

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 MgSO₄
1000 mg NaCl

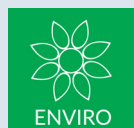
Summary:

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 MgSO₄ 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
Quinoxifen	Quintozone	Tecnazene
Tetraconazole	Tetramethrin	

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



Procedure:

1. Botanical Preparation

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

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

2. Solid-phase Cleanup

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

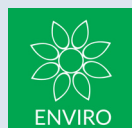
3. Cartridge Elution

- Elute cartridge with 12 mL of 3:1 acetone:toluene
- Reduce extract to approximately 100 µL with a gentle N₂ stream in a water bath at 50-55 °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
- Centrifuge at 3500 rpm x 5 min
- 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 x 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.¹⁴

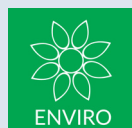


Representative Recoveries (RSD) and Percent LOQ's in Each Botanical Matrix

Representative Recoveries (mean, n=4) $\pm$ percent relative standard deviation (RSD) for pesticides by botanical, at 10 and 500 $\mu\text{g}/\text{kg}$ and the number not detected (ND) at each fortification concentration

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