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利用氣相層析串聯質譜法及超高效液相層析串聯質譜法同時檢測土壤中 352 種農藥殘留

施念昊 [1]　許得美 [1]　徐慈鴻 [1]　初建 [1*]

摘要

施念昊、許得美、徐慈鴻、初建。2019。利用氣相層析串聯質譜法及超高效液相層析串聯質譜法同時檢測土壤中 352 種農藥殘留。臺灣農藥科學　6：1-36。

作物在耕作期間，為防治病蟲草害會施用不同種類的農藥，因此需要建立多重殘留分析方法，以便同時準確檢測土壤中的農藥殘留，本研究建立之土壤中農藥多重殘留檢測方法，可供未來執行臺灣農田環境中土壤之農藥殘留檢測及環境風險評估。供試土壤樣品以自動索氏萃取法 (Soxhlet extraction) 進行前處理，萃取液分別以氣相層析串聯質譜儀 (GC-MS/MS) 及超高效液相層析串聯質譜儀 (UPLC-MS/MS)，檢測 195 及 157 項農藥。GC-MS/MS 基質匹配檢量線範圍為 5~500 μg/L，土壤基質分別添加 10 及 40 μg/kg 農藥標準品，以 GC-MS/MS 分析，回收率達 64.5~115.6% 及 60.1~119.1%，相對標準偏差 (relative standard deviation, RSD) 低於 20%。另外，UPLC-MS/MS 基質匹配檢量線範圍為 2~200 μg/L，回收試驗添加濃度為 4 及 20 μg/kg，回收率分別達 64.3~115.4% 及 63.6~110.0%，相對標準偏差低於 20%。建立之檢測方法參加 ERA (Environmental Resource Associates) 所舉辦之土壤中有機氯農藥能力測試，20 種有機氯農藥皆通過能力測試，顯示此方法亦適用於土壤中有機氯農藥之檢測。

關鍵詞：土壤、農藥、氣相層析串聯質譜儀、超高效液相層析串聯質譜儀

緒言

現今農業生產過程中，為增進作物產量及品質常施用農藥防治農作物病蟲草害，但施用後的農藥也會進入環境中 (21)。

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* 通訊作者。E-mail: chu@tactri.gov.tw

[1] 臺中市 行政院農業委員會農業藥物毒物試驗所

農藥可藉由不同途徑進入土壤，作物地上部在噴施農藥時，農藥會進入土壤 [18]，最直接的方式是施於土壤中，防治雜草或植物寄生性線蟲。殘留於土壤的農藥，可能影響下期作，其中部分農藥會經由植物根部吸收轉移至食用部位 [15]。此外，進入土壤中的農藥也會經由土壤水的移動，進入到地表水或地下水 [20]，而再次進入食物鏈，因此需監測土壤中的農藥殘留，以評估可能對人體健康和環境的影響。

土壤樣品具多樣性和複雜性，如何從土壤中萃取農藥是關鍵，通常農藥容易被吸附於黏粒及有機質含量高的土壤，而質地較粗的砂土則較不易吸附農藥。農田土壤中含有腐植質和營養鹽，會影響農藥的吸附，需要適當的萃取方法 [12]，才能把被吸附的殘留農藥 (bound residue) 萃取出來，常用的萃取技術有索氏萃取、加速溶劑萃取 (accelerated solvent extraction, ASE)、微波輔助萃取 (microwave-assisted extraction, MAE)、超臨界流體萃取 (supercritical fluid extraction, SFE) 及固相萃取 (solid-phase extraction, SPE) 等 [18, 21, 25]，其中索氏萃取自 1879 年建立以來 [22]，由於操作簡單且回收率高，有詳盡的操作程序 [4, 9, 24, 21]，是常用於萃取土壤中農藥的方法。自動索氏萃取法 [2, 7, 23]，保有索氏萃取的優點，並將過程自動化，減少溶劑使用量及加速萃取時間。本研究即以自動索氏萃取法進行前處理，再利用兼具靈敏度及選擇性優勢的 GC-MS/MS 及 UPLC-MS/MS 進行分析。

材料與方法

一、土壤樣品

試驗對照組用空白土壤樣品，於 2017 年 2 月採集自花蓮縣臺 11 線公路 66.735 公里處，道路施工時開挖之土壤，以確保未施用農藥，並委託國立中興大學土壤調查試驗中心進行土壤性質分析，項目包含有機質、酸鹼值、質地、陽離子交換能力及總體密度等 (表一)。

供試農田土壤樣品，分別於 2017 年 5~8 月至宜蘭、彰化、雲林、嘉義、臺南、高雄及花蓮等 10 處水稻田採集，採樣前先應用衛星定位儀定位採樣點的經緯度，用混樣 (composites) 方式採樣，在一塊田區中採樣人員以 Z 字方式前進，以不銹鋼製手動式土鑽採樣器 (hand-held auger) 採集 0~15 cm 深度的土壤樣品，採集十個位置土壤，混合成一個樣品。採集之樣品置於 PE 塑膠袋中，送回實驗室後

表一、空白土壤樣品特性

Table 1. Summary of blank soil properties

Analytical item	Measured value
Organic matter	1.78%
pH	7.90
Soil texture	Clay
Sand	24.0%
Silt	35.5%
Clay	40.5%
CEC	15.4 $cmol_c/kg$
Bulk density	1.47 g/cm^3

去除石礫及樹枝等雜物，於陰涼處自然風乾約 5~7 天，再以木鎚打碎樣品，經 2 mm 標準篩 (No. 10 Mesh) 過篩，置入 HDPE 材質之樣品瓶並於室溫保存。

二、試藥

349 種農藥標準品，除益多松 (etrimfos) 及阿納寧 (acrinathrin) 純度較低，分別為 63.4 及 88.7% 外，純度範圍皆介於 93.5% 至 100.0%。分別購自 Accu Standard、Chem Service、Dr. Ehrenstorfer Gmbh、Sgima-Aldrich fluka、Wako 等公司，另殺芬草 (saflufenacil) 來自臺灣巴斯夫股份有限公司。其他相關分析試藥包括丙酮 (≥99.0%, Merck)、二氯甲烷 (≥99.0%, Merck)、正己烷 (≥98.0%, Merck)、甲醇 (≥99.9%, Merck)、乙腈 (≥99.9%, J. T. Baker)、甲酸 (≥98.0%, Merck)、醋酸銨 (≥98.0%, Merck) 及無水硫酸鈉 (≥99.0%, Merck) 等。

三、標準品溶液配製

精秤農藥標準品 (取樣克數大於 0.02 g 以 4 位數天平秤取，0.02 g 以下以 5 位數天平秤取)，並分別以適量溶劑 (如丙酮、正己烷、甲醇及乙腈等) 溶解及定量，作為標準品儲備液 (stock solution)。再取適量標準儲備溶液，分別配製成數個 10,000 μg/L 標準品混合液，於 -20℃ 條件下避光保存。使用時，置於室溫回溫約 1 小時，取適量標準品混合液，稀釋成 2~500 μg/L 之標準品工作液 (working solution)。

四、樣品前處理

土壤及無水硫酸鈉各秤取 10 g，置入圓筒濾紙 (Cellulose Soxhlet Extraction Thimble, 38 mm × 80 mm, GE Healthcare Life Sciences) 後，攪拌均勻靜置 5 分鐘，以自動索式萃取裝置 (Soxtec Extraction System Model 2050 Foss/Sweden) 萃取農藥。萃取溶劑為 120 mL 丙酮與二氯甲烷混合液 (1:1, v/v)，先加熱沸騰 (金屬板溫度 180℃) 90 min，再迴流萃取 (金屬板溫度 180℃) 60 min，萃取液濃縮至微乾後，以 2 mL 丙酮與正己烷混合液 (1:1, v/v) 定量，取其中 1 mL 檢液經 0.2 μm PTFE (Advantec, JP020AN) 濾膜過濾後，以氣相層析串聯質譜儀 (Waters Micromass Quattro micro GC) 分析，另剩下 1 mL 檢液以氮氣吹至微乾，以 1 mL 甲醇定量，經 0.2 μm PTFE 濾膜過濾後，以超高效液相層析串聯質譜儀 (Waters ACQUITY UPLC/Waters Premier XE) 分析。

五、分析儀器及條件

氣相層析串聯質譜儀，載體氣體 (carrier gas) 為氦氣 (純度≥ 99.9995%)，流速為 1.0 mL/min，樣品注射體積為 1 μL。層析管柱採用 Agilent HP-5MS (30 m

× 0.25 mm × 0.25 μm)，層析管柱升溫為：90℃ 維持 2 min，以升溫速率 7 (℃/min) 達到 300℃，並維持 4 min。離子化模式為 electron impact (EI)，離子化能量為 70 eV，界面溫度 (interface temperature) 為 250 ℃，離子源溫度 (ion source temperature) 為 180℃。分析參數：偵測離子對、滯留時間 (retention time, RT) 與碰撞能量 (collision energy, CE)，(如表二)。

超高效液相層析串聯質譜儀，層析管柱為 Waters ACQUITY UPLC BEH C18 (2.1 mm × 100 mm × 1.7 μm)，保護管柱為 Waters ACQUITY UPLC BEH C18 VanGuard Pre-Column (2.1 mm × 5 mm × 1.7 μm)。移動相：A 液含 5 mM 醋酸銨水溶液 (含 0.1%甲酸)；B 液含 5 mM 醋酸銨之甲醇溶液，移動相梯度分析條件，(如表三)。離子化模式採用電灑法 (ESI)，離子噴霧電壓 (ionspray voltage) 為 3kV，離子源溫度為 120℃，溶媒揮散溫度 (desolvation temperature) 為 400℃，進樣錐氣體流速 (cone gas flow)：50 L/hr，溶媒揮散流速 (desolvation flow)：900 L/hr。分析參數：偵測離子對、滯留時間、進樣錐電壓 (cone voltage, CV) 與碰撞能量，(如表四)。

六、標準檢量線之製作

取標準品工作溶液 5、10、20、50、100、200 及 500 μg/L，進行 GC-MS/MS 分析；2、5、10、20、50、100 及 200 μg/L，進行 UPLC-MS/MS 分析，以波峰面積對濃度作圖，至少 5 種濃度繪製成標準檢量線。

七、基質效應 (matrix effect, ME)

以空白土壤樣品檢液 (來源如前述材料方法四、樣品前處理)，添加 195 種農藥標準品，使其最終濃度為 5、10、20、50、100、200 及 500 μg/L 以 GC-MS/MS 分析，其檢量線決定係數皆在 0.99 以上 (表二)。另以空白土壤樣品檢液添加 157 種農藥標準品，使其最終濃度為 2、5、10、20、50、100 及 200 μg/L 以 UPLC-MS/MS 分析，其檢量線決定係數皆可達 0.99 以上 (表四)。

基質效應計算公式如下：

ME ＝(基質匹配檢量線之斜率－純溶劑檢量之線斜率)／純溶劑檢量之線斜率 × 100%。

八、添加回收試驗

取 10 g 空白對照組土壤樣品，置入圓筒濾紙後，加入含 195 種農藥的工作液，使其濃度為 10 及 40 μg/kg 靜置 5 分鐘，依樣品前處理操作流程，以 GC-MS/MS 進行分析；另 157 種農藥，使其濃度為 4 及 20 μg/kg，以 UPLC-MS/MS 進行分析。同時進行空白試驗 (blank analysis) 作為對照分析比對，以檢液所測得各農藥離子碎片質量波峰之滯留時間及

表二、土壤中農藥之 GC-MS/MS 分析條件及回收試驗結果

Table 2. Parameters used in the determination of 195 pesticide residues in soil and recovery test results obtained by GC-MS/MS

Pesticides	Chinese name	Pesticide type [1)]	RT (min)	Quantitative		Qualitative		r^2	Spiked 10 μg/kg		Spiked 40 μg/kg		ME (%)
				ion pairs (m/z)	CE (eV)	ion pairs (m/z)	CE (eV)		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	
bromopropylate	新殺蟎	acaricide	26.09	341>183	15	341>155	15	1.000	87.5	1.8	88.2	0.7	112.4
fluacrypyrim		acaricide	24.33	145>115	25	145>102	15	1.000	91.1	3.6	93.9	1.9	86.0
tetradifon	得脫蟎	acaricide	26.79	159>131	10	159>111	20	1.000	99.8	5.5	98.5	1.6	77.0
azaconazole		fungicide	23.09	217>173	20	217>145	20	1.000	87.4	2.2	86.5	0.6	77.0
bitertanol	比多農	fungicide	28.45	170>115	30	170>141	10	0.991	87.9	1.7	81.9	3.9	173.6
bromuconazole	溴克座	fungicide	25.99-26.63	295>173	10	173>145	20	1.000	90.5	2.2	91.1	2.1	88.8
bupirimate	布瑞莫	fungicide	23.09	273>193	15	208>165	15	1.000	86.6	3.7	86.2	3.3	95.6
chinomethionat	蟎離丹	fungicide	21.73	234>206	15	206>148	15	0.992	98.1	5	98.7	1.8	75.6
chlorothalonil	四氯異苯腈	fungicide	17.62	266>205	25	266>168	10	1.000	93.6	7.2	93.8	1.8	-81.5
chlozolinate	克氯得	fungicide	21.22	331>259	5	188>153	15	1.000	64.5	4.1	60.1	2.6	72.1
cyproconazole	環克座	fungicide	23.34	222>125	15	222>82	5	1.000	89.3	2.3	89.1	1.9	115.0
dichlofluanid	益發靈	fungicide	19.83	224>123	10	167>124	15	1.000	88.4	5.1	87.4	2	-54.6
dicloran	大克爛	fungicide	16.4	206>176	10	176>148	8	0.991	94.8	4.4	93.2	2	82.6
difenoconazole	待克利	fungicide	31.74	323>265	15	323>202	26	1.000	88.3	3.9	88.2	2.1	86.2
diniconazole	達克利	fungicide	23.76	268>232	10	268>171	15	1.000	80	6.3	82.3	4.4	144.4
edifenphos	護粒松	fungicide	24.63	173>109	6	310>173	15	1.000	81.9	1.5	83.7	2.8	105.9
epoxiconazole	依普座	fungicide	25.61	192>138	10	192>157	12	1.000	92.2	1.3	92.6	2.3	103.0
fenarimol	芬瑞莫	fungicide	27.74	251>139	15	139>111	10	1.000	90.8	1.3	91.6	1	123.5
fluazinam	扶吉胺	fungicide	24.34	417>387	15	387>359	15	1.000	81.6	7.2	82.1	2.8	-4.2

表二（續）、土壤中農藥之 GC-MS/MS 分析條件及回收試驗結果

Table 2 (continued). Parameters used in the determination of 195 pesticide residues in soil and recovery test results obtained by GC-MS/MS

Pesticides	Chinese name	Pesticide type [1)]	RT (min)	Quantitative		Qualitative		r^2	Spiked 10 μg/kg		Spiked 40 μg/kg		ME (%)
				ion pairs (m/z)	CE (eV)	ion pairs (m/z)	CE (eV)		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	
flutolanil	福多寧	fungicide	22.5	173>145	15	281>173	15	0.996	108.8	3	112.4	2.2	86.4
folpet	福爾培	fungicide	22.25	130>102	20	130>120	20	0.999	95.9	2	104.7	4.4	61.9
fthalide (phthalide)	熱必斯	fungicide	20.66	243>215	14	243>179	24	1.000	89.4	2	87.3	2.7	72.9
HCB (hexachlorobenzene)	六氯苯	fungicide	16.18	284>249	20	286>214	35	0.992	81.7	0.9	72.3	2.5	59.2
imibenconazole	易胺座	fungicide	33.36	125>89	10	253>82	15	1.000	85.6	1.5	85.9	1	44.5
iprobenfos	丙基喜樂松	fungicide	18.1	204>91	10	204>122	15	0.991	102.3	4.6	96.8	2.5	108.2
iprodione	依普同	fungicide	25.87	314>245	15	314>271	10	1.000	96.7	8.8	91.1	1.9	174.5
kresoxim-methyl	克收欣	fungicide	23.13	116>89	10	206>116	10	0.990	102.2	7.8	95.7	1.3	42.9
mepronil	滅普寧	fungicide	24.18	119>91	10	269>119	10	1.000	89.9	3.4	90.4	3.7	106.9
nitrothal-isopropyl		fungicide	20.44	236>194	15	236>148	20	1.000	87	2.7	85.4	3.3	76.8
nuarimol	尼瑞莫	fungicide	25.17	235>139	10	235>123	10	1.000	90.6	2.2	89.6	1.3	93.1
PCNB	五氯硝苯	fungicide	17.1	249>214	25	237>143	12	0.992	90.7	2	82.3	1.8	85.8
penconazole	平克座	fungicide	21.13	248>157	20	248>192	20	1.000	90.9	3	88.5	0.4	76.1
pyrazophos	白粉松	fungicide	27.89	221>193	10	232>204	15	1.000	87.7	0.8	89.2	0.9	98.5
pyroquilon	百快隆	fungicide	17.23	173>130	16	173>144	18	1.000	90	3.6	86.2	2.4	80.2
tebuconazole	得克利	fungicide	25.16	250>125	15	250>153	10	1.000	87.9	2.6	86.8	1.9	93.7
tecnazene		fungicide	14.42	261>203	10	215>144	25	0.993	77.2	6.9	66.8	7.6	90.0

表二（續）、土壤中農藥之 GC-MS/MS 分析條件及回收試驗結果

Table 2 (continued). Parameters used in the determination of 195 pesticide residues in soil and recovery test results obtained by GC-MS/MS

Pesticides	Chinese name	Pesticide type [1)]	RT (min)	Quantitative		Qualitative		r^2	Spiked 10 μg/kg		Spiked 40 μg/kg		ME (%)
				ion pairs (m/z)	CE (eV)	ion pairs (m/z)	CE (eV)		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	
tetraconazole	四克利	fungicide	20.47	336>218	12	336>204	20	1.000	90.8	3.3	89.7	2.1	70.9
thifluzamide	賽氟滅	fungicide	23.13	194>166	15	194>125	30	1.000	90.7	3.4	89.6	1.9	78.7
tolclofos-methyl	脫克松	fungicide	18.96	265>250	15	250>220	10	1.000	90.1	1.5	87.9	1.3	74.1
trans-chlordane	trans-可氯丹	fungicide	21.74	373>266	20	373>301	10	1.000	99	1.9	91.3	3.2	48.0
triflumizole	賽福座	fungicide	21.67	278>73	5	206>179	15	1.000	81	5.4	79.6	3.7	46.5
vinclozolin	免克寧	fungicide	18.83	285>212	5	212>145	20	0.992	94.8	10.2	98.3	3.4	65.8
captafol	四氯丹	fungicide	25.31	107>79	10	183>79	15	0.999	108.5	4.5	110.8	5.1	-
ditalimfos	普得松	fungicide	22.24	130>102	15	209>130	15	1.000	83.7	4.7	84.1	1.2	61.6
fenbuconazole	芬克座	fungicide	29.41	198>129	15	198>102	25	1.000	92.3	1.8	91.4	2.3	63.4
fenpropimorph	芬普福	fungicide	20.16	128>70	10	303>128	5	1.000	93.9	2.7	90.3	4.8	95.1
molinate	稻得壯	fungicide	13.25	126>55	10	187>126	10	0.995	70.6	11.5	60.6	9	57.8
oxadixyl	毆殺斯	fungicide	23.98	163>132	10	163>117	25	1.000	89.8	2.8	89.9	1.3	96.1
propiconazole	普克利	fungicide	24.87	173>145	15	259>69	15	1.000	86.2	1.8	88.3	1.7	93.2
pyrimethanil	派美尼	fungicide	17.41	198>156	10	198>118	15	1.000	91.3	4.5	89.4	2.2	83.1
triadimefon	三泰芬	fungicide	20.3	208>181	5	208>111	10	1.000	92.8	4.2	89.7	3.7	71.2
alachlor	拉草	herbicide	19.06	188>160	15	160>132	15	0.993	100.9	5.6	99.3	2.2	72.2
benfluralin	倍尼芬	herbicide	15.67	292>264	15	292>206	16	0.992	90	4.4	85.2	1.1	72.1

表二（續）、土壤中農藥之 GC-MS/MS 分析條件及回收試驗結果

Table 2 (continued). Parameters used in the determination of 195 pesticide residues in soil and recovery test results obtained by GC-MS/MS

Pesticides	Chinese name	Pesticide type [1)]	RT (min)	Quantitative		Qualitative		r^2	Spiked 10 μg/kg		Spiked 40 μg/kg		ME (%)
				ion pairs (m/z)	CE (eV)	ion pairs (m/z)	CE (eV)		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	
benoxacor		herbicide	18.2	259>120	20	120>65	15	1.000	93.2	5.3	92.3	2.4	25.0
bifenox	必芬諾	herbicide	26.55	341>310	6	341>189	16	1.000	84.7	3.7	84.2	1.2	127.4
butachlor	丁基拉草	herbicide	22.16	237>160	8	176>147	10	1.000	92.6	3	90.5	1.4	93.9
butralin	比達寧	herbicide	20.66	266>190	10	224>132	20	1.000	87.2	7.8	88.4	3.3	100.0
chlorpropham	克普芬	herbicide	15.19	213>171	6	127>65	18	1.000	81.2	4.5	84.1	3.1	66.6
cyhalofop-butyl	丁基賽伏草	herbicide	27.27	256>120	10	120>91	10	1.000	87.6	2.5	87.3	1.1	112.1
diclofop-methyl		herbicide	25.21	340>253	10	340>281	10	1.000	89.8	1	87.9	1.3	81.2
dimepiperate		herbicide	21.41	119>91	8	145>112	10	1.000	94.1	5.5	89.8	1.6	58.7
dimethametryn		herbicide	21.1	212>122	10	212>94	18	1.000	88.6	4.9	89.2	2.7	84.1
diphenamid	大芬滅	herbicide	20.72	167>152	15	239>167	5	1.000	90.9	7.2	92.2	2.7	62.6
fenoxaprop-ethyl	芬殺草	herbicide	28.17	361>288	15	361>261	10	1.000	87.8	1.6	86.4	0.9	81.9
flamprop-methyl		herbicide	22.97	105>77	15	276>105	10	1.000	93.4	2.6	90.5	0.7	71.7
flumiclorac-pentyl		herbicide	32.31	423>318	10	423>308	15	1.000	88.4	1.8	87.4	2.3	80.2
hexazinone	菲殺淨	herbicide	25.09	171>71	15	171>85	15	1.000	89.4	2.9	89.3	2.3	106.9
isoproturon	異丙隆	herbicide	7.67	146>128	5	161>146	5	1.000	90.4	4.7	89	2.1	65.8
mefenacet	滅芬草	herbicide	27.32	192>136	15	192>109	25	1.000	91.6	1.9	92.4	1.5	109.8
metazachlor	滅草胺	herbicide	21.06	133>117	20	209>132	15	1.000	87.4	3.1	86.9	3	89.5
metolachlor	莫多草	herbicide	20.07	238>162	8	162>133	15	0.990	99.5	1.6	100.2	3.2	88.3

表二（續）、土壤中農藥之 GC-MS/MS 分析條件及回收試驗結果

Table 2 (continued). Parameters used in the determination of 195 pesticide residues in soil and recovery test results obtained by GC-MS/MS

Pesticides	Chinese name	Pesticide type [1)]	RT (min)	Quantitative		Qualitative		r^2	Spiked 10 μg/kg		Spiked 40 μg/kg		ME (%)
				ion pairs (m/z)	CE (eV)	ion pairs (m/z)	CE (eV)		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	
mirex	滅蟻樂	herbicide	27.3	272>237	15	237>117	15	0.991	101.4	2.3	100.7	1.6	20.4
myclobutanil	邁克尼	herbicide	22.97	179>125	14	179>152	6	1.000	91	2.8	87.7	1.8	84.5
oxadiazon	樂滅草	herbicide	22.84	258>175	15	258>112	30	1.000	88.8	6.7	90.4	2	66.9
oxyfluorfen	復祿芬	herbicide	22.99	302>274	10	252>146	25	1.000	83.6	3.7	84.4	2.6	153.2
pendimethalin	施得圃	herbicide	21.09	252>162	8	252>191	8	1.000	85.7	3.7	87.8	1.9	94.8
picolinafen		herbicide	26.19	238>145	30	238>190	10	1.000	90.2	1.8	88.4	1.1	98.8
piperophos		herbicide	26.24	320>122	8	122>81	8	1.000	86.1	2.5	84.4	0.4	119.4
propachlor	雷蒙得	herbicide	14.55	120>77	20	176>57	10	0.993	93.3	4.5	88.1	0.6	71.3
propazine	普拔根	herbicide	16.87	214>172	10	214>104	15	0.997	113.7	4	114.8	2.5	67.3
pyraflufen-ethyl	派芬草	herbicide	24.94	412>349	15	349>307	10	1.000	87.4	5.8	83.5	2.6	90.3
quinoclamine	莫克草	herbicide	19.88	207>172	10	172>89	25	1.000	83.7	2.7	82.9	2.2	88.7
thenylchlor	欣克草	herbicide	25.17	288>141	10	127>59	6	1.000	87.5	0.7	86.2	1.1	82.9
tribufos		herbicide	22.72	202>147	10	169>57	8	0.990	97.7	2.8	96.5	2.3	77.3
tridiphane	三地芬	herbicide	19.22	187>159	10	173>145	15	1.000	95.4	5.4	95.5	2.4	-7.1
bromacil	克草	herbicide	19.84	205>188	12	205>162	15	1.000	93.8	1.8	94.1	0.7	97.5
chlornitrofen		herbicide	24.45	289>108	15	236>173	10	1.000	87.8	1	86.1	3.3	139.8
chlorthal-dimethyl	大克草	herbicide	20.33	301>223	25	332>301	10	1.000	89	4.1	85.2	1.9	56.0
dinitramine	撻乃安	herbicide	17.74	261>241	15	305>216	10	0.999	108.5	6.4	114	2.9	100.0

表二（續）、土壤中農藥之 GC-MS/MS 分析條件及回收試驗結果

Table 2 (continued). Parameters used in the determination of 195 pesticide residues in soil and recovery test results obtained by GC-MS/MS

Pesticides	Chinese name	Pesticide type [1)]	RT (min)	Quantitative		Qualitative		r^2	Spiked 10 μg/kg		Spiked 40 μg/kg		ME (%)
				ion pairs (m/z)	CE (eV)	ion pairs (m/z)	CE (eV)		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	
dithiopyr	汰硫草	herbicide	19.53	354>306	6	354>286	12	0.990	98.6	3.9	94.2	1.6	83.4
fluroxypyr-meptyl	氟氯比代謝物	herbicide	25.25	209>181	10	181>161	15	1.000	93	2.3	89.8	2.7	76.5
prometryn	佈滅淨	herbicide	19.2	241>199	5	184>69	10	1.000	88.1	5.4	89	2.4	79.9
propyzamide		herbicide	17.25	173>145	10	173>109	22	1.000	89.6	6.6	88.7	3.2	68.5
tebuthiuron	得匍隆	herbicide	13.02	171>156	10	156>62	20	0.996	99.2	5.4	102.6	2.1	85.2
tri-allate		herbicide	17.85	268>184	15	128>86	5	0.991	91.8	1.9	87.7	1.7	76.0
trifluralin	三福林	herbicide	15.61	306>264	10	306>160	20	0.994	90.9	3.1	85.1	1.1	84.9
acetochlor		herbicide	18.78	146>130	25	223>146	20	0.991	98.5	9.9	99.7	1.6	88.8
napropamide	滅落脫	herbicide	22.4	271>128	4	128>72	4	0.991	104.3	4	98.2	2.6	116.2
aldrin	阿特靈	insecticide	19.96	263>193	25	263>228	20	0.992	96.7	4.5	84.6	2.6	34.4
bifenthrin	畢芬寧	insecticide	26.17	181>166	10	165>115	20	0.998	113.1	4.6	115.6	1.8	93.3
cadusafos		insecticide	15.75	159>131	15	159>97	5	0.990	91.8	1.9	85.7	2.5	85.9
carbophenothion	加芬松	insecticide	24.5	342>157	15	342>296	8	1.000	90.8	2.4	88.5	1.9	92.5
chlorfenapyr	克凡派	insecticide	23.43	247>227	10	247>75	15	1.000	92.7	0.9	91.5	2.5	74.9
chlorfenvinphos	氯芬松	insecticide	21.03-21.35	267>159	14	323>267	10	1.000	90.2	8.6	89.5	4.6	92.7
chloropropylate	克氯蟎	insecticide	23.59	251>139	15	251>111	25	0.991	101.8	2.6	100.7	2	118.6
chlorpyrifos	陶斯松	insecticide	20.19	314>258	12	314>286	6	1.000	87.1	5	86.8	1	76.7
chlorpyrifos-methyl	甲基陶斯松	insecticide	18.83	286>93	16	286>271	10	1.000	91.4	2.9	86.5	2.3	67.5

表二（續）、土壤中農藥之 GC-MS/MS 分析條件及回收試驗結果

Table 2 (continued). Parameters used in the determination of 195 pesticide residues in soil and recovery test results obtained by GC-MS/MS

Pesticides	Chinese name	Pesticide type [1)]	RT (min)	Quantitative		Qualitative		r^2	Spiked 10 μg/kg		Spiked 40 μg/kg		ME (%)
				ion pairs (m/z)	CE (eV)	ion pairs (m/z)	CE (eV)		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	
chlorthiophos	克硫松	insecticide	24.05	325>269	15	325>297	5	1.000	87.7	2.6	86.8	1.4	93.6
cis-chlordane	cis-可氯丹	insecticide	22.14	373>266	20	373>301	10	0.990	95.5	8.2	94.9	2.9	60.2
coumaphos	蠅毒磷	insecticide	28.89	362>109	15	362>334	5	1.000	89.2	1.8	87.8	1.2	108.0
cyanofenphos	施力松	insecticide	24.63	169>141	5	185>157	5	1.000	90	4.1	90.8	2.1	69.7
cyanophos	氰乃松	insecticide	17.15	243>109	15	109>79	8	0.990	95.1	3.9	92.3	2.5	70.8
cyfluthrin	賽扶寧	insecticide	29.68	163>127	5	206>151	16	1.000	93.5	0.8	92.7	1.3	76.7
cypermethrin	賽滅寧	insecticide	29.82	163>127	5	181>152	10	0.990	100.8	1.5	101.8	1.9	89.0
cyphenothrin	賽芬寧	insecticide	28.23	123>81	10	181>152	20	1.000	97.6	6.8	90.1	2.9	96.6
deltamethrin	第滅寧	insecticide	32.09	253>172	8	253>93	15	1.000	91.4	2.5	91.1	1.2	75.8
dialifos	得拉松	insecticide	28.08	208>181	10	208>89	15	1.000	92.8	2.5	89.9	1	95.0
diazinon	大利松	insecticide	17.51	304>179	12	179>137	14	0.992	95.5	4.5	91.3	3.4	85.2
dieldrin	地特靈	insecticide	22.76	263>193	30	263>228	25	0.992	96.1	5	95.9	2.8	47.4
diofenolan		insecticide	24.55	300>186	15	186>158	10	1.000	91	2.4	89.3	2	96.2
disulfoton	二硫松	insecticide	17.61	88 >60	7	274>88	5	0.997	83.6	4.6	80.6	3.4	41.7
endrin	安特靈	insecticide	23.34	263>193	30	263>228	25	1.000	98.4	6	93.3	2.1	9.4
EPN	一品松	insecticide	26.14	157>110	10	157>77	18	1.000	86.8	1.9	89.5	1.2	115.8
ethion	愛殺松	insecticide	23.96	231>129	20	231>175	20	0.991	97	4.6	95.9	2.6	115.2
ethoprophos	普伏松	insecticide	14.9	200>158	4	158>114	6	0.992	90.2	3	85.7	0.5	75.4

表二（續）、土壤中農藥之 GC-MS/MS 分析條件及回收試驗結果

Table 2 (continued). Parameters used in the determination of 195 pesticide residues in soil and recovery test results obtained by GC-MS/MS

Pesticides	Chinese name	Pesticide type [1)]	RT (min)	Quantitative		Qualitative		r^2	Spiked 10 μg/kg		Spiked 40 μg/kg		ME (%)
				ion pairs (m/z)	CE (eV)	ion pairs (m/z)	CE (eV)		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	
etofenprox	依芬寧	insecticide	30.22	163>135	5	163>107	14	0.999	115.4	1.7	119.1	1.6	83.2
etrimfos	益多松	insecticide	17.94	292>181	5	292>153	16	0.993	93.3	2.7	92.3	3.6	92.4
fenchlorphos	樂乃松	insecticide	19.24	285>270	15	285>240	20	0.990	99.1	3.9	94.1	2.9	61.7
fenitrothion	撲滅松	insecticide	19.63	277>260	10	277>109	15	1.000	88.3	9.4	89.2	2.9	110.8
fenpropathrin	芬普寧	insecticide	26.33	181>152	18	208>181	10	0.997	108.3	3.6	113.6	0.1	93.5
fensulfothion	繁福松	insecticide	23.72	156>141	10	292>109	15	1.000	82.9	2.4	84.2	1.7	83.7
fenvalerate	芬化利	insecticide	31.09/31.36	167>125	8	125>89	15	1.000	92.8	1.7	92.8	1.9	72.7
flucythrinate	護賽寧	insecticide	30.12/30.39	199>157	10	451>199	10	1.000	92.8	2.2	92.8	1.3	67.8
fluvalinate	福化利	insecticide	31.43	250>55	10	250>200	15	1.000	90.4	1	90.9	1.5	92.9
fonofos	大福松	insecticide	17.22	246>137	10	246>109	25	0.990	89.8	2.1	86.3	1.4	71.8
formothion	福木松	insecticide	18.25	170>93	10	170>63	20	0.997	82.7	6.8	88	2.5	83.7
halfenprox	合芬寧	insecticide	29.88	263>235	15	263>115	30	1.000	88.7	0.5	89	1.8	81.2
heptenophos	飛達松	insecticide	14	124>89	15	124>63	30	0.994	87.9	3.5	82.4	0.4	79.4
isoxathion	加福松	insecticide	23.25	313>177	10	313>130	10	1.000	93.4	4.4	96.9	2.4	-26.2
leptophos	福賜松	insecticide	27.09	171>77	20	375>360	20	1.000	88.9	2.4	89.2	1.6	91.2
lindane (γ-BHC)	靈丹	insecticide	16.96	219>183	10	181>145	10	0.992	99.5	4.2	94.7	2.8	30.3
malaoxon	馬拉松代謝物	insecticide	18.91	127>99	10	127>109	15	1.000	88.8	4.7	89.1	3	161.0
malathion	馬拉松	insecticide	19.92	173>127	5	173>99	10	1.000	88.7	6	90.2	1.9	103.0

表二（續）、土壤中農藥之 GC-MS/MS 分析條件及回收試驗結果

Table 2 (continued). Parameters used in the determination of 195 pesticide residues in soil and recovery test results obtained by GC-MS/MS

Pesticides	Chinese name	Pesticide type [1)]	RT (min)	Quantitative		Qualitative		r^2	Spiked 10 μg/kg		Spiked 40 μg/kg		ME (%)
				ion pairs (m/z)	CE (eV)	ion pairs (m/z)	CE (eV)		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	
mephosfolan	美福松	insecticide	21.38	196>168	5	196>140	5	1.000	86.2	2.1	88.8	2.1	121.6
methacrifos	滅克松	insecticide	12.73	125>79	5	125>62	5	0.996	75.9	8.9	67.1	9.2	63.4
methidathion	滅大松	insecticide	21.79	145>85	6	145>58	12	1.000	91.8	4.1	92.1	1.8	56.7
methoxychlor		insecticide	26.28	227>169	20	227>212	10	1.000	104.2	6.6	109.7	1.1	-4.3
mevinphos	美文松	insecticide	11.49	127>109	10	192>127	10	0.995	79.9	3.6	73.2	4.1	-4.9
o,p'-DDD	2,4-滴滴滴	insecticide	22.96	235>165	18	235>199	20	0.993	94.2	4.4	91.9	2	49.7
o,p'-DDT	2,4-滴滴涕	insecticide	23.91	235>165	18	235>199	20	1.000	100.9	5.7	100.3	2.1	-11.2
p,p'-DDD	4,4-滴滴滴	insecticide	23.4	235>165	18	235>199	20	0.999	86.7	3.5	83.3	2.3	-91.1
p,p'-DDT	4,4-滴滴涕	insecticide	23.71	235>165	15	235>200	12	0.999	86	6.2	83.7	1.2	-86.9
o,p'-DDE	2,4-滴滴依	metabolite of DDT	21.88	246>176	15	318>246	25	1.000	94	4.2	90.9	1.3	60.1
p,p'-DDE	4,4-滴滴依	metabolite of DDT	22.85	246>176	15	318>246	25	0.999	87.3	4.8	82	2.2	-90.1
paraoxon	巴拉松代謝物	insecticide	19.23	149>119	5	149>91	15	1.000	85.3	2.4	86.3	1.8	102.1
parathion	巴拉松	insecticide	20.23	291>109	15	291>142	5	1.000	89.3	6.3	88.7	3	98.0
parathion-methyl	甲基巴拉松	insecticide	18.89	263>109	15	263>127	20	1.000	86.9	0.9	88.8	2.8	111.2
permethrin	百滅寧	insecticide	28.57-28.74	163>127	5	183>153	10	1.000	90.9	1.5	92.9	1.4	97.6
phenothrin	酚丁滅蝨成分之一	insecticide	26.84	183>168	15	183>153	12	0.982	115.7	2.4	90.2	5	107.6
phenthoate	賽達松	insecticide	21.42	274>246	4	274>121	7	1.000	89.3	4.2	87.7	2.1	86.1

表二（續）、土壤中農藥之 GC-MS/MS 分析條件及回收試驗結果

Table 2 (continued). Parameters used in the determination of 195 pesticide residues in soil and recovery test results obtained by GC-MS/MS

Pesticides	Chinese name	Pesticide type [1)]	RT (min)	Quantitative		Qualitative		r^2	Spiked 10 μg/kg		Spiked 40 μg/kg		ME (%)
				ion pairs (m/z)	CE (eV)	ion pairs (m/z)	CE (eV)		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	
phorate	福瑞松	insecticide	15.86	260>75	8	260>231	10	0.991	76.8	2.1	71.5	1.9	76.4
phosalone	裕必松	insecticide	27.04	182>111	12	182>138	6	1.000	89.3	1.2	89.8	0.8	105.3
phosmet	益滅松	insecticide	26.07	160>133	10	160>105	14	1.000	91.9	0.8	92.9	1.4	98.3
pirimiphos-ethyl	乙基亞特松 (必滅松)	insecticide	20.82	318>166	10	318>182	15	1.000	93	5.1	90.7	2	91.4
pirimiphos-methyl	亞特松	insecticide	19.67	290>125	20	290>151	20	1.000	91	1.6	87.6	2.1	89.5
propaphos	加護松	insecticide	21.83	220>140	10	220>125	30	1.000	84.6	3.4	81.3	2.2	95.7
prothiofos	普硫松	insecticide	28.07	360>194	8	360>139	14	1.000	86.7	3.5	85.3	2	80.3
pyridaphenthion	必芬松	insecticide	25.98	340>199	15	340>109	16	1.000	89.3	1.2	87.7	0.8	141.9
pyrimidifen	畢汰芬	insecticide	30.83	184>169	20	161>135	30	1.000	91.6	2	91.9	1.8	96.7
pyriproxyfen	百利普芬	insecticide	27.14	136>96	8	136>78	18	1.000	93.1	0.8	93.4	0.4	92.9
quinalphos	拜裕松	insecticide	21.42	146>118	10	157>129	10	1.000	94.7	1.8	90.3	3.2	67.3
salithion (dioxabenofos)	殺力松	insecticide	15.49	216>201	6	216>138	10	0.992	87.2	3.9	82.9	1.7	70.4
silafluofen	矽護芬	insecticide	30.42	179>151	10	179>91	15	0.991	101.3	1.2	100.5	1.6	77.8
tefluthrin	汰福寧	insecticide	17.84	177>127	15	197>141	10	0.991	95.5	4.6	92.8	2.5	53.6
terbufos	托福松	insecticide	17.12	231>175	10	153>97	8	0.992	86.3	1.7	79.2	1.1	62.0
thiometon	硫滅松	insecticide	16.16	125>79	6	125>47	15	0.994	72.5	1.9	65.3	1.7	58.4
triazophos	三落松	insecticide	24.32	257>162	10	257>119	22	1.000	81.8	7.6	83.5	0.8	149.1
δ-BHC	δ-蟲必死	insecticide	17.74	219>183	10	181>145	10	0.996	115.3	5.6	114.4	1.5	59.9
λ-cyhalothrin	賽洛寧	insecticide	27.56	208>181	10	181>152	10	1.000	87.1	2.6	91.5	1.9	80.3

表二（續）、土壤中農藥之 GC-MS/MS 分析條件及回收試驗結果

Table 2 (continued). Parameters used in the determination of 195 pesticide residues in soil and recovery test results obtained by GC-MS/MS

Pesticides	Chinese name	Pesticide type [1)]	RT (min)	Quantitative		Qualitative		r^2	Spiked 10 μg/kg		Spiked 40 μg/kg		ME (%)
				ion pairs (m/z)	CE (eV)	ion pairs (m/z)	CE (eV)		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	
bromophos-ethyl	乙基溴磷松	insecticide	21.85	359>303	25	359>331	5	1.000	95.4	3.2	91.1	2.4	57.2
heptachlor	飛佈達	insecticide	18.99	272>237	15	237>167	30	1.000	97.4	1.2	90.9	2.6	8.8
heptachlor epoxide	環氧飛佈達	metabolite of heptachlor	21.09	353>263	15	353>289	15	0.991	98.2	3.7	94.8	2.5	37.7
isofenphos	亞芬松	insecticide	21.33	213>185	15	213>121	10	1.000	94.4	5.9	91.5	2.8	86.2
tetramethrin	治滅寧	insecticide	25.99-26.17	164>107	10	164>135	5	1.000	101.8	4.3	90	3.5	120.2
acrinathrin	阿納寧	insecticide	27.82	208>181	10	181>152	10	1.000	93.5	2.2	92.1	1	116.3
azinphos-methyl	谷速松	insecticide	27.07	160>132	5	160>77	15	1.000	87.6	1.6	86.8	1.4	102.0
bromophos-methyl	(甲基)溴磷松	insecticide	20.68	331>316	20	331>286	25	0.990	97.8	5.3	95.2	3.3	47.6
esfenvalerate	益化利	insecticide	31.36	167>125	8	125>89	15	0.999	86.7	3.5	82.3	1.4	64.8
α-BHC	α-蟲必死	insecticide	15.97	219>183	10	181>145	10	0.995	92.1	6.1	88.6	1	47.0
α-cypermethrin	亞滅寧	insecticide	28.9-29.16	163>127	5	181>152	10	0.999	85.3	3.6	82	1.2	-89.2
α-endosulfan	α-安殺番	insecticide	22.06	241>206	10	195>159	6	0.992	99.7	4	95.7	0.5	63.3
β-BHC	β-蟲必死	insecticide	16.03	219>183	10	181>145	10	0.999	82.7	9.8	78	2.2	-90.7
β-endosulfan	β-安殺番	insecticide	23.6	195>159	6	241>206	10	1.000	89.7	3.9	88.9	1.2	47.8
endosulfan-sulfate	安殺番代謝物	metabolite of endosulfan	24.73	272>237	10	387>253	10	1.000	89.9	0.8	89	2.7	46.2
4,4'-dichlorobenzo-phenone (DCBP)	大克蟎降解物	degradation of dicofol	19.41	139>111	10	250>139	5	1.000	91.6	1.8	93.9	2.4	88.7

[1)] Data from PPDB [(8)].

表三、液相層析移動相梯度條件

Table 3. Parameters of the UPLC mobile phase elution used for the (A) ESI^+ mode and (B) ESI^- mode

(A)

Time (min)	Flow rate (mL/min)	Mobile phase A (%) [1)]	Mobile phase B (%) [2)]
0	0.3	99	1
2	0.3	50	50
8	0.3	30	70
10	0.3	10	90
12	0.3	1	99
13	0.3	1	99
13.5	0.3	99	1
15	0.3	99	1

(B)

Time (min)	Flow rate (mL/min)	Mobile phase A (%) [1)]	Mobile phase B (%) [2)]
0	0.3	99	1
1	0.3	10	90
2	0.3	1	99
3.2	0.3	1	99
3.5	0.3	99	1
5	0.3	99	1

[1)] Mobile phase A solution: 5 mM ammonium acetate solution (containing 0.1% formic acid).

[2)] Mobile phase B solution: 5 mM ammonium acetate in methanol.

表四、土壤中農藥之 LC-MS/MS 分析條件及回收試驗結果

Table 4. Parameters used for the determination of 157 pesticide residues in soil and recovery test results obtained by LC-MS/MS

Pesticides	Chinese name	Pesticide type [1)]	RT (min)	Precursor ion (m/z)	Cone voltage (V)	Quantitative		Qualitative		r^2	Spiked 4 μg/kg		Spiked 20 μg/kg		ME (%)
						Product ion (m/z)	CE (eV)	Product ion (m/z)	CE (eV)		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	
etoxazole	依殺蟎	acaricide	10.83	360	35	141	35	304	17	0.996	98.3	1.7	96.6	6.5	-10.5
fenothiocarb	芬硫克	acaricide	7.88	254	17	160	11	107	26	0.996	97.4	8.2	88.3	8.1	-4.8
fenpyroximate	芬普蟎	acaricide	10.93	422	32	366	15	138	32	0.999	93.9	2.1	93.5	6	8.9
hexythiazox	合賽多	acaricide	10.64	353	30	228	14	168	26	0.995	97.4	5.7	95.4	9	19.3
propargite	毆蟎多	acaricide	10.83	368	15	231	11	175	17	0.996	100.1	5.8	94.2	7.9	-3.8
spirodiclofen	賜派芬	acaricide	10.97	411	25	313	11	71	14	0.997	92.6	4	92.6	5.4	-3.6
clofentezine	克芬蟎	acaricide	9.08	303	25	138	23	102	44	0.998	90.9	4.4	100.2	12.7	3.5
tebufenpyrad	得芬瑞	acaricide	10.3	334	52	117	34	145	28	0.997	95.8	10.1	94	5.2	2.9
azoxystrobin	亞托敏	fungicide	5.9	404	28	372	15	329	30	0.994	93.6	0.1	91.4	4.7	6.0
benalaxyl	本達樂	fungicide	8.65	326	26	148	20	91	34	0.998	92.9	4.7	95	3.4	2.3
benthiazole	佈生	fungicide	5.88	239	15	180	12	218	20	0.998	90.1	4.2	90.7	5.7	1.1
boscalid	白克列	fungicide	6.36	343	41	307	20	140	20	0.999	100	5.7	98.2	7.1	18.9
carbendazim	貝芬替	fungicide	2.72	192	33	160	18	132	28	0.998	64.3	6.3	63.6	4.2	0.6
carboxin		fungicide	4.17	236	34	143	16	87	22	0.996	66	9.6	78.9	9.7	-0.3
carpropamid	加普胺	fungicide	8.52	334	20	139	20	196	14	0.996	99.4	1.8	100.7	8.5	-1.6
cyazofamid	賽座滅	fungicide	7.61	325	26	108	20	261	10	0.999	98.7	6.2	99.2	6.1	-4.8
cymoxanil	克絕	fungicide	3.15	199	17	128	8	111	18	0.992	88.7	4.6	88.3	2.5	-39.0
cyprodinil	賽普洛	fungicide	8.13	226	56	93	33	108	25	0.999	89.6	6.1	97.2	5.8	1.6
dimethomorph	達滅芬	fungicide	6.93	388	41	301	20	165	30	0.997	97.9	2.2	98.5	5.3	8.4
dimoxystrobin		fungicide	8.19	327	24	205.2	10	116	21	0.999	99	2	98.8	4.6	-7.8

表四（續）、土壤中農藥之 LC-MS/MS 分析條件及回收試驗結果

Table 4 (continued). Parameters used for the determination of 157 pesticide residues in soil and recovery test results obtained by LC-MS/MS

Pesticides	Chinese name	Pesticide type [1)]	RT (min)	Precursor ion (m/z)	Cone voltage (V)	Quantitative		Qualitative		r^2	Spiked 4 μg/kg		Spiked 20 μg/kg		ME (%)
						Product ion (m/z)	CE (eV)	Product ion (m/z)	CE (eV)		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	
famoxadone	凡殺同	fungicide	9.01	392	20	331	11	238	20	0.990	97.3	6.8	84.7	5.3	8.8
fenoxanil		fungicide	8.07	329	25	302	16	189	24	0.999	94.1	3.3	93.5	7.6	3.2
fluopicolide	氟比來	fungicide	6.67	385	29	175	23	147	49	0.998	99.9	4.4	96.8	7.2	1.0
fluquinconazole		fungicide	7.09	378	35	351	19	309	25	0.994	97.1	17.5	89.6	15	13.9
flusilazole	護矽得	fungicide	8.31	316	32	165	26	247	16	0.999	95.8	5.9	96.5	7.2	5.6
flutriafol	護汰芬	fungicide	4.85	302	26	70	18	123	29	0.999	90.5	3.5	90.7	5.5	9.1
furametpyr	福拉比	fungicide	4.84	334	28	157	32	131	24	0.999	95.6	2.9	95.7	5.5	1.1
imazalil	依滅列	fungicide	5.08	297	40	159	22	69	22	0.999	79.1	8.1	80.8	8.2	21.7
iprovalicarb		fungicide	7.17	321	22	119	16	203	10	0.997	101.3	5.6	100.8	5.5	0.6
isoprothiolane	亞賜圃	fungicide	6.77	291	26	189	22	231	12	0.996	114.8	3.8	105.7	4.6	-17.8
mepanipyrim	滅派林	fungicide	7.02	224	38	106	24	131	22	0.997	106	4.1	105.3	4.6	6.1
metalaxyl	滅達樂	fungicide	5.06	280	26	220	13	192	17	0.999	93.8	2.7	94.3	5.3	3.8
metrafenone	滅芬農	fungicide	9.3	409	20	209	17	227	29	0.999	96.7	2.4	94	7.9	3.5
oxycarboxin	嘉保信	fungicide	3.15	268	26	175	16	147	25	0.996	94.9	4	93.2	4.9	1.2
prochloraz	撲克拉	fungicide	9.16	376	17	308	11	266	14	0.998	98	5.8	96	8.3	-2.9
pyraclostrobin	百克敏	fungicide	9.04	388	31	194	12	163	25	0.997	97	7.2	96.1	6.8	0.4
pyrifenox	比芬諾	fungicide	7.51	295	29	93	22	263	14	1.000	87	5.8	89.3	5.7	5.7
quinoxyfen	快諾芬	fungicide	10.59	308	60	197	32	162	44	0.996	96.2	9.3	95.5	6.1	-22.9
spiroxamine		fungicide	6.51	298	32	144	20	100	32	0.997	92.3	6.1	95.1	5	35.6
triticonazole		fungicide	7.42	318	25	70	16	125	35	0.998	97.9	5.8	92.3	7.2	10.7

表四（續）、土壤中農藥之 LC-MS/MS 分析條件及回收試驗結果

Table 4 (continued). Parameters used for the determination of 157 pesticide residues in soil and recovery test results obtained by LC-MS/MS

Pesticides	Chinese name	Pesticide type [1)]	RT (min)	Precursor ion (m/z)	Cone voltage (V)	Quantitative		Qualitative		r^2	Spiked 4 μg/kg		Spiked 20 μg/kg		ME (%)
						Product ion (m/z)	CE (eV)	Product ion (m/z)	CE (eV)		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	
pencycuron	賓克隆	fungicide	9.46	329	40	125	22	136	26	0.999	78.3	2	79.8	5.1	1.2
tricyclazole	三賽唑	fungicide	3.3	190	38	163	20	148	50	0.996	99.3	18.9	89.6	10.6	-0.3
amisulbrom	安美速	fungicide	9.99	468	20	229	16	125	36	0.998	105.3	4.8	95.5	4.1	4.7
metconazole-cis	滅特座	fungicide	9.08	320	38	70	22	159	38	0.999	93.9	1.6	93.8	4.2	5.3
zoxamide	座賽胺	fungicide	8.67	336	32	187	25	136	30	0.995	99.2	2.7	84.6	10.8	6.8
alloxydim	亞汰草	herbicide	7.78	324	25	234	15	266	11	0.999	93.3	5.9	92.1	7.2	-4.3
ametryn	草殺淨	herbicide	5.71	228	32	186	25	96	19	1.000	93.5	1	90.7	4.8	4.0
atrazine	草脫淨	herbicide	4.87	216	39	174	18	96	23	0.999	90.2	1.8	91.7	4.6	-4.6
azafenidin	草芬定	herbicide	5.08	338	35	264	29	112	56	0.997	95.6	4.7	91.3	4.6	4.3
bensulfuron-methyl	免速隆	herbicide	5.44	411	33	149	22	182	20	0.997	70	7.4	72.5	5.3	2.1
bentazone	本達隆	herbicide	1.8	239	-37	132	-26	197	-22	0.991	95.2	1.8	77.7	7	-3.6
bromobutide		herbicide	7.39	312	17	194	11	119	29	1.000	83.4	3.1	87.9	2.9	1.2
butafenacil		herbicide	7.26	492	20	331	26	180	40	0.998	108.2	5.6	108.3	6.3	4.2
carfentrazone-ethyl	乙基克繁草	herbicide	8.28	412	36	346	24	366	18	0.997	94.1	12.7	94.8	9.1	-3.6
clomazone	可滅蹤	herbicide	5.62	240	32	125	18	89	46	0.997	79.9	4.3	87.7	7	1.1
clomeprop	克普草	herbicide	10.25	324	25	203	17	120	15	0.995	104.9	14.2	100.2	7.3	11.6
cyanazine	氰乃淨	herbicide	3.65	241	41	214	17	96	25	0.998	93.9	5.2	92.7	5.1	36.6
cyclosulfamuron	環磺隆	herbicide	6.97	422	25	261	18	218	26	0.999	92.8	3.7	94.2	3.8	-2.9
diuron	達有龍	herbicide	5.08	233	23	72	15	160	27	0.994	90.6	4.3	93.8	5.2	0.6

表四（續）、土壤中農藥之 LC-MS/MS 分析條件及回收試驗結果

Table 4 (continued). Parameters used for the determination of 157 pesticide residues in soil and recovery test results obtained by LC-MS/MS

Pesticides	Chinese name	Pesticide type [1)]	RT (min)	Precursor ion (m/z)	Cone voltage (V)	Quantitative		Qualitative		r^2	Spiked 4 μg/kg		Spiked 20 μg/kg		ME (%)
						Product ion (m/z)	CE (eV)	Product ion (m/z)	CE (eV)		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	
dymron	汰草龍	herbicide	6.63	269	30	151	10	91	40	0.999	98.2	1.1	97.1	8.7	4.2
ethofumesate	益覆滅	herbicide	5.97	287	36	121	15	259	10	0.996	94.9	14.5	94.4	8.7	6.6
fluazifop-P-butyl	伏寄普	herbicide	10.25	384	38	282	22	328	16	0.995	96.5	3.5	94.2	5.4	-18.3
isouron	愛速隆	herbicide	4.15	212	30	167	15	72	23	0.998	93.2	0.1	92.1	3.3	3.5
lenacil		herbicide	4.89	235.2	21	153.1	16	136.1	32	0.997	91.8	3.3	93.6	4.5	5.9
linuron	理有龍	herbicide	5.9	249	21	160	21	182	18	0.994	100.4	9.8	98.3	6.8	5.6
metobromuron	撲多草	herbicide	4.71	259	25	170	20	148	15	0.999	91.1	6.4	91.9	5.7	3.9
naproanilide	奈普草	herbicide	7.85	292	22	171	14	120	24	0.997	91	1.3	94.3	7.2	4.4
norflurazon		herbicide	5.18	304	39	284	24	160	33	0.999	91.4	1	93.2	6.3	3.2
penoxsulam	平速爛	herbicide	4.21	484	36	195	32	164	34	0.996	86.1	6.1	87.2	4.3	2.3
pretilachlor	普拉草	herbicide	9.86	312	18	252	18	176	27	0.998	110.5	5.1	107.6	12.8	-21.9
propanil	除草靈	herbicide	5.97	218	40	162	16	127	22	0.999	86	2.8	96.3	5.7	8.7
quizalofop-ethyl	快伏草	herbicide	10.07	373	40	299	18	91	32	0.999	90.3	3.8	95.8	8.6	76.4
simazine	草滅淨	herbicide	3.99	202	40	124	16	96	22	0.992	97.5	0.8	92.8	5	-0.3
tepraloxydim	得殺草	herbicide	7	342	20	250	15	166	23	1.000	100.7	15	85.3	18.7	-5.1
thiobencarb	殺丹	herbicide	9.32	258	25	125	18	100	12	0.998	106	5	105.6	9.1	1.5
dimethinamid	汰草滅	herbicide	6.19	276	26	244	14	168	26	0.999	88.5	0.8	89.5	5.8	8.2
pyrazoxyfen	普芬草	herbicide	8.61	403	45	91	37	105	21	0.999	111	11.7	99.7	7.7	7.2
pyridate	必汰草	herbicide	11.47	379	19	207	18	351	10	0.999	90.7	3	90.4	7.1	-3.1

表四（續）、土壤中農藥之 LC-MS/MS 分析條件及回收試驗結果

Table 4 (continued). Parameters used for the determination of 157 pesticide residues in soil and recovery test results obtained by LC-MS/MS

Pesticides	Chinese name	Pesticide type [1)]	RT (min)	Precursor ion (m/z)	Cone voltage (V)	Quantitative		Qualitative		r^2	Spiked 4 μg/kg		Spiked 20 μg/kg		ME (%)
						Product ion (m/z)	CE (eV)	Product ion (m/z)	CE (eV)		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	
abamectin	阿巴汀	insecticide	11.35	890.5	20	567	11	305	23	0.999	96	7.2	94.6	6.1	19.7
acetamiprid	亞滅培	insecticide	2.97	223	26	126	21	90	35	0.994	103.9	1.1	97.5	7.1	98.5
amitraz	三亞蟎	insecticide	11.11	294	20	163	14	122	32	0.995	69.1	4	70.3	8.5	-53.8
bendiocarb	免敵克	insecticide	3.97	224	26	167	8	109	18	0.991	90.1	4.2	91.4	5.5	-7.4
buprofezin	布芬淨	insecticide	10.35	306	20	201	13	116	15	0.998	103.9	5.6	98.4	7.8	-15.3
carbaryl	加保利	insecticide	4.23	202	28	145	22	117	28	0.997	95.4	2	90.2	5	-6.3
carbofuran	加保扶	insecticide	3.99	222	34	165	16	123	16	0.997	96	2.5	97.5	5.3	-0.6
chlorantraniliprole	剋安勃	insecticide	5.45	484	24	453	22	286	14	0.998	88.3	3.9	92.6	6.6	8.8
chromafenozide	可芬諾	insecticide	7.19	395	15	175	17	339	8	0.997	109	3.9	105.2	6.5	5.4
clothianidin	可尼丁	insecticide	2.82	250	24	169	12	132	18	0.990	96.1	2.9	95.3	4.9	-4.6
dicrotophos	雙特松	insecticide	2.69	238	28	193	10	112	10	0.992	84.2	1.6	86.8	4.9	26.7
diethofencarb		insecticide	5.88	268	19	226	10	124	40	0.993	91.9	12.5	87.2	4.5	-9.6
dimethoate	大滅松	insecticide	3	230	14	199	11	125	20	0.992	95.9	1.3	95.4	2.6	72.4
dinotefuran	達特南	insecticide	2.15	203	20	157	8	129	14	0.995	97.1	6.4	97.4	5.6	-3.4
fenamiphos	芬滅松	insecticide	7.93	304	27	217	24	109	25	0.996	94.3	7.5	93.7	7.5	7.0
fenazaquin	芬殺蟎	insecticide	11.19	307	29	161	17	131	47	0.996	101.4	3.4	96.4	6.6	11.3
fenbutatin-oxide	芬佈賜	Insecticide	12.44	519.4	44	197	54	351	32	0.999	102.3	8	100.5	7.2	-4.3
fenobucarb	丁基滅必蝨	insecticide	5.9	208	22	152	8	95	14	0.999	87.4	9.6	89	8.5	-2.3
fenoxycarb	芬諾克	insecticide	8.09	302	28	116	11	88	20	0.995	89	1.4	92.1	3	1.1
fipronil	芬普尼	insecticide	2.17	435	-29	330	-15	250	-27	0.990	97.5	14.2	99.5	8.5	-30.9

表四（續）、土壤中農藥之 LC-MS/MS 分析條件及回收試驗結果

Table 4 (continued). Parameters used for the determination of 157 pesticide residues in soil and recovery test results obtained by LC-MS/MS

Pesticides	Chinese name	Pesticide type [1)]	RT (min)	Precursor ion (m/z)	Cone voltage (V)	Quantitative		Qualitative		r^2	Spiked 4 μg/kg		Spiked 20 μg/kg		ME (%)
						Product ion (m/z)	CE (eV)	Product ion (m/z)	CE (eV)		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	
flonicamid	氟尼胺	insecticide	2.52	230	32	203	18	174	18	0.990	96.7	4.3	97.1	6.9	-21.7
flufenoxuron	氟芬隆	insecticide	10.85	489	40	158	22	141	46	0.996	98.7	2.1	94.4	8.5	4.9
imidacloprid	益達胺	insecticide	2.77	256	34	175	20	209	15	0.993	92.5	4.6	90.6	6.8	55.7
indoxacarb	因得克	insecticide	9.88	528	34	203	40	150	22	0.998	91.3	8.4	96.5	7.8	-37.3
isazofos	依殺松	insecticide	7	314	20	162	17	120	32	0.998	96.1	4	90.9	6.3	0.0
mecarbam	滅加松	insecticide	7.28	330	21	227	8	97	35	0.996	109.6	7.6	105.3	11.4	0.0
metaflumizon	美氟綜	insecticide	10.45	507	40	287	26	267	32	0.997	107.6	5.4	106.3	6.5	-11.7
methiocarb	滅賜克	insecticide	6.12	226	28	169	10	121	22	0.997	93.7	4.6	88	7.9	1.3
methoxyfenozide	滅芬諾	insecticide	6.7	369	34	149	18	313	8	0.993	91.8	2.9	92.4	4	11.4
monocrotophos	亞素靈	insecticide	2.58	224	26	127	16	98	12	0.997	94.1	0.8	94.2	4.8	41.6
omethoate	歐滅松	insecticide	2.08	214	20	183	10	155	15	0.998	101	5.2	84.1	19.7	-3.6
oxamyl	歐殺滅	insecticide	2.31	237	21	72	10	90	10	0.996	80.5	5.8	89.7	6.3	4.8
oxydemeton methyl	滅多松	insecticide	2.42	247	20	169	14	313	-31	0.999	82	16.4	84.7	10.9	41.0
paraoxon-methyl	甲基巴拉松代謝物	insecticide	3.48	248	40	202	19	109	31	0.996	68.5	1.2	75.5	6.5	45.8
phosphamidon	福賜米松	insecticide	3.58	300	23	127	14	227	23	0.996	91.8	1.5	91.4	5.8	14.6
phoxim	巴賽松	insecticide	9.02	299	20	129	11	153	7	0.992	88.6	2	84.4	4	-0.6
pirimicarb	比加普	insecticide	4.29	239	34	72	18	182	15	0.991	95.9	1.3	93.2	4.4	2.8
pirimicarb-desmethyl	比加普代謝物	insecticide	3.12	225	25	168	15	180	13	0.998	85	7.3	83.1	3.8	2.5

表四（續）、土壤中農藥之 LC-MS/MS 分析條件及回收試驗結果

Table 4 (continued). Parameters used for the determination of 157 pesticide residues in soil and recovery test results obtained by LC-MS/MS

Pesticides	Chinese name	Pesticide type [1)]	RT (min)	Precursor ion (m/z)	Cone voltage (V)	Quantitative		Qualitative		r^2	Spiked 4 μg/kg		Spiked 20 μg/kg		ME (%)
						Product ion (m/z)	CE (eV)	Product ion (m/z)	CE (eV)		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	
profenophos	佈飛松	insecticide	10.12	373	36	345	20	128	40	0.998	92.2	1.1	91.6	4.9	-17.9
promecarb	普滅克	insecticide	6.5	208	26	151	9	109	15	0.993	82.7	3.2	82.9	6.2	-1.1
propoxur	安丹	insecticide	3.95	210	21	111	16	168	10	0.996	75.7	12.2	80.8	3.6	0.7
pyridaben	畢達本	insecticide	11.21	365	28	147	24	309	12	1.000	115.4	5.9	110	6.1	-27.3
spinetoram J	賜諾特 J	insecticide	10.28	748	80	142	31	98	62	0.992	89.4	9.3	89.6	5.6	-7.9
spinetoram L	賜諾特 L	insecticide	10.81	760	80	142	29	98	40	0.999	95.6	0.6	95.5	6.6	-25.6
spinosad A	賜諾殺 A	insecticide	9.65	732.6	56	142	31	98	59	0.994	92	4.4	95.8	6.7	6.7
spinosad D	賜諾殺 D	insecticide	10.23	746.5	51	142	31	98	53	0.991	98.7	3	97.3	7.7	5.4
spirotetramat	賜滅派	insecticide	7.29	374.3	25	302	17	216	35	0.996	90.7	6	92	10.6	13.0
tebufenozide	得芬諾	insecticide	8.07	353	19	297	8	133	20	0.999	88.2	4.1	92.4	6.9	2.0
tetrachlorvinphos	樂本松	insecticide	8.19	367	26	127	14	206	35	0.993	107.3	6.1	104.2	3.4	-12.5
thiacloprid	賽果培	insecticide	3.15	253	41	126	20	90	40	0.998	95.4	1	94.6	5.4	-1.7
thiodicarb	硫敵克	insecticide	4.27	355	26	88	16	108	16	0.999	94.1	12.5	96.3	5.2	10.1
tolfenpyrad	脫芬瑞	insecticide	10.43	384	45	197	32	145	26	1.000	92.5	1.3	92.6	4.4	-6.7
trichlorfon	三氯松	insecticide	3.02	257	28	109	18	79	30	0.998	83.3	4.5	85.2	5.2	-32.9
vamidothion	繁米松	insecticide	2.95	288	17	146	14	118	23	0.999	93.5	2.1	94.1	4.6	-22.1
ethiprole	益斯普	insecticide	6.28	397	34	351	18	255	36	0.999	79.6	5.9	74.6	16.5	11.1
isoprocarb	滅必蝨	insecticide	4.87	194	24	95	14	137	8	0.997	85.1	7	88.9	5.7	1.6

表四（續）、土壤中農藥之 LC-MS/MS 分析條件及回收試驗結果

Table 4 (continued). Parameters used for the determination of 157 pesticide residues in soil and recovery test results obtained by LC-MS/MS

Pesticides	Chinese name	Pesticide type [1)]	RT (min)	Precursor ion (m/z)	Cone voltage (V)	Quantitative		Qualitative		r^2	Spiked 4 μg/kg		Spiked 20 μg/kg		ME (%)
						Product ion (m/z)	CE (eV)	Product ion (m/z)	CE (eV)		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	
thiamethoxam	賽速安	insecticide	2.52	292	28	211	12	132	22	0.998	87.4	0.5	91.1	6.1	34.5
XMC (macbal)	滅克蝨	insecticide	4.33	180	20	123	13	108	29	0.997	98.6	3.2	96.2	4.6	-6.8
xylycarb (meobal) (MPMC)	滅爾蝨	insecticide	4.5	180	20	123	13	108	29	0.995	100.2	2.8	97.5	5	2.0
acephate	毆殺松	insecticide	1.97	184	17	143	8	125	18	0.998	86.9	2.2	86.4	9.8	-2.6
aldicarb	得滅克	insecticide	3.45	208	10	89	20	116	8	0.994	80.5	16.6	85	9.5	2.7
demeton-S-methyl	滅賜松	insecticide	4.05	231	10	89	10	61	30	1.000	89.4	9.6	90.9	9.8	-3.2
acequinocyl-OH	亞醌蟎代謝物	metabolite of acequinocyl	3.14	341	-60	186	-35	86	14	0.998	90.1	3.6	90.3	5.8	-54.5
aldicarb-sulfone	得滅克颯	metabolite of aldicarb	2.26	223	31	148	10	89	14	1.000	95.9	3.1	93.7	5.5	15.6
aldicarb-sulfoxide	得滅克亞颯	metabolite of aldicarb	2.16	207	22	132	10	161	18	0.998	78.4	7.3	87.4	5.6	-5.7
3-keto carbofuran	3-酮基加保扶	metabolite of carbofuran	3.37	236	24	179	12	181	10	0.999	95.4	6.1	94.2	4.7	1.9
3-OH carbofuran	3-羥基加保扶	metabolite of carbofuran	2.97	238	34	163	16	308	15	0.995	101.9	11.8	92.7	6.7	9.8

表四（續）、土壤中農藥之 LC-MS/MS 分析條件及回收試驗結果

Table 4 (continued). Parameters used for the determination of 157 pesticide residues in soil and recovery test results obtained by LC-MS/MS

Pesticides	Chinese name	Pesticide type [1)]	RT (min)	Precursor ion (m/z)	Cone voltage (V)	Quantitative		Qualitative		r^2	Spiked 4 μg/kg		Spiked 20 μg/kg		ME (%)
						Product ion (m/z)	CE (eV)	Product ion (m/z)	CE (eV)		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	
demeton-S-methyl-sulfone	滅賜松代謝物	metabolite of Demeton-S-Methyl	2.49	263	26	169	17	121	17	0.996	80	5	81.1	5.2	39.4
fenamiphos-sulfone	芬滅松代謝物	metabolite of fenamiphos	4.09	336	35	266	19	171	21	0.996	97	6.3	89.8	3.5	7.4
fenamiphos-sulfoxide	芬滅松代謝物	metabolite of fenamiphos	3.97	320	144	233	21	216	25	0.994	72.2	17.8	78.4	10.7	12.2
fenthion-oxon	芬殺松代謝物	metabolite of fenthion	5.53	263	35	231	15	104	23	0.999	88	4.8	83.7	3.6	9.2
fenthion-oxon-sulfone	芬殺松代謝物	metabolite of fenthion	3.02	295	35	217	19	109	28	0.992	97.3	3.7	92.2	5.2	-7.3
fenthion-sulfone	芬殺松代謝物	metabolite of fenthion	4.27	311	32	125	22	109	32	0.999	86.6	0.6	90.2	5	4.4
fenthion-sulfoxide	芬殺松代謝物	metabolite of fenthion	4.09	295	32	280	18	282	-27	0.997	93.5	2.5	89.7	4.7	7.7
fipronil-desulfinyl	芬普尼代謝物	metabolite of fipronil	2.17	387	-24	351	-15	282	-27	0.999	94.3	1.6	94.9	5.3	-11.9
fipronil-sulfone	芬普尼代謝物	metabolite of fipronil	2.19	451	-33	415	-15	79	29	0.999	95.1	1.4	94.8	5.9	-41.7

表四（續）、土壤中農藥之 LC-MS/MS 分析條件及回收試驗結果

Table 4 (continued). Parameters used for the determination of 157 pesticide residues in soil and recovery test results obtained by LC-MS/MS

Pesticides	Chinese name	Pesticide type [1)]	RT (min)	Precursor ion (m/z)	Cone voltage (V)	Quantitative		Qualitative		r^2	Spiked 4 μg/kg		Spiked 20 μg/kg		ME (%)
						Product ion (m/z)	CE (eV)	Product ion (m/z)	CE (eV)		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	
methiocarb-sulfone	滅賜克代謝物	metabolite of methiocarb	3.02	258	25	122	19	107	38	0.997	96.6	16.2	94	4	-3.6
methiocarb-sulfoxide	滅賜克代謝物	metabolite of methiocarb	2.87	242	20	185	14	122	28	0.998	91.7	1	90.2	5.7	92.4
DMST		metabolite of tolylfluanid	4.1	215	20	106	15	202	36	0.996	100.7	0.6	109.4	4.7	-3.0

[1)] Data from PPDB [(8)].

面積，分別與標準溶液比較鑑別並定量之，求取回收率。

結果與討論

一、基質效應

考量土壤樣品是一種含大量化合物的複雜基質，這些化合物會干擾分析物信號，產生基質效應，為了減少基質效應的影響，需使用基質匹配檢量線來進行定量[19]。進一步以標準品溶於純溶劑和基質的檢量線斜率評估基質效應，如基質效應微弱 (增強或抑制 0~20%)，可忽視基質干擾，但具中等 (增強或抑制 20~50%) 或強烈 (增強或抑制> 50%) 基質效應，則必須使用基質匹配檢量線來克服基質的影響[11, 12, 13, 14]。以 GC-MS/MS 分析的 195 種農藥，高達 188 種基質效應超過 ± 20%，且多屬基質增強效應 (表二)。UPLC-MS/MS 分析之 157 種農藥，只有 27 種基質效應超過 ± 20% (表四)。GC-MS/MS 基質效應明顯大於 UPLC-MS/MS，更需以相同基質來製備檢量線作為精確定量之方法。

二、添加回收試驗

黏土因土壤中黏粒含量較高，比表面積較大，容易吸附農藥，如所用檢測方式萃取效率不佳，將無法獲得良好的回收試驗結果，本試驗選擇有機質含量 1.78% 之黏土作為空白土壤 (表一)。GC-MS/MS 基質匹配檢量線範圍為 5~500 μg/L，將 GC-MS/MS 分析之 195 種農藥添加於土壤中，使其濃度分別為 10 及 40 μg/kg，進行方法回收率試驗 (n = 3)。添加濃度為 10 μg/kg 時，195 種農藥回收率介於 64.5~115.6%，相對標準偏差皆小於 20%。添加濃度為 40 μg/kg 時，195 種農藥回收率介於 60.1~119.1%，相對標準偏差在 10% 以下。

UPLC-MS/MS 基質匹配檢量線範圍為 2~200 μg/L，將 UPLC-MS/MS 分析之 157 種農藥添加於土壤中，使其濃度分別為 4 及 20 μg/kg。添加濃度為 4 μg/kg 時，157 種農藥回收率介於 64.3~115.4%，相對標準偏差皆小於 20%。添加濃度為 20 μg/kg 時，157 種農藥回收率介於 63.6~110.0%，相對標準偏差皆在 20% 以下。

此檢驗方法分析黏土土壤中 352 種農藥殘留時，在高及低濃度添加回收試驗之回收率皆可在 60~120% 範圍內，相對標準偏差小於 20%，GC-MS/MS 及 UPLC-MS/MS 分析農藥之定量極限，分別為 10 及 4 μg/kg。土壤農藥殘留分析方法之確效，通常要求回收率介於 70~120%之間，相對偏差 20%以下[13, 19]，97% 以上之農藥可達此範圍，無法達到的農藥品項為克氯得、tecnazene、稻得壯、滅克松、硫滅松、貝芬替、carboxin、三亞蟎和歐滅松，共計 9 種。

三、土壤有機氯農藥檢測能力測試 (proficiency testing, PT)

大多數國家已禁止使用有機氯農藥多年，臺灣於 1974 年起禁止使用，但至今在環境基質中仍可檢測到其殘留，但殘留量通常都很低，因此需要開發一個可靠及靈敏的分析技術 [11]。氣相層析電子捕捉偵測器 (GC-ECD) 是檢測有機氯農藥最常使用的方法 [2, 17, 26]，但由於易受樣品基質的干擾，常常導致偽陽性 [11]，GC-MS/MS 則有較高的專一性 (specificity) [11, 15]。利用所建立之土壤多重農藥殘留分析方法參加 ERA (Environmental Resource Associates) 所舉辦之土壤中有機氯農藥能力測試，其結果顯示，20 種有機氯農藥 Z-Score 絕對值皆小於 2，其中 18 種有機氯農藥 Z-Score 絕對值更是小於 1 (圖一)，顯示此方法亦適宜執行土壤中有機氯農藥之檢測。

四、土壤真實樣品檢測

利用建立之方法進行實際土壤樣品農藥殘留檢測調查，於宜蘭、彰化、雲林、嘉義、臺南、高雄及花蓮等地區，共採集

Summary PT Performance Evaluation Report

Organochlorine Pesticides in Soil — **Lot Number D100-728**

	Reported PT Result	Satisfactory Range	z Score	Reported Method	Performance Evaluation
4,4'-DDD	221 µg/kg	154 - 360	-0.707	NIEA M193.00C	Satisfactory
4,4'-DDE	123 µg/kg	87.9 - 190	-0.62	NIEA M193.00C	Satisfactory
4,4'-DDT	91.6 µg/kg	54.9 - 173	-0.756	NIEA M193.00C	Satisfactory
Aldrin	49.7 µg/kg	32.3 - 67.4	-0.0156	NIEA M193.00C	Satisfactory
alpha-BHC	87.6 µg/kg	50.9 - 142	-0.387	NIEA M193.00C	Satisfactory
alpha-Chlordane	314 µg/kg	219 - 442	-0.296	NIEA M193.00C	Satisfactory
beta-BHC	67.6 µg/kg	44.2 - 106	-0.492	NIEA M193.00C	Satisfactory
delta-BHC	266 µg/kg	173 - 393	-0.308	NIEA M193.00C	Satisfactory
Dieldrin	67.3 µg/kg	47.0 - 95.5	-0.327	NIEA M193.00C	Satisfactory
Endosulfan I	267 µg/kg	148 - 406	-0.159	NIEA M193.00C	Satisfactory
Endosulfan II	276 µg/kg	159 - 402	-0.076	NIEA M193.00C	Satisfactory
Endosulfan sulfate	150 µg/kg	73.0 - 219	0.111	NIEA M193.00C	Satisfactory
Endrin	180 µg/kg	105 - 240	0.225	NIEA M193.00C	Satisfactory
Endrin aldehyde	116 µg/kg	73.0 - 214	-0.782	NIEA M193.00C	Satisfactory
Endrin ketone	146 µg/kg	114 - 330	-1.4	NIEA M193.00C	Satisfactory
gamma-BHC(Lindane)	284 µg/kg	186 - 439	-0.447	NIEA M193.00C	Satisfactory
gamma-Chlordane	94.9 µg/kg	62.7 - 125	0.0817	NIEA M193.00C	Satisfactory
Heptachlor	36.8 µg/kg	26.1 - 70.2	-1.03	NIEA M193.00C	Satisfactory
Heptachlor epoxide	145 µg/kg	92.8 - 196	0.026	NIEA M193.00C	Satisfactory
Methoxychlor	138 µg/kg	43.7 - 190	0.576	NIEA M193.00C	Satisfactory

圖一、參加 ERA 所舉辦之土壤中有機氯農藥能力測試結果。

Fig. 1. ERA PT performance evaluation report.

10 個水稻土壤樣品進行多重農藥殘留檢測，結果顯示每個土壤樣品中，至少可被檢出 1 種農藥，所有樣品共檢出 30 種農藥，包含有殺菌劑 8 種，除草劑 8 種，殺蟲劑 11 種，及其代謝物 3 種，詳如 (表五)。

30 種農藥中有 9 種不是水稻登記用藥，分別為亞托敏、護矽得、達有龍、芬佈賜、福瑞松、普硫松及有機氯農藥地特靈、4,4-滴滴涕和及其代謝物 4,4-滴滴依等。其中亞托敏、護矽得、達有龍、芬佈賜、福瑞松及普硫松等 6 種農藥，根據 PPDB (Pesticide Properties Data Base)[8] 文獻資料均屬中度持久性 (moderately persistent) 農藥，田間消散半量時間 (field half life) 最低為 45 天，最高為 180.7 天 [8]，有機氯農藥地特靈、4,4-滴滴涕、4,4-滴滴依具高持久性 (vry persistent)，在環境中不易消散，故以上 9 種藥劑，易於土壤中檢出。地特靈檢出殘留量為 23.68 μg/kg，低於本國土壤污染管制標準 40 μg/kg [1]。滴滴涕最高檢出殘留量為 37.84 μg/kg，遠低於本國土壤污染管制標準 3000 μg/kg (total DDT) 及加拿大環境品質準則 (CCME) 700 μg/kg (total DDT) [10]。10 件土壤樣品中，有 2 件驗出滴滴涕及滴滴依，比較 2014 年調查臺灣地區農田土壤有機氯農藥殘留結果，於 200 個監測農田土壤樣品，檢出率最高的滴滴依為 13.5% (殘留量範圍 ND~3.2 μg/kg)，其次是滴滴涕檢出率為 11% (殘留量範圍 ND~6.24 μg/kg) [5]。

10 件土壤樣品中農藥殘留檢出次數，以除草劑丁基拉草檢出 7 次最多，檢出濃度範圍介於 11.20~50.80 μg/kg。其次依序是殺蟲劑益達胺驗出 6 次，檢出濃度範圍為 6.70~51.12 μg/kg。殺菌劑三賽唑分別檢出 4 次，檢出濃度為 4.54~154.20 μg/kg。檢出 3 次的農藥有亞托敏、賓克隆、草殺淨、達有龍、施得圃、剋安勃、芬佈賜等。

丁基拉草於土壤的田間消散半量期為 11.5 天，非屬於持久性農藥，在環境中殘留期並不長，初等 (2007) 監測雲林地區水田灌溉水中農藥殘留，丁基拉草被檢出率最高，因丁基拉草及含此成份之混合劑廣泛被用於水稻田雜草防治，故在水田土壤樣品中被檢出機率高 [6]。殺蟲劑益達胺在水稻田中主要推薦用以防治水稻水象鼻蟲，殺菌劑三賽唑則被推薦用於防治稻熱病，田間消散半量期分別為 174 及 130 天，均為具有環境持久性藥劑，故使用後易在環境中被檢測出。

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表五、土壤真實樣品檢測結果

Table 5. Results of soil sample analysis

Pesticide	Chinese name	Pesticide type	DT_{50} in a field [1)] (days)	Pesticides authorized for use on rice in Taiwan	Residue (μg/kg)									
					Chang-hua	Chang-hua	Chang-hua	Chia-yi	Hua-lien	Kao-hsiung	Tai-nan	Yi-lan	Yun-lin	Yun-lin
azoxystrobin	亞托敏	fungicide	180.7	No	ND	4.10	ND	ND	5.06	ND	ND	ND	ND	4.26
flusilazole	護矽得	fungicide	94	No	ND	ND	ND	ND	ND	ND	ND	ND	ND	47.84
difenoconazole	待克利	fungicide	85	Yes	ND	ND	10.64	ND	ND	ND	ND	ND	ND	11.18
flutolanil	福多寧	fungicide	234	Yes	ND	ND	ND	ND	ND	12.90	ND	ND	ND	ND
isoprothiolane	亞賜圃	fungicide	-	Yes	ND	ND	ND	11.18	ND	10.34	36.60	ND	ND	ND
pencycuron	賓克隆	fungicide	37.7	Yes	13.28	ND	ND	ND	14.26	ND	ND	ND	ND	8.80
propiconazole	普克利	fungicide	35.2	Yes	ND	ND	ND	ND	ND	ND	ND	ND	ND	9.44
tricyclazole	三賽唑	fungicide	130	Yes	116.46	ND	154.2	ND	4.54	ND	ND	ND	20.76	ND
diuron	達有龍	herbicide	89	No	7.16	23.98	ND	ND	59.58	ND	ND	ND	ND	ND
ametryn	草殺淨	herbicide	37	Yes	4.44	26.62	ND	ND	10.58	ND	ND	ND	ND	ND
bensulfuron-methyl	免速隆	herbicide	8.2	Yes	4.56	ND	ND	ND	ND	ND	ND	ND	ND	ND
butachlor	丁基拉草	herbicide	11.5	Yes	29.20	50.80	13.74	16.02	ND	ND	11.20	24.68	ND	22.92
mefenacet	滅芬草	herbicide	-	Yes	9.20	ND	121.36	11.22	ND	ND	ND	ND	ND	ND
oxadiazon	樂滅草	herbicide	165	Yes	ND	ND	83.98	ND	ND	ND	ND	ND	ND	ND
pendimethalin	施得圃	herbicide	100.6	Yes	ND	71.20	ND	ND	ND	15.62	ND	ND	ND	34.82
pretilachlor	普拉草	herbicide	-	Yes	ND	ND	32.96	ND	ND	ND	ND	ND	ND	ND
dieldrin	地特靈	insecticide	-	No	ND	ND	ND	ND	ND	23.68	ND	ND	ND	ND
fenbutatin-oxide	芬佈賜	insecticide	95	No	ND	ND	13.58	ND	ND	6.80	4.00	ND	ND	ND
p,p'-DDT	4,4-滴滴涕	insecticide	-	No	ND	11.96	19.54	ND	ND	ND	ND	ND	ND	ND
phorate	福瑞松	insecticide	63	No	145.40	ND	ND	ND	37.78	ND	ND	ND	ND	ND

表五（續）、土壤真實樣品檢測結果

Table 5 (continued). Results of soil sample analysis

Pesticide	Chinese name	Pesticide type	DT_{50} in a field [1)] (days)	Pesticides authorized for use on rice in Taiwan	Residue (μg/kg)									
					Chang-hua	Chang-hua	Chang-hua	Chia-yi	Hua-lien	Kao-hsiung	Tai-nan	Yi-lan	Yun-lin	Yun-lin
prothiofos	普硫松	insecticide	45	No	6.00	ND	ND	ND	ND	ND	ND	ND	ND	ND
buprofezin	布芬淨	insecticide	45.6	Yes	12.64	3.60	ND	ND	ND	ND	ND	ND	ND	ND
carbofuran	加保扶	insecticide	14	Yes	ND	3.56	ND	ND	ND	ND	ND	ND	ND	ND
chlorantraniliprole	剋安勃	insecticide	204	Yes	ND	4.96	ND	ND	ND	9.88	ND	ND	ND	15.66
chlorpyrifos	陶斯松	insecticide	27.6	Yes	19.80	ND	ND	ND	ND	ND	ND	ND	ND	22.38
fipronil	芬普尼	insecticide	65	Yes	ND	ND	ND	ND	ND	ND	ND	ND	ND	40.38
imidacloprid	益達胺	insecticide	174	Yes	23.64	38.72	51.12	29.40	ND	ND	ND	ND	6.70	9.86
p,p'-DDE	4,4-滴滴依	metabolite of DDT	-	-	ND	ND	ND	37.84	ND	ND	ND	ND	ND	17.70
fipronil-desulfinyl	芬普尼代謝物	metabolite of fipronil	-	-	ND	ND	ND	ND	ND	ND	ND	ND	ND	10.44
fipronil-sulfone	芬普尼代謝物	metabolite of fipronil	-	-	ND	ND	ND	ND	ND	3.62	ND	ND	ND	34.98

[1)] Data from PPDB [(8)].

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Gas chromatography-tandem Mass Spectrometry and Ultra Performance Liquid chromatography-tandem Mass Spectrometry for the Simultaneous Determination of 352 Pesticide Residues in Soil

Nien-Hao Shih[1], De-Mei Hsu[1], Tsyr-Horng Shyu[1], Chien Chu[1*]

Abstract

Shih, N. H., Hsu, D. M., Shyu, T. H., and Chu, C. 2019. Gas chromatography-tandem mass spectrometry and ultra performance liquid chromatography-tandem mass spectrometry for the simultaneous determination of 352 pesticide residues in soil. Taiwan Pestic. Sci. 6: 1-36.

Pesticides are applied widely in agriculture to protect plants from disease, weeds, and insect damage. As diverse classes of pesticides exist, conducting a credible risk assessment requires the use of multi-residue methods that allow for pesticide residues to be accurately and simultaneously measured in soil. Accordingly, the purpose of this study was to establish a multi-residue method which is capable of assessing the risk of various pesticides used in agricultural soil. To test the efficacy of our proposed method, we extracted soil samples using automatic Soxhlet extraction. A total of 195 and 157 pesticide compounds were analyzed by GC-MS/MS and UPLC-MS/MS, respectively. The matrix-matched calibration range for GC-MS/MS was 5~500 μg/L, and the average recoveries of the 195 pesticides analyzed by GC-MS/MS at two spike levels (10 and 40 μg/kg) were 64.5~115.6% and 60.1~119.1%, respectively, with relative standard deviations (RSDs) of less than 20%. The matrix-matched calibration range for UPLC-MS/MS was 2~200 μg/L, and the average

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* Corresponding author, E-mail: chu@tactri.gov.tw

[1] Taiwan Agricultural Chemicals and Toxic Substances Research Institute, Council of Agriculture, Taichung

recoveries of the 157 pesticides analyzed by UPLC-MS/MS at two spike levels (4 and 20 μg/kg) were 64.3~115.4% and 63.6~110.0%, respectively, with RSDs of less than 20%. The established analytical method participated in the proficiency testing of organochlorine pesticides in soil held by Environmental Resource Associates (ERA). Results showed that 20 organochlorine pesticides passed proficiency testing, which also revealed that our proposed method is suitable for the detection of organochlorine pesticides in soil. Therefore, the method is likely to be useful in the analysis and assessment of pesticide residues in agricultural soil.

Key words: soil, pesticides, GC-MS/MS, UPLC-MS/MS