SHIMADZU
APPLICATION NEWS
色谱分析
NO.GCMS-006
岛津分析应用报告

应用 GPC-GCMS 和 GC-MS 快速测定蔬菜中的 97 种农药残留

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。

GC-MS 的分析条件

◆ GC(GC-2010)

Column	:Rtx-5ms[0.25mm(ID)x30(L),Thicknes 0.25μm]
Injector	:Splitless
Injection volume	:2μL
Injection temperature	:260℃
Oven temperature program	:80℃(2min)-(20℃/min)-180℃-(5℃/min)-280℃(20min)
Carrier gas	:He
Linear velocity	:45.0cm/sec

◆ MS(GCMS-QP2010)

Ion Source temperature	:230℃
Interface temperature	:260℃
SCAN	
Start time	:4.0min
End time	:47min
Mass range	:M/Z 86-450
Interval	:0.5sec

GPC-GCMS 的分析条件

◆ GPC

Mobile phase	:Acetone/Cyclohexane(3/7 by volume)
Flow rate	:0.1mL/min
Column	:Shodex CLNpak EV-200AC(2mmx150mm)

Oven temperature :40˚C

Injection Volume :10μL

Fraction time :3.32-5.32min

Fraction volume :200μL

◆ GC(GC-2010)

Column :deactivated silica tubing[0.53mm(ID)x5m(L)]
+pre-column DB5-ms[0.25mm(ID)x5m(L)]
+DB5-ms[0.25mm(ID)x30m(L),Thickness0.25μm]

Injector :PTV

Injector time program :120˚C (5min)-(100˚C /min)-250˚C (31.7min)

Oven temperature program :82˚C (5min)-(8˚C /min)-300˚C (5.75min)

Carrier gas :He

Linear velocity :45.0cm/sec

◆ MS(GCMS-QP2010)

Ion Source temperature :200˚C

Interface temperature :250˚C

SCAN

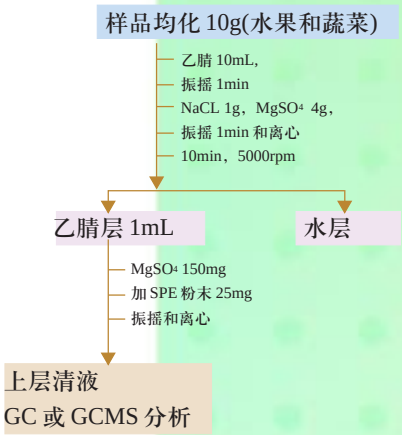
Start time :10.2min

End time :37min

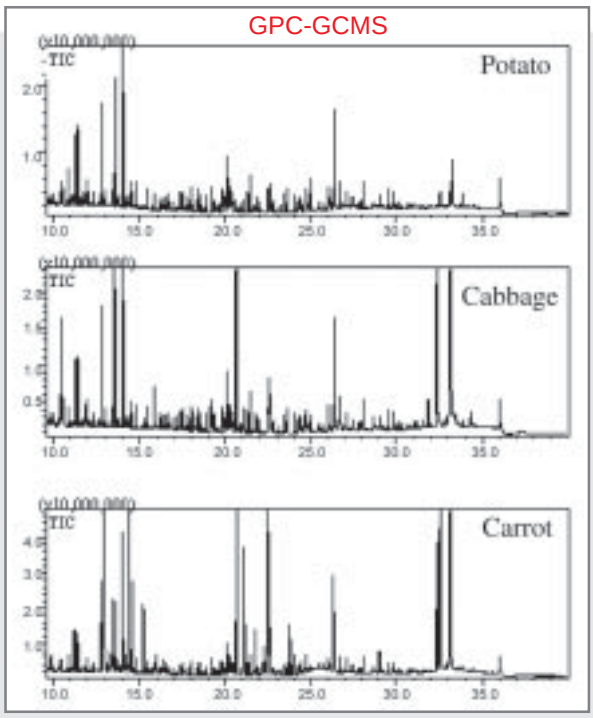
Mass range :m/z 86-450

Interval :0.5sec

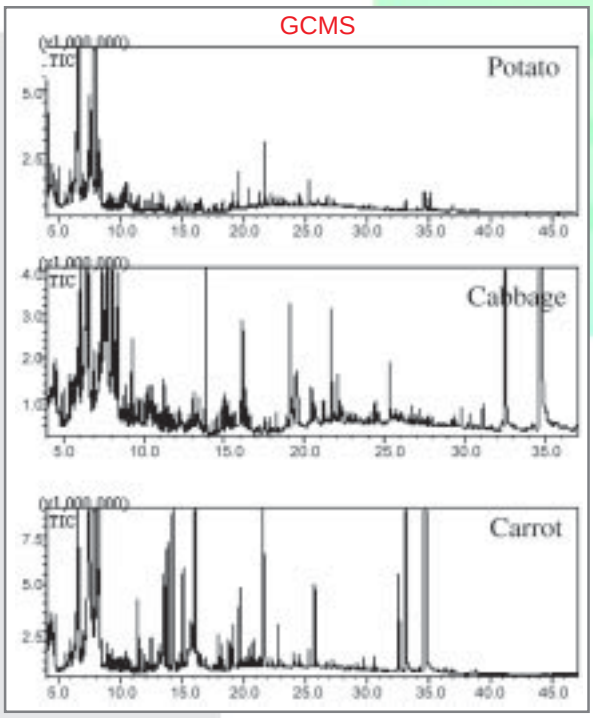
样品前处理：QuEchERS 法



实验结果



土豆、白菜、胡萝卜的 TIC 图



土豆、白菜、胡萝卜的 TIC 图

土豆、白菜、胡萝卜的回收率— GPC-GCMS 与 GC-MS 的比较

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	107.22
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	Tebufenpyrad	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
Isoprocarb	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	Pyriproxyfen	99.45	87.44	102.62	89.26	105.51	93.15
BPMC	97.80	78.55	97.00	85.94	99.89	74.02	α-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	Cyhalothrin 1	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	Pyrifenox-1	98.44	79.22	95.08	80.82	106.51	84.63	Cyhalothrin 2	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	Isophenphos	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	Permethrinl	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	Pyridaben	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	Permethrin 2	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	Cyfluthrin 1	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	Paclobutrazol	105.54	83.56	101.54	82.85	111.64	92.41	Cyfluthrin 2	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	Pyrifenox-2	96.94	80.70	93.56	79.81	102.07	83.97	Cyfluthrin 3	109.67	82.12	116.31	98.91	117.18	75.74
δ-BHC	104.60	65.79	106.33	82.29	108.39	75.08	Flutolanil	112.70	84.92	109.50	88.11	109.87	103.70	Cyfluthrin 4	82.81	69.91	103.46	140.52	114.93	79.03
Etrimfos	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	Cypermethrin 1	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	Tricyclazole	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	Pretilachlor	113.77	88.26	113.38	82.54	118.38	100.93	Cypermethrin 2	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	p,p'-DDE	100.45	81.81	96.81	82.12	94.57	80.58	Cypermethrin 3	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	Myclobutanil	91.46	83.94	91.85	84.37	98.42	93.20	Cypermethrin 4	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	Flusilazole	92.76	80.42	92.26	85.26	97.36	87.21	Flucythrinate 1	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	Cyprocpnazole	106.20	83.16	104.99	83.74	117.38	90.86	Flucythrinate 2	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	Silafluofen	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
Pirimiphos-methy 1	102.80	75.55	101.86	81.74	107.89	83.95	p,p'-DDD	104.72	82.19	103.52	86.88	106.79	88.53	Fenvalerate 1	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	Mepronil	108.99	85.29	109.73	85.14	118.66	93.12	Fenvalerate 2	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	Fluvalinate 1	135.00	91.10	154.83	132.96	161.08	79.40
Thiobencarb	96.25	76.55	96.53	78.33	100.73	80.60	Propiconazole 1	101.81	84.52	100.24	86.37	110.44	92.14	Fluvalinate 2	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	Difenoconazole 1	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	Propiconazole 2	96.88	84.52	98.07	86.37	104.77	92.14	Difenoconazole 2	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)-Dimethylvinpl	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							

GPC-GCMS 和 GC-MS 的检索相似度的比较

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	αα-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	Cyhalothrinl	87	56	87	62	88	57
Chlorpropham	91	53	90	61	90	59	Pyrifenox-1	83	65	81	64	84	63	Cyhalothrin2	80	43	84	48	83	42
Bendiocarb	95	54	94	57	77	49	Isophenphos	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	Acrinathrin	76	58	81	70	81	60
α-BHC	92	80	91	72	91	63	Captan	47	38	23		23	47	Pyraclofos	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-II	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
Terbufos	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	Paclobutrazol	93	82	89	82	90	80	Cyfluthrin2	78	45	79	49	79	42
Tefluthrin	55	65	58	55	67	60	Pyrifenox-2	87	79	87	79	88	62	Cyfluthrin3	68	36	72	41	69	38
δ-BHC	91	71	92	75	91	51	Flutolanil	61	86	68	74	69	24	Cyfluthrin4	68	41	77	47	73	38
Etrimfos	84	76	84	82	87	78	Prothiofos	82	60	83	30	66	18	Cypermethrin1	69	35	76	44	26	30
Pirimicarb	95	76	95	80	92	83	Tricyclazole	37	57	36	42	37	44	Halfenprox	90	80	92	78	91	80
Ethiofencarb	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	P,P育 DDE	94	91	92	90	87	87	Cypermethrin3	61	34	76	45	67	32
Methyl-Parathion	66	63	69	55	67	61	Myclobutanil	90	74	90	71	91	76	Cypermethrin4	59	48	78	54	74	43
Tolclofos-methyl	89	87	87	87	89	85	Flusilazole	91	77	91	78	92	78	Flucythrinate1	77	63	79	65	79	62
NAC	91	52	91	59	90	19	Cyprocpnazole	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
Pirimiphos-methyl	88	73	88	65	86	68	P,P育 DDD	93	89	94	89	93	89	Fenvalerate1	84	65	85	62	84	60
Esprocarb	65	58	65	55	67	54	Mepronil	92	91	92	90	89	91	Fenvalerate2	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
Thiobencarb	90	77	90	66	88	71	Propiconazolel	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	Thenylchlor	86	87	90	84	79	86	Imibenconazole	78	66	84	67	84	69
(Z)-Dimethylvinph	87	39	87	36	82	34	Difolatan	27	-	18	-	24	-							

结论

GPC-GC/MS 系统的进样量为 10μL，比 GC-MS 高 5 倍，因此可得到更高的灵敏度。

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-GC/MS 系统可得到优于 GC-MS 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 GC-MS 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 GC-MS 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 GC-MS 中，分别有 47，50，53 种。

应用 GPC-GC/MS 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十分之一。

采用 QuEChERS 法 +GPC-GC/MS，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。