

High sensitivity analysis of pesticides in dried hops cones and hops pellets by liquid chromatography-triple quadrupole mass spectrometry Jeff Dahl and Robert Clifford Shimadzu Scientific Instruments, Columbia, Md.

Introduction

Hops (Humulus lupulus) are an essential ingredient in brewing beer but agricultural production of this plant is threatened by insects and other dangers. Pesticides and other chemicals may be used to protect hops and increase yield, but certain chemical residues may be harmful to consumers. Chemical residues may also have unintended negative effects on non-target insects such as honeybees. Sensitive and selective detection of chemical residues in hops is necessary to ensure protection of consumers and the environment. Methods using LC-MS provide efficient and effective detection of chemical residues in a complex sample matrix such as hops. We have developed an LC-MS method for detection of over 150 analytes in hops and carried out a market survey of over 50 different hops pellets samples.

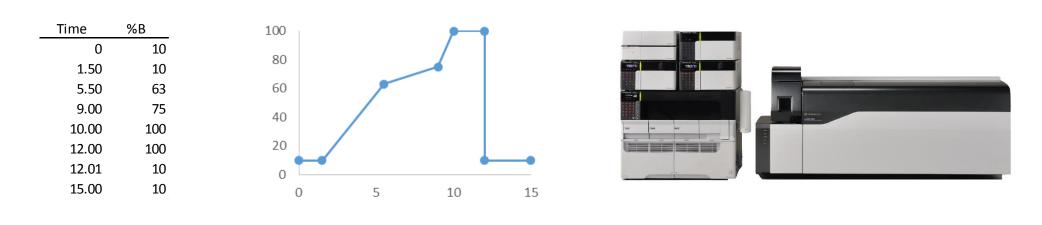


Hops pellets

Figure 1 Sample preparation procedure

Method

Test portions of hops pellets (1.5 grams) were homogenized with a SPEX Genogrinder and extracted using a modified QuEChERS extraction with dispersive SPE cleanup (Restek cat no. 26237 and 26243). Detection was carried out by LC-MS-MS using a Shimadzu Prominence HPLC with LCMS-8050 triple quadrupole mass spectrometer. Electrospray ionization was used with continuous polarity switching to measure analytes in both modes throughout the run. Pesticide recovery was determined using spiking experiments and matrix-matched calibration curves.



LC Column Mobile Phase A	: Restek ARC-18 (2.1×100 mm, 3 µm) : 5 mM NH4OAC + 0.1% Formic Acid	Interface Temp Nebulizing Gas	: 400 °C : 3 L/min
Mobile Phase B	: Methanol	Drying Gas	: 10 L/min
LC Flow Rate	: 0.5 mL/min	DL Temp	: 250 °C
Heater Gas	: 10 L/min	Heat Block Temp	: 400 °C

Figure 1 Gradient time program (top left), LCMS-8050 (top right) and MS conditions

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Results and Discussion

The method was performed with calibration curves and quality control samples in triplicate in three different representative sample matrices to verify recovery, check interferences, and matrix effects. Recovery was in the range of 70–120% for nearly all analytes. Quantitation limits were compound dependent but established at the 20, 50, 200 or 1000 ng/gram fixed levels as appropriate. The calibration curve was established over the range of 16 to 4000 ng/gram dried pellet level.

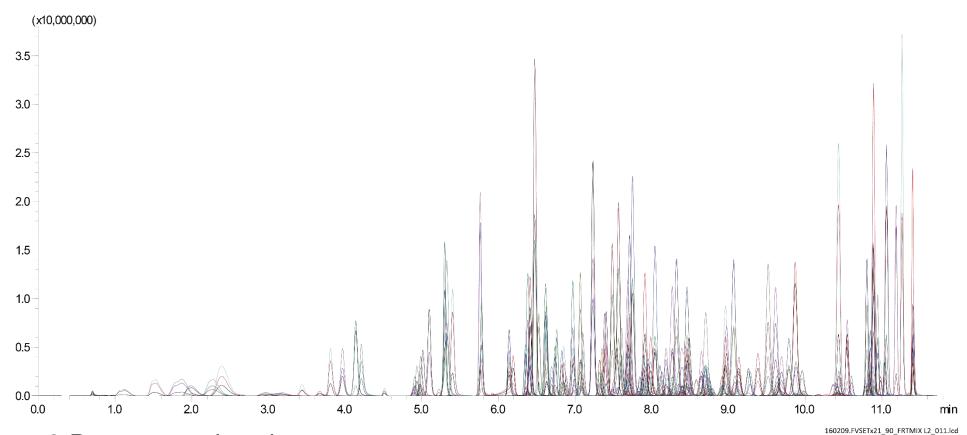


Figure 3 Representative chromatogram

Over fifty hops pellets samples were obtained from various manufacturers and represent growers from major hops-growing regions of the world. Pesticides were detected in most of the samples with the notable exception of Australia and New Zealand. A few pesticides such boscalid were detected in nearly every sample while some pesticides were found only infrequently. Certain pesticides such as azoxystrobin and myclobutanil were found with high frequency in European samples while not detected or infrequently detected in samples from North America.

3-hydroxycarbofuran	Chlorpyrifos	Ethiofencarb	Flutolanil Metalaxyl		Penconazole	Sulfentrazone
Acephate	Clethodim	Ethiprole	Flutraifol	Metconazole	Phosmet	Tebuconazole
Acetamiprid	Clofentazine	Ethoprophos	Formetanate	Methabenzthiazuron	Picoxystrobin	Tebufenozide
Aldicarb	Clothianidin	Etofenprox	Furalaxyl	Methamidophos	Piperonyl Butoxide	Tebufenpyrad
Aldicarb Sulfoxide	Cyazofamid	Etoxazole	Furathiocarb	Methiocarb	Prallethrin	Tebuthiuron
Aldoxycarb	Cycluron	Fenamidone	Hexaconazole	Methomyl	Prochloraz	Temephos
Azoxystrobin	Cyproconazole	Fenarimol	Hexaflumuron	Methoprotryne	Promecarb	Tetraconazole
Benalaxyl	Cyromazine	Fenazaquin	Hexythiazox	Methoxyfenozide	Propamocarb	Thiacloprid
Bendiocarb	Diazinon	Fenbuconazole	Imidacloprid	Metobromuron	Propargite	Thiamethoxam
Bifenazate	Dichlorvos	Fenhexamid	Indoxacarb	Metribuzin	Propiconazole	Thidiazuron
Bitertanol	Dicrotophos	Fenobucarb	Ipconazole	Mevinphos	Propoxur	Thiobencarb
Boscalid	Diethofencarb	Fenoxycarb	Iprovalicarb	MGK-264	Pyracarbolid	Thiophanate-methyl
Bromuconazole	Difenoconazole	Fenpyroximate	Isoprocarb	Monocrotophos	Pyraclostrobin	Triadimefon
Bupirimate	Diflubenzuron	Fenuron	Isoproturon	Monolinuron	Pyridaben	Triadimenol
Butafenacil	Dimethoate	Fipronil	Kresoxym-methyl	Myclobutanil	Pyriproxyfen	Trichlorfon
Carbaryl	Dimethomorph	Flonicamid	Linuron	Neburon	Quinoxyfen	Tricyclazole
Carbetamide	Dimoxystrobin	Fluazinam	Malathion	Nitenpyram	Rotenone	Trifloxystrobin
Carbofuran	Diniconazole	Fludioxonil	Mandipropamid	Novaluron	Siduron	Triflumizole
Carboxin	Dinotefuran	Flufenacet	Mefenacet	Omethoate	Spinetoram	Triflumuron
Carfentrazone-ethyl	Diuron	Fluometuron	Mepanipyrim	Oxadixyl	Spinosad A	Triticonazole
Chloantraniliprole	Emamectin B1a	Fluoxastrobin	Mepronil	Oxamyl	Spirotetramat	Vamidothion
Chlorotoluron	Epoxiconazole	Fluquinconazole	Metaflumizone	Paclobutrazol	Spiroxamine	Zoxamide
Chlorovuron	Enrinomoctin	Flucilazolo				

Table 1 List of analytes measured in the method

								e									
	Country of Origin		×	oin a			ailipro		6. 7	orph		. nat	2 . N	ot	6	amid	MGK 26A+H
	ATHOI	de	AZOMSHOY BI	henatate Boscalid	Bupitimate Sta	A ant	(all of ta	All vianio	, otaminath	onion	azole	WOT'N.	amilati	1 ²¹⁰ 20	opi dipro	alat	× 1,260,00
	Conn	sample	ALOT. BI	ter post	BUDI Caro	Chilos	Clote o	Cloth C	Pair Dime	OIUN.	trot ten	2. tlour	Hef	Imilor	Marris	Neto	MOT MYC
	Australia	A1		141													
	Australia	A2	No	Pesticides [Detected												
Oceana	New Zealand	A3	No	Pesticides [Detected												
	New Zealand	A4		Pesticides [
0	New Zealand	A5		Pesticides [
	New Zealand	A6		Pesticides [
	New Zealand	A7	NO	Pesticides [Detected												
	Austria France	A8 A9	25														761
	Germany	A9 A10	451	18627					9111		4	9 403			1162		101
	Germany	A10	118	10417					244		-	5 405			20994		38
	Germany	A12	316	2375				21	1563				418		3032		189
Ð	Germany	A13	3419	49104		24			6109			79			3518		
Europe	Germany	A14	6037	40383				15	5166			77			4399		1873
Ē	Germany	A15	6711	9691					2152					31		67	1913
	Germany	A16	1491						2049			110	15			32	686
	Germany	A17	436	8498	_				4113			195			3666		1555
	United Kingdom	A18		409	1027				_								948
	United Kingdom	A19	5414	107	34		79		680			570		21		68	1488
	United Kingdom	A20	16	487	31				280					100	429	324	635
	USA USA	A21 A22	-	2578 2402 12586									565	162 205			811
	USA	A22 A23		4231 23904									480	519			
	USA	A24		149 19685						54			32	255			
	USA	A25	3	3402 30770		148				27	190		209	425			218
	USA	A26							8803				33	56			
	USA	A27	1	1492 8223									1866	153			
	USA	A28	22	2140 37854							136 11	2	259	136			
	USA	A29		2501									1157	285			
	USA	A30		168 242									35	303			
	USA	A31		3435	44	89					87		1295	663			279
	USA	A32	17	37923					2072	24			6.4	76	110		
	USA USA	A33	26	334					39	41	46		64	2/11	119		17
<u>e</u>	USA	A34 A35	20	87730 172 1624						41	40 56		716	241 661			309
ner	USA	A35	20	26007							50		1745	312			1365
h Ai	USA	A37	20	83 2004					79				416	163			61
North America	USA	A38		118 1868					65				456	159			
Z	USA	A39		502 4558		21							191				
	USA	A40	7	7323 12287		45				28	51			133	3307		
	USA	A41		13324					1155				225	38			24
	USA	A42	_						481	16							
	USA	A43		8213 4332		56					181	7	1691	61			22
	USA	A44		2256 331									468	255			
	USA	A45		5573 16561		34			217	27			458	192			
	USA	A46		15662		22			217	27 25				22			
	USA USA	A47 A48		23 710 6109		145				35	54		477	245			588
	USA	A48 A49	s	8279 1736		143		2	52 1942		J-1		1251	108	837		500
	USA	A50		10187				2	15				1231	21	007		
	USA	A51		168 68		16					40		261				
	USA	A52	9	9092 16310					56		49	7	45	75	2093		412

Table 2 Pesticides detected in market survey samples.
 Levels reported in ng/gram hops pellets.

Conclusion

An LCMS method was developed for detection of chemical residues in hops. A market survey was carried out with more than 50 samples representing growers worldwide. Pesticides were efficiently and effectively detected with good sensitivity and selectivity.

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