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Fast screening of pesticides in foods and agricultural products with probe electrospray ionization (PESI) tandem mass spectrometry

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Introduction

Pesticides screening in food and agricultural products have been intensively emphasized due to the increasing food safety requirement. Recently, high resolution mass has been thought to a promising screening method, but it is very costly. Pesticides usually have broad polar range and both GCMS and LCMS methods should be used for their determination. Probe electrospray ionization (PESI) source, as an ambient ionization technique, which could be used for the determination of both polar and semi-polar compounds. Meanwhile, as an in situ ionization, PESI source usually needs less sample pretreatments. In this study, 80 pesticides are selected as research targets, which are commonly monitored in vegetables every year in China. A PESI-MS/MS approach is developed aiming at both high throughput and quantification using MRM acquisition.

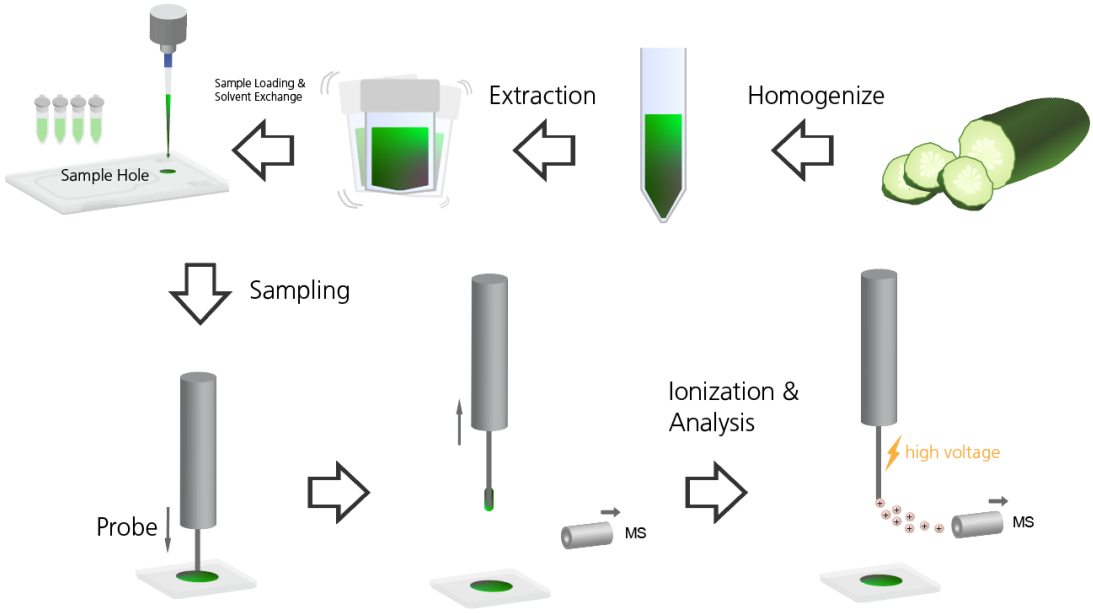

Figure 1 Sample pretreatment flow and schematic diagram of PESI

Material and Methods

Commercially available pesticides were used for this experiment. Standards of pesticides were diluted with water / isopropanol = 1/1 to an appropriate concentration and then analysed by DPiMS-8060. The water / isopropanol (1/1) solution consisted of 2 mM ammonium acetate buffer and 0.2% formic acid. The commercially available pesticides were used for the confirmation of MS spectrum and the optimization of MRM conditions.
Automated MRM parameter optimization with both APCI and ESI source were carried out by flow injection analysis of authentic standards with a function of the LabSolutions LCMS control software. The DPiMS-8060 consisted of PESI source (Shimadzu) and a triple quadrupole mass spectrometer (LCMS-8060, Shimadzu).

For sample pretreatment, 1.5 kg of fresh cucumber was pulverized with a fruit and vegetable processing machine (AUX-20B, Aux) for 3 min, and stored in 50 ml polyethylene centrifuge tube for use. 10 (±0.01) g sample were put in a 50 ml centrifuge tube, 5ml ultrapure water and 10 ml of acetonitrile (5% acetic acid) were added and then vortexed for 3min. Afterwards, 4g Mg_2SO_4 and 1g NaCl were added and vortexed for another 3min. Finally, the sample was centrifuged at 4200 rpm for 5 min and supernatant was stored for use.

For sample analysis, 10 µl of the supernatant was loaded in the sample plate and after evaporation at room temperature (ca.10mins), 10 µl of the water / isopropanol was added in the same sample plate.

Table1 Instruments Parameters for DPiMS-8060

PESI	LCMS-8060
Ionization Outage time: 200 msec	Desolvent line: 200 ℃
Take sample time: 50 msec	Heat block: 30 ℃
Discharge voltage: 2.3 kV(+)/-3.0 kV(-)	Sample amount: 10 µL
Cleaning time: 0.05 min(+)/0.05 min(-)	MRM method: 0.075 min/5 pesticides
Cycle time of probe: 2.78 Hz	Switch time: 1 msec
Ionization time: 250 msec	Residence time: 2 msec

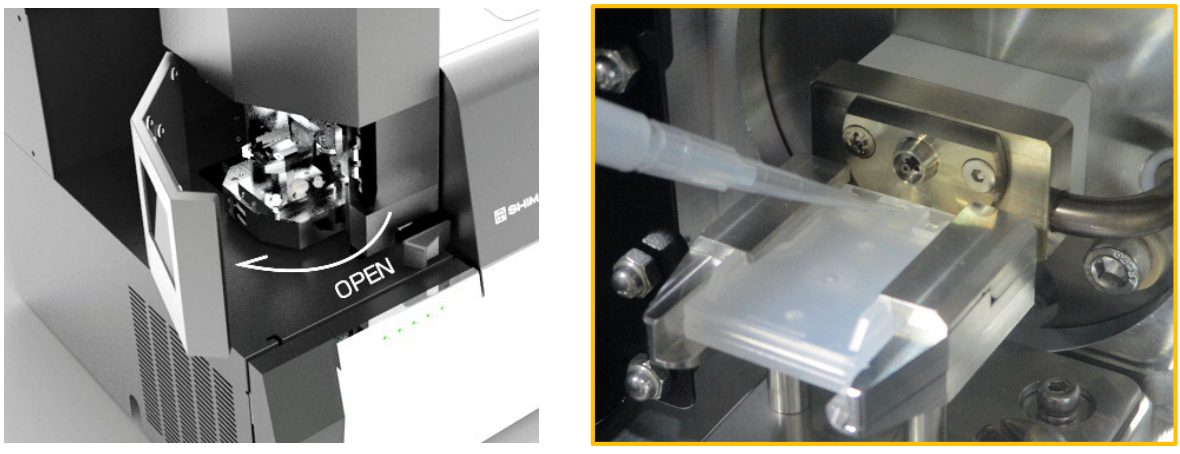

Figure 2 Injection mode for DPiMS-8060

Results

Ionization confirmation and sensitivity check

Automated MRM parameter optimization with ESI or APCI source were carried out by flow injection analysis with an embedded function of Labsolutions. Afterwards, ionization confirmation of 80 pesticides was applied using DPiMS-8060. Fortunately, among the 80 pesticides, 74 compounds can be confirmed by DPiMS-8060 in water/isopropanol (1/1) solution. The unconfirmed compounds include dicofol, fugiclor and hexacyclohexane (4 isomers), which are usually detected with GCMS.

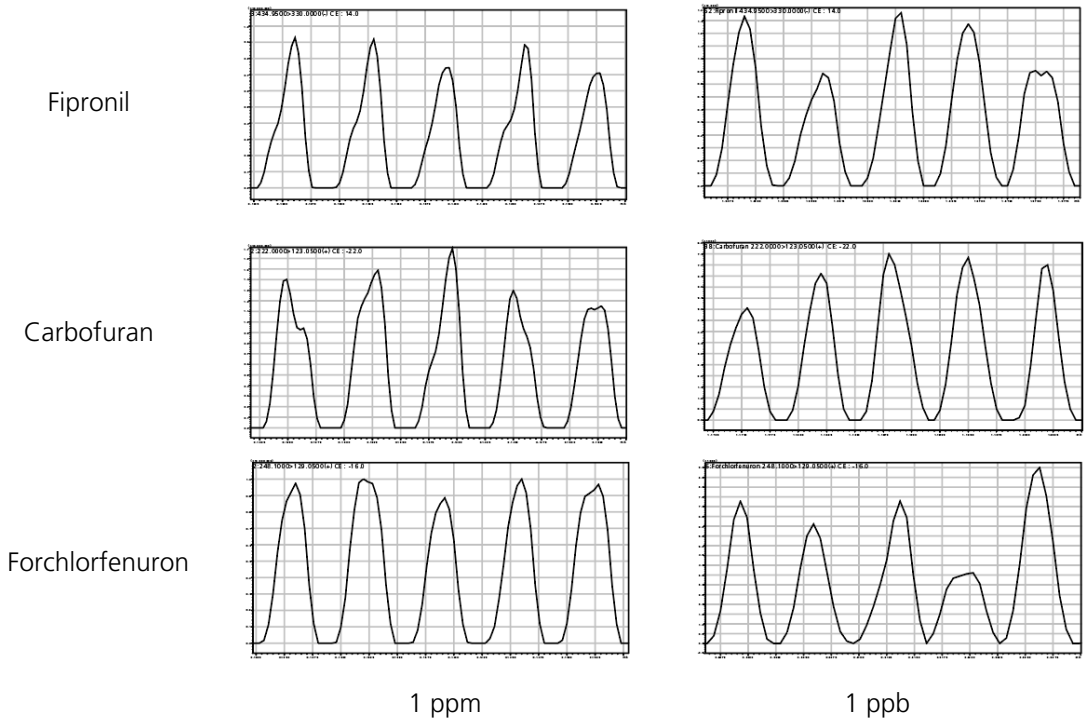

Figure 3 Typical mass chromatograms of isocarbophos, carbofuran, and forchlorfenuron
(1ppm for ionization confirmation and 1ppb for sensitivity check)

Single pesticide standard solution was prepared in 1, 10, and 100ppb for sensitivity check on DPiMS-8060. Among the 74 compounds, 27 compounds are traditionally detected with GCMS method and 47 compounds are with LCMS methods.

Generally, over 90% pesticides can be detected at lower than 10ppb, which demonstrated the high sensitivity of DPiMS-8060 (Table 2).1ppb responses of typical pesticides are shown in Figure 3.

Table 2 Linearity of typical pesticides

Traditional Method	Total	1 ppb	10 ppb	100 ppb	>100 ppb
GCMS	27	12	8	3	4
LCMS	47	45	2	0	0

Quantitative Analysis of real samples

Blank matrix was obtained the same way as normal samples. 1ppm stock solution was diluted to 5, 10, 20, 50, and 100ppb with water / isopropanol. The calibration curves were treated the same way as samples but standard solutions were added. Among the 74 compounds, the linear correlation coefficient of 36 compounds are over 0.98 (Table 3). The mass chromatogram of cucumber blank matrix with 100ppb standard are show in Figure 4. DPiMS-8060 can test 74 pesticides within 1.5 min, which is suitable for fast screening of pesticides in vegetables.For most compounds traditionally detected with GCMS, they show poor or no linearity under PESI detection. This is probably due to the matrix component strongly affect the ionization of these compounds. Especially for pyrethroids, their precursors are usually ammonium adducts. Under current pretreatment procedure, none of them could be detected.

Table 3 Linearity of typical pesticides

No.	Name	Equations	R^2
1	Methamidophos	y=10271x-3973	0.997
2	Acephate	y=242.1x+121.7	0.988
3	Omethoate	y=1324x-1757	0.995
5	Sulfone aldicarb	y=597.4x+1027.3	0.997
7	Thiamethoxam	y=436.4x+1740.4	0.998
8	Imidacloprid	y=347.2x-57.9	0.998
9	Carbofuran-3-hydroxy	y=1371x+1863	0.998
10	Dimethoate	y=503.7x+2466	0.996
11	Acetamiprid	y=335.8x+282.2	0.998
13	Aldicarb	y=271.5x+17.6	0.992
14	Carbofuran	y=545.7x+3104	0.984
15	Carbaryl	y=78.14x-327.39	0.999
16	Phosemet	y=63.11x+218.85	0.995
17	Azoxystrobin	y=858.1x+6042.2	0.999
18	Malathion	y=99.25x+10389.78	0.99
19	Dimethomorph	y=787.7x+5140.4	0.992
20	Triadimefon	y=58.36x+2903.33	0.989
21	Triazophos	y=794.9x-1005.5	0.997
24	Diazinon	y=12809x+3795	0.999
26	Phoxim	y=72.14x+3293.62	0.992
29	Difenoconazole	y=214.5x+3198.5	0.998
30	Profenofox	Y=146.2x+1198.6	0.99

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31	Tridemorph	y=911.2x+4730.8	0.998
32	Chlorpyrifos	y=47.29x+2052.55	0.998
35	Pyridaben	y=487.3x+14122.1	0.982
37	Cyromazine	y=830.1x+100260.9	0.999
40	Paclobutrazol	y=188.1x+587.0	0.997
43	Chlorantraniliprole	y=94.29x+306.3	0.997
45	Phorate	y=43.58x+343.69	0.993
46	Isofenphos-methyl	y=164.7x+868.7	0.992
60	Pyrimethanil	y=1535x+7138	0.999
64	Etofenprox	y=133.8x+6467.5	0.998
68	Fipronil	y=708.3x+13232.6	0.986
69	Fipronil Desulfinyl	y=369.8x+21422.8	0.987
70	Fipronil sulfide	y=1083x+7228	0.993
71	Fipronil Sulfone	y=1562x+13836 0.996	0.996

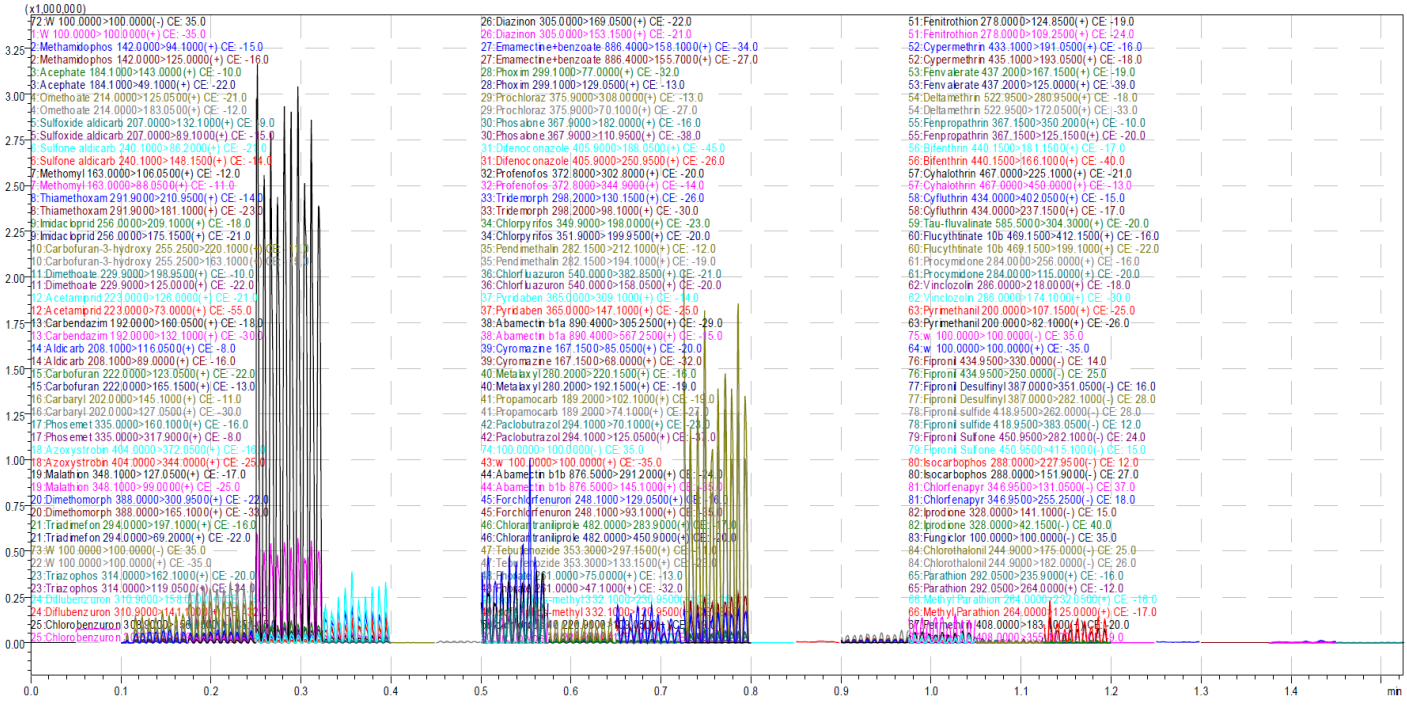

Figure 4 Typical mass chromatograms for 74 pesticides (100ppb)

10 µg/kg and 100 µg/kg spike recovery experiments were performed in cucumber. Table 4 shows the spike recovery rate for some pesticides, which demonstrate the DPiMS-8060 can be used for the fast screening analysis. For the other pesticides, the recovery rate is not within the range of 60-120%.
Another easy and simple extraction method should be developed for them.

Table 4 Pesticides spike recovery in cucumber

No.	Name	10(µg/kg) spike	100(µg/kg) spike	MRL(µg/kg)*
1	Methamidophos	122%	66.6%	50
2	Acephate	85.4%	74.5%	300
3	Omethoate	99.5%	67.4%	20
5	Sulfone aldicarb	85.6%	85.0%	20
7	Thiamethoxam	85.0%	113%	500
8	Imidacloprid	70.6%	111%	200
9	Carbofuran-3-hydroxy	73.0%	93.0%	20
10	Dimethoate	67.1%	116%	200
14	Carbofuran	89.9%	124%	20
15	Carbaryl	93.7%	102%	1000
25	Emamectine	66.0%	86.8%	20
29	Difenoconazole	79.8%	130%	200
40	Paclobutrazol	63.9%	123%	50
43	Chlorantraniliprole	95.4%	147%	20
60	Pyrimethanil	69.1%	127%	2000
64	Etofenprox	124%	81.7%	500

Conclusion

- On DPiMS-8060, the analytical work flow is presented as high-throughput and robust measurement for pesticides in agriculture products.
- MRM methods of 74 pesticides have been confirmed on DPiMS-8060, which enables fast screening analysis in short time.
- Matrix calibration curves are necessary to obtain satisfactory recovery.

References

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