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Rapid and simultaneous analysis of dichlorvos, malathion, carbaryl, and 2,4-dichlorophenoxy acetic acid in citrus fruit by flow-injection ion spray ionization tandem mass spectrometry

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Abstract

A simple method for the rapid and simultaneous analysis of dichlorvos (DDVP), malathion, carbaryl, and 2,4-dichlorophenoxy acetic acid (2,4-D) in citrus fruit, which uses flow-injection ion spray ionization tandem mass spectrometry, has been developed for the first time. The method involves the combined use of stable isotopically labeled internal standards (DDVP-d_6, malathion-d_{10}, carbaryl-d_7, and 2,4-D-d_5) and a multiple reaction monitoring technique. The average recoveries for the pesticides at the same concentrations as their tolerance levels (DDVP: 0.1–0.2 $\mu g\,g^{-1}$; malathion: 0.5–4.0 $\mu g\,g^{-1}$; carbaryl: 1.0 $\mu g\,g^{-1}$; 2,4-D: 1.0–2.0 $\mu g\,g^{-1}$) ranged from 90 to 119% with the relative standard deviation (R.S.D.) ranging from 1.0 to 13.1% ($n = 5$). Analysis time, including sample preparation and determination, was only 15 min. The present method is effective for screening DDVP, malathion, carbaryl, and 2,4-D in citrus fruit.

Keywords: Dichlorvos (DDVP); Malathion; Carbaryl; 2,4-Dichlorophenoxy acetic acid (2,4-D); Tandem mass spectrometry; Flow-injection analysis

1. Introduction

In order to combat a variety of pests that destroy citrus fruit and to improve fruit quality, dichlorvos (DDVP), malathion, carbaryl, and 2,4-dichlorophenoxy acetic acid (2,4-D) are widely used as pesticides (Fig. 1) [1]. In Japan, the tolerance levels of 0.2 $\mu g\,g^{-1}$ for DDVP, 4.0 $\mu g\,g^{-1}$ for malathion, 1.0 $\mu g\,g^{-1}$ for carbaryl and 2.0 $\mu g\,g^{-1}$ for 2,4-D have been established in citrus fruit. In order to provide safe citrus fruit products to consumers, these pesticides should be quantified. If the residual concentrations of these pesticides in a citrus fruit sample exceed their tolerance levels, the citrus fruit has to be recalled and discarded for the benefit of the consumers. Therefore, it is vital to not only determine the residual pesticides in citrus fruit, but also obtain rapidly the results of determination. However, these pesticides are analyzed separately by liquid chromatography (LC) [2,3] or gas chromatography (GC) [4–13] because of their different physicochemical properties. DDVP and malathion are usually analyzed by GC/MS [4–6] or a GC-flame photometric detector [7,8] without derivatization. On the other hand, 2,4-D and carbaryl are analyzed by GC/MS [9–13] or an LC-fluorometric detector [2,3] after derivatization. Thus, it is difficult to analyze simultaneously the four pesticides in citrus fruit by conventional analytical methods such as chromatography. Furthermore, those methods require labor-intensive sample cleanup, strictly controlled chromatographic conditions, and a long separation time. Consequently, there is an urgent need for a simple analytical method for the rapid and simultaneous determination of DDVP, malathion, carbaryl, and 2,4-D at concentrations near their tolerance levels in citrus fruit.

The combination of tandem mass spectrometry (MS/MS) and direct sample injection to an MS/MS system, named flow-injection-tandem mass spectrometry (FI-MS/MS), can be successfully applied to food analysis, similar to LC/MS

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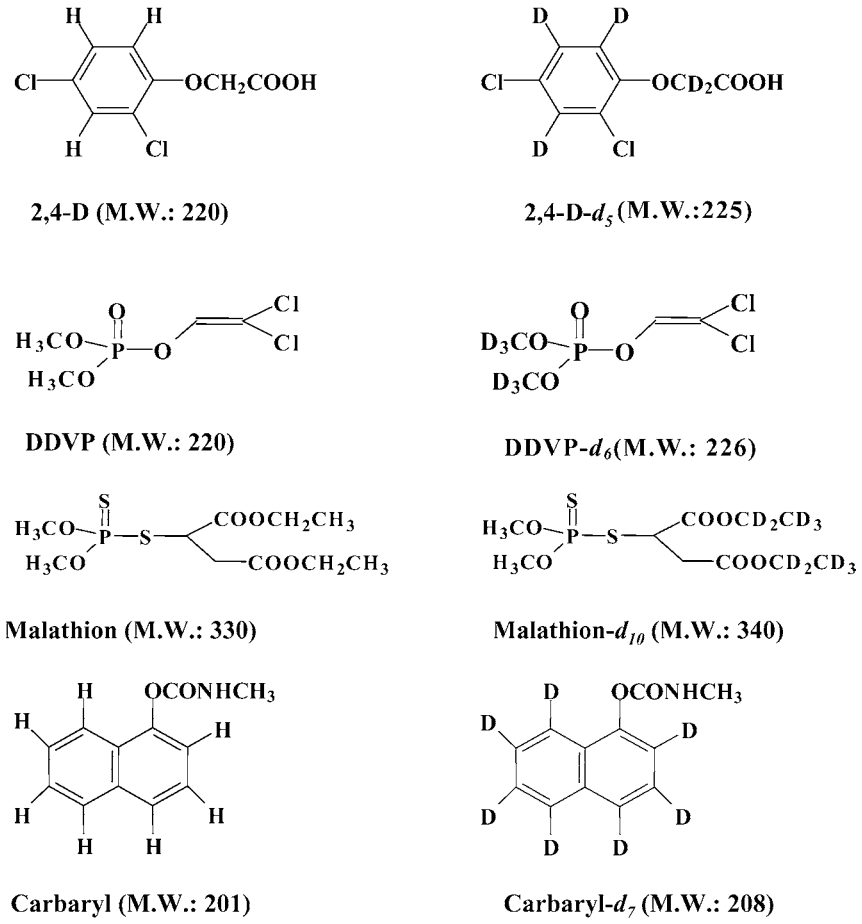

Fig. 1. Structures of dichlorvos, malathion, carbaryl, and 2,4-dichlorophenoxy acetic acid.

or GC/MS described in our previous paper [14]. Because the first MS of the MS/MS is used for the separation of target compounds from all ionized compounds according to mass difference, the second one is used for the detection of the target compounds, the determination of the target compounds in food extract does not require any separation systems such as chromatography. In addition, long separation times are unnecessary and it is easy to develop a method for rapidly analyzing compounds having different physicochemical properties. Accordingly, we have developed a simple method for the rapid and simultaneous determination of DDVP, malathion, carbaryl, and 2,4-D in citrus fruit, which uses flow-injection ion spray ionization tandem mass spectrometry (ISP MS/MS).

2. Materials and methods

2.1. Reagents and standard solution

Pesticide-grade acetone, ethyl acetate, *n*-hexane, methanol, acetonitrile, and anhydrous disodium sulfate (Na_2SO_4) were purchased from Wako Pure Chemicals Industries, Ltd. (Osaka, Japan). The pesticide standards, 2,4-D, DDVP, malathion, and carbaryl, and the stable isotopically labeled internal standards, 2,4-D-d_5, DDVP-d_6, malathion-d_{10}, and carbaryl-d_7, were purchased from Hayashi Pure Chemical Industries, Ltd. (Osaka, Japan). Water purified by a Milli-Q water purification system (Millipore, Bedford, MA, USA) was used. Stock solutions (1.0 mg mL^{-1}) of these pesticides and internal standards were prepared in methanol, and dilutions were made as required by the addition of acetone. All the working standard solutions were stored in 10 mL vials at −80 °C.

2.2. Citrus fruit samples

Samples (orange, grapefruit, lemon, and lime) were obtained from various grocery stores in Tokyo and were confirmed to be pesticide-free by a blank test. About 500 g of each sample was chopped by a conventional food processor and then stored at −80 °C.

2.3. Apparatus

FI-MS/MS was performed using an API series binary pump (Waters 600s controller, 616 pump), an auto-sampler (MIDAS, Spark Holland), and an API 300 triple quadrupole

tandem mass spectrometer (PE-Sciex, Thornhill, Canada) equipped with a turbo ion spray interface. A PEEK tube (1.0 m × 0.50 mm i.d.) was used for connecting the MS/MS interface to the auto-sampler.

2.4. FI-MS/MS conditions

FI experiments were performed at room temperature using methanol:water (95:5, v/v) as the carrier liquid at a flow rate of 0.1 mL min^{-1}. The injection volume was 1 μL.

The conditions for ISP MS/MS were as follows: the nebulizer probe temperature was 375 °C; the flow rate of heated auxiliary nitrogen gas was 7 L min^{-1}; the ionization mode was both positive and negative; and collision-induced dissociation was performed using nitrogen as the collision gas at a pressure of 3.2 mPa. The other MS/MS parameters (ion spray voltage, orifice voltage, and offset voltage) for each pesticide are shown in Table 1.

2.5. Sample preparation

Citrus fruit sample was sliced and homogenized by a mixer. About 25 g of sample was added into a 250 mL centrifuge tube and spiked with 0.5 mL of mixed internal standard in acetone (final concentration: 0.1 μg mL^{-1}). The mixture was blended with 25 g of anhydrous Na_2SO_4 and 50 mL of *n*-hexane using a high-speed blender. After centrifugation (3100 rpm, 8 min), a 1 μL aliquot of the supernatant was injected into the flow-injection ISP MS/MS system.

2.6. Quantitation

Calibration curves were constructed from the peak-area ratios of the pesticides to their respective internal standards. Recoveries were calculated as the ratio of the peak-area ratio of the analyte to the internal standard from the fortified samples, to the corresponding peak-area ratio of the pesticide standard and the internal standard solutions.

3. Results and discussion

3.1. Optimization of flow-injection ISP MS/MS conditions

Compound-specific MS/MS parameters, namely, ion mode, precursor ion, monitor ion under multiple reaction monitoring (MRM), ion spray voltage, orifice voltage, and offset voltage, were set. The performance of the FI ISP MS/MS system was optimized by evaluating the effects of sample injection parameters (carrier liquid composition, carrier flow rate, injection volume, and size of the tube connecting the MS/MS interface to the injection port) on mass spectral ion intensity. The optimization of these sample injection parameters is discussed below.

3.1.1. MS/MS conditions

The ion spray ionization mass spectra recorded for DDVP, malathion, and carbaryl gave $[M+H]^+$ at *m/z* 221, 331, and 202 in the positive ion mode, respectively, and that recorded for 2,4-D gave $[M-H]^-$ at *m/z* 219 in the negative ion mode. When each of these molecular ion species was used as the precursor ion for full-scan ISP tandem MS/MS, all of the pesticides gave product ion spectra with clear cleavage of the precursor ions. The following product ions that showed the highest intensity were selected for MRM: 2,4-D, *m/z* 161 $[M - CH_2COOH]^-$; DDVP, *m/z* 127 $[M + H\text{-}C_2HCl_2]^+$; malathion, *m/z* 127 $[M+H\text{-}(CH_3O)_2PS_2C_2H_5O]^+$; and carbaryl, *m/z* 145 $[M + H\text{-}CH_3NHCO]^+$. We paid special attention to the intensities of these precursor ions and monitor ions in order to optimize ion spray voltage, orifice voltage, and offset voltage.

For high-sensitivity MRM, ion spray voltage and orifice voltage should be adjusted for each pesticide. Accordingly, each solution of the pesticides in *n*-hexane (1 μg mL^{-1}) was flow-injected into the ISP MS/MS and the $[M + H]^+$ intensities for DDVP at *m/z* 221, malathion at *m/z* 331, and carbaryl at *m/z* 202, and the $[M-H]^-$ intensity for 2,4-D at *m/z* 219 were monitored under selected ion spray voltages (3500–5000 V) and orifice voltages (15–35 V) by selected ion monitoring (SIM). The ion spray voltages and the orifice voltages that gave the highest intensities for the pesticides are shown in Table 1.

Table 1
Compound-specific ISP MS/MS parameters for the pesticides and corresponding internal standards

Compound	MRM (precursor/product ion)	Ion spray voltage (V)	Orifice voltage (V)	Offset voltage (V)	Ion mode (ESI)
2,4-D	219/161	−4000	−21	9	−
2,4-D	224/164	−4000	−21	9	−
DDVP	221/127	4250	30	−10	+
DDVP-d_6	227/133	4250	30	−10	+
Malathion	331/127	4600	31	−7	+
Malathion-d_{10}	341/132	4600	31	−7	+
Carbaryl	202/145	4000	16	−6	+
Carbaryl-d_7	209/152	4000	16	−6	+

−: Negative mode; +: Positive mode.

In order to obtain the optimal MS/MS conditions for the determination of the pesticides, we measured the intensity of each monitor ion (2,4-D, *m*/*z* 161; DDVP, *m*/*z* 127; malathion, *m*/*z* 127; carbaryl, *m*/*z* 145) appearing on the MRM profiles under selected offset voltages (−15 to +15 V) using the same procedures as those described above. The optimized offset voltages for the pesticides are shown in Table 1.

As the nebulizer probe temperature could not be changed for each target compound, the optimal temperature was selected by comparing the intensities of the precursor ions. In the temperature range examined (300–425 °C) in this study, the intensities increased as the temperature increased. In the cases of malathion, DDVP, and carbaryl, an increase in temperature was found to increase the precursor ion intensity on SIM profiles; however, temperatures exceeding 375 °C decreased the intensity. On the other hand, in the case of 2,4-D, the difference in precursor ion intensity on the SIM profile was very small between 325 and 425 °C. Therefore, the nebulizer probe temperature was set at 375 °C.

3.1.2. Carrier liquid

The flow-injection ISP MS/MS requires that the carrier liquid promote the ionization of the precursor ion. Methanol, acetonitrile, water and their mixed solutions are usually used in flow-injection ISP MS/MS as the carrier liquid. The ionization-promoting effects of these solvents increase in the following order: acetonitrile, methanol, and water. On the other hand, it is well-known that the higher the concentration of the organic solvent used as carrier liquid, the lower the surface tension of the sprayed droplet, the larger the surface area of the sprayed droplet, and the larger the number of ions detected by ion spray ionization. Because methanol has both effects of promoting ionization and decreasing surface tension of the sprayed droplet, we examined whether it can be used as the carrier liquid for the determination of 2,4-D, malathion, DDVP, and carbaryl. When each of the pesticides in *n*-hexane solution was analyzed by flow-injection ISP MS/MS, the monitor ions of malathion and DDVP on each MRM profile showed satisfactory intensities, whereas those of 2,4-D and carbaryl did not, indicating that methanol does not sufficiently promote the ionization of 2,4-D and carbaryl. Therefore, we decided to add promoter chemicals to methanol. In the case of ion spray ionization, formic acid and acetic acid in the positive ion mode and ammonia and triethylamine in the negative ion mode are well-known additives for promoting ionization. However, we could not use any of these additives because both positive and negative ion modes were necessary for the simultaneous determination of 2,4-D, malathion, DDVP, and carbaryl in this study. Although water increases the surface tension of the sprayed droplet, it promotes ionization more effectively than methanol. Therefore, we examined the effects of selected concentrations (5–50%) of water on the precursor ion intensities of the pesticides. The intensities were increased when the concentration of water was increased, whereas an increase of 5% decreased the precursor ion intensities. Therefore, we decided to use a mixture of methanol:water (95:5, v/v) as the carrier liquid.

In flow-injection ISP MS/MS, the carrier liquid flow rate has a marked influence on the precursor ion intensity. We investigated the optimal flow rate under selected flow rates (0.05–0.5 mL min^{-1}). The flow rate of 0.1 mL min^{-1} gave the highest intensities for the pesticides and therefore was selected as the carrier liquid flow rate.

3.1.3. Sample injection

When 100 μL of a mixed standard solution of the pesticides in *n*-hexane (1 μg mL^{-1}, each) was injected into the flow-injection ISP MS/MS system, two peaks appeared on each MRM profile of the pesticides. As described in our previous paper [14], this means that the pesticides in the completely mixed sample solution with carrier liquid are ionized and the pesticides in a lone sample solution (*n*-hexane) are not ionized or are difficult to ionize. Therefore, to realize the efficient ionization of each of the pesticides, the sample solution should be mixed completely with the carrier liquid. The key parameters for controlling the mixing of these solutions are sample volume, mixing time, which is the same as the moving time of sample solution from the injection port to the MS/MS interface, and the contact surface area between the sample solution and the carrier liquid. As it was obvious that a small volume of the sample solution facilitated mixing with the carrier liquid, we set the sample volume at 1 μL. On the other hand, the mixing time is related to the tube length, and the contact surface area between the sample solution and the carrier liquid is related to the tube inside diameter. As described in our previous paper [14], we have determined the optimized tube length and the inside diameter. In the present study, we used a tube 100 cm in length by 0.5 mm in inside diameter, which was previously optimized [14].

3.2. Selection of internal standards

In order to improve reproducibility and accuracy, it is essential to use an internal standard. In particular, a stable isotopically labeled internal standard is effective for MS analysis because it can correct the effects of the sample matrix on suppressing or promoting analyte ionization. In this study, the relative contribution of the analyte to the total ion current might be decreased because the crude citrus fruit extract without cleanup was directly injected into the MS/MS interface for rapid analysis. Therefore, we used commercially available pesticides labeled with stable isotopes: 2,4-D-d_5, DDVP-d_6, malathion-d_{10}, and carbaryl-d_7.

The flow-injection ISP MS/MS conditions (ionization mode, precursor ion, monitor ion, ion spray voltage, orifice voltage, and offset voltage; Table 1) for all the internal standards were optimized in the same manner as described above.

Next, all the precursor ions (molecular ion species) and the isotopic ions of the pesticides and their internal standards

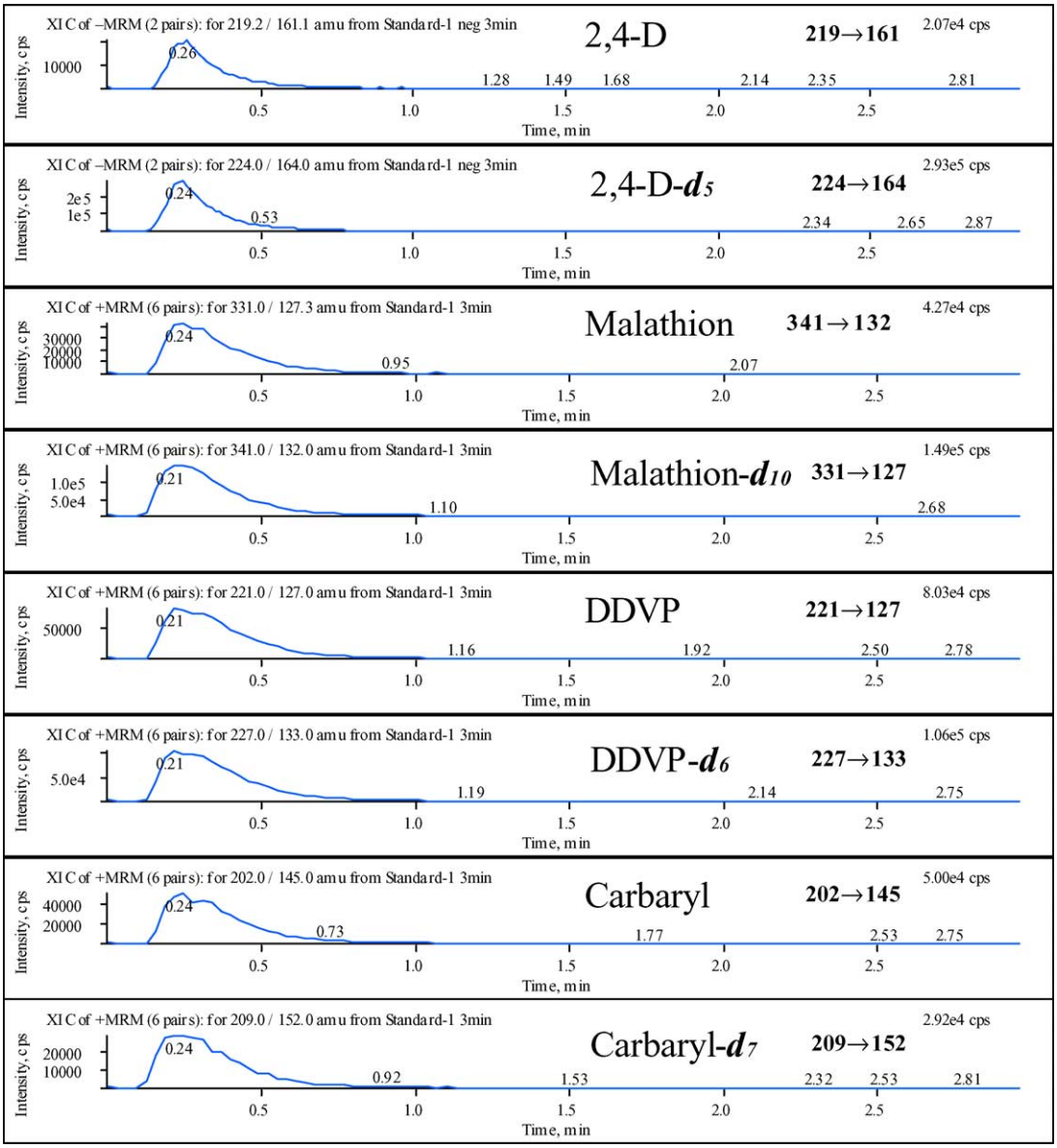

Fig. 2. MRM profiles of standard pesticides under flow-injection ISP MS/MS conditions.

were compared because overlapping of the ions could lead to serious error in MRM by flow-injection ISP MS/MS. The precursor ions of the pesticides and those of the corresponding internal standards did not overlap with each other, including their isotopic ions. Accordingly, we confirmed that 2,4-D-d_5, DDVP-d_6, malathion-d_{10}, and carbaryl-d_7 could be used as the internal standards for MRM of the pesticides.

3.3. Sample preparation

In the conventional method, two or three extractions and several segmental cleanup steps are required for highly sensitive and accurate determination, and these operations consume time. In order to develop a simple method for the rapid analysis of pesticides in citrus fruit, it is necessary that the sample preparation, including extraction and cleanup steps, be as simple as possible. As a stable isotopically labeled internal standard shows the same physicochemical behavior as its corresponding compound, the addition of the internal standard immediately after sample weighing enables correction for sample loss. Using this technique, the extraction time is reduced while maintaining good recovery. Moreover, the use of a stable isotopically labeled internal standard can also correct for the effects of the sample matrix on the ionization of analyte, and thus cleanup steps can be omitted. Accordingly, we selected the combination of only one extraction after the addition of internal standards and no cleanup steps for the present sample preparation.

Because the crude citrus fruit extract without cleanup, which contained high concentrations of co-existing substances, was directly injected into the MS/MS interface, the influence of the extraction solvent and its volume on the

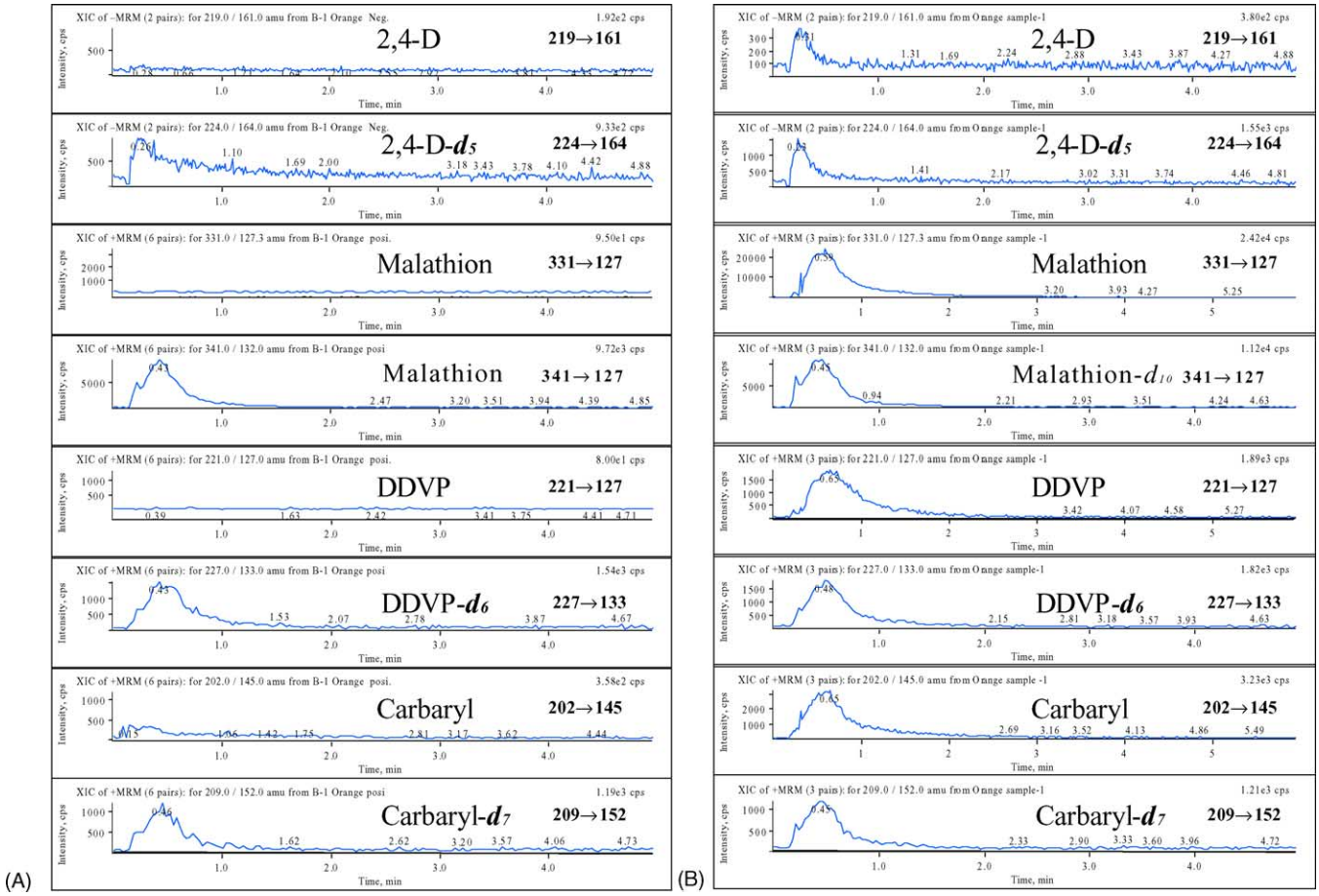

Fig. 3. Typical MRM profiles of orange samples under flow-injection ISP MS/MS conditions. (A) Non-fortified orange (blank). (B) Spiked at concentrations half the tolerance levels.

results of quantification was expected. According to the conventional method, methanol, acetonitrile, acetone, ethyl acetate, and *n*-hexane were examined for use as the extraction solvent. These solvents caused peak tailing on the MRM profile of each analyte, and their influence increased in the following order: *n*-hexane, ethyl acetate, acetone, acetonitrile, and methanol. Although the stable isotopically labeled internal standard could correct for the influence of the sample matrix on the ionization of analyte, it could not correct for the significant influence of the high concentration of the sample matrix. Therefore, we extracted 25 g of lemon samples with 50 mL each of *n*-hexane, ethyl acetate, acetone, acetonitrile, and methanol, and added the pesticides and their corresponding internal standards at concentrations near their tolerance levels, in order to examine the influence of the concentration of the sample matrix. Only *n*-hexane showed satisfactory quantitative results with no ion suppression or peak tailing. Methanol, acetonitrile, and acetone exhibited significant ion suppression for all the four pesticides, whereas ethyl acetate exhibited the same suppression for malathion. Therefore, we decided to use *n*-hexane as the extraction solvent.

Typical MRM profiles of the pesticides and the corresponding internal standards are shown in Fig. 2. These profiles were obtained under the optimal flow-injection ISP MS/MS conditions described above. Fig. 2 indicates satisfactory intensities of the pesticides and their internal standards at their tolerance levels.

3.4. Quantitation

Calibration curves were linear over the range of 0.001–2.5 $\mu g\,mL^{-1}$ with correlation coefficients over 0.999. These concentrations were equivalent to 0.002–5.0 $\mu g\,g^{-1}$ as the concentrations in citrus fruit in the present study.

3.4.1. Recoveries

Citrus fruit samples were fortified with the pesticides at concentrations equal to or half their tolerance levels, and analyzed as given in Section 2.5. Typical MRM profiles of orange samples fortified with the pesticides at concentrations half their tolerance levels and non-fortified orange (blank) are shown in Fig. 3. The recoveries and corresponding relative standard deviation (R.S.D.) are listed in Table 2. The average recoveries for 2,4-D and malathion ranged from 95 to 112 and 95 to 110% with the R.S.D.s ranging from 1.3 to 11.4 and 2.1 to 7.4%, respectively. For

Table 2
Recoveries of pesticides from citrus fruit samples ($n = 5$)

Pesticide	Sample	Spiked conc. ($\mu g\,g^{-1}$)	Recovery ± S.D. (%)	R.S.D. (%)
2,4-D	Orange	2	112 ± 1.8	1.6
		1	95 ± 11.0	11.4
	Lemon	2	110 ± 1.4	1.7
		1	108 ± 9.0	8.3
	Grapefruit	2	110 ± 1.9	1.3
		1	104 ± 4.0	3.4
	Lime	2	106 ± 4.0	3.9
		1	99 ± 9.0	9.4
Malathion	Orange	4	98 ± 2.4	2.4
		2	99 ± 7.0	7.4
	Lemon	4	97 ± 2.1	2.1
		2	106 ± 3.0	2.4
	Grapefruit	4	95 ± 3.8	4.0
		2	102 ± 7.0	7.4
	Lime	4	104 ± 2.0	5.5
		2	110 ± 3.0	3.1
DDVP	Orange	0.2	110 ± 1.8	1.6
		0.1	109 ± 6.0	5.1
	Lemon	0.2	109 ± 1.1	1.0
		0.1	107 ± 6.0	5.4
	Grapefruit	0.2	108 ± 2.6	2.4
		0.1	105 ± 6.0	5.5
	Lime	0.2	106 ± 3.0	3.1
		0.1	103 ± 6.0	5.7
Carbaryl	Orange	1	102 ± 4.3	4.2
		0.5	101 ± 3.0	2.8
	Lemon	1	103 ± 3.1	3.0
		0.5	119 ± 7.0	6.3
	Grapefruit	1	105 ± 6.1	5.8
		0.5	90 ± 12.0	13.1
	Lime	1	106 ± 9.0	8.6
		0.5	101 ± 5.0	4.8

DDVP and carbaryl, the average recoveries ranged from 103 to 110 and 90 to 119% with the R.S.D.s ranging from 1.0 to 5.5 and 2.8 to 13.1%, respectively. The recoveries and the R.S.D.s were not influenced by the kind of sample, and continuous analyses of 50 citrus fruit samples did not adversely affect MRM profiles.

3.4.2. Quantification limit

On the basis of the results of the recovery tests and the MRM profiles of the samples fortified with pesticides at concentrations half their tolerance levels, the limits of quantification were estimated to be $0.005\,\mu g\,g^{-1}$ for 2,4-D, DDVP and carbaryl, and $0.001\,\mu g\,g^{-1}$ for malathion in citrus fruit (S/N ratio >10).

3.4.3. Analysis of commercial samples

In order to investigate the availability of this method, citrus fruit samples on the market (10 each of orange, lemon, grapefruit and lime) were analyzed according to the present method. 2,4-D was detected from two lemon samples and its concentrations were 0.1 and $0.2\,\mu g\,g^{-1}$. These concentrations are significantly lower than the tolerance levels established by Japan in lemon. For DDVP, carbaryl and malathion, they were not detected in all samples. Analysis of these pesticides was finished simultaneously in <15 min from cutting the citrus fruit sample, which is quite shorter than that of using the conventional analytical method.

4. Conclusions

Flow-injection ion spray ionization tandem mass spectrometry was developed for the simultaneous determination of DDVP, malathion, carbaryl, and 2,4-D in citrus fruit, and has the following characteristics: (1) The high selectivity of tandem mass spectrometry makes simple and rapid determination possible without the need for chromatographic separation. (2) The internal standards labeled with a stable isotope are effective for correcting the influence of the directly injected sample extract without cleanup on the ionization of analytes and sample loss due to only one extraction. (3) The reproducibility and accuracy of the quantification of pesticides at concentrations near their tolerance levels in citrus fruit were realized by adding an internal standard. (4) The analysis time, which includes the time from sample preparation to obtaining the results of determination, is only 15 min.

Because of these characteristics, we strongly recommend the simultaneous quantification method presented herein for the analysis of DDVP, malathion, carbaryl, and 2,4-D in citrus fruit.

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