in food products must be given together with that of its metabolites, namely, 2-[N-(6-chloro-3-pyridylmethyl)-N-ethyl]amino-2-methyliminoacetic acid (CPMA) and N-(6-chloro-3-pyridylmethyl)-N-ethyl-N'-methylformamidine (CPMF).¹⁾ In the official analytical method of the Japanese Ministry of Health, Labor, and Welfare, CPMA and CPMF are first converted to N-(6-chloro-3-pyridylmethyl)-N-ethylformamide (CPF) and determined by GC, and those contents are added to the concentration of nitenpyram and not given separately. Furthermore, the method is complicated due to a troublesome procedure that requires use of many reagents and a purification column.

Another problem to determine CPMA and CPMF discrimi-

nately is that CPMA tends to change to CPMF in an organic solvent, such as acetone and ethylacetate.²⁾ Organic solvent extraction and subsequent concentration are usually adopted in the analytical procedure for organic compounds. Tsumura *et al.* reported that 80.4% of CPMA in a water/acetone (20:150) mixture was converted to CPMF during rotary evaporator concentration and recovery was only 9.0%.³⁾ In addition, CPMA is highly polar,^{2,3)} and a chromatogram peak is not as good in shape as twin peaks in separation by common reversed-phase chromatography.⁴⁾ Consequently, a novel analytical procedure is required for the measurement of CPMA that would be entail extraction with a lower-ratio-organic solvent and would not require a concentration procedure. A separation process is also needed to investigate to handle the relatively highly polar compounds.

We investigated extractions of pesticides from many kinds of agricultural products using an acetonitrile/water mixture⁵⁾ in which a relatively hydrophilic medium was used and preconcentration for analysis was not needed. Recently, hydrophilic interaction liquid chromatography (HILIC) has become popular to analyze highly polar compounds.^{6–11)} HILIC is a kind of normal-phase chromatography which entails use of a water/organic solvent mixture eluent and a stationary phase having higher polarity than the mobile phase. Whereas a non-polar organic solvent

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is used for conventional normal-phase chromatography and handling of hydrophilic compounds is normally difficult, CPMA is expected to have good affinity for both the mobile and stationary phases of the HILIC system.

In this work, a novel method was investigated to measure nitenpyram, CPMA, and CPMF simply and discriminatively using HILIC. As CPF is not produced under natural conditions,³⁾ the targets for analysis were the other three compounds. A water-mixed solvent was selected for the extraction to prevent conversion of CPMA to CPMF. Using the optimal extraction medium, a recovery test was performed by standard addition to agricultural samples. The presented HILIC-MS/MS was applied to the measurement of the three compounds, and the obtained data were compared to those by the official analytical method of the Japanese Ministry of Health, Labor, and Welfare,¹⁾ which requires two methods: HPLC-UV for nitenpyram and gas chromatography-flame thermionic detection (GC-FTD) for the total of CPMA and CPMF.

Materials and Methods

1. Standard solution

Nitenpyram, CPMA, CPMF, and CPF were obtained from Wako Pure Chemical Industries (Osaka, Japan). CPMA was dissolved in water, and the other compounds were dissolved in methanol to obtain 500 mg/L stock solutions.

2. Sample treatment

The effect of water content in the extraction solvent was examined using asparagus containing nitenpyram, CPMA, and CPMF. Recovery was examined with sweet pepper, mandarin orange (pulp without peel), onion, and brown rice; all were confirmed not to contain nitenpyram or any metabolites. Brown rice was pulverized using a food cutter into particles that could be passed through a 425 μm standard sieve, and the other vegetables/fruit were prepared using a food cutter and a homogenizer, then, each of the three nitenpyram compounds was added to be 0.005 or 0.5 mg/kg for the recovery tests. Two asparagus samples and a melon (pulp without peel) sample containing nitenpyram and the metabolites were used for the evaluation of contaminated samples analysis.

The extraction process is shown in Fig. 2. Test samples (5 g each) prepared as mentioned above were treated in 20 mL of an acetonitrile-water mixture, typically, 65:35, with the help of ultrasonication (Nissei Ultrasonic Cleaner NS-605, 600W, 28 kHz, Nihonseiki Kaisha Ltd., Tokyo, Japan) for 5 min; then, they were centrifuged for 5 min at 1882 $\times g$. The solid was treated with the same solvent one more time in the same way, and the top clear layers of the first and second extractions were collected and mixed with an acetonitrile-water mixture to obtain a volume of 50 mL. The solution was filtered with a hydrophobic 0.45 μm filter (Chromatodisk 25N, GL Sciences, Tokyo, Japan) for chromatographic analysis. The calibration curve was obtained using matrix-matched standard solutions prepared using an extracted solution from contaminant-free samples.

Fig. 1. Chemical structures of nitenpyram, CPMA, CPMF, and CPF.

Fig. 2. Sample treatment for HILIC-MS/MS analysis.

3. HILIC-MS/MS analysis for nitenpyram, CPMA, and CPMF

The instrument used in this analysis was an HPLC (Waters 2795, Waters, MA) coupled with a tandem mass spectrometer (Quattro Premier, Waters). The separation column was a non-modified silica gel column (Atlantis HILIC, 4.6 mm i.d. $\times$ 150 mm L, 3 μm , Waters). In addition, the amide type (TSKgel Amide 80, 2.0 mm i.d. $\times$ 150 mm L, 3 μm , Waters), the sulfobetaine type (ZIC-pHILIC, 4.6 mm i.d. $\times$ 150 mm L, 5 μm , Merck KGaA, Darmstadt, Germany), the diol type (Inersil HILIC, 4.6 mm i.d. $\times$ 150 mm L, 3 μm , GL Sciences), and the triazole type (COSMOSIL HILIC, 3.0 mm i.d. $\times$ 150 mm L, 5 μm , Nacalai Tesque, Kyoto, Japan) were tested for comparison of HILIC columns.

The sample injection was 10 μL in volume, the column temperature was 40°C, and the eluent was distilled water-acetonitrile-500 mM ammonium acetate (25:70:5). The flow rate used for the amide type (2.0 mm i.d.) was 0.1 mL/min, 0.2 mL/min for the triazole type (3.0 mm i.d.), and 0.5 mL/min for the other columns (4.6 mm i.d.). Each analyte was ionized by electrospray ionization (ESI) in the positive mode, and the quantitative measurement was performed by selected reaction monitoring (SRM). During the ESI process, the capillary voltage was 3.45 kV, the source temperature was 120°C, the desolvation temperature was 350°C, and the total nitrogen flow and cone flow rate were 1000 L/h and 100 L/h, respectively.

Table 1. Chromatographic and SRM parameters for nitenpyram, CPMA, and CPMF

Compound	t_R , ^{a)} min	Ion type	Quantification transition	Cone, V	CE, ^{b)} eV	Confirmatory transition	Cone, V	CE, ^{b)} eV	Ion ratio
Nitenpyram	4.6	$[M+H]^+$	270.66→125.62	25	25	270.66→188.78	25	25	13.6
CPMA	5.1	$[M+H]^+$	256.18→126.12	25	25	256.18→176.45	25	10	2.3
CPMF	9.4	$[M+H]^+$	212.30→126.33	35	20	212.30→ 90.47	35	35	4.6

^{a)} Retention time, ^{b)} collision energy. **Fig. 3.** Chromatograms obtained for extracts from sweet pepper spiked with 0.005 mg/kg nitenpyram (a1), CPMA (b1), and CPMF (c1) and sweet pepper extract (a2), (b2), and (c2).

4. Nitenpyram analysis by HPLC-UV

Nitenpyram was also analyzed using HPLC-UV according to the standard method. A 5-g agricultural product sample was homogenized with 20 mL of acetone and filtered through glass wool. The treatment was repeated once. Both filtrates were gathered and concentrated using a rotary evaporator. The solution was then placed on the head of a column packed with porous diatomaceous earth (InertSep K-solute 20 mL, GL Sciences); 15 min later 50 mL of hexane was added to the column, and the eluent was wasted. Then, 50 mL of diethyl ether–hexane mixture (1:1) and 50 mL of dichloromethane were successively introduced into the column, and the eluent was transferred to another column (15 mm i.d.×300 mm L) packed with 10 g of silica gel (for gas chromatography use, 63–200 μ m, Merck KGaA) which was sintered in dichloromethane before use. The sample-loaded column was washed with 50 mL of an acetone–dichloromethane mixture (1:1), and the compounds were then eluted with 50 mL of acetone. The eluent was concentrated using a rotary evaporator, and a methanol–50 mM potassium dihydrogen phosphate mixture (3:17) was added to achieve a volume of 2 mL for HPLC analysis.

The HPLC system used comprised a high-pressure pump (LC-10AD), a column oven (CTO-10A), and a UV detector (SPD-M10Avp), all purchased from Shimadzu, Kyoto, Japan. Ten microliters of sample was injected into a carrier stream consisting of a methanol–50 mM potassium dihydrogen phosphate aqueous solution (3:17) flowing at 1 mL/min. Nitenpyram separated from the coexisting compounds using a column (Mightysil RP-18 GP, 4.6 mm i.d.×150 mm L, 5 μ m, Kanto Chemical,

Tokyo, Japan) was monitored as the absorbance at 270 nm.

5. GC-FTD analysis for CPMA and CPMF

For comparison, CPMA and CPMF were also determined by GC-FTD after derivatization to CPF according to the official analytical method of the Japanese Ministry of Health, Labor, and Welfare. An agricultural product sample (5 g) was homogenized with 20 mL of acetone twice as described in Section 4, and the filtrate obtained through glass wool was treated at 50°C for 90 min and concentrated using an evaporator. The concentrated solution was kept in a 50°C water bath for 30 min after addition of 0.2 mL triethylamine. The solution was treated with a diatomaceous earth column and a silica gel column as for nitenpyram, described in Section 4. The difference from the pretreatment for nitenpyram was that an acetone–hexane mixture (1:4, 50 mL) was used instead of acetone–dichloromethane and the final concentrated eluent was 4 mL with acetone.

The GC instrument used was a Shimadzu GC-2010 equipped with a capillary column (0.25 mm i.d.×30 m, 0.25 μ m thickness, J&W DB-1701, Agilent, CA). The extract sample (2 μ L) was injected in the splitless mode into an injector heated at 250°C. The column oven temperature was kept at 80°C for 1 min and then increased to 180 and up to 250°C at the rate of 30°C/min in both cases; temperatures of 180 and 250°C were maintained for 15 min and 20 min, respectively. The detector temperature was set at 280°C.

Table 2. Recoveries of nitenpyram, CPMA, and CPMF from four kinds of agricultural samples

Compound	Sample	Concentration/mg/kg	Recovery		
			Average and RSD/% (<i>n</i> =6)	LOD/ μ g/kg (<i>S/N</i> =3)	LOQ/ μ g/kg (<i>S/N</i> =10)
Nitenpyram	Sweet pepper	0.005	98.7 4.0	0.24	0.80
		0.5	103.0 1.9		
	Mandarin orange (pulp without peel)	0.005	93.0 3.0	0.36	1.20
		0.5	103.3 3.5		
	Onion	0.005	105.0 3.1	0.31	1.05
		0.5	103.8 1.7		
CPMA	Brown rice	0.005	99.3 2.4	0.36	1.20
		0.5	103.7 3.9		
	Sweet pepper	0.005	99.3 4.7	0.14	0.47
		0.5	102.0 4.6		
	Mandarin orange (pulp without peel)	0.005	99.3 3.3	0.18	0.60
		0.5	101.8 3.3		
CPMF	Onion	0.005	98.3 5.4	0.19	0.64
		0.5	105.3 3.6		
	Brown rice	0.005	93.0 5.0	0.12	0.42
		0.5	95.4 7.4		
	Sweet pepper	0.005	99.0 5.2	0.17	0.56
		0.5	106.6 2.5		
	Mandarin orange (pulp without peel)	0.005	106.3 7.0	0.18	0.58
		0.5	98.6 6.8		
	Onion	0.005	103.7 3.1	0.13	0.43
		0.5	105.0 5.5		
	Brown rice	0.005	99.3 4.9	0.13	0.44
		0.5	105.5 2.1		

Results and Discussion

1. Chromatography analysis conditions

In the HILIC separation, a water-rich liquid layer is formed on solid particles, and analytes move between the hydrophilic layer in the stationary phase and the mobile phase. The separation performance is largely affected by the condition of the water-rich layer, in which water is supplied from the mobile phase. Therefore, the retention time and peak height tend to vary when column equilibrium is not sufficiently achieved. Accordingly, the isocratic mode was selected, in which the composition of the mobile phase was constant and the column was equilibrated with the mobile-phase matrix.

Selection and tuning of the SRM parameters were performed by direct injection of a 1 mg/L standard solution of each analyte. The optimized MS/MS transitions as well as specific cone voltages and collision energies are summarized in Table 1. Two transitions were measured for analyte identification and confirmation, and one of them was used for quantification.

Five kinds of HILIC columns, which are explained in the Materials and Methods section, were tested for the chromatographic analysis of nitenpyram and the metabolites with distilled water–acetonitrile–500 mM ammonium acetate (25:70:5) as the carrier stream. For the amide-type, sulfo betaine-type, diol-type,

and triazole-type columns, the analytes did not interact well in the stationary phase, and the retention times were less than 5 min. On the other hand, good chromatogram peaks were obtained with the non-modified silica gel column, as shown in Fig. 3. The retention times were 4.6 min for nitenpyram, 5.1 min for CPMA, and 9.4 min for CPMF. The estimated numbers of plates were 5100–5200 for these three compounds. Thus, a non-modified silica gel column was chosen for the subsequent experiments.

2. Chromatography performance

Under optimal conditions, good performance was obtained for chromatographic analysis. Figure 3 shows the chromatograms for sweet pepper samples with and without the addition of nitenpyram, CPMA, and CPMF obtained with the non-modified silica gel column. In this method, the analytes were separated by HILIC and detected by tandem mass spectrometry, which was sensitive as well as selective. Thus, the diluted sample could be introduced to the determination system without any purification procedure. A good peak shape was obtained for each compound, and an interference peak was not observed in the real sample chromatograms.

The calibration curves for nitenpyram, CPMA, and CPMF were straight ($R^2 > 0.999$) in the range from 0.2 to 200 μ g/L.

Table 3. Nitenpyram, CPMA, and CPMF found in agricultural samples by HILIC-MS/MS and conventional methods

Sample	Compound	Residue level ^{a)} /mg/kg		Ratio, % ^{d)}
		HILIC-MS/MS	Conventional method ^{c)}	
Asparagus 1	Nitenpyram	0.162±0.0069	0.155±0.0125	104.5
	CPMA	0.113±0.0028	—	—
	CPMF	0.191±0.0096	—	—
	CPF	0.267 ^{b)}	0.274±0.0051	97.4
Asparagus 2	Nitenpyram	0.100±0.0044	0.094±0.0028	106.4
	CPMA	0.045±0.0012	—	—
	CPMF	0.035±0.0010	—	—
	CPF	0.068 ^{b)}	0.070±0.0065	97.1
Melon (pulp without peel)	Nitenpyram	0.031±0.0005	0.031±0.0009	100.0
	CPMA	0.009±0.0005	—	—
	CPMF	0.033±0.0018	—	—
	CPF	0.038 ^{b)}	0.036±0.0021	105.6

^{a)} Results of residue level are indicated as average and standard deviation of values obtained three times. ^{b)} CPMA and CPMF values are measured in terms of CPF value. ^{c)} Nitenpyram was measured by HPLC-UV and CPF was by GC-FTD. ^{d)} Ratios are HILIC-MS/MS data to conventional methods data.

Fig. 4. Effect of acetonitrile concentration in extraction solvent on nitenpyram, CPMA, and CPMF extracted from an asparagus sample.

The linear range corresponded to 0.002–2 mg/kg for 5 g of agricultural product sample. From the signal-to-noise ratio (S/N), the limits of detection (LOD, $S/N=3$) and limits of determination (LOQ, $S/N=10$) were obtained as shown in Table 2: LODs and LOQs were 0.24–0.36 and 0.80–1.20 $\mu\text{g/kg}$ for nitenpyram, 0.12–0.19 and 0.42–0.64 $\mu\text{g/kg}$ for CPMA, and 0.13–0.18 and 0.43–0.58 $\mu\text{g/kg}$ for CPMF, respectively. Accordingly, the presented method had enough sensitivity to determine 1/10 of the uniform limit (10 $\mu\text{g/kg}$) determined by the Japanese Ministry of Health, Labor, and Welfare.

3. Examination of extraction solvent

Contaminated asparagus was treated with different water/acetonitrile mixtures for the extraction of nitenpyram, CPMA, and CPMF. The obtained compound concentrations were plotted against the acetonitrile content in Fig. 4. The nitenpyram and CPMF values increased with an increase in the acetonitrile concentration up to 65%. This suggested that a higher organic

solvent ratio was required for effective extraction from agricultural samples. At 100%, however, the extracted CPMA amount decreased, probably due to the high polarity of CPMA or conversion to CPME, as mentioned in the Introduction.²⁾ Accordingly, the ratio of acetonitrile and water was adjusted at 65:35 for the subsequent experiments, such as the recovery test and comparison with the conventional methods for contaminated samples.

4. Analysis of agricultural products

LC-MS/MS analysis sometimes gives errors due to ion suppression or ion enhancement in the ionization if the sample contains a matrix in high content.²⁾ Ion enhancement was observed in the HILIC-MS/MS analysis of the agricultural samples. For example, the SRM chromatogram peak areas of matrix-matched standard solutions increased by 103–126% for nitenpyram, 110–129% for CPMA, and 103–125% for CPMF relative to standard solutions. Therefore, recovery tests were performed for samples containing a variety of matrices, namely, samples containing a high content of chlorophyll (sweet pepper), acidic samples (mandarin orange), samples highly containing sulfide groups (onion), and samples rich in lipid (brown rice). For all samples, the added concentrations were 0.005 and 0.5 mg/kg, and good chromatographic peaks were obtained for all samples without an interference peak. The recovery tests were repeated 6 times for each sample. The results of recovery tests are shown in Table 2. Recoveries at a lower concentration (0.005 mg/kg) were 93.0–105.0% for nitenpyram, 93.0–99.3% for CPMA, and 99.0–106.3% for CPMF. When the chemicals were added at a higher concentration (0.5 mg/kg), the results were 103.0–103.8% for nitenpyram, 95.4–105.3% for CPMA, and 98.6–106.6% for CPMF. Thus, the extraction was quantitative for a variety of samples with different concentrations. For dry samples, such as brown rice, it is reportedly required to inject water into samples before organic solvent extraction to cause the tissues to

swell.^{12,13)} On the other hand, in this method, although a water injection was not used, good recovery was obtained by using a water-mixed solvent even in the extraction from brown rice. In our experiments without a water injection, the extraction efficiency of real residue from dry samples is quantitatively uncertain. The inter-day deviations for nitenpyram, CPMA, and CPMF were 7.0, 3.9, and 3.9%, respectively, which were obtained for sweet pepper tested (0.5 mg/kg, $n=1$) for 6 days.

In order to confirm the applicability of this method, we searched for samples containing the compounds that we sought to evaluate. From 60 samples obtained in the Kumamoto prefectural research center and retail stores, two asparagus samples and a melon sample were found to contain nitenpyram, CPMA, and CPMF. For these three samples, the compounds were analyzed by the presented water/acetonitrile extraction followed by HILIC-MS/MS and the conventional methods. In the conventional methods, nitenpyram was determined by HPLC-UV, and CPMA and CPMF were converted to CPF and analyzed by GC-FTD as the sum of the two compounds. Those results are compared in Table 3. The ratio of the HILIC-MS/MS data against the conventional method was 100.0–106.4% for nitenpyram and 97.1–105.6% for the sum of CPMA and CPMF (CPF). The data by HILIC-MS/MS agreed well with those by the conventional methods from highly contaminated asparagus to the less contaminated melon sample. Furthermore, the three compounds were determined simply and simultaneously by the proposed method, whereas two complicated analytical methods were required in the conventional methods. In addition, the concentrations of CPMA and CPMF were given individually only in the proposed method. This showed that HILIC-MS/MS is a useful and reliable analytical method for nitenpyram and its metabolites contained in real agricultural product samples.

Conclusions

A simple analytical method was developed for nitenpyram, CPMA, and CPMF individually using HILIC-MS/MS, which is advantageous for highly polar compounds. Recovery tests and real sample analyses were performed, and good results were obtained for all samples tested. Purification was not needed

because HILIC-MS/MS was a highly selective determination method and pretreatment of the sample is simple and less time-consuming, requiring no specialized skills. In addition, those three compounds could be extracted simultaneously with a throughput of 6 samples/hr, which was one seventh of conventional analytical procedure according to the official analytical method of the Japanese Ministry of Health, Labor, and Welfare. The present method analyzes CPMA and CPMF separately, and the metabolism of nitenpyram to these compounds can be monitored. The method is expected to be of use in the research of the metabolism dynamics of the pesticide. Moreover, it is environmentally safer because it requires only a small amount of organic solvent. The proposed method is useful for the analysis of nitenpyram, CPMA, and CPMF contained in agricultural products.

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