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应用GPC-GCMS和GC-MS快速测定蔬菜中的97种农药残留

No. GCMS-006

摘要： GPC-GCMS是GPC提纯系统与GC/MS在线连接而成的装置。应用GPC提纯系统可将油脂、色素成分与农药分离，通过切换阀排出油脂、色素等杂质，将要分析的农药导入GC-MS。实现了从试样的提纯到农药的分析完全自动化。采用快速的QuEChERS方法做样品的前处理，分别应用GPC-GCMS和GC-MS快速测定了三种蔬菜中的97种农药残留，并对结果做了比较。

关键词： GPC-GCMS 蔬菜 农药残留 快速测定

GC-MS的分析条件

◆GC(GC-2010)

Column	: Rtx-5ms [0.25 mm(ID) x 30 m(L), Thickness 0.25 um]
Injector	: Splitless
Injection volume	: 2 uL
Injection temperature	: 260 °C
Oven temperature program	: 80 °C (2 min) - (20 °C/min) - 180 °C/min - (5 °C/min) - 280 °C (20 min)
Carrier gas	: He
Linear velocity	: 45.0 cm/sec

◆MS(GCMS-QP2010)

Ion Source temperature	: 230 °C
Interface temperature	: 260 °C

SCAN

Start time	: 4.0 min
End time	: 47 min
Mass range	: m/z 86 - 450
Interval	: 0.5 sec

GPC-GCMS的分析条件

◆GPC

Mobile phase	: Acetone / Cyclohexane (3 / 7 by volume)
Flow rate	: 0.1 mL/min
Column	: Shodex CLNpak EV-200AC (2 mm x 150 mm)
Oven temperature	: 40 °C
Injection Volume	: 10 uL
Fraction time	: 3.32 - 5.32 min
Fraction volume	: 200 uL

◆GC(GC-2010)

Column	: deactivated silica tubing [0.53 mm(ID) x 5 m(L)] + pre-column DB5-ms[0.25 mm(ID) x 5 m(L),] + DB5-ms [0.25 mm(ID) x 30 m(L), Thickness 0.25 um] PTV
Injector	
Injector time program	: 120 °C(5 min) - (100 °C/min) - 250 °C(31.7 min)
Oven temperature program	: 82 °C(5 min) - (8 °C/min) - 300 °C(5.75 min)
Carrier gas	: He
Linear velocity	: 45.0 cm/sec

◆MS(GCMS-QP2010)

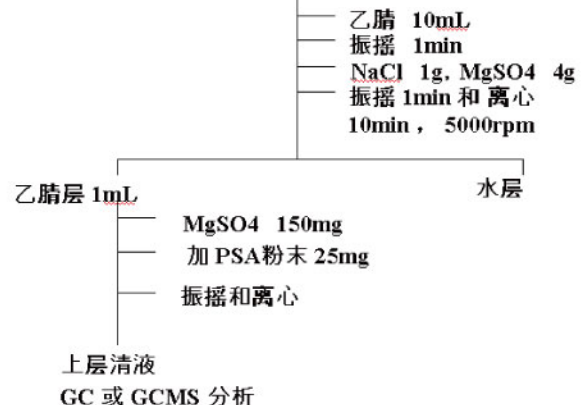
Ion Source temperature	: 200 °C
Interface temperature	: 250 °C

SCAN

Start time	: 10.2 min
End time	: 37 min
Mass range	: m/z 86 - 450
Interval	: 0.5 sec

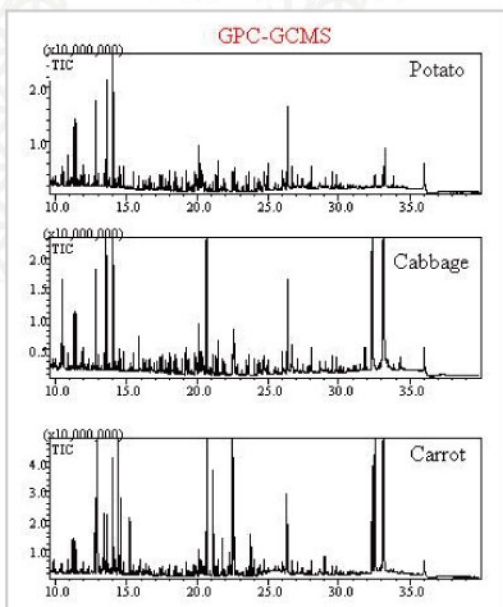
样品前处理：QuEChERS 法

样品均化 10g (水果和蔬菜)

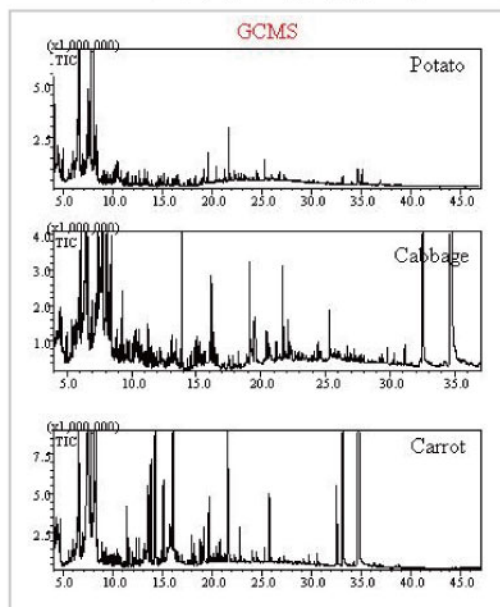


实验结果

土豆、白菜、胡萝卜的TIC图



土豆、白菜、胡萝卜的TIC图



GPC-GCMS与GC-MS中土豆、白菜、胡萝卜的回收率 (%) 及相似度检索结果

Name	Potato		Cabbage		Carrot		Name	Potato		Cabbage		Carrot		Name	Potato		Cabbage		Carrot	
	GPC-GCMS	GCMS	GPC-GCMS	GCMS	GPC-GCMS	GCMS		GPC-GCMS	GCMS	GPC-GCMS	GCMS	GPC-GCMS	GCMS		GPC-GCMS	GCMS	GPC-GCMS	GCMS	GPC-GCMS	GCMS
Methamidophos	68.20	70.99	72.36	83.82	70.79	67.88	Chlorpyrifos	96.88	69.74	95.26	70.92	100.21	73.09	Iprodione	103.40	137.83	103.87	156.43	112.31	90.84
DDVP	87.88	71.60	87.54	77.98	91.06	73.34	Parathion	113.57	83.00	108.31	77.35	120.19	96.46	Acetamiprid	70.63	89.10	91.16	99.73	99.33	107.72
EPTC	98.56	68.53	96.56	68.98	101.35	70.13	DCBP	103.76	78.30	107.55	81.73	120.14	80.34	EPN	109.60	95.34	112.45	96.52	137.74	113.07
Butylate	109.67	68.00	110.90	69.46	109.71	69.12	Isofenphos Oxon	119.89	118.23	116.89	112.04	87.97	109.91	Tebuufenpyrad	111.70	88.54	108.01	91.19	118.66	91.72
Acephate	72.50	234.31	73.97	255.41	70.36	489.84	Fosthiazate	107.65	127.06	105.25	126.76	118.50	129.15	Phosalone	111.25	87.39	115.74	95.34	119.95	103.02
Isoprocab	94.98	80.16	95.75	86.65	96.28	68.88	Fosthiazate	107.63	114.55	105.24	133.73	114.19	125.49	Pyrproxyfen	99.45	87.44	102.62	89.26	105.51	93.15
BPAC	97.80	78.55	97.00	85.94	99.89	74.02	g-CVP	102.78	91.23	103.87	94.59	107.15	94.05	Mefenacet	103.96	92.75	107.88	95.03	116.04	107.11
Ethoprophos	99.19	77.87	99.68	78.42	102.99	81.98	Pendimethalin	110.07	85.02	108.06	78.90	120.11	96.30	Cyhalothrin1	111.95	85.59	121.13	111.91	118.31	109.72
Chlorpropham	112.01	71.91	113.36	76.88	115.20	75.95	Pyrifenoxy-1	98.44	79.22	95.08	80.82	106.51	84.63	Cyhalothrin2	118.06	81.80	130.48	112.44	94.65	85.05
Bendiocarb	85.79	71.40	86.85	94.41	91.71	75.25	Isofenphos	115.58	79.62	114.24	83.08	120.08	88.17	Fenarimol	99.78	84.66	99.31	85.24	111.24	95.34
Cadusafos	104.05	73.71	101.76	76.55	107.60	80.31	β-CVP	104.09	91.13	100.10	94.53	106.26	93.98	Acrinathrin	115.00	85.00	134.71	113.14	224.86	87.75
α-BHC	96.52	76.29	97.27	78.63	102.31	79.48	Captan	90.50	68.91	65.72	0.00	76.83	51.48	Pyraclofos	107.68	140.60	107.40	157.46	190.84	161.42
Thiometon	103.32	73.76	107.00	75.08	107.38	78.98	Quinalphos	97.53	79.96	98.14	83.63	103.81	88.87	Bitertanol	125.36	94.72	118.90	90.50	100.24	114.43
Dimethipin	77.24	84.40	78.80	88.83	79.16	73.47	Triadimenol-11	101.63	78.70	97.15	82.48	109.20	90.60	Permethrin1	112.83	92.12	110.87	95.15	114.86	97.90
β-BHC	106.71	80.36	106.40	82.97	112.33	82.69	PAP	98.38	78.46	94.93	80.01	105.69	89.05	Pvridaben	120.35	89.34	120.63	95.76	83.49	102.61
γ-BHC	98.53	75.96	100.97	76.68	105.60	76.04	Triadimenol-22	105.07	78.63	102.99	82.42	112.49	90.57	Permethrin2	104.62	92.15	109.92	95.59	116.08	97.91
Terbufos	120.30	75.09	122.45	78.40	119.99	80.53	Chinomethionat	55.85	48.61	54.65	49.49	54.73	48.35	Cyfluthrin1	92.12	67.19	100.96	79.38	124.44	75.20
Diazinon	105.90	75.76	103.92	78.33	109.19	79.45	Paclotabrazol	105.54	83.56	101.54	82.85	111.64	92.41	Cyfluthrin2	109.31	75.73	126.81	107.15	134.14	74.64
Tefluthrin	117.73	76.36	116.12	79.34	117.15	79.85	Pyrifenoxy-2	96.94	80.70	93.56	79.81	102.07	83.97	Cyfluthrin3	109.67	82.12	116.31	98.91	117.18	75.74
δ-BHC	104.60	65.70	106.33	82.29	108.39	75.08	Flutolanil	112.70	84.92	109.50	88.11	109.87	103.70	Cyfluthrin4	82.81	69.91	103.46	140.52	114.93	79.03
Etrinfos	103.07	73.90	100.95	75.02	106.58	77.73	Prothiofos	103.20	79.65	100.76	83.42	85.77	84.87	Cvpermethrin1	105.90	55.10	103.94	85.49	103.03	54.17
Pirimicarb	92.40	76.07	89.03	78.00	96.66	80.26	Trietelazole	94.42	94.03	100.11	100.32	103.82	110.94	Halfenprox	93.69	91.57	97.11	99.11	103.49	115.33
Ethiofencarb	93.55	105.36	91.88	121.24	91.13	97.54	Pretlathlor	113.77	88.26	113.38	82.54	118.38	100.93	Cvpermethrin2	87.84	90.91	99.82	120.27	104.92	92.45
Benfuresate	94.47	75.28	94.14	76.96	102.22	76.67	n,p-DDE	100.45	81.81	96.81	82.12	94.57	80.58	Cvpermethrin3	94.43	80.56	131.37	96.25	93.40	79.00
Methyl-Parathion	103.97	85.38	119.78	82.06	115.21	92.39	Mvelobutanil	91.46	83.94	91.85	84.37	98.42	93.20	Cvpermethrin4	81.74	69.61	109.84	112.83	102.34	92.21
Tolclofos-methyl	96.87	76.10	97.18	79.61	101.06	81.63	Fenilazole	92.76	80.42	92.26	85.26	97.36	87.21	Flucythrinate1	105.36	94.07	106.86	110.59	117.49	101.58
NAC	99.17	78.32	105.79	124.35	108.64	78.38	Cyproconazole	106.20	83.16	104.99	83.74	117.38	90.86	Flucythrinate2	113.89	93.30	119.75	118.98	119.62	110.04
Methiocarb	112.42	89.99	113.50	126.23	117.53	79.56	Chlorobenzilate	113.91	86.36	111.02	83.89	116.86	92.39	Silaflofen	88.41	90.49	119.23	91.73	118.31	91.90
MEP	100.26	80.74	101.72	73.77	111.66	94.35	Fensulfothion	98.56	88.93	102.08	97.02	119.16	122.23	Pyrimidufen	82.03	93.50	84.51	101.10	86.11	106.55
Priniphos-methyl	102.80	75.55	101.86	81.74	107.89	83.95	n,p-DDD	104.72	82.19	103.52	86.88	106.79	88.53	Fenvalerate1	100.61	73.75	101.50	104.85	103.60	88.61
Esprocarb	99.30	77.32	98.12	78.96	102.94	82.34	Mepromil	108.99	85.29	109.73	85.14	118.66	93.12	Fenvalerate2	104.94	81.36	106.73	110.72	111.77	84.62
Dichlofluanid	71.65	62.79	62.22	57.91	50.04	61.48	EDDP	107.49	131.51	107.09	142.62	117.90	128.06	Fluralinate1	135.00	91.10	154.83	132.96	161.08	79.40
Thioencarb	96.25	76.55	96.53	78.33	100.73	80.60	Propiconazole1	101.81	84.52	100.24	86.37	110.44	92.14	Fluralinate2	141.81	81.87	155.01	136.95	152.11	75.08
Malathion	97.33	82.57	95.35	90.76	103.67	90.23	Lenacil	108.62	90.74	106.57	91.54	118.97	104.00	Difenoconazole1	143.31	89.80	117.42	86.90	186.62	120.87
Diethofencarb	116.68	86.47	106.31	84.19	114.50	89.03	Propiconazole2	96.88	84.52	98.07	86.37	104.77	92.14	Difenoconazole2	123.32	95.26	115.22	86.89	136.73	117.12
Metolachlor	101.85	80.18	99.37	79.61	106.58	85.71	Tebuconazole	108.98	82.08	102.33	83.96	117.25	92.81	Deltamethrin	108.75	78.32	94.89	81.47	110.71	107.65
MPP	62.67	76.22	57.34	80.67	56.28	83.26	Thenylchlor	99.55	88.00	100.73	85.04	109.03	97.78	Imibenconazole	157.38	88.31	155.53	98.96	180.13	113.40
(Z)-Dimethylsiphos	96.72	94.14	94.37	99.44	102.41	96.69	Difolatan	89.84	0.00	58.20	0.00	112.40	0.00							

Name	Potato		Cabbage		Carrot		Name	Potato		Cabbage		Carrot		Name	Potato		Cabbage		Carrot	
	GPC-GCMS	GCMS	GPC-GCMS	GCMS	GPC-GCMS	GCMS		GPC-GCMS	GCMS	GPC-GCMS	GCMS	GPC-GCMS	GCMS		GPC-GCMS	GCMS	GPC-GCMS	GCMS	GPC-GCMS	GCMS
Methamidophos	88	74	64	72	93	73	Chlorpyrifos	85	83	83	82	77	77	Iprodione	74	38	78	43	77	31
DDVP	95	69	95	66	96	60	Parathion	87	68	87	62	68	57	Acetamiprid	53	91	87	90	87	89
EPTC	83	85	81	86	82	81	DCBP	87	87	78	31	51	88	EPN	92	66	92	49	88	63
Butylate	87	69	87	63	80	64	Isofenphos Oxon	73	57	53	57	25	42	Tebufenpyrad	91	73	91	79	91	82
Acephate	88	19	86	19	83	14	Fosthiazate	88	44	88	46	74	22	Phosalone	89	80	92	80	90	79
Isoprocarb	95	43	95	49	95	41	Fosthiazate	88	40	88	45	73	22	Pyriproxyfen	92	89	89	89	89	89
BPMC	97	88	97	87	97	88	α -CVP	86	61	88	62	88	60	Mefenacet	81	71	80	72	78	74
Ethoprophos	92	60	74	58	92	56	Pendimethalin	83	65	61	44	75	36	Cyhalothrin1	87	56	87	62	88	57
Chlorpropham	91	53	90	61	90	59	Pyrifenoxy-1	83	65	81	64	84	63	Cyhalothrin2	80	43	84	48	83	42
Bendiocarb	95	54	94	57	77	49	Isofenphos	67	79	66	81	75	80	Fenarimol	88	84	88	82	77	85
Cadusafos	94	66	93	73	86	72	β -CVP	35	61	37	62	39	60	Azinathrin	76	58	81	70	81	60
β -BHC	92	80	91	72	91	63	Captan	47	38	23		23	47	Pyraclafos	86	60	90	55	89	49
Thiometon	49	70	49	69	45	71	Quinalphos	85	86	85	84	86	84	Bitertanol	93	75	92	74	96	70
Dimethipin	56	37	50	38	62	36	Triadimenol-11	90	54	89	62	80	60	Permethrin1	93	80	94	66	93	76
β -BHC	83	58	86	57	85	60	PAP	74	81	72	79	75	81	Pyridaben	87	75	87	75	89	75
γ -BHC	89	77	86	78	90	76	Triadimenol-22	80	54	91	62	32	60	Permethrin2	55	80	56	66	56	76
Tebufofos	92	85	93	82	92	80	Chinomethionat	58	28	24	28	20	23	Cyfluthrin1	79	36	80	46	79	32
Diazinon	86	76	88	77	88	77	Paclbutazol	93	82	89	82	90	80	Cyfluthrin2	78	45	79	49	79	42
Tefluthrin	55	65	58	55	67	60	Pyrifenoxy-2	87	79	87	79	88	62	Cyfluthrin3	68	36	72	41	69	38
δ -BHC	91	71	92	75	91	51	Flutolani	61	86	68	74	69	24	Cyfluthrin4	68	41	77	47	73	38
Etrinfos	84	76	84	82	87	78	Prothiofos	82	60	83	30	66	18	Cypermethrin1	69	35	76	44	26	30
Pririmcarb	95	76	95	80	92	83	Triacyclazole	37	57	36	42	37	44	Halfenprox	90	80	92	78	91	80
Ethiofenarb	93	78	91	53	70	37	Pretilachlor	87	79	87	72	25	70	Cypermethrin2	85	38	86	47	88	35
Benfuresate	87	77	88	77	87	72	<i>p,p'</i> -DDE	94	91	92	90	87	87	Cypermethrin3	61	34	76	45	67	32
Meth1-Parathion	66	63	69	55	67	61	Myclobutani	90	74	90	71	91	76	Cypermethrin4	59	48	78	54	74	43
Tolelofos-methyl	89	87	87	87	89	85	Flusiazole	91	77	91	78	92	78	Flucythrinate1	77	63	79	65	79	62
NAC	91	52	91	59	90	19	Cyproconazole	92	81	88	78	91	79	Flucythrinate2	73	56	74	59	78	56
Methiocarb	93	59	93	65	89	44	Chlorobenzilate	96	93	96	83	96	90	Silafluofen	93	92	94	89	94	88
MEP	66	69	73	56	68	58	Fensulfothion	76	73	79	72	80	74	Pyrimidufen	96	90	95	90	96	89
Pririmphos-methyl	88	73	88	65	86	68	<i>p,p'</i> -DDD	93	89	94	89	93	89	Fenvalerate 1	84	65	85	62	84	60
Eprocarb	65	58	65	55	67	54	Mepromil	92	91	92	90	89	91	Fenvalerate 2	80	54	76	60	82	55
Dichlofluanid	90	35	25	25	64	31	EDDP	94	78	93	79	94	32	Fluvalinate1	74	36	69	40	75	24
Thiofenarb	90	77	90	66	88	71	Propiconazole1	74	70	73	70	73	61	Fluvalinate2	59	30	57	41	58	33
Malathion	75	49	85	49	81	47	Lenacil	91	76	92	77	89	75	Difenoconazole1	79	59	77	54	82	63
Diethofencarb	81	64	82	63	79	60	Propiconazole2	89	70	88	70	90	61	Difenoconazole2	84	65	83	61	84	63
Metolachlor	77	84	91	84	82	80	Tebuconazole	90	63	90	59	90	62	Deltamethrin	87	40	88	35	86	37
MPP	56	84	61	81	51	72	Themlchlor	86	87	90	84	79	86	Imibenzconazole	78	66	84	67	84	69
(Z)-Dimethilvinip	87	39	87	36	82	34	Difolatan	27	-	18	-	24	-							

5. 结论

GPC-GCMS系统的进样量为10 μ L, 比GCMS高5倍, 因此具有更高的灵敏度。

在100ppb 97种农残的添加回收实验中, 由于GPC的净化作用, 应用GPC-GCMS系统可得到优于GCMS的结果。土豆、白菜、胡萝卜中农药回收率超出70-120%范围的分别有7, 12, 10种; 而在GCMS中, 分别有15, 16, 13种。

由于GPC能去除干扰物质, 减少基质影响, 应用GPC-GC/MS系统可得到优于GCMS的质谱图和定性结果, 其中, 土豆、白菜、胡萝卜中农药的检索相似度SI值低于70的分别有19, 19, 24种; 而在GCMS中, 分别有47, 50, 53种。

应用GPC-GCMS系统, 可在50分钟内完成从GPC提纯到GCMS分析的过程。添加的97种农药中, 有80多种回收率在70%到120%的范围内, 结果良好。

采用快速样品前处理-QuEChERS法, 只需30分钟即可完成样品的前处理。溶剂消耗量只有10mL, 是常规样品前处理的几分之一。

采用QuEChERS法+GPC-GCMS, 可快速分析蔬菜中的农药残留, 从样品前处理到GCMS分析, 仅用1.5小时左右便可完成。适用于蔬菜中农药残留的筛查分析。