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Improved Detection of Pesticide Residues in Botanicals by LCMS

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Introduction

Pesticides and other chemicals are used in the production of many agricultural products, including botanicals for use as dietary supplements. Supplements are widely used but their raw materials, often sourced from remote locations, are subjected to fewer regulatory controls than staple foods. To ensure quality the US FDA requires identity and quality testing, but most botanicals do not have specific regulations. To analyze complex botanicals for residual chemicals such as pesticides, LC-MS-MS is needed for high sensitivity, high confidence results. We developed an LCMS method with improved detection sensitivity for chemical residues in botanicals.

Photo credits: Echinacea, Giancarlo Dessì; Cayenne, H. Zell; Valerian, Lairich Rig; Ginseng, National Institute of Korean Language; Tumeric, Simon A. Eugster; Passionflower, Bob Peterson; St Johns Wort, Glyn Baker. All photos obtained through wikimedia commons under creative commons attribution-share alike 2.0 or higher

Echinacea *E. purpurea*

Passionflower (tea) *Passiflora sp.*

Cayenne *Capsicum annuum*

Valerian *Valeriana officinalis*

St. Johns Wort *Hypericum perforatum*

Tumeric
Curcuma Longa

Korean Ginseng *Panax ginseng*

Figure 1 A selection of popular dietary supplements tested. Various parts of the above-pictured plants may be used in actual dietary supplement formulations.

Method

Representative samples of powdered botanicals were removed from their gelatin capsules, homogenized and extracted with acetonitrile accompanied by shaking and sonication. Samples were additionally cleaned up using dispersive solid phase extraction to remove unwanted matrix components. Analysis was carried out by LC-MS-MS using a triple quadrupole mass spectrometer. The mass spectrometer interface parameters were carefully adjusted to improve the signal for the majority of the analytes. Spiking experiments were used to determine recovery and matrix-matched standards were used to prepare calibration curves.

Table 1 Instrument parameters used for analysis

LC Column	: Raptor ARC18 (2.1×150 mm, 2.7 µm)
Mobile Phase A	: 0.1% Formic Acid with 5 mM Am. Formate
Mobile Phase B	: Methanol
Flow Rate	: 0.5 mL/min
Probe Voltage	: +0.5 kV or –0.5kV
Interface Temp	: 100 ˚C
Nebulizing Gas	: 3 L/min
Drying Gas	: 10 L/min
DL Temp	: 100 ˚C
Heat Block Temp	: 100 ˚C

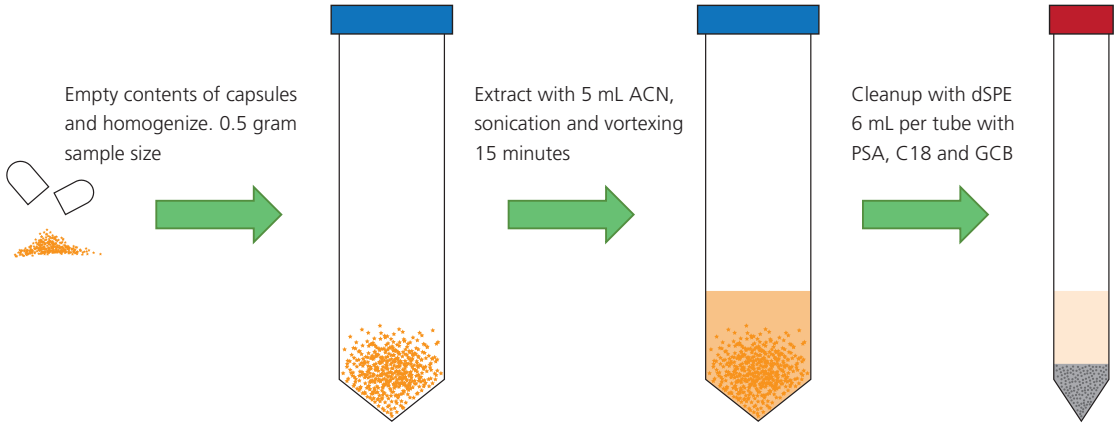

Figure 2 Sample preparation of botanicals for LC-MS analysis

Results and Discussion

Eight popular botanical supplements were selected for testing, including Cayenne, Valerian, Passionflower tea, Korean Ginseng, St. John's Wort, Tumeric and two varieties of Echinacea. The Tea and Echinacea variety 1 were labeled as organic, while the other supplements were not labeled as organic. For each sample, a single-point standard addition sample at 500 ng/g dried material was prepared in addition to check matrix-specific effects. Compared with a conventional method, we found significant improvement in instrument response for many analytes by careful adjustment of interface temperature and spray voltage. For quantitation, matrix matched calibration curves were linear within the quantitation limits established for each compound, which was compound dependent. Detection limits and quantitation limits were required to have 3:1 and 10:1 signal to noise respectively, and quantitation limits were required to have less than 20% RSD in triplicate injections. Using our newly developed method, we are able to characterize the extent of residual pesticides t in popular botanicals.

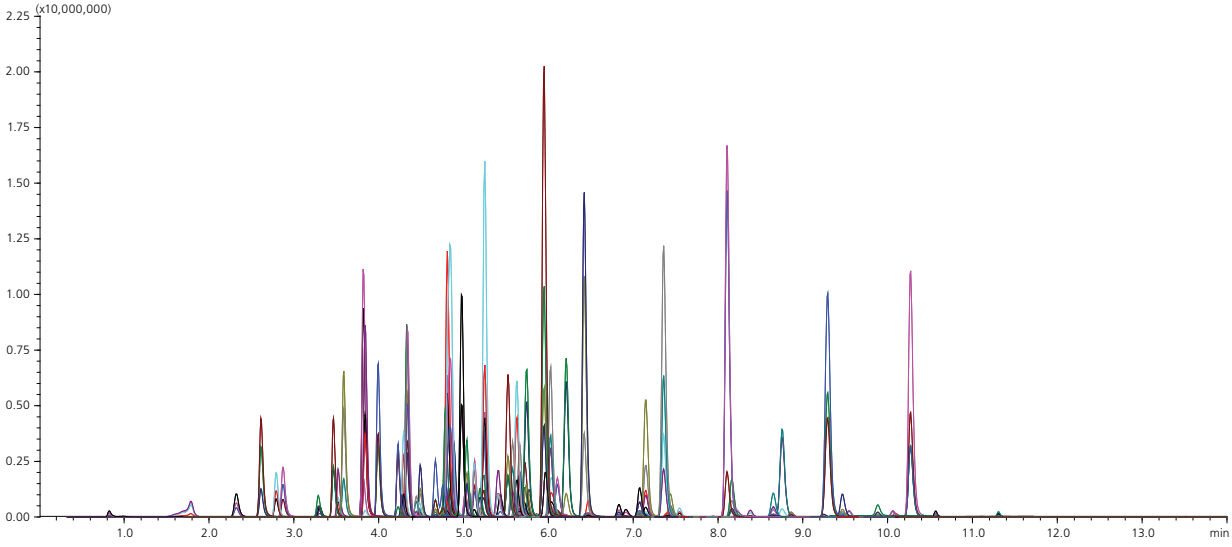

Figure 3 Representative chromatogram of pesticides spiked into a sample of Korean Ginseng at the 500 ng/g of dried material level.

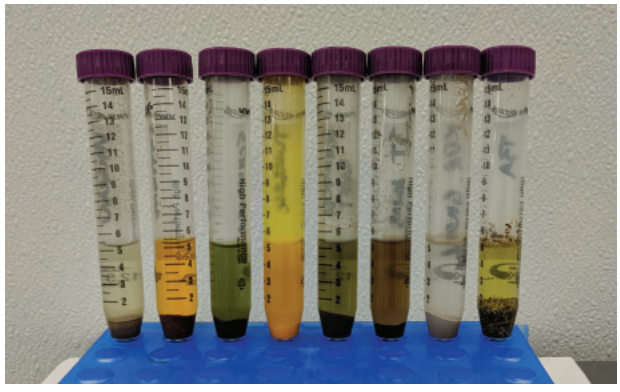

Figure 4 Acetonitrile extracts (before dSPE cleanup) of various botanicals. From left: Valerian, Cayenne, Echinacea-1, Tumeric, Echinacea-2, St. John's Wort, Korean Ginseng, and Passionflower Tea.

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Table 2 Chemical residues detected in botanical extracts. Values reported in ng/g dry material.

	Cayenne	Echinacea-1	Echinacea-2	Korean Ginseng	St. John's Wort	Passionflower tea	Tumeric	Valerian root
Azoxystrobin	15	ND	ND	7	ND	ND	ND	ND
Carbaryl	ND	ND	ND	ND	ND	35	ND	ND
Carbofuran	3.7	ND	ND	ND	ND	ND	ND	ND
Chlorpyrifos	ND	ND	ND	ND	ND	ND	9.4	ND
Cypermethrin	140	ND	ND	ND	ND	ND	ND	ND
Dimethomorph	ND	ND	ND	36	ND	ND	ND	ND
Imidacloprid	11	ND	ND	ND	ND	ND	ND	ND
Metalaxyl	ND	ND	ND	ND	ND	ND	8.3	ND
Methoprene	196	ND	ND	ND	ND	ND	ND	ND
Novaluron	24	ND	ND	ND	ND	ND	ND	ND
Propiconazole	ND	ND	ND	24	ND	ND	ND	ND
Pyraclastrobin	6.5	ND	ND	ND	ND	ND	ND	ND
Tebuconazole	59	ND	ND	4.8	ND	ND	ND	ND
Trifloxystrobin	10	ND	ND	ND	ND	ND	ND	ND

Table 3 List of compounds measured and limits of quantitation in ng/g.

Abamectin	30	Daminozide	15	Hexythiazox	15	Propiconazole	60
Acephate	5	Deltamethrin	30	Imazalil	10	Propoxur	2
Acequinocyl	60	Diazinon	<2	Imidacloprid	4	Pyraclostrobin	10
Acetamiprid	<2	Dichlorvos	15	Kresoxim-methyl	4	Pyrethrin I	100
Aldicarb	<2	Dimethoate	<2	Malathion	2	Pyridaben	2
Allethrin	50	Dimethomorph	5	Metalaxyl	2	Resmethrin	35
Azoxystrobin	4	Dinotefuran	2	Methiocarb	4	Spinetoram	2
Bifenazate	2	Dodemorph	4	Methomyl	<2	Spinosad	<2
Bifenthrin	4	Endosulfan-sulfate	4	Methoprene	50	Spirodiclofen	10
Boscalid	4	Ethoprophos	2	Mevinphos	4	Spiromesifen	20
Buprofezin	<2	Etofenprox	4	MGK-264	500	Spirotetramat	2
Carbaryl	10	Etoxazole	<2	Myclobutanil	10	Spiroxamine	2
Carbofuran	<2	Fenhexamid	20	Naled	2	Tebuconazole	2
Chlorantraniliprole	2	Fenoxycarb	2	Novaluron	15	Tebufenozide	5
Chlorpyrifos	10	Fenpyroximate	10	Oxamyl	2	Teflubenzuron	15
Clofentazine	4	Fensulfothion	5	Paclobutrazol	2	Tetrachlorvinphos	4
Clothianidin	4	Fenthion	10	Permethrin	10	Tetramethrin	4
Coumaphos	4	Fenvalerate	100	Phenothrin	10	Thiacloprid	<2
Cyantraniliprole	2	Fipronil	2	Phosmet	10	Thiamethoxam	<2
Cyfluthrin	500	Flonicamid	25	Piperonyl butoxide	5	Thiophanate-methyl	5
Cypermethrin	60	Fludioxonil	2	Pirimicarb	2	Trifloxystrobin	<2
Cyprodinil	10	Fluopyram	2	Prallethrin	10		

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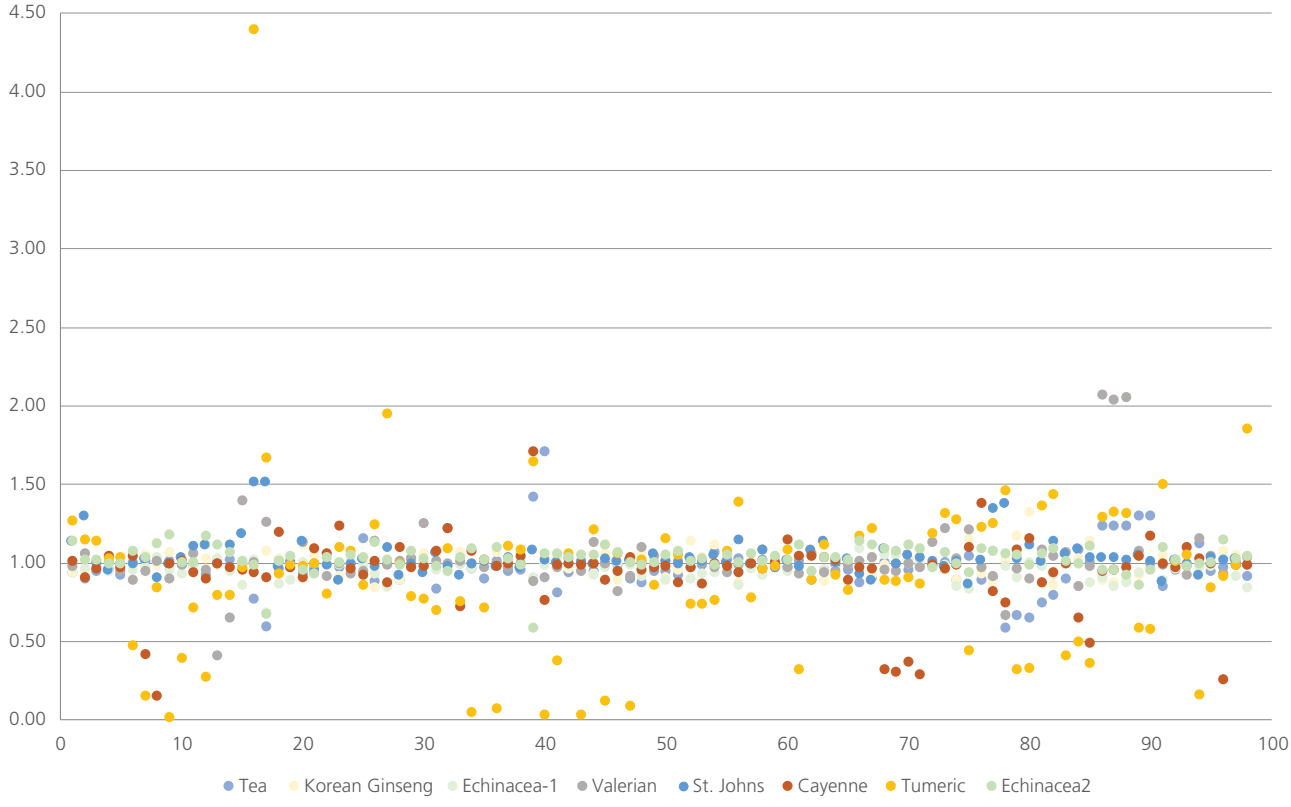

Figure 5 Recovery for each analyte in a 500 ng/g spike of each sample. Tumeric and Cayenne had the greatest number of analytes with low recovery, due to signal suppression.

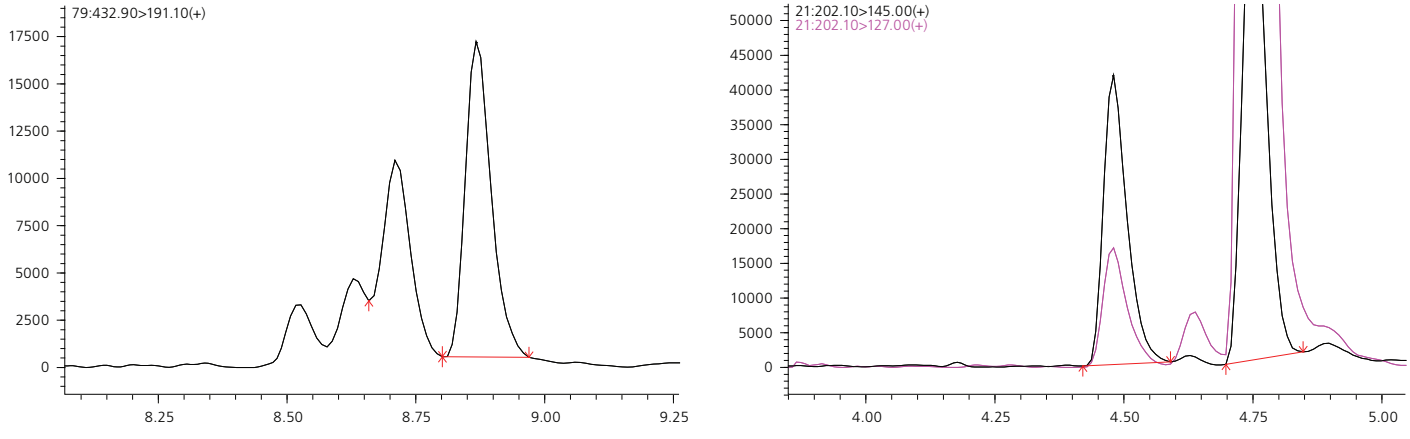

Figure 6 (Left) Cypermethrin (four isomers) detected in Cayenne sample. (Right) Carbaryl detected in organic passionflower tea sample.

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Conclusion

We developed a high performance method for sensitive detection of pesticides in popular botanical supplements with a simple sample preparation and applied the method to measure pesticides in selected botanical products offered for retail sale. We found matrix effects to be minimal with the exception of Tumeric and Cayenne. For these matrices, additional sample cleanup may be useful to minimize signal suppression by the matrix.

Several pesticides were detected in some of the dietary supplements. Cayenne had the greatest number of detections and with the highest levels approaching 200 ng/g. Significantly, the Passionflower tea, which was labeled as organic, was found to contain 35 ng/g carbaryl. Our rapid, sensitive, and selective method is well-suited to high throughput detection of pesticide residues in popular botanical products.

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