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# Determination of 55 Residual Pesticides in Onion and Leek Samples Using GC-MS/MS

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## 1. Introduction

Determination of residual pesticides in vegetables is an important topic in food safety. Most commonly, pesticide residues in the matrix have been analyzed by GC/MS. But applying GC/MS method to onion and leek samples is often difficult, since many of the pesticide peaks are overlapped by matrix compounds. Triple quadrupole GC-MS/MS provides excellent sensitivity and selectivity in analyzing compounds in complex matirces. In this report, a novel approach for determination of 55 residual pesticides in onion and leek samples using a GC-MS/MS in multiple reaction monitoring (MRM) mode has been developed. The established method was sensitive and reliable for analysis of the 55 pesticides in onion and leek samples.

## 2. Methods and Materials

**Sample Preparation**

The samples were extracted by acetonitrile and purified by Carb/PSA solid-phase extraction (SPE) cartridges. Internal standard substance (heptachlor-endo-epoxide, 0.028 mg/L) was used to overcome matrix effect and achieve quantitative determination.

Organic onion and leek samples were purchased from local food market.

The samples were homogenized in a food processor.

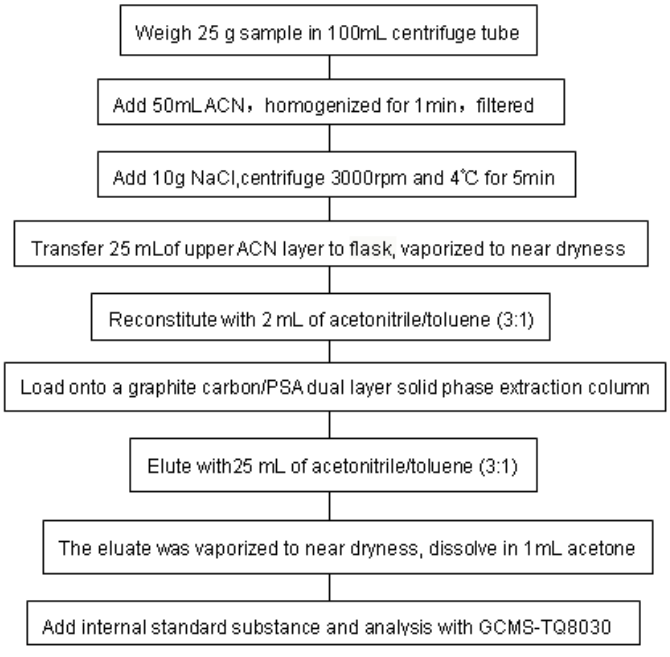


Fig. 1 Sample pretreatment step

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Table 1 List of pesticides

| NO | NAME | CAS | Quantitative ion-pair | Collision voltage(V) | Qualitative ion-pair | Collision voltage(V) | Ret. Time |
|---|---|---|---|---|---|---|---|
| 1 | Methamidophos | 10265 - 92 - 6 | 141.0>95.0 | 8 | 141.0>126.0 | 4 | 5.913 |
| 2 | Dichlorvos | 62 - 73 - 7 | 185.0>93.0 | 14 | 185.0>109.0 | 14 | 6.033 |
| 3 | Omethoate | 1113 - 02 - 6 | 156.0>110.0 | 8 | 156.0>141.0 | 4 | 9.686 |
| 4 | Sulfotep | 3689 - 24 - 5 | 322.0>202.0 | 10 | 322.0>294.0 | 4 | 10.559 |
| 5 | Phorate | 298 - 02 - 2 | 260.0>75.0 | 8 | 260.0>231.0 | 4 | 10.799 |
| 6 | alpha-HCH | 319 - 84 - 6 | 218.9>182.9 | 8 | 218.9>144.9 | 20 | 10.916 |
| 7 | Dimethoate | 60 - 51 - 5 | 125.0>79.0 | 8 | 125.0>47.0 | 14 | 11.157 |
| 8 | beta-HCH | 319 - 85 - 7 | 218.9>182.9 | 8 | 218.9>144.9 | 20 | 11.447 |
| 9 | Quintozene | 82 - 68 - 8 | 294.8>236.8 | 16 | 294.8>264.8 | 12 | 11.502 |
| 10 | gamma-HCH | 58 - 89 - 9 | 218.9>182.9 | 8 | 218.9>144.9 | 20 | 11.598 |
| 11 | Terbufos | 13071 - 79 - 9 | 231.0>174.9 | 14 | 231.0>128.9 | 26 | 11.672 |
| 12 | Fonofos | 944 - 22 - 9 | 246.0>109.1 | 18 | 246.0>137.1 | 6 | 11.761 |
| 13 | Diazinon | 333 - 41 - 5 | 304.1>179.1 | 10 | 304.1>162.1 | 8 | 11.797 |
| 14 | Pyrimethanil | 53112 - 28 - 0 | 198.1>183.1 | 14 | 198.1>158.1 | 18 | 11.908 |
| 15 | delta-HCH | 319 - 86 - 8 | 218.9>182.9 | 10 | 218.9>144.9 | 20 | 12.171 |
| 16 | Vinclozolin | 50471 - 44 - 8 | 285.0>212.0 | 12 | 285.0>178.0 | 14 | 12.828 |
| 17 | Parathion-methyl | 298 - 00 - 0 | 263.0>109.0 | 14 | 263.0>136.0 | 8 | 12.869 |
| 18 | Fenitrothion | 122 - 14 - 5 | 277.0>260.0 | 6 | 277.0>109.1 | 14 | 13.365 |
| 19 | Malathion | 121 - 75 - 5 | 173.1>99.0 | 14 | 173.1>127.0 | 6 | 13.535 |
| 20 | Chlorpyrifos | 2921 - 88 - 2 | 313.9>257.9 | 14 | 313.9>285.9 | 8 | 13.683 |
| 21 | Fenthion | 55 - 38 - 9 | 278.0>109.0 | 20 | 278.0>125.0 | 20 | 13.76 |
| 22 | Parathion | 56 - 38 - 2 | 291.1>109.0 | 14 | 291.1>137.0 | 6 | 13.828 |
| 23 | Triadimefon | 43121 - 43 - 3 | 208.1>181.0 | 10 | 208.1>127.0 | 14 | 13.895 |
| 24 | Isocarbophos | 24353 - 61 - 5 | 289.1>136.0 | 14 | 289.1>113.0 | 6 | 13.909 |
| 25 | Dicofol | 115 - 32 - 2 | 250.0>139.0 | 14 | 250.0>215.0 | 8 | 13.988 |
| 26 | Isofenphos-methyl | 83733-82-8 | 199.0>121.0 | 14 | 241.1>121.1 | 22 | 14.217 |
| 27 | Fipronil | 120068 - 37 - 3 | 366.9>212.9 | 30 | 366.9>254.9 | 22 | 14.414 |
| 28 | Phosfolan | 947-02-4 | 255.0>227.0 | 6 | 255.0>140.0 | 22 | 14.524 |
| IS | Heptachlor-exo-epoxide | 1024 - 57 - 3 | 352.8>262.9 | 14 | 352.8>281.9 | 12 | 14.536 |
| 29 | Phenthoate | 2597 - 03 - 7 | 273.9>125.0 | 20 | 273.9>246.0 | 6 | 14.62 |
| 30 | Quinalphos | 13593 - 03 - 8 | 157.1>129.0 | 14 | 157.1>93.0 | 10 | 14.643 |
| 31 | Procymidone | 32809 - 16 - 8 | 283.0>96.0 | 10 | 283.0>255.0 | 12 | 14.714 |
| 32 | Methidathion | 950 - 37 - 8 | 145.0>85.0 | 8 | 145.0>58.0 | 14 | 14.915 |
| 33 | Profenofos | 41198 - 08 - 7 | 336.9>266.9 | 14 | 336.9>308.9 | 6 | 15.549 |
| 34 | p,p'-DDE | 72 - 55 - 9 | 246.0>176.0 | 30 | 246.0>211.0 | 22 | 15.643 |
| 35 | p,p'-DDD | 72 - 54 - 8 | 235.0>165.0 | 24 | 235.0>199.0 | 14 | 16.436 |
| 36 | o,p'-DDT | 789 - 02 - 6 | 235.0>165.0 | 24 | 235.0>199.0 | 16 | 16.491 |
| 37 | Triazophos | 24017 - 47 - 8 | 257.0>162.0 | 8 | 257.0>134.0 | 22 | 16.685 |
| 38 | p,p'-DDT | 50 - 29 - 3 | 235.0>165.0 | 24 | 235.0>199.0 | 16 | 17.146 |
| 39 | Iprodione | 36734 - 19 - 7 | 314.0>245.0 | 12 | 314.0>56.0 | 22 | 17.853 |
| 40 | Phosmet | 732 - 11 - 6 | 160.0>133.0 | 14 | 160.0>77.0 | 24 | 17.989 |
| 41 | Bifenthrin | 82657 - 04 - 3 | 181.1>166.1 | 12 | 181.1>153.1 | 8 | 18.007 |
| 42 | Fenpropathrin | 39515 - 41 - 8 | 265.1>210.1 | 12 | 265.1>172.1 | 14 | 18.192 |
| 43 | Phosalone | 2310 - 17 - 0 | 182.0>111.0 | 14 | 182.0>138.0 | 8 | 18.664 |
| 44 | Cyhalothrin-1 | 68085 - 85 - 8 | 197.0>161.0 | 8 | 197.0>141.0 | 12 | 18.802 |
| 45 | Cyhalothrin-2 | 68085 - 85 - 8 | 197.0>161.0 | 8 | 197.0>141.0 | 12 | 18.982 |
| 46 | Coumaphos | 56-72-4 | 362.0>109.0 | 16 | 362.0>226.0 | 14 | 19.929 |
| 47 | Pyridaben | 96489 - 71 - 3 | 147.1>117.1 | 22 | 147.1>132.1 | 14 | 19.969 |
| 48 | Cyfluthrin-1 | 68359 - 37 - 5 | 226.1>206.1 | 14 | 226.1>199.1 | 6 | 20.331 |
| 49 | Cyfluthrin-2 | 68359 - 37 - 5 | 226.1>206.1 | 14 | 226.1>199.1 | 6 | 20.428 |
| 50 | Cyfluthrin-3,4 | 68359 - 37 - 5 | 226.1>206.1 | 14 | 226.1>199.1 | 6 | 20.488 |
| 51 | Cypermethrin-1 | 52315 - 07 - 8 | 163.1>127.1 | 6 | 163.1>91.0 | 14 | 20.655 |
| 52 | Cypermethrin-2 | 52315 - 07 - 8 | 163.1>127.1 | 6 | 163.1>91.0 | 14 | 20.756 |
| 53 | Cypermethrin-3,4 | 52315 - 07 - 8 | 163.1>127.1 | 6 | 163.1>91.0 | 14 | 20.813 |
| 54 | Flucythrinate-1 | 70124 - 77 - 5 | 199.1>157.1 | 10 | 199.1>107.1 | 22 | 20.815 |
| 55 | Flucythrinate-2 | 70124 - 77 - 5 | 199.1>157.1 | 10 | 199.1>107.1 | 22 | 21.007 |
| 56 | Fenvalerate-1 | 51630 - 58 - 1 | 419.1>225.1 | 6 | 419.1>167.1 | 12 | 21.546 |
| 57 | Fluvalinate-1 | 69409 - 94 - 5 | 250.1>55.0 | 20 | 250.1>200.0 | 20 | 21.66 |
| 58 | Fenvalerate-2 | 51630 - 58 - 1 | 419.1>225.1 | 6 | 419.1>167.1 | 12 | 21.724 |
| 59 | Fluvalinate-2 | 69409 - 94 - 5 | 250.1>55.0 | 20 | 250.1>200.0 | 20 | 21.755 |
| 60 | Difenoconazole-1 | 119446 - 68 - 3 | 323.0>265.0 | 14 | 323.0>202.0 | 28 | 22.02 |
| 61 | Difenoconazole-2 | 119446 - 68 - 3 | 323.0>265.0 | 14 | 323.0>202.0 | 28 | 22.089 |
| 62 | Deltamethrin-1 | 52918 - 63 - 5 | 252.9>93.0 | 20 | 252.9>171.9 | 8 | 22.126 |
| 63 | Deltamethrin-2 | 52918 - 63 - 5 | 252.9>93.0 | 20 | 252.9>171.9 | 8 | 22.345 |

## GC/MS/MS Analysis

Treated samples were analyzed in MRM mode using a gas chromatograph coupled with a triple quadrupole mass spectrometer (GCMS-TQ8030, Shimadzu Corporation, Japan). The MRM transitions and collision energies for every compound were acquired from the pesticide MRM database provided by Shimadzu Corporation which contains 440 pesticides.

Analytical Conditions

GC

| | |
|---|---|
| Carrier gas | : He |
| Linear velocity | : 47.2 cm/sec |
| Injection mode | : splitless (1 min) |
| Injection port temperature | : 250°C |
| Column | : Rxi-5 Sil ms, 30 m × 0.25 mm, 0.25 µm |
| Temperature program | : 50°C (1 min)-25°C/min-125°C-10°C/min-300°C (15 min) |

MS/MS

| | |
|---|---|
| Ionization | : EI |
| Collision gas | : argon |
| Solvent cutting time | : 4 min |
| Ion source temperature | : 200°C |
| Interface temperature | : 250°C |
| Detector voltage | : tuning voltage + 0.6 kV |
| Monitoring mode | : MRM |

# 3. Results and Discussion

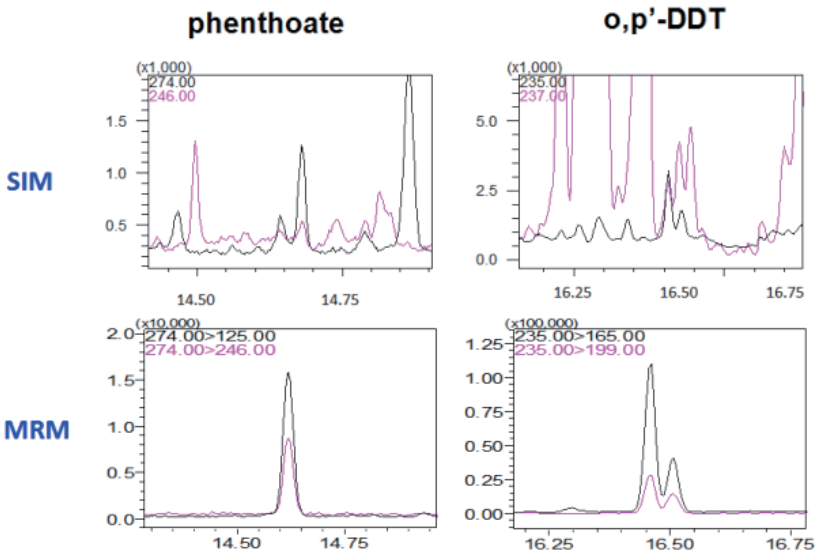


Fig. 2 SIM, MRM chromatograms of phenthoate and o, p-DDT spiked in onion samples (0.005 mg/L)

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Pesticide analysis by GC/MS has mostly been performed in SIM (Selected Ion Monitoring) mode, but especially for complex matrices the analytical selectivity achieved was often not sufficient. Fig. 2 shows chromatograms phenthoate and o, p-DDT spiked in onion matrix (0.005 mg/L) in both SIM and MRM modes. The results showed a clear improvement in sensitivity and selectivity when using MRM.

In order to assess the method linearity, calibration curves were constructed for the 55 pesticides spiked in the sample matrix, using heptachlor-endo-epoxide as the internal standard. The linear relation between peak area ratio and concentration ratio of target and internal standard substance were good from 0.001 mg/L to 0.1 mg/L ($r^2$ > 0.99). The limits of detection (LODs) of all the pesticides studied were 0.0001 mg/kg. The average recoveries were 70%-120% of target compounds and the relative standard deviations (%RSDs, n=6) were less than 11% in two spiked levels at 0.001 mg/kg and 0.005 mg/kg.

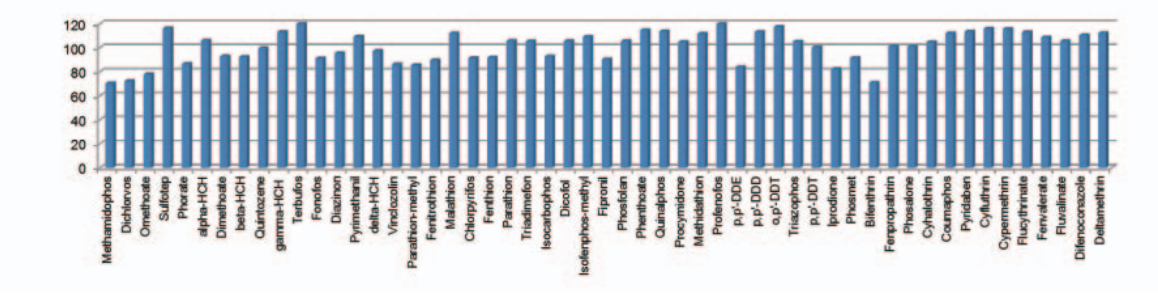


Fig. 3 Recovery of pesticides at 0.001mg/L spiked in onion sample

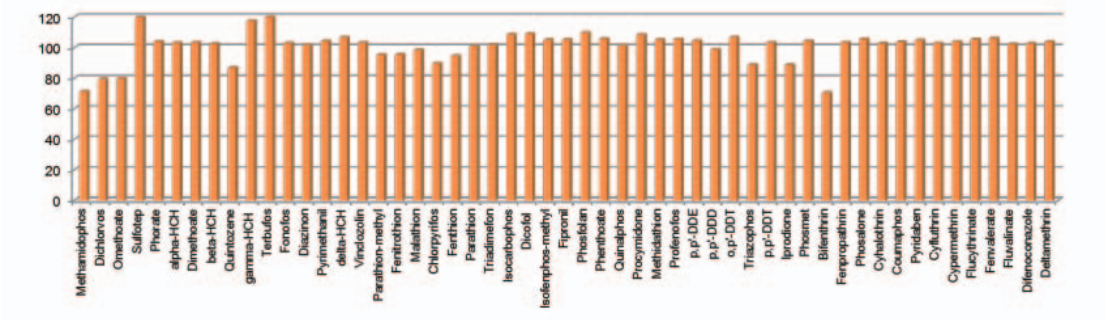


Fig. 4 Recovery of pesticides at 0.001mg/L spiked in leek sample

# 4. Conclusions

- The developed method is sensitive, rapid, precise, and widely linear, therefore it is suitable for the determination of pesticides.
- The recoveries were acceptable for multi-residue pesticide determination in onion and leek samples. GC/MS/MS technique (MRM) compared to SIM provides excellent sensitivity and selectivity for analysis of pesticides in complex matrices.

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