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Ultra-fast screening of pesticides in foods and agricultural products with desorption corona beam ionization (DCBI) tandem mass spectrometry

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Introduction

Pesticides screening in food sample has traditionally counted on analytical confirmation with a quantitative method such as GC/MS, HPLC and LC/MS. The chromatographic technique provide a high sensitivity and high reliability solution for pesticides analysis but introduce the relatively low throughput with time-consuming pretreatment technique.
Desorption corona beam ionization (DCBI) source for direct analysis in mass spectrometry can work under ambient conditions with minimal sample pretreatments. In DCBI, a visible thin corona beam are generated from helium gas and impact the solid sample surface, and then the analyte molecules on the surface were ionized in the gas phase (1). DCBI was used in the field of drug development, environmental, homeland security, etc (2 - 5).
In this study, we attempted to develop a DCBI-MS approach to determine pesticides amount aiming at high throughput and comprehensive methods using MRM acquisition. Ambient mass spectrometry coupled with ultra-fast triple quadrupole mass spectrometry permits this data acquisition in 30 seconds per sample as compared with the conventional chromatographic run of about 20 - 40 minutes.

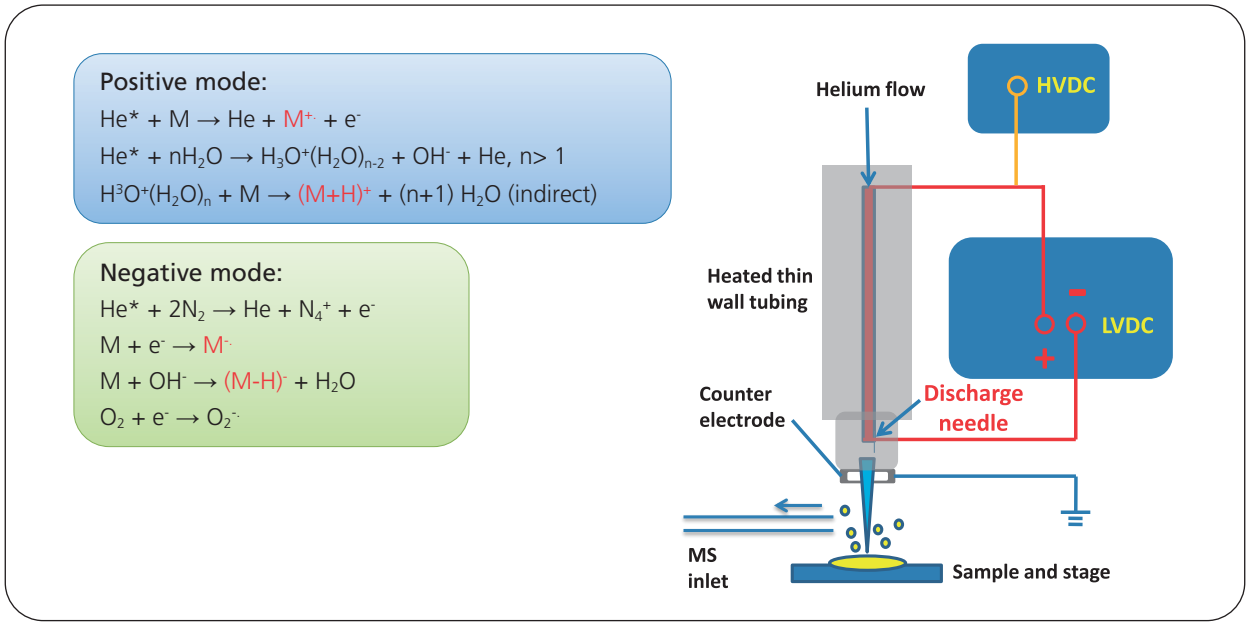

Figure 1 Ionization mechanism and schematic diagram of DCBI

Materials and Methods

The commercially available pesticides were used for the confirmation of MS spectrum and the optimization of MRM conditions. Automated MRM parameter optimization with ESI or APCI source were carried out by flow injection analysis of authentic standards with a function of the LabSolutions LC/MS control software. The DCBI source (Shimadzu Corporation) was mounted on a triple quadrupole mass spectrometer (LCMS-8040 or LCMS-8050, Shimadzu Corporation) with the capability of simultaneously acquiring 555 MRM channels per second. Samples were introduced to the DCBI source by inserting a glass capillary or a glass sample cup. The DCBI source was operated at 150 - 300 C as heater temperature and 2 - 3 kV as discharge voltage. Measurements of mass spectrum or MRM chromatogram were conducted in both positive or negative polarity mode. Samples were introduced to the DCBI source by inserting a glass capillary or a glass sample cup. Analytical conditions are shown in Table 1.

Table 1 Experimental conditions for DCBI Analysis

DCBI Conditions	
He gas flow (L/min)	: 1
High voltage, discharge (kV)	: 2.5
Gas temperature (C)	: 250
MS Conditions	
Nebulizing gas flow, N_2 (L/min)	: 0.6
Desolvent line temperature (C)	: 220
Heat block temperature (C)	: 150

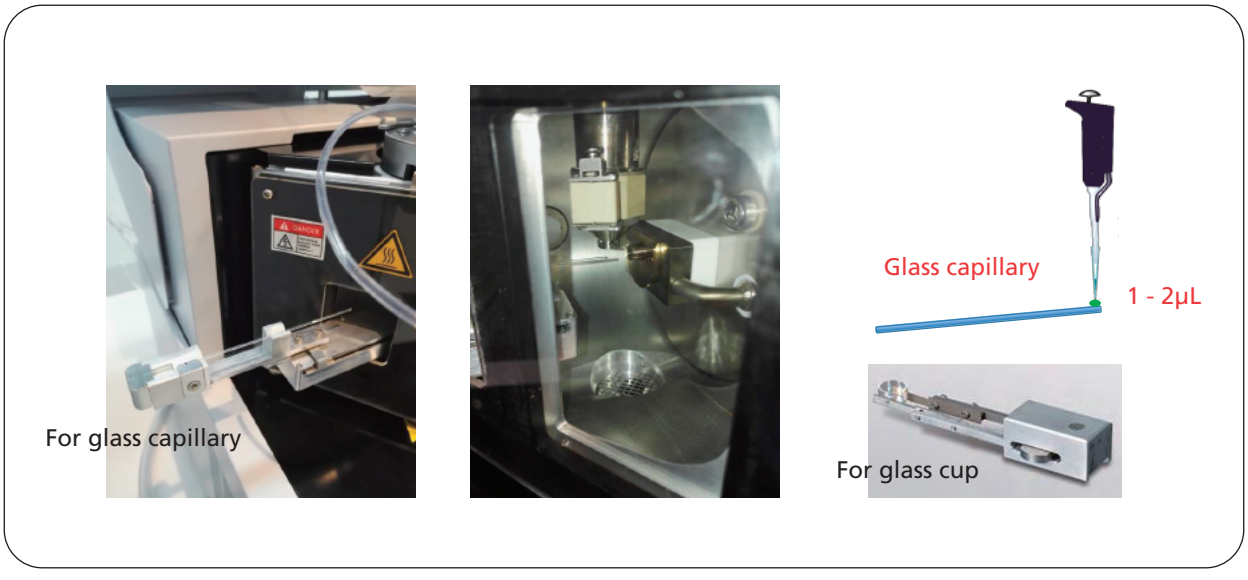

Figure 2 Injection mode for DCBI analysis (LCMS-8040)

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Results

Ionization confirmation of pesticides by DCBI

Ionization confirmation of 37 pesticides was applied using DCBI with LCMS-8040 triple quadrupole mass spectrometer, and compared with ESI and APCI source. 1 ppm or 10 ppm methanol solutions of authentic standard were introduced to the ion source. Full scan measurement was conducted to determine the optimum ionization polarity of target compounds by glass capillary sampling (DCBI, Figure 2) and by flow injection analysis with 50% methanol (ESI and APCI).

As a consequence, different type of adduct ions are observed in three different ion source for the same target pesticide (Figure 3). The results of 37 pesticides are summarized in Table 2. The protonated molecule was detected mainly under DCBI conditions. Its simple and no sodium adduct spectrum resembles a result of APCI and it will be suitable for the MRM mode measurement.

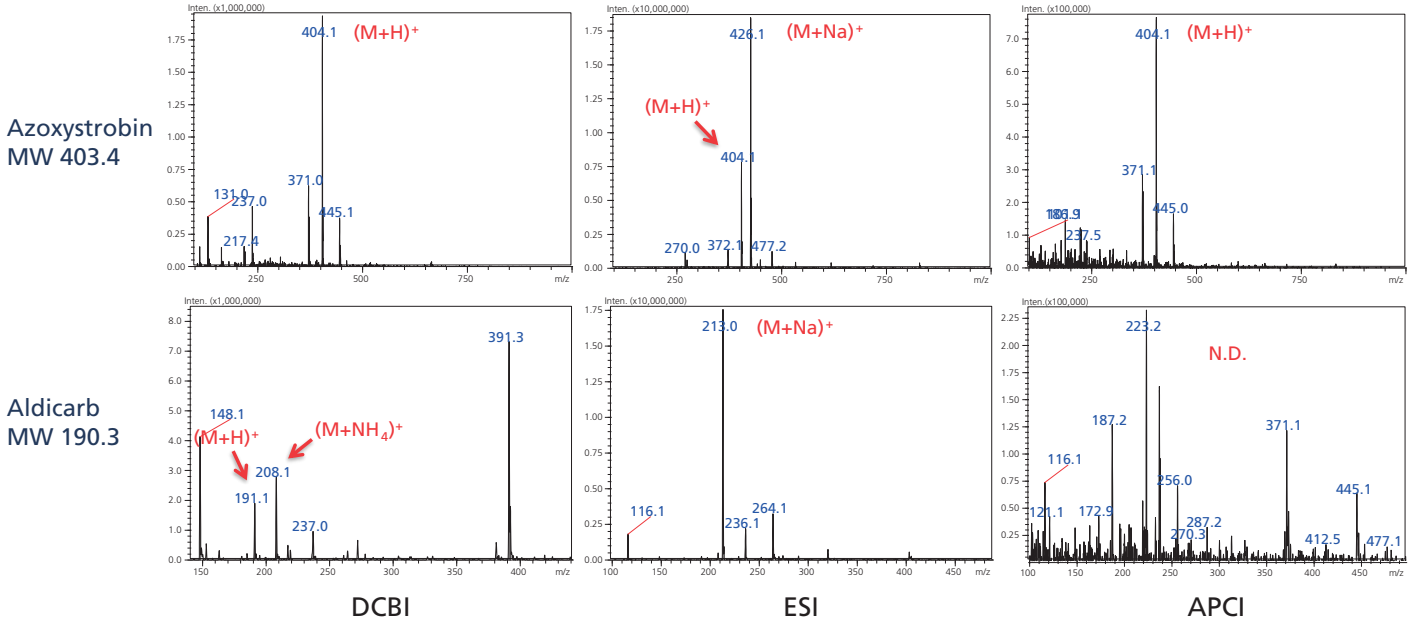

Figure 3 Typical mass spectra of pesticides by DCBI, ESI and APCI.

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Table 2 Comparison of ionization pattern of 37 pesticides

No.	Name	Formula	Molecular weight	Detected ions		
				DCBI	ESI	APCI
1	Methamidophos	C2H8O2NPS	141.1	$(M+H)^+$	$(M+Na)^+$, $(M+H)^+$	$(M+H)^+$
2	Acephate	C4H10NO3PSi	183.2	$(M+H)^+$	$(M+Na)^+$, $(M+H)^+$	$(M+H)^+$
3	Omethoate	C5H12NO4PS	213.2	$(M+H)^+$	$(M+Na)^+$, $(M+H)^+$	$(M+H)^+$
4	Sulfoxide aldicarb	C7H14N2O3S	206.3	$(M+H)^+$	$(M+Na)^+$, $(M+H)^+$	nd
5	Sulfone aldicarb	C7H14N2O4S	222.3	$(M+NH_4)^+$, $(M+H)^+$	$(M+NH_4)^+$, $(M+Na)^+$, $(M+H)^+$	nd
6	Methomyl	C5H10N2O2S	162.2	$(M+H)^+$	$(M+H)^+$	$(M+H)^+$
7	Thiamethoxam	C8H10ClN5O3S	291.7	$(M+H)^+$	$(M+H)^+$	$(M+H)^+$
8	Imidacloprid	C9H10ClN5O2	255.1	$(M+H)^+$	$(M+H)^+$	$(M+H)^+$
9	Carbofuran-3-hydroxy	C12H15NO4	237.3	$(M+H-H_2O)^+$	$(M+Na)^+$, $(M+NH_4)^+$, $(M+H-H_2O)^+$, $(M+H)^+$	$(M+H-H_2O)^+$
10	Dimethoate	C5H12NO3PS2	229.3	$(M+H)^+$	$(M+Na)^+$, $(M+H)^+$	$(M+H)^+$
11	Acetamiprid	C10H11ClN4	222.7	$(M+H)^+$	$(M+Na)^+$, $(M+H)^+$	nd
12	Carbendazim	C9H9N3O2	191.2	$(M+H)^+$	$(M+H)^+$	$(M+H)^+$
13	Aldicarb	C7H14N2O2S	190.3	$(M+NH_4)^+$, $(M+H)^+$	$(M+Na)^+$	nd
14	Carbofuran	C12H15NO3	221.3	$(M+H)^+$	$(M+Na)^+$, $(M+H)^+$	$(M+H)^+$
15	Carbaryl	C12H11NO2	201.2	$(M+H)^+$	$(M+Na)^+$, $(M+H)^+$	$(M+H)^+$
16	Phosemet	C11H12NO4PS2	317.3	$(M+H)^+$	$(M+Na)^+$, $(M+H)^+$	$(M+H)^+$
17	Azoxystrobin	C22H17N3O5	403.4	$(M+H)^+$	$(M+Na)^+$, $(M+H)^+$	$(M+H)^+$
18	Malathion	C10H19O6PS2	330.4	$(M+H)^+$	$(M+Na)^+$, $(M+H)^+$	$(M+H)^+$
19	Dimethomorph	C21H22ClNO4	387.1	$(M+H)^+$	$(M+Na)^+$, $(M+H)^+$	$(M+H)^+$
20	Triadimefon	C14H16ClN3O2	293.1	$(M+H)^+$	$(M+Na)^+$, $(M+H)^+$	$(M+H)^+$
21	Triazophos	C12H16N3O3PS	313.3	$(M+H)^+$	$(M+Na)^+$, $(M+H)^+$	$(M+H)^+$
22	Fipronil	C12H4Cl2F6N4OS	435.9	$(M+H)^+$	$(M-H)^-$	$(M-H)^-$
23	Diflubenzuron	C14H9ClF2N2O2	310.0	$(M+H)^+$	$(M+Na)^+$/, $(M-H)^-$	$(M+H)^+$/, $(M-H)^-$
24	Chlorobenzuron	C14H10Cl2N2O2	308.0	$(M+H)^+$	$(M+Na)^+$/, $(M-H)^-$	$(M+H)^+$/, $(M-H)^-$
25	Diazinon	C12H21N2O3PS	304.4	$(M+H)^+$	$(M+H)^+$, $(M+Na)^+$	$(M+H)^+$
26	Emamectin benzoate	C49H75NO13	885.5	$(M+H)^+$	$(M+H)^+$	$(M+H)^+$
27	Phoxim	C12H15N2O3PS	298.3	$(M+H)^+$	$(M+Na)^+$, $(M+H)^+$	$(M+H)^+$
28	Prochloraz	C15H16Cl3N3O2	375.0	$(M+H)^+$	$(M+H)^+$	$(M+H)^+$
29	Phosalone	C12H15ClNO4PS2	367.0	$(M+H)^+$	$(M+Na)^+$, $(M+H)^+$	$(M+H)^+$
30	Difenoconazole	C19H17Cl2N3O3	405.1	$(M+H)^+$	$(M+Na)^+$, $(M+H)^+$	$(M+H)^+$
31	Profenofos	C11H15BrClO3PS	371.9	$(M+H)^+$	$(M+Na)^+$, $(M+H)^+$	$(M+H)^+$
32	Tridemorph	C19H39NO	297.3	$(M+H)^+$	$(M+H)^+$	$(M+H)^+$
33	Chlorpyrifos	C9H11Cl3NO3PS	348.9	$(M+H)^+$	$(M+Na)^+$, $(M+H)^+$	$(M+H)^+$
34	Pendimethalin	C13H19N3O4	281.3	$(M+H)^+$	$(M+H)^+$	$(M+H)^+$
35	Chlorfluazuron	C20H9Cl3F5N3O3	539.0	$(M+H)^+$	$(M-H)^-$	$(M-H)^-$
36	Ppyridaben	C19H25ClN2OS	364.1	$(M+H)^+$	$(M+Na)^+$, $(M+H)^+$	$(M+H)^+$
37	Abamectin B1a	C48H72O14	872.5	$(M+NH_4)^+$, $(M+H)^+$	$(M+Na)^+$	$(M-H)^-$

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Confirmation of optimal MRM transitions

For improvement of the selectivity of target compound, we tried to be detected in MRM mode by DCBI-MS with higher sensitive LCMS-8050 triple quadrupole mass spectrometer. Multiple MRM transition candidates were selected and compound dependent parameters were optimized to each MRM transition using each authentic standard. The performance of the DCBI-MS was evaluated by the analysis of the mixture of 37 pesticides solution. Semi-quantification was accomplished based on peak areas in the ion chromatograms.

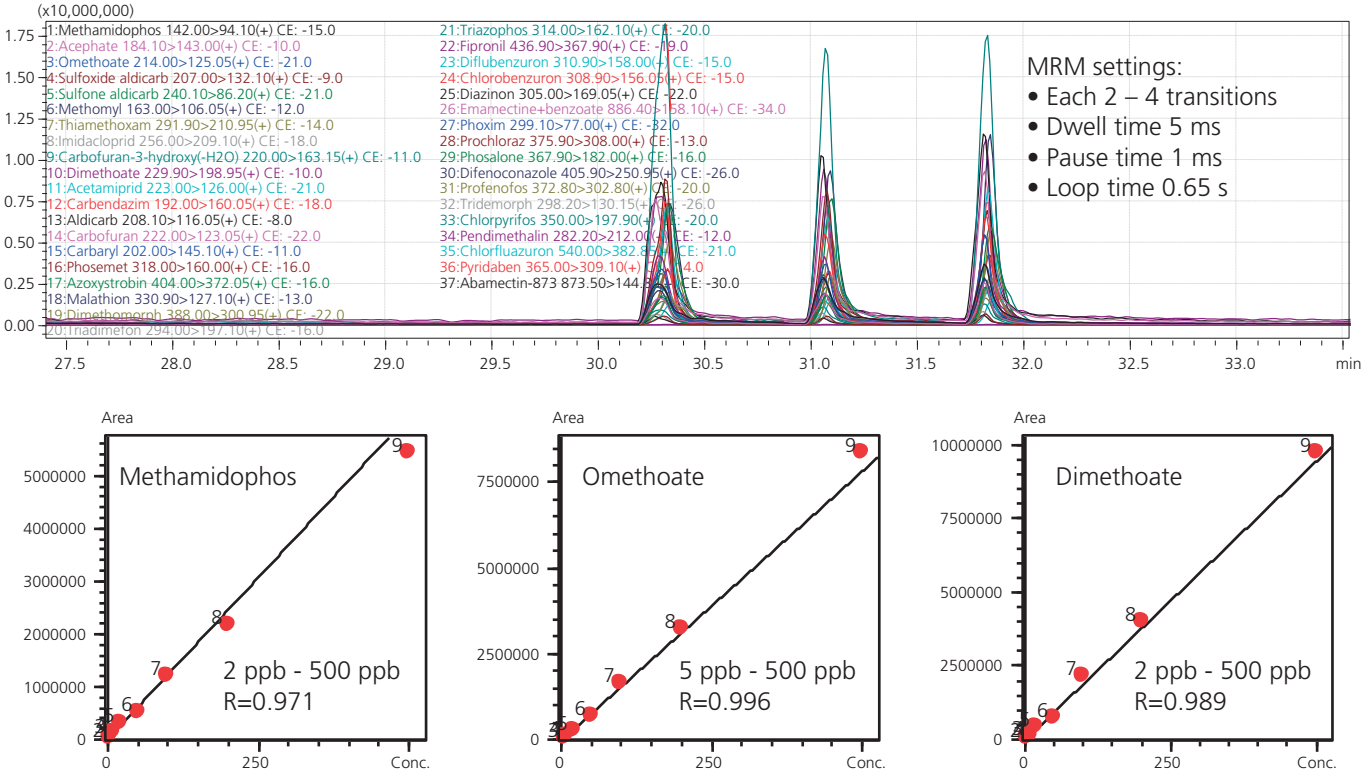

Figure 4 MRM chromatogram of 37 pesticides mixture (3 injections, 1 ppm) and response linearity of typical pesticides.

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Screening analysis of real agricultural sample

To find out the optimal transition number and optimal dwell time of each MRM transition, we performed the detection and reproducible test using the plant homogenates. Approximately 20 g of cucumber were put in a food processor and processed it for 1 minutes. Without dilution and centrifugation, homogenates were directly applied to DCBI-MRM analysis with 108 MRM transitions of 5 ms dwell time. The matrix samples spiked with 10 ppb standards were prepared for the analytical test. Several target compounds have shown good recoveries (Figure 5), however there is room for the improvement, for example sample treatment, ionization parameter and MS parameter for this approach.

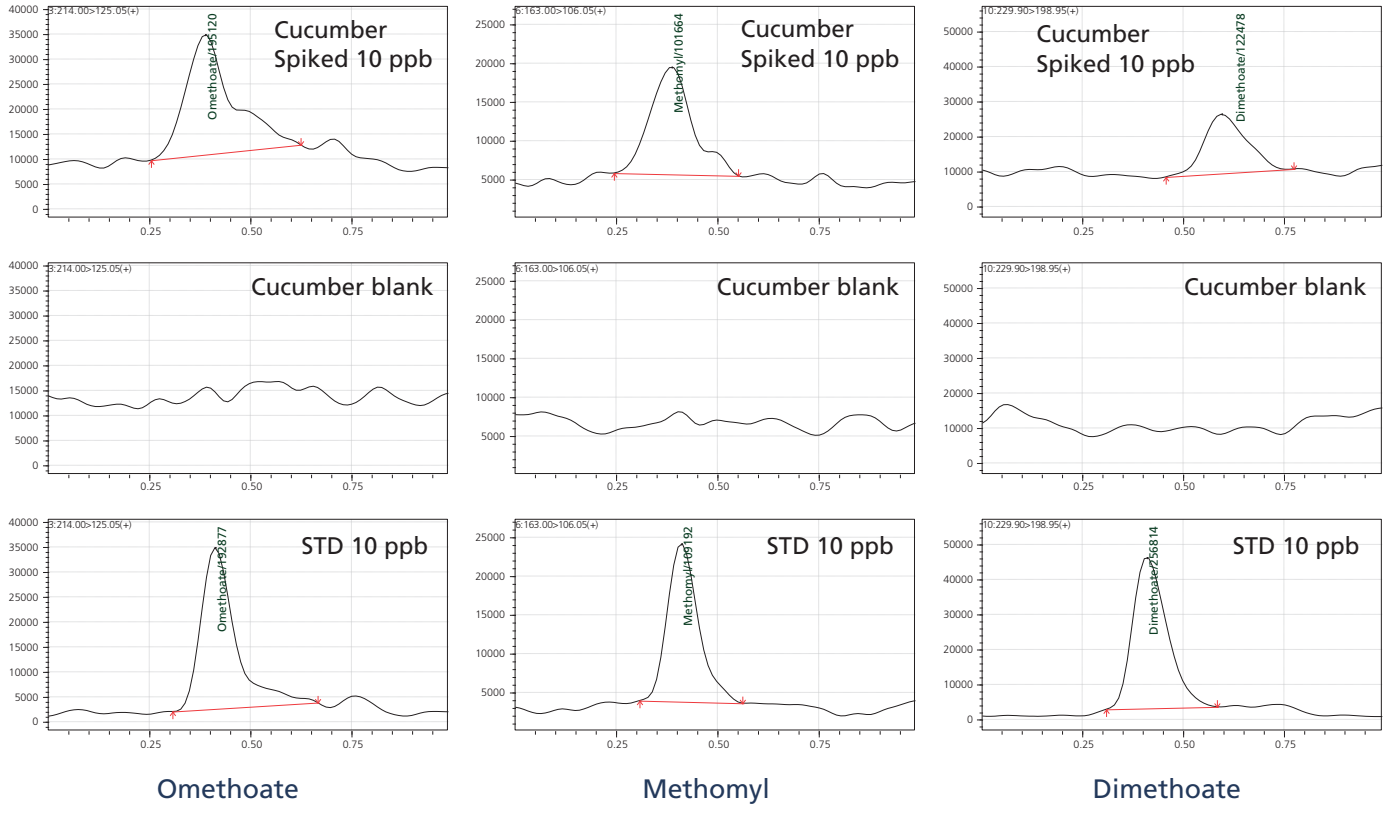

Figure 5 Measurement results of the matrix sample spiked with 10 ppb standards

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Conclusions

- DCBI-MRM-based analytical workflow is presented as high-throughput and robust measurement for agricultural pesticides.
- DCBI-MS approach enables screening analysis of short time.
- We performed the optimization of approximately 40 pesticides and obtained MRM parameters for each compound with DCBI analysis.
- The results demonstrate that simultaneous MRM analysis with ultra-fast MRM acquisition instrument and direct ionization technique improves the throughput for analysis of pesticides in agricultural sample.

References

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DCBI+LCMS-8050

Disclaimer: Shimadzu LCMS-8040, LCMS-8050 and DCBI are intended for Research Use Only (RUO). Not for use in diagnostic procedures.

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