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Introduction

Advanced screening methods based on liquid chromatography-mass spectrometry (LC-MS) for detection of un-predicted residues of pesticides and veterinary drugs in agriculture products and food have been reported in recent years [1]. Without spectrum libraries like in GCMS, LC/MS/MS was initially not used in screening analysis. Whereas, high resolution LC-TOF was selected for screening analysis due to its accurate mass capability [1-2]. However, with rapid progress in data acquisition technique speed like UFMS (ultrafast MS) and high MRM capacity, new generation triple quadrupole LC/MS/MS has been used for targeted screening, e.g., of over a few hundred of pesticides in one analysis [3]. It is interesting to know the advantages and limitations of the two different screening approaches for pesticide residues in agriculture and food matrixes. We describe here a comparative study on targeted screening analysis based on MRM method on a UFMS-TQ system and un-targeted screening analysis based on high resolution MS full spectrum method on a LC-TOF system using same sample sets of mixed pesticides aiming at unveiling their capabilities and limitations in the challenging screening analysis.

Experimental

Mixed pesticide samples were obtained from a third party without information of compound number and names before completion of analysis. The unknown pesticide samples were analysed by two different screening methods on two LC-MS systems. A MRM-based targeted screening method was carried out on LCMS-8050, an ultrafast (UFMS) triple quadrupole system. Un-targeted screening ana-lysis of the same samples was carried out on LCMS-IT-TOF, a high resolution MS system. The two systems, analytical conditions and parameters are compiled into Table 1.

Table 1: Un-targeted	screening	analysis	conditions	of I CMS-IT-TOF
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System & items		LCMS-8050*	LCMS-IT-TOF		
LC conditions	Column	Shim-pack XR-ODS III	Shim-pack XR-ODS III		
		(150 mmL. x 2mmi.D., 2.2µm)	(150L x 2.0, 2.2µm)		
	Flow Rate	0.4 mL/min	0.3 mL/min		
	Mobile Phase	A : Water 5mM ammonium formate	A : Water 5 mmol/L NH4 formate,		
		with 0.1% formic acid	0.1% formic acid		
		B : MeOHwith 5mM NH4 formate	B : MeOHwith 5 mmol/L NH4 formate,		
		with 0.1% formic acid	0.1% FA		
	Elution Mode	Gradient elution, 20 minute	Gradient elution, 35 min		
		B: 5% (0 min) -> 100% (16min ~ 18min)	B: 15% (0min) -> 100% (25mins to 31min)		
		-> 5% (18.1min ~20min)	-> 15% (31.1min to 35min)		
	Oven Temp.	45 °C	50 °C		
MS conditions	Interface	ESI heated	ESI (not heated)		
	MS Mode	Schedule MRM, in positive and negative mode	Multi-event TIC, Positive and negative		
	Interface Temp.	300 °C	RT		
	Block Temp.	400 °C	250 °C		
	DL Temp.	250 °C	200 °C		
	Nebulizing Gas	Nitrogen, 2.0 L/min	Nitrogen, 1.5 L/min		
	Heating Gas	Zero Air, 10 L/min	N.A.		
	Drying Gas Flow	Nitrogen, 10 L/min	Nitrogen, 10 L/min		
Inj Vol	Inj. Volume	1.0 μL	10 uL		

* Refereed to method 1. The LC conditions of Method 2 and method 3 are different.

Results and Discussion

Description of targeted and un-targeted screening approaches

It has been accepted with unanimity that the MRM technique is one of best analytical methods in quantitative analysis of trace level organic compounds in complex matrix. Although MRM method has been used widely in quantitative analysis of thousands of compounds, it had not been used for screening analysis aiming at detection of concerned chemicals like pesticides in agriculture products until a recent time. The conventional method for screening analysis of pesticide residues is by GCMS with well-established spectrum library. However, GCMS with El or CI ion source could not detect and guantify less and non-volatile pesticides effectively. In recent years, LC-MS with ESI interface has been increasingly used in analysis of pesticide residues using MRM method or high resolution TOF-MS method [1]. The so-called HRMS instruments like LC-TOF with its high mass-resolving power were first adopted in un-targeted screening analysis for pesticides and other chemical contaminants in agriculture products and food. A different methodology from GCMS isemployed, in which data analysis of the full spectra data is searched against a compound (molecular formula) database via

accurate mass matching (+/-5ppm or better) to find candidates. The key advantages of this approach are: it does not need to restrict the retention time and the raw data can be re-analysed using different molecular formula database of any concerned compound or compounds group. On the hand, with rapid progress in instrumentation technology in recent years, new generation LC/MS/MS systems with ultrahigh data acquisition speed and extremely high capacity of MRM are invoked to use in screening analysis in food safety field. Targeted screening methods based on pre-loaded MRMs of hundred pesticides have been used increasingly as an alternative. This study is aimed at a comprehensive comparison between MRM-based targeted screening method and HRMS-based un-targeted screening method in detection and identification of pesticides in the unknown samples. Table 2 outlines the two methods used in this study, which were carried out on LCMS-8050, a latest model of LC/MS/MS with the highest performance specification of Shimadzu series, and LCMS-IT-TOF, a high resolution hydride MS system.

Item	Targeted Screening MRM method	Un-targeted screening HRMS method			
No. of pesticides	fixed number (347, 167 & 121)*	not limited			
Detection and	Two pre-set MRM for each pesticide, intensity ratio	Accurate mass matching mass window (+/-) 5ppm			
identification method	Pre-determined RT with (+/-) 0.5 min window	lsotope pattern matching (scope > 50%)			
Data analysis	Pre-set method, automated	allow re-process with specific database for data mining			

Table 2: Comparison of targeted & un-targeted screening methods

* three method packages are used with different numbers of pesticides

in Residual Pesticides Analysis

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Results of targeted and untargeted screening of mixed pesticide samples

Figure 1 shows the MRM chromatograms of targeted screening analysis of the unknown mixed pesticide sample by three methods covering different numbers of compounds on LCMS-8050. The results of the screening by using three methods are shown in Figure 2. The total number of unique pesticides found in the unknown sample is 189.

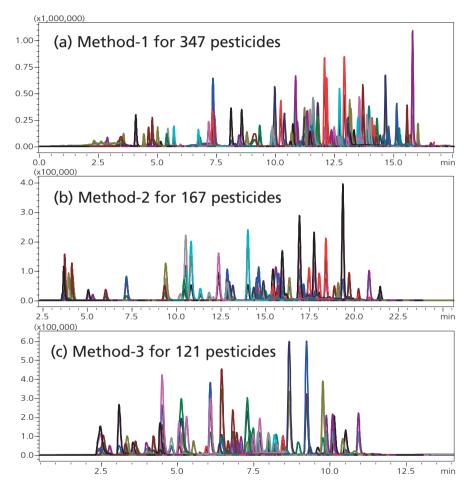


Figure 1: MRM chromatograms of targeted screening analysis of an unknown sample by three methods on LCMS-8050. The numbers of pesticides screened by the three methods are 347, 167 and 121, respectively.

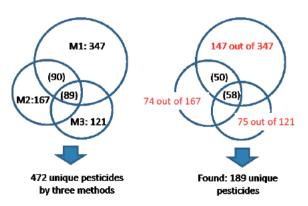


Figure 2: Numbers of pesticides of three MRM method packages covered are Method-1: 347, Method-2: 167 and Method 3: 121 (left). A total of 189 pesticides were found in the unknown mixed pesticide sample by the three methods (right).



Figure 3 shows multi-event TICs of un-targeted screening analysis of the unknown mixed pesticide sample on LCMS-IT-TOF. The so-called multi-event method was described elsewhere [4]. Instead of a single event of full mass range (m/z100~900), the data acquisition was performed in ten separate events, each covering a narrow mass range. This method was proven to be more sensitive than a single event method due to a lower baseline [4]. A total of 83 pesticides was detected and confirmed from this un-targeted screening analysis using a compound database of 450 pesticides (see Table 3). Fifty-three out of the eighty-three (70%) found pesticides were also found in targeted screening by LCMS-8050. In addition, 37 candidates were suspected present in the sample. Nine out of 37 suspected candidates (24%) were also found in the targeted screening analysis by LCMS-8050.

Comparison of targeted and untargeted screening

As shown in Figure 4, nine pesticides found in the unknown sample by both targeted and untargeted screening methods are selected randomly to compare the detection results individually. A general impression is that for those firmly detected pesticides, the detection results by both HRMS method on LC-TOF and MRM method on LC/MS/MS are gualified as screening candidates. The absolute detection sensitivity of MRM-based targeted screening are obviously higher than that of HRMS-based un-targeted screening. There are instrumentation factors and methodology factors. The LCMS-8050 is a latest model of triple quadrupole system with extremely high sensitivity, which contributes at least partially to the results of more pesticides found. However, this study is focused on the methodology factors. One of the key ideas of un-targeted screening by HRMS is that the method should avoid discrimination of any mass in data acquisition step. This

means that all ions of a sample including matrix and solvent clusters are detected equally. As a result, some peaks of interesting compounds may be interfered to become shoulder or tailing peaks or submerged peaks due to high baseline. These can make peak detection more difficult in the subsequent data analysis step due to inappropriate integration parameters being applied. This was proven by reversed searching of those pesticides that were not found by un-targeted screening but found by MRM method in the LC-TOF raw data. By entering the exact masses of these pesticides to extract the corresponding EIC, additional 69 pesticides were found from the LC-TOF raw data. Figure 5 shows a few examples of the EICs obtained by this method. It can be that all these peaks in TICs are severely disturbed or merged by the baseline.

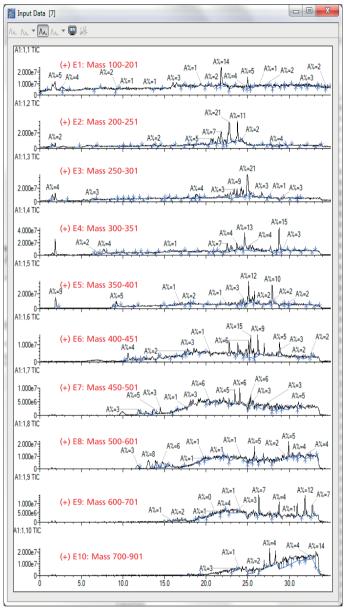


Figure 3: Multi-event TICs of un-targeted screening of an unknown mixed pesticide sample on LC-MS-IT-TOF.

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34 21.8 937.44.00 199.1805 Cylum C11.H22.R0 M+H -10 yms y 35 22.3 177.9304 220.055 Imax C12.H15.R0.027.5 M+H -1.6 yms y 36 22.3 27.73.41.47 220.011 227.031.47 27.011 247.0211 <td< td=""><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td>yes yes</td></td<>											yes yes
35 22.3 13.95.843 290.055 190.0414 C14.H14.B0.021 M-H1 -1.8 ymc ymc ymc 36 22.3 277.93.04 240.055 290.055 290.0414 Automation C12.H15.02.075 M-H1 -3.5 ymc ymc </td <td></td> <td>yes</td>											yes
27 22.3 27.52.4 247.0318 247.0325 Fuldoonil C12 He N2.0272 [M+H] -7.6 yes y 38 22.4 6.888,062 Abl1225 404.1122 404.1124 Abugytomic C21 HI N2 OC QL M+H] -1.6 Wes y 39 22.5 35.615.97 331.1150 331.108 Billofenzade C18 HI N2 OZ QL M+H] -1.6 Wes Y 41 22.5 4.282,73 302.1387 fremosyche C1 2 HI N N4 M+H] -2.6 Y Yes Y 42 22.6 42.30,049 228.1862 228.127 Arrespin C1 HI N N5 M+H] -2.6 Y Yes Y 43 22.6 22.00,069 324.1105 324.1206 futubal C1 HI N N5 M+H] -1.6 Yes											yes
37 22.3 27.5.4.147 247.013 247.0232 Filadoanii C12 He N2 0272 [M+H] -7.6 yes y 38 22.4 6.889.06 40.122 40.4128 40.4148 10.6 50.4128 <td< td=""><td></td><td></td><td></td><td></td><td></td><td></td><td>C12 H15 N2 O3 P S</td><td></td><td></td><td></td><td>no</td></td<>							C12 H15 N2 O3 P S				no
39 22.5 35.01.597 331.120 Huldemade Cli H19 N2 OZ (M-H1 -0.8 Yes y 40 22.5 7.491.568 331.186 332.186 333.187 333.137 <	37	22.3		247.0318		Fludioxonil		[M-H]-	-0.7	yes	yes
40 22.5 7.461.968 332.188 332.189 332.189 7.672.937 7.672.942.94 7.672.942.94 <t< td=""><td>38</td><td>22.4</td><td>6,889,062</td><td>404.1225</td><td>404.1241</td><td>Azoxystrobin</td><td>C22 H17 N3 O5</td><td>[M+H]+</td><td>-1.6</td><td>yes</td><td>yes</td></t<>	38	22.4	6,889,062	404.1225	404.1241	Azoxystrobin	C22 H17 N3 O5	[M+H]+	-1.6	yes	yes
41 22.5 4.22.23 302.1387 ferrowyarb C17 H18 NG M-HH -2.7 yes y 42 22.6 4.25.25.73 302.1387 ferrowyarb C17 H18 NG M-HH -2.7 yes y 43 22.6 22.00.09 228.162 228.127 Ametyn C1417 N5 M-HH -2.4 wys y 44 22.9 45.39.136 223.127 Ametyn C17 H15 N0 ZH M-HH -0.6 yss r 45 23.0 15.69.200 223.1005 didiofon ullone C17 H15 N0 ZH M-HH -1.0 yss ys 47 23.0 1.66.29.44 727.066 227.005 didiofon ullone C8 H19 G4 P3 M-HH -0.8 yss ys 48 23.1 1.06.29.44 290.051 290.088 melenact C16 H14 N2 O25 M-HH -0.8 yss ys 50 23.3 10.652.94 290.088 10.00005 C16 H14 NH 0.4											yes
42 22.6 15.55.878 233.1648 Saturon C14120120 M-H1 -2.9 yms yms 43 22.6 22.200.09 22.200.09 22.200.09 Yms											no
43 22.6 22.00.049 228.1628 228.127 Ametyn C94171855 Mettie -1.4 yer y 44 22.9 43.31,38 224.127 Ametyn C917 1181 MA Methal -0.6 yer Y 45 23.0 45.34,06 324.1195 324.1205 fluxbali C17.H16 N0.271 Methi -1.0 yes Y 46 23.0 13.662,800 324.1195 doldforb C17.H16 N0.271 Methi -1.0 yes Y 47 23.0 14.664,170 323.00075 distifton stillore C18.H10 AP 53 Methi -1.0 yes Y 50 23.3 10.765,544 290.0851 290.0885 Chonuon C18.H13 NO 2 / V Methi -3.8 yes Y 51 23.5 32.83.87 372.0280 372.0280 372.0278 traconable C18.H13 NO 2 / V Methi -3.8 yes Y 52 2.6 2.62.2787 331.0										· · ·	yes
44 22.9 45.391.86 227.142 fermione (2 or f) C15 HIS M4 [M-H4]+ -1.0 yes yes 45 23.0 15.954.66 232.7065 327.0165 diodop C15 HIS M4 [M-H4]+ -1.0 yes yes 46 23.0 1.6694.170 232.0002 322.0005 diodop C15 HIS 20 4C2 [M-H4]+ -4.3 yes yes 48 23.1 8.170,765.42 388.1310 dimetomorph C1 HIS 20 4C1 [M-H4]+ -0.8 yes yes <td< td=""><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td>no</td></td<>											no
46 230 95.4.406 324.119 324.1205 fluxbanl C17.H16.N.0278 M.H.H.H. -1.0 yes 46 230 11.662.200 327.066 327.067 327.07 327.07 327.2117 327.117 11.17.17 10.17.17 10.17.17 10.17.17 10.17.17 10.17.17 10.17.17 10.17.17 10.17.17 10.17.17.17 10.17.17.17 <td< td=""><td></td><td></td><td></td><td></td><td></td><td>Ametryn</td><td></td><td></td><td></td><td></td><td>yes no</td></td<>						Ametryn					yes no
46 21.0 11.6 (20.200 327.005 327.015 dicklopp C15.H12 04.C2 M-H1 -1.9 Yes F 47 23.0 14.694.170 320.002 320.007 dicklopp C15.H12 04.C2 M-H14) -4.3 yes y 48 23.1 8.70.32 388.130 disclopp C11.H22 M OL C1 M-H14) -0.8 yes y 50 23.3 10.706.544 291.0892 291.0895 Chonxuran C11.H14 02.021 M-H14) -0.3 yes y 51 23.5 3.81.88.664 21.119 21.217.13 Statumant C11.H20 AC2.0 M-H14 -1.1 yes ye 52 2.6.5 2.42.33.13.077 331.037											no
47 23.0 14.64.170 329.0075 dullotions suffore CR-H19.04.P3 MA-Hair -4.3 yes y 48 23.1 A170.342 S28.1020 383.100 Mail -4.3 yes y 49 23.3 10.765.44 229.0851 299.0847 metracut C16.H14.20.205 MAHH -0.8 yes y 51 23.5 8.18.8468 374.1912 Synothermat C16.H14.20.25 MAHH -0.8 yes y 52 23.5 4.28.84.66 374.1912 Synothermat C12.H27.M05 MAHH -5.6 Yes y 54 25.6 2.20.2173 321.117 321.121 Barlinghom C18.H18.20 MAHH -5.6 Yes y 55 2.5.6 2.20.2173 321.1037 Handmate mon suftee C1.H17.018.5 MAHH -1.8 yes y 56 2.5.6 2.45.2.573 242.1420 242.1434 Informin C1.H17.018.5 MAHH											no
44 23.1 6.17.0.342 388.130 antestrongh C1 1422 40.4C1 M-HH -0.8 yes yes yes 49 23.3 10.765.44 290.051 290.061 290.061 290.051 <											no
48 21.3 10.76,544 290.088 1290.088 International Constraints Cli H1 M2 O25 M-H1 0.2 yes y 50 21.3 10.632,34 290.088 201.0885 Chorumon C1 H1 M2 O25 M-H1 0.3 yes y 51 21.5 8.186,46 374.1951 374.1962 Sprotestramat C1 H27 NOS M-H1 -3.6 yes y 52 22.5 4.238.37 372.0288 traconacide C1 H11 NG O1 472 M-H1 -3.8 yes y 53 23.6 2.02.241.17 221.111 Margangem C1 H11 NG O1 472 M-H1 -3.8 yes y 55 23.6 2.02.27,07 301.0377 functachon com aufora C1 H11 NG O1 472 M-H1 -3.8 yes											yes
50 23.3 10.652.944 291.0895 Chronuum C15.H15.V2.02 (M-H1+ -1.1 west yest	49	23.3	10,796,544	299.0851	299.0849		C16 H14 N2 O2 S		0.2		no
52 23.5 3.25.2,198 22.1.2173 genularity C18.142.8 LO3 M-H1 -5.6 Yes y 53 23.5 4.238.437 22.21.028 32.22.028 12.2028 transmitted C18.118.014.024.01 -9.8 yes y 54 23.6 2.22.47.17 224.116.4 224.118 Manapryrim C1.4113.91.0 M-H1 -1.8 yes y 55 23.6 1.709.030 364.0728 364.0737 filternext C1.4113.910.274.5 M-H1 -1.4 yes y 57 23.6 1.709.030 364.0728 364.0737 filternext C1.4113.910.274.5 M-H1 -1.4 yes y 58 23.7 3.85.955 325.049 325.021 Cyaudamid C1.811.94.074.5 M-H1 -2.4 yes y 60 2.37 4.849.44 337.118 Gatestroite C1.911.7 M-L1 M-H1 -3.3 yes y 61 2.28 2.937.92 373.125<	50	23.3	10,632,934	291.0898	291.0895	Chloroxuron	C15 H15 N2 O2 CI	[M+H]+	0.3		yes
53 22.5 4.29.8,877 372.0280 servoncode C13.H11 N0.D4-C2 MuHi -0.8 yes y 54 32.6 22.28.477 322.04166 22.04.178 MuHi -0.8 yes y 55 25.6 2.29.24.717 331.0376 file Clinitities Clinitities Number -0.8 yes y 56 25.6 2.60.278 331.0376 file Clinitities Clinitities Number -0.8 yes y 57 25.6 2.62.2737 331.0376 file Clinitities Clinitities Number -0.8 yes y 58 2.57 7.28.55.25.03 325.0509 325.051 Clinitities Clinitities Number -2.3 yes y 60 2.37 5.897.050 44.89314 Strona Clinitities Clinitities Clinitities -2.3 yes y yes yes yes yes yes yes yes						Spirotetramat		[M+H]+		yes	yes
Sta 28.6 22.24.217.7 224.118.8 224.118.8 224.118.2 Martin Natrin Natrin <t< td=""><td>52</td><td>23.5</td><td>3,252,198</td><td>321.2117</td><td>321.2173</td><td>Iprovalicarb</td><td>C18 H28 N2 O3</td><td></td><td>-5.6</td><td>Yes</td><td>yes</td></t<>	52	23.5	3,252,198	321.2117	321.2173	Iprovalicarb	C18 H28 N2 O3		-5.6	Yes	yes
5 23.6 26.2 27.7 311.037.6 functionable some autow C11 H17 OC PS MAHali -0.1 yes y 56 23.6 1709.030 5640278 640478 640478 640478 640478 640478 640478 640478 640478 640477 functionable C10 H19 M5 MMH1 -0.9 yes y 57 23.6 24.52273 22.550.699 25.0507 Casafand C10 H19 M5 MMH1 -2.2 yes y 60 23.7 4849.643 331.183 337.1185 337.1215 febroancable C10 H17 M4 C1 MMH1 -2.2 yes y 61 23.8 427.760 331.2018 131.0018 finderhoxacke C16 H21 M4 O1 MH1 -2.3 yes y ge 62 23.8 2.037.702 373.1276 373.0326 faderhoxacke C16 H22 M4 O15 MH1 -2.9 yes yes y ge 2.2.037.031 M8488 Meanaleyhon <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td>yes</td> <td>yes</td>										yes	yes
56 23.6 1.79.030 364.072 Milemaxit C1411310.074 fs M-H1 -1.0 yes yes 57 23.6 24.32,257 24.242,273 24.120 224.140 textury C1411310.074 fs M-H1 -1.0 yes yes </td <td></td> <td>yes</td>											yes
57 23.6 24.52.97.31 242.142 tethulyn C10.H19.N5 [M-H] -1.4 yme y											no
58 23.7 38.85,955 325.029 325.021 Cyaudamid C13.H13.MG.25 Cl M-HH -2.2 yes y 59 23.7 5.997.593 424.929 434.931 figual C13.H13.MG.25 Cl M-HH -2.3 yes y 60 23.7 4.884.934 437.118 337.1215 finbuonacic C13.H13.MG.25 Cl M-HH -3.3 yes y 61 23.8 2.877.792 373.1375 fichuonacic C13.H13.MG.25 Sl M-HH -3.4 yes yes <td></td> <td>yes</td>											yes
99 23.7 5.997.939 444.9314 fipmoil C1214NA0 F5 C2 [M-H] -2.3 yes y 60 23.7 5.997.939 444.93114 [fipmoil C1214NA0 F5 C2 [M-H] -2.3 yes y 61 23.8 4.897.940 351.208 351.2018 thickmonde C1214NA0 F5 C2 [M-H] -2.3 yes y 61 23.8 4.297.950 351.208 351.2078 tote/monde C1214DA C2 [M-H] -2.9 yes y 63 24.9 1.055.021 755.05072 273.0515 McP C11H13.012 [M-H] -1.2 yes y 64 22.9 1.055.021 755.05072 750.51378 Hydramethylnon C23.142.140.02 [M-H] -1.2 yes yes y 66 24.0 0.2937.021 495.05072 726.0178 Hydramethylnon C12.1416.14.020 [M-H] -1.2 yes y 67 24.1 6.013.153 <											no
60 23.7 4.88.944 337.128 fmbuonacity C19.H17.N4.C M-H41 -2.7 yes y 61 23.8 4.827.360 337.128 fmbuonacity C19.H17.N4.C M-H41 -1.3 yes y 62 23.8 4.287.360 373.126 fmbuonacity C16.H22.N4.035 M-H41 -1.3 yes y 63 23.9 1.753.805 220.075 23.0355 MCR C11.H17.N4.C M-H41 -1.2 yes yes f 64 23.9 1.055.021 705.0712 Fibendamide C23.H22.N2.047.51 M-H41 -1.2 yes											yes yes
61 22.8 4.287.360 351.2078 tablemonde C12.128.10.20 [M-H] 1.3 yes y 62 22.8 2.037.79 371.767 371.3076 stalledmonde C12.128.10.20 [M-H] -2.9 yes y 63 23.9 1.753.3065 273.0575 XIM78 C11.113.0 [M-H] -2.9 Yes r 64 21.9 1.753.3005 273.0575 XIM78 C11.113.0 [M-H] -2.9 Yes r 65 24.0 2.03.070.1 455.1666 455.1078 Hybersethylon C23.162.04176 M-H] -1.2 yes y 66 24.0 6.955.008 227.0569 270.0721 Mound C11.116.10.0 C12 M-H] -1.2 yes											yes yes
62 23.8 2.927,792 373.127 373.1375 adiastocic C16.H22.M 0.35 MA+Lajh -29 yes yes 63 23.9 1.753.805 273.075 23.0555 MCIR C11.H22.M 0.35 ML+H40-Opl 4.0 yes yes 64 23.9 1.053.001 705.007 705.0175 Huberdamid C23.H22.N2 0.477.51 MA+Lajh -35 yes yes 66 24.0 6.053.068 275.0792 705.0712 Huberdamidyon C23.H22.N2 0.477.51 MA+Lajh -1.2 yes yes 67 24.1 6.011.315 271.0730 Dranopartohn C13.H23.12 MH+1 -1.2 yes ye 68 24.2 4.664.272 284.076 284.0716 perionazale C13.H15.N2.012 MH+1 -0.8 yes yes<											yes
63 21.9 175.8305 273.055 MCPB C11H13 01 C1 M-HCOOL Vec Yes Yes </td <td></td> <td>no</td>											no
64 22.9 10.55/21 705.007 705.0125 Filzendamide C23122.N2 0.475 S1 MeHal -5.5 yes y 65 24.0 20.307.021 405.166 405.1078 Hydamethydam C2312.87 0.475 S1 MeHal -1.2 y y 66 24.0 6.95.508 275.0712 Neburon C12.118.N2 0.62 MeHi -1.3 ys y 67 24.1 6.011.315 271.02 207.073 Dinosyntrohn C13.1418.N2 0.62 MeHi -2.6 ys y 68 24.2 4.644.272 284.0716 prinosnazie C13.1415.N3 0.22 MeHi -0.8 ys y 70 24.3 1.70.664 342.0213 342.0217 prinosnazie C13.117.N3 0.5212 MeHi -0.8 ys y 71 24.4 5.14.68.92 342.0217 342.0217 prinosnazie C13.117.N3 0.522 MeHi -0.8 ys y 72 24.4 5.14.68.92 342.0											no
66 24.0 6955,068 275,0712 Networn C12.H16.N2 OC2 (M-H1) -1.3 yes y 67 24.1 6013,153 271,229 271,7129 Diray,71703											no
67 24.1 6.011.315 327.129 327.1703 Dimospherobin C19H22/H2.03 MAH1 -4.0 ymc						Hydramethylnon		[M+H]+		yes	yes
66 24.2 4.68.4/27 284.0776 perconazale C13.H15 M3 C12 M-H1 -4.0 yes y 69 24.2 2.68.4/27 284.0776 perconazale C13.H15 M3 C12 M-H1 -4.0 yes y 70 24.3 1.70.084 342.021 Biotocazal C13.H15 M3 C12 M-H1 -0.8 yes y 71 24.4 5.756.66 72.4687 32.0207 perconazale C13.H17 M3 C2 C1 M-H1 -0.8 yes y 72 24.4 5.146.822 342.0271 872.0277 perconazale C13.H17 M3 C2 C1 M-H1 -0.8 yes y 73 24.7 5.588,165 326.0008 356.021 Diroconazale C13.H17 M3 C2 C2 M-H1 -1.3 yes y 74 2.48 5.582,85 746.4070 748.492 pinetram C42.H69 N101 M-H1 -1.4 yes y 75 2.49 1.70.51.27 746.4920 171.110.2012	66	24.0	6,955,098	275.0699	275.0712	Neburon	C12 H16 N2 O Cl2	[M+H]+	-1.3	yes	yes
69 24.2 21.02.426 308.15124 teluconazole C16.H22.N3.01 MuH1 -0.8 Yes y 70 24.3 1700.864 308.15124 teluconazole C16.H22.N3.01 MuH1 -2.8 Yes y 71 24.4 5.556.866 732.4681 Symoph A C41.H55.05.02 MuH1 -0.6 yes y 72 24.4 5.144.822 342.0771 324.02011 320.02011 progromazole C15.H17.N3.03.022 MuH1 -0.6 yes y 73 24.7 2.568.166 32.6081 32.6021 Dinconazole C15.H17.N3.03.022 MuH1 -1.3 yes y 74 24.8 5.382.85 748.4994 Spinteriam C42.H59.N1010 MuH1 -1.4 yes y 75 24.9 J.959.821 50.1075 50.1107 50.1107 S0.1107 MuH1 -1.4 yes y 76 25.1 4.00.662 38.1643 383.155											yes
70 24.3 1.700.864 342.0218 342.0249 Profitzionalistic C14.H15.H0.502.2 [M-H] -2.2 yes y 71 24.4 5.756.806 3576.806 spinopino C14.H15.H0.502.2 [M-H] -0.6 yes y 72 24.4 5.756.806 352.007.0 proconazole C15.H17.H0.502.2 [M-H] -0.6 yes y 73 24.7 2.588.168 506.008 352.001.0 IAH-II -1.3 yes y 74 24.8 5.358.255 748.490.1 20.801.0 IAH-II -1.3 yes y 75 24.9 1.791.82.01 748.492.5 1748.492.5 1748.492.5 yes y 76 25.1 4.002.62 383.1635 functincazino C18.H15.N0.07.62.01 HM-H] -1.4 yes yes 76 25.1 4.002.62 383.1635 functincazino C18.H26.N0.275 M-H] -3.0 yes y 77											yes
71 24.4 5575,696 732.4887 732.4881 732.4481 5174,892 742 744 742.4881 742.4881 742.4881 742.4881 742.4881 742.4881 742.4881 742.4881 742.4881 742.4881 742.4881 742.4881 742.4881 742.4881 742.4881 742.4881 742.4881 742.4883 742.4891 742.4891 742.4891 742.4891 742.4891 742.4891 742.4891 742.4891 742.4891 742.4891 742.4891 742.4891 742.4891 742.4891 742.4892 742.4891 742.4891 742.4892 742.4891 742.4892 742.4891 742.4892 742.4892 742.4892 742.4892 742.4892 742.4892 742.4891 742.4892 742.4891 742.49181 742.49181											yes
72 24.4 51.46.832 342.071 macroanse C15.H17.H0.02 C2 M-H1+ -0.0 ymc ymc 73 24.7 2588,166 326.0608 326.0121 Diraconsele C15.H17.H0.02 C2 M-H1+ -1.3 90. ymc y										· · ·	no
73 24.7 2.588,186 326.0808 326.0821 Diriconazole C15.H17.M3 OC12 M-H1H -1.3 yets y 74 2.48 5.388,287 A84.07 7.48.9444 Sintenzana C21.BH17.M3 OC12 M-H1H -2.4 yets y 75 2.49 1.791.821 346.0923 Sintunziole C15.H15.M3 O15.3C M-H1H -2.4 yets y 76 2.51 4.002,662 383.1684 338.1565 functionazole C15.H15.M3 O15.3C M-H1H 5.9 yets y 77 2.52 9.059.096 505.105 Metallinizoria C118.H26.10.255 M-H1H -3.0 yets y 78 2.55 12.471.642 360.175 505.1105 Metallinizoria C21.H23.N0.272 [M-H1H -3.8 yets y 79 2.5.7 2.655.777 422.066 422.0214 Forynomizate (or f) C21.H23.N0.272 [M-H1H -0.6 yets y 90 2.5.6 <t< td=""><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td>yes</td></t<>											yes
74 24.8 53.88,285 748.4970 748.4994 Spinestram C42.1469.MOI0 M-H1 -2.4 yes y 75 24.9 1,791.821 366.015 364.0012 C11 C11 C11 Virtik Yes y											yes
75 24.9 17.71 J21 346.0015 346.0023 Trillmanzde C15.H15.Nd 0.F3 Cl MeH1 -5.9 yes y 76 25.1 4.002,663 363.1664 383.1664 3											no
76 25.1 4.00.2662 883.1694 383.1635 functionable C18.162.06.2055 [M-H]+ 5.9 yes y 77 25.2 9.059.065 50.1075 50.51.107											yes
77 25.2 9.050,006 505.1075 505.1105 Metallumicone C24.H16.Mu 2076 [M-H] -3.0 yes y 78 25.5 12.471,642 360.1752 360.1770 etosazole C21.H123.N 02.F2 [M-H]+ -1.8 yes y 79 25.7 2.695,757 422.2064 422.2074 Fengroundmate (E or F) C24.H27.N0.04 (M-H]+ -0.6 yes y 80 25.8 2.013,440 37.0978 374.0934 Fengroundmate (E or F) C24.H27.N0.04 (M-H]+ -0.6 yes y 81 25.8 7.307.520 373.0971 373.0905 Quadopt=UTIN TAR C4 (M-H]+ 2.1 yes r											yes
78 25.5 12,471,642 360.1752 360.1770 etoxazole C21 H23 N 02 F2 (M+H)+ -1.8 yes y 79 25.7 2,655,757 422.2064 422.2074 ferproximate (E or F) C24 H27 N3 04 (M+H)+ -0.6 yes y 80 25.8 2,013,440 374.0934 Pyrazophos C14 H20 N3 05 P5 [M+H]+ 4.4 yes r 81 25.8 7,30571 370.0975 Quadop 50 Quadopt-P4 C19 H171 N2 04 C1 (M+H)+ 2.1 yes r											yes yes
79 25.7 2,695,757 422.2068 422.2074 Fengroximate (E or F) C 24 H27 N3 O4 [M-H]+ -0.6 yes y 80 25.8 2,013,440 374.0373 374.0393 Myraophos C 14/120 N3 O5 P5 [M-H]+ -4.4 yes r 81 25.8 7,30572 373.0397 373.0395 Qualopt-Unit C 19/117 N2 O4 C1 (M-H]+ 2.1 yes r											yes yes
80 25.8 2,013,440 374,0978 374,0934 Pyrazophos C14 H20 N3 05 P S [M+H]+ 4.4 yes r 81 25.8 7,307,520 373,0971 373,0950 Quizalofop-Ethyl C19 H17 N2 O4 Cl [M+H]+ 2.1 yes r											yes yes
81 25.8 7,307,520 373.0971 373.0950 Quizalofop-Ethyl C19 H17 N2 O4 Cl [M+H]+ 2.1 yes r											no
											no
82 26.2 8,095,296 447.1116 447.1057 orthosulfamuron C16 H20 N6 O6 S [M+Na]+ 5.9 Yes r	82		8,095,296		447.1057	orthosulfamuron	C16 H20 N6 O6 S		5.9		no

Table 2 Result of un-targeted screening of pesticides of unknown mixed pesticide sample on LCMS-IT-TOF

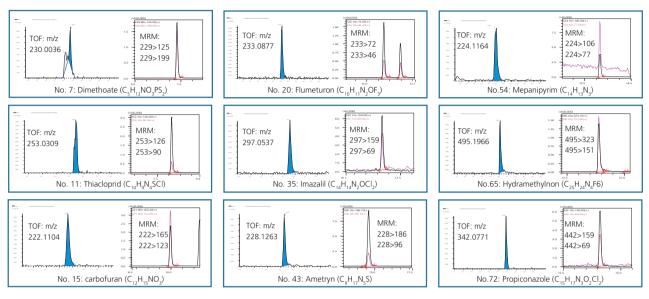


Figure 4: Individual comparisons of detection of nine pesticides (out of 83) in an unknown sample by targeted and un-targeted screening methods.

But, they could be detected if their EICs were extracted successfully. This results indicate that HRMS based un-targeted screening is highly depending on the data analysis method. The current peak picking algorithm could not find effectively the distorted and submerged peaks. More sensitive peak picking programs (different algorithm) are required for effective detection of distorted and submerged peaks in LC-TOF data.

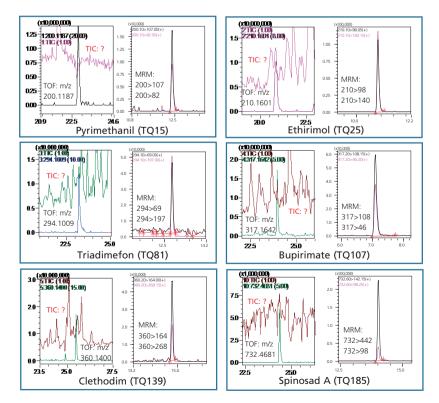


Figure 4 Sixty-nine additional pesticides were confirmed exist in the unknown sample by re-exploring the LC-TOF raw data through extracting the exact masses of pesticides found by MRM method (displaying 6 only).

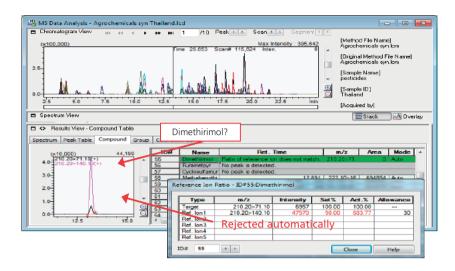


Figure 5: The Identification of a peak for dimethirimol was rejected automatically by the method due to un-matching of intensity ratio of MRMs.

In contrast, the MRM targeted screening method does not affected by data analysis. While, matrix effect is the only factor that may cause false positive and false negative detection. The screening reliability of MRM method is considerably high due to the excellent mass selectivity and specific RT of every compounds. In addition, the confirmation MRM (reference ion) and its intensity ratio with the main MRM (quantifier ion) provides additional selectivity and confirmation, which could reduce further false positive results. Figure 6 shows one example, a peak corresponding to dimethirimol appeared at the expected RT with two MRMs. However, the data analysis program rejected it as a found pesticide due to the intensity ratio of the MRM pair was out of the defined range. This result may have two possibilities: it is another compound or there is a co-elute peak which MRM is same as the confirmation MRM (210>140) of dimethirimol. The MRM-based targeted screening methods have been increasingly adopted in analysis of pesticides and other chemical contaminants in food safety analysis due to several facts. First, the number of pesticides that can be covered (screened) in a single run has increased drastically due to the improvements in triple quadrupole instrumentation and software technologies. Second, MRM database of most pesticides become available for various LC/MS/MS systems from vendors or research institutes. Third, MRM targeted screening approach can be fully automated from data acquisition to data analysis and reporting, which is favorited in routine inspection analysis in food safety labs.

Conclusions

This is a preliminary comparative study of MRM-based targeted screening method and HRMS based un-targeted screening method for detection of pesticides. HRMS method on LC-TOF is an ideal approach for screening of un-limited pesticides in samples. This approach requires advanced data acquisition method and high sensitivity in full spectrum mode to detect all ions without discrimination. However, data analysis may be very challenging in peak picking of distorted and submerged peaks due to matrix interference of actual food samples. On the other hand, the MRM-based targeted screening approach has been increasingly adopted in food safety analysis because of its operation easiness and high reliability in detection and identification of targeted pesticides. Further studies with more quantitative comparison of the two screening approaches and their performances for different samples are needed.

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