

# Simultaneous Analysis of 250 Pesticide Residues in Plants by LC-MS/MS using 500 Selected Reaction Monitoring (SRM) Transitions

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## Overview

**Purpose:** To develop a multi-pesticides residue LC-MS/MS screening method for sensitive detection of 250 analytes in ginseng matrix at both positive and negative ESI mode, using a single experiment on a triple quadrupole system with a novel timed-SRM (t-SRM) setup.

**Methods:** The 250 pesticides were spiked into the ginseng matrix. The multi-pesticides mixture was separated by a 35-min gradient on a conventional C18 column, detected on a triple stage quadrupole mass spectrometer with a heated electrospray ionization source. Two SRM transitions were selected per residue.

**Results:** A sensitive and efficient LC-MS/MS method has been developed to identify approximately 250 pesticides in a single run. The Limits of Quantitation (LOQ) for most pesticides were 1 µg/kg (1 ppb) or lower.

## Introduction

The research data suggests that the pesticide residues existing in commercially grown produce can cause serious health problems when consumed. It leads to a growing public concern over the amount of pesticide residues in foods. Therefore, there is a need for an efficient analysis method to identify and confirm the pesticide residues in different food matrices.

Most commonly, residues in the matrix were detected by GC-MS or HPLC-UV. Recently LC-MS/MS is emerging as the technique of choice to assay environmental and food matrices. Especially, SRM (selected reaction monitoring) scanning mode on a triple quadrupole mass spectrometer, provides a selective and effective way to identify and quantify pesticides.

In this study, we have developed a sensitive and rapid method for the detection of approximately 250 pesticides at both positive and negative modes in a single LC-MS/MS run, by using a triple stage quadrupole mass spectrometer. The timed-SRM (T-SRM) experiment allows us to efficiently detect a large list of SRM transitions without compromising the dwell time for each SRM.

## Methods

### Sample preparation:

The pesticides included in this study are listed in Table 1. A stock mix solution of all the pesticides was spiked into a ginseng extract, to prepare at 1 µg/µl (1 ppb) and 10 µg/µl (10 ppb) of concentrations, respectively.

### LC conditions:

LC: Thermo Scientific Accela Pump and Autosampler  
Column: Thermo Scientific Hypersil GOLD PFP 100 mm x 2.1 mm, 1.9 µm

Column temperature: 45 °C

Mobile phase: A: 5mM ammonium formate in water

B: 2mM ammonium formate in methanol

Gradient: starting from 5%B to 25%B in 2 min, and increasing to 100%B in 28 min, then holding at 100%B for 5 min

Flow rate: 300 µL/min

Injection: 5 µL (with loop)

### MS conditions:

Mass spectrometer: Thermo Scientific TSQ Vantage EMR

Source: Heated ESI

Ion polarity: positive and negative

Spray voltage: 3000 V

Sheath gas pressure (N<sub>2</sub>): 65 units

Auxiliary gas pressure (N<sub>2</sub>): 15 units

Ion transfer capillary temperature: 250 °C

Scan type: SRM

CID conditions: Ar at 1.5 mTorr

Cycle time: 0.4 s

The SRM transitions that were monitored are summarized in Table 1. The setup of timed SRM can be seen in Figure 1.

## Results

Table 1 summarized all 250 pesticides detected in this study. The MS/MS parameters for some pesticides were adopted from a previous study<sup>1,2</sup>. The rest of the pesticides have been optimized individually on the TSQ Vantage™. Those parameters can be expanded to any TSQ Series triple quadrupole mass spectrometer, for the pesticides screening application.

TABLE 1. Retention times and compound-specific ESI-MS/MS parameters. (pesticides #1-#125 on left, #126-#250 on right)

Compound	RT	Parent Ion	Quantity Ion	Quantity Ion	Compound	RT	Parent Ion	Quantity Ion	Quantity Ion
Methoxychlor	1.6	142	94	125	Flurothymidol	23.3	204	130	147
Malathion	3.9	165	95	106	Disinone	16.6	205	105	109
Permethrin	5.0	185	45	72	Phenolphthalein	16.6	206	106	104
Phenolphthalein	12.8	115	145	157	Phenolphthalein	16.6	207	107	105
Propylam	11.1	180	130	138	Flurothymidol	23.3	207	107	101
Carbaryl	2.2	185	143	149	Salicylic acid	22.8	207	107	102
Fenitrothion	8.6	185	130	127	Tolmethion	18.2	208	107	105
Propoxycarb	7.0	180	160	144	Ortho-methoxy-pyridine	17.4	208	108	209
Triprozinol	8.0	180	130	163	Fluorobenzene	18.2	208	108	201
Carbendazim	6.7	192	132	160	Chlorobenzene	17.4	201	109	203
Imazacarb	10.6	194	101	127	Fluorobenzene	18.2	209	110	204
Cypermethrin	7.0	199	111	120	Fluorobenzene	18.2	210	110	102
Cyfluthrin	10.0	199	72	93	Hexachlorocyclopentadiene	17.4	210	110	102
Pyrimethanil	15.4	200	82	107	Hexachlorocyclopentadiene	17.4	210	110	102
Chlorpyrifos	12.8	201	82	107	Hexachlorocyclopentadiene	17.4	210	110	102
Thiodiazinon	8.0	200	131	175	Hexachlorocyclopentadiene	17.4	210	110	102
Carbaryl	10.0	200	127	145	Hexachlorocyclopentadiene	17.4	210	110	102
Diazinon	3.3	200	114	129	Hexachlorocyclopentadiene	17.4	210	110	102
Aldicarb	3.4	207	89	132	Hexachlorocyclopentadiene	17.4	210	110	102
Imidacloprid	11.6	207	72	103	Hexachlorocyclopentadiene	17.4	210	110	102
Fluorocarb	13.0	200	109	151	Hexachlorocyclopentadiene	17.4	210	110	102
Metidathion	6.9	200	80	116	Hexachlorocyclopentadiene	17.4	210	110	102
Subacarb	13.0	200	91	109	Hexachlorocyclopentadiene	17.4	210	110	102
Azinphosmethyl	8.0	209	137	152	Hexachlorocyclopentadiene	17.4	210	110	102
Propoxycarb	8.2	209	101	168	Hexachlorocyclopentadiene	17.4	210	110	102
Chlorpyrifos	14.2	211	136	140	Hexachlorocyclopentadiene	17.4	210	110	102
Chlorpyrifos	11.6	210	142	153	Hexachlorocyclopentadiene	17.4	210	110	102
Omethoate	3.0	214	105	133	Hexachlorocyclopentadiene	17.4	210	110	102
Chlorpyrifos	11.6	210	142	153	Hexachlorocyclopentadiene	17.4	210	110	102
Metidathion	10.0	210	99	120	Hexachlorocyclopentadiene	17.4	210	110	102
Metidathion	7.0	210	110	121	Hexachlorocyclopentadiene	17.4	210	110	102
Permethrin	4.0	210	79	105	Hexachlorocyclopentadiene	17.4	210	110	102
Permethrin	3.2	210	97	125	Hexachlorocyclopentadiene	17.4	210	110	102
Thiodiazinon	10.6	210	102	152	Hexachlorocyclopentadiene	17.4	210	110	102
Formetanidolol	12.2	222	120	165	Hexachlorocyclopentadiene	17.4	210	110	102
Subacarb	8.0	222	81	143	Hexachlorocyclopentadiene	17.4	210	110	102
Methoxychlor	1.6	230	100	145	Hexachlorocyclopentadiene	17.4	210	110	102
Carbendazim	6.7	230	100	145	Hexachlorocyclopentadiene	17.4	210	110	102
Acetamiprid	7.0	230	90	138	Hexachlorocyclopentadiene	17.4	210	110	102
Metidathion	3.0	230	80	108	Hexachlorocyclopentadiene	17.4	210	110	102
Monrothion	4.0	234	127	193	Hexachlorocyclopentadiene	17.4	210	110	102
Chlorpyrifos	5.4	234	123	167	Hexachlorocyclopentadiene	17.4	210	110	102
Metoprolol	15.5	234	77	104	Hexachlorocyclopentadiene	17.4	210	110	102
Carbaryl	3.0	234	80	107	Hexachlorocyclopentadiene	17.4	210	110	102
Aldicarb	3.4	234	89	132	Hexachlorocyclopentadiene	17.4	210	110	102
Cypermethrin	7.0	234	93	108	Hexachlorocyclopentadiene	17.4	210	110	102
Methoxychlor	1.6	234	100	145	Hexachlorocyclopentadiene	17.4	210	110	102
Chlorpyrifos	5.4	234	123	167	Hexachlorocyclopentadiene	17.4	210	110	102
Metoprolol	15.5	234	77	104	Hexachlorocyclopentadiene	17.4	210	110	102
Carbaryl	3.0	234	80	107	Hexachlorocyclopentadiene	17.4	210	110	102
Aldicarb	3.4	234	89	132	Hexachlorocyclopentadiene	17.4	210	110	102
Cypermethrin	7.0	234	93	108	Hexachlorocyclopentadiene	17.4	210	110	102
Methoxychlor	1.6	234	100	145	Hexachlorocyclopentadiene	17.4	210	110	102
Chlorpyrifos	5.4	234	123	167	Hexachlorocyclopentadiene	17.4	210	110	102
Metoprolol	15.5	234	77	104	Hexachlorocyclopentadiene	17.4	210	110	102
Carbaryl	3.0	234	80	107	Hexachlorocyclopentadiene	17.4	210	110	102
Aldicarb	3.4	234	89	132	Hexachlorocyclopentadiene	17.4	210	110	102
Cypermethrin	7.0	234	93	108	Hexachlorocyclopentadiene	17.4	210	110	102
Methoxychlor	1.6	234	100	145	Hexachlorocyclopentadiene	17.4	210	110	102
Chlorpyrifos	5.4	234	123	167	Hexachlorocyclopentadiene	17.4	210	110	102
Metoprolol	15.5	234	77	104	Hexachlorocyclopentadiene	17.4	210	110	102
Carbaryl	3.0	234	80	107	Hexachlorocyclopentadiene	17.4	210	110	102
Aldicarb	3.4	234	89	132	Hexachlorocyclopentadiene	17.4	210	110	102
Cypermethrin	7.0	234	93	108	Hexachlorocyclopentadiene	17.4	210	110	102
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Chlorpyrifos	5.4	234	123	167	Hexachlorocyclopentadiene	17.4	210	110	102
Metoprolol	15.5	234	77	104	Hexachlorocyclopentadiene	17.4	210	110	102
Carbaryl	3.0	234	80	107	Hexachlorocyclopentadiene	17.4	210	110	102
Aldicarb	3.4	234	89	132	Hexachlorocyclopentadiene	17.4	210	110	102
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Metoprolol	15.5	234	77	104	Hexachlorocyclopentadiene	17.4	210	110	102
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Metoprolol	15.5	234	77	104	Hexachlorocyclopentadiene	17.4	210	110	102
Carbaryl	3.0	234	80	107	Hexachlorocyclopentadiene	17.4	210	110	102
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