# Multi-residue Pesticide Analysis of Botanical Dietary Supplements using SPE Cleanup and GC-Triple Quadrupole MS/MS*

## UCT Part Numbers

**ECPSACB256**
500 mg PSA,
250 mg GCB/6 mL cartridge

**ECMSSC50CT-MP**
4000 mg $MgSO_4$
1000 mg NaCl


## Summary:

A screening method for the analysis of 310 pesticides, isomers of organohalogen, organophosphorus, organonitrogen and pyrethroid pesticide metabolites in a variety of dried botanical dietary supplements, spices, medicinal plants, herbals, teas, and phytomedicines is described. Acetonitrile/water is added to the dried botanical along with anhydrous $MgSO_4$ and NaCl for extraction. This is followed by clean-up using a tandem cartridge SPE cartridge consisting of graphitized carbon black (GCB) and primarysecondary amine sorbent (PSA). Pesticides in the study were spiked at 10, 25, 100 and 500 µg/kg. Mean pesticide recoveries were 97%, 91%, 90% and 90%. Percent RSDs were 15%, 10%, 8%, and 6% respectively.


**Some Pesticides Screened by this Method**

| | | |
|---|---|---|
| Azoxystrobin | Chlorpyrifos | DDT |
| Diazinon | Dimethomorph | Hexachlorobenzene |
| Hexachlorocyclohexanes | methamidophos | Pentachloroaniline |
| Pentachloroanisole | Pentachlorobenzene | Pentachlorothioanisole |
| Quinoxyfen | Quintozene | Tecnazene |
| Tetraconazole | Tetramethrin | |

Prepare stock solutions of individual standards by dissolving 25–100 mg of pesticide in 25 mL of toluene

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## Procedure:

### 1. Botanical Preparation

a) Add dry botanical powder (1.00 ± 0.02 g) to the 50 mL centrifuge tube
b) Add 10 mL water and 10 mL extraction solvent (60 µg/L of the internal standard, tris-(1,3-dichloroisopropyl)phosphate in acetonitrile)
c) Shake vigorously to insure the botanical is completely wetted
d) Allowed to stand for 15 minutes
e) Add the contents of **ECMSSC50CT-MP** pouch to each centrifuge tube
f) Shake vigorously after addition to disperse the salts
g) Shake samples vigorously for 1 minute

**Note:** Centrifuge at 4500 rpm (4200g) x 5 min

### 2. Solid-phase Cleanup

a) Condition **ECPSACB256** cartridge(s) on a manifold using 3 x 6 mL acetone
b) Do not let cartridge go to dryness after last acetone wash
c) Insert 15 mL disposable centrifuge tubes in the vacuum manifold
d) Add a layer of anhydrous sodium sulfate to the top of each cartridge
e) Add a 1.25 mL aliquot of the extract to the cartridge
f) Allow to percolate through the cartridge. Apply low vacuum if needed
g) Rinse cartridge with 1 mL of acetone and continue to collect

### 3. Cartridge Elution

a) Elute cartridge with 12 mL of 3:1 acetone:toluene
b) Reduce extract to approximately 100 µL with a gentle $N_2$ stream in a water bath at 50-55 °C
c) Add 0.5 mL toluene, QC standards (50 µL of deuterated polycyclic aromatic hydrocarbons mixture, 500 µg/L), and 25 mg of magnesium sulfate
d) Centrifuge at 3500 rpm x 5 min
e) Divide the toluene extracts between two GC vials with 250 µL vial inserts keeping one vial as a reserve spare

### 4. GC-MS/MS Analysis

| GC-MS/MS Parameters | |
|---|---|
| **GC** | TRACE Ultra Gas Chromatograph |
| **MS** | TSQ Quantum triple quadrupole |
| **Autosampler** | TriPlus (Thermo Fisher Scientific) |
| **Column** | 30 m x 0.25 188 mm id HP-5MS fused silica capillary column (Agilent Technologies, Santa Clara, CA, USA) |
| **Guard Column** | deactivated 5 m × 0.25 mm I.D, Restek Corp., Bellefonte, PA |
| **Oven Temperature** | Program, initial 105° C for 3 min, 130° C/ @ 10° C/min, 200° C @ 4°C/min, 290° C @ 8° C/min. Hold 6 min. |
| **Column Flow Rate** | 1.4 mL/min He |
| **Injector** | PTV 100° C for 0.05 min, ramp 12° C/sec to 280° C |
| **Autosampler** | TriPlus Thermo Fisher Scientific |
| **Auto-sampler Temperature** | 10 °C |
| **Injection Volume** | 2.0 µL splitless mode |
| **Injection Liner** | 2 mm id x 120 mm open baffled fused silica deactivated |
| **Ion Source & Transfer T** | 250 °C and 280 °C, respectively |
| **Electron Multiplier V** | auto-tune approx. 1400 V |
| **Ar Collision gas** | 1.5 mTorr |
| **Cycle Time** | 0.5 sec |
| **Q1 entrance mass width (FWHM)** | 0.7 amu |
| **Stock pesticide standards** | Full scan 50-550 m/z |

There is not complete agreement over which transitions for a given pesticide are optimal for foods or dietary supplements. Reference information on SRM transitions for these analytes is provided in references.[1-4]

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## Representative Recoveries (RSD) and Percent LOQ's in Each Botanical Matrix

Representative Recoveries (mean, n=4) ± percent relative standard deviation (RSD) for pesticides by botanical, at 10 and 500 µg/kg and the number not detected (ND) at each fortification concentration

| Botanical | | 10 µg/kg | ND | 500 µg/kg | ND |
|---|---|---|---|---|---|
| Astralagus | Astragalis membranaceus | 94 ± 13 | 68 | 92 ± 3 | 15 |
| Bitter Orange Peel | Citrus aurantium | 112 ± 15 | 63 | 90 ± 5 | 23 |
| Black Cohosh Root | Cimicifuga racemosa | 84 ± 11 | 39 | 82 ± 4 | 14 |
| Chamomile | Matricaria chamonmilla | 87 ± 11 | 68 | 91 ± 4 | 29 |
| Cinnamon | Cinnamom verum | 63 ± 26 | 149 | 101 ± 7 | 9 |
| Comfrey Root | Symphytum officinale | 89 ± 18 | 69 | 83 ± 10 | 15 |
| Dong Quai | Angelica sinensis | 107 ± 19 | 156 | 97 ± 8 | 16 |
| Echinacea | Echinacea purpurea | 97 ± 16 | 61 | 101 ± 8 | 11 |
| Fenugreek | Trigonella foenum | 99 ± 14 | 82 | 81 ± 7 | 11 |
| Garlic | Allium sativum | 98 ± 18 | 78 | 87 ± 6 | 15 |
| Ginger | Zingiber | 103 ± 14 | 211 | 104 ± 6 | 59 |
| Gingko Biloba | Ginko biloba | 99 ± 16 | 89 | 80 ± 7 | 14 |
| Ginseng | Panax quinquefolius | 88 ± 11 | 64 | 86 ± 6 | 8 |
| Green Tea | - | 91 ± 13 | 43 | 79 ± 6 | 11 |
| Hoodia | Hoodia gordonii | 104 ± 19 | 94 | 93 ± 5 | 20 |
| Hops | Humulus lupulus | 111 ± 10 | 233 | 102 ± 6 | 53 |
| Jasmine | Jasminum odoratissmum | 100 ± 14 | 65 | 84 ± 4 | 10 |
| Kava Kava | Piper methysticum | 111 ± 10 | 164 | 100 ± 4 | 59 |
| Licorice Root | Glycyrrhiza glabra | 93 ± 14 | 43 | 87 ± 6 | 15 |
| Milk Thistle | Silybum marianum | 90 ± 13 | 73 | 77 ± 10 | 17 |
| Psyllium | Plantago psyllium | 99 ± 11 | 39 | 95 ± 4 | 16 |
| Saw Palmetto | Serenoa serrulata | 103 ± 13 | 111 | 98 ± 7 | 13 |
| St. John's Wort | Hpericum perforatum | 93 ± 10 | 100 | 83 ± 6 | 16 |
| Valerian Root | Valeriana wallichii | 101 ± 19 | 68 | 94 ± 10 | 13 |

* Adapted from, Douglas G. Hayward, Jon W. Wong, Feng Shi, Kai Zhang, Nathaniel S. Lee, Alex L. DiBenedetto, & Mathew J. Hengel. "Multi-residue Pesticide Analysis of Botanical Dietary Supplements using Salt-out Acetonitrile Extraction, Solidphase extraction cleanup column and Gas Chromatography-Triple Quadrupole Mass Spectrometry" DOI: 0.1021/ac400481w

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## References:

[1] Pang, G. F.; Fan, C. L.; Liu, Y. M.; Cao, Y. Z.; Zhang, J. J.; Li, X. M.; Li, Z. Y.; Wu, Y. P.; Guo, T. T J. AOAC Int. 2006, 89, 740– 771

[2] Walorczyk, S.; Gnusowski, B. J. Chromatogr. A. 2006, 1128(1-2), 236-243

[3] Okihashi, M.; Takatori, S.; Kitagawa, Y.; Tanaka, Y. J. AOAC Int. 2007, 90(4), 1165-1179

[4] Frenich, A. G.; González-Rodríquez, M. J.; Arrebola, F. J.; Vidal, J. L. M. Anal. Chem.2005, 77, 4640-4648

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