**Pirimiphos-methyl**

CIPAC 239/TC/M/3

Method extension

Studies for Method Extension of existing CIPAC method for pirimiphos-methyl

Long Lasting Insecticidal Nets.

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1. **Introduction**
* The CIPAC method 239/TC/M/3 is suitable for determining pirimiphos-methyl technical. This method of determination is an extension of the CIPAC method 239/TC/M/3. This report was prepared to demonstrate the revised method suitable for determining pirimiphos-methyl in coated insecticidal nets in the presence of deltamethrin.
* The study is method extension of CIPAC method 239/TC/M/3 for the evaluation of pirimiphos-methyl in Yorkool NG2 long lasting insecticidal nets. The study was conducted by Yorkool International Trading Co., Ltd.
1. **Modified method.**

**Outline of CIPAC Method**: The pirimiphos-methyl in long lasting insecticidal net is dissolved in acetone, containing an internal standard, and the pirimiphos-methyl content determined by capillary gas chromatography.

**Reagents***Pirimiphos-methyl* standard of known purity. Even a purified standard of pirimiphos-methyl is not very stable at room temperature. It is important to keep the standard in a refrigerator. Before taking out standard from the bottle, ensure that the temperature of the bottle has reached room temperature. Depending on the amount in the bottle this may take up to 4 hours. Accelerating this process by putting the bottle into a water bath with a temperature above 25°C is not recommended because this can cause degradation of the active substance.

*Acetone*

*4,4'-Dimethoxybenzophenone* internal standard. Must not contain impurities with the same retention time as pirimiphos-methyl.

*Internal standard solution.* Dissolve 0.025 g of 4,4- dimethoxybenzophenone in acetone (250 ml). Prepare sufficient solution for the calibration solutions and the all samples to be analysed.

*Calibration solutions.* Prepare calibration solutions in duplicate. Warm the material at 25°C, prior to weighing, to ensure it is completely liquid. Weigh (to the nearest 0.1 mg) 20 - 30 mg (s mg) of standard pirimiphos-methyl into a volumetric flask (100 ml). Fill to the mark with internal standard solution. Then place it in an ultrasonic bath for 5 min to ensure complete solution (solutions CA and CB).

**Apparatus**

*Gas chromatograph* equipped with split/splitless injection and a flame ionization detector

*Capillary column* fused silica, 15 m x 0.25 (i.d.) mm coated with crosslinked dimethyl polysiloxane (DB-1 or equivalent); film thickness: 0.25 μm

*Electronic integrator or data system*

**Procedure**

* 1. *Operating conditions(typical)*

*Column* Fused silica, 15 mx 0.25 mm (i. d.) coated with crosslinked dimethyI polysiloxane (DB-1 or equivalent); film thickness: 0.25 μm

*Injection system*

 Injector Split injection

Injection volume 1 µl

Split ratio 10:1

Detector flame ionisation

*Temperatures*

Injector port 170°C (Depending on the equipment used, an injection port temperature higher than 170°C may be used, but it has to be carefully checked to avoid any degradation of pirimiphos-methyl in the injection system)

 Detector 310°C

 Oven programme

 temp 1: 60°C, hold 0min, ramp rate 25°C /min

temp 2: 100°C, hold 0min, ramp rate 40°C /min

temp 3: 280°C, hold 4min

*Gas flow rates*

 Helium(carrier) 2 ml/min(typically 86kPa at 60°C);run at constant flow

 Air 400 ml/min

 Hydrogen 30 ml/min

 Nitrogen(make up) to 30 ml/min

 Retention times pirimiphos-methyl: about 4.9 min

 Internal standard: about 5.6 min

* 1. *System equilibration*Prepare two calibration solutions. Inject 1 μl portions of solution CA until the response factors (fi) obtained for two consecutive injections differ by less than 1.0%. Then inject a 1 μl portion of solution CB. The response factor, fi, for this solution should not deviate by more than 1.0% from that of solution CA, otherwise prepare new calibration solutions. If the peak retention times differ significantly from the values given, then adjust the flow rate accordingly.
	2. *Preparation of sample.*Prepare solutions in duplicate for each sample. Cut the sample into small pieces of less than 2×2 cm and homogenise. Weigh(to the nearest 0.1 mg) about 500 mg (w mg) LN sample to contain 4.5-5.5 mg of pirimiphos-methyl into a suitable flask or bottle (50 ml). Add by pipette or calibrated dispenser the internal standard solution (20.0 ml). Cap the container and place it in an ultrasonic bath for 30 min. Cool the sample to room temperature and filter the solution through a 0.45μm PTFE filter membrane. Transfer the sample to a GC vial (solutions SA and SB).
	3. *Determination*Inject in duplicate 1 μl portions of each sample solution bracketing them with duplicate injections of the calibration solution as follows calibration solution CA, calibration solution CB. Calibration solution CA sample solution S1A, sample solution S1B, calibration solution CA, sample solution S2A sample solution S2B, calibration solution CA, and so on for further samples. Measure the relevant peak areas. If the peak shapes and precision of the analysis deteriorate, due to e.g. build-up of formulation residue in the GC, replace injection liners, gold seals and/or split vent lines.
	4. *Calculation*Calculate the mean value of each pair of response factors bracketing the two injections of a sample (f) and use this value for calculating the pirimiphos-methyl contents of the bracketed sample injections.

$$fi=\frac{Ir×s×P}{Hs}$$

content of pirimiphos-methyl $=\frac{f×Hw}{Iq×w×5}$ g/kg

where:

fi = individual response factor

f= mean response factor

Hs = peak area of pirimiphos-methyl in the calibration solution

Hw= peak area of pirimiphos-methyl in the sample solution

Ir = peak area of the internal standard in the calibration solution

Iq = peak area of the internal standard in the sample solution

s = mass of the pirimiphos -methyl reference standard in the calibration solution (mg)

w = mass of sample taken (mg)

P = purity of pirimiphos-methyl reference standard (g/kg)



Figure 1 GC Chromatogram of a calibration solution

Figure 2 GC Chromatogram of a sample solution

1. **Results**

Day 1 results from *Test Center for Chemical Products of Zhejiang Chemical Industry Research Institute*

Sample A:

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Sample A | peak area of pirimiphos-methyl | peak area of 4,4'-dimethoxybenzophenone |  weight of subsamples(mg) | individual response factor fi | average peak area of pirimiphos-methyl in sample solutions | average peak area of 4,4'-dimethoxybenzophenone in sample solutions |
| Calibration solution CA | 178.00227 | 111.77453 | × | 16374.38  | × | × |
| Sample solution A-1  | 169.20293 | 111.65657 | 496.1 | 　 | 169.41655 | 112.68654 |
| Sample solution A-1  | 169.63017 | 113.71651 | 　 |
| Calibration solution CA | 173.57332 | 111.61768 | × | 16768.63  | × | × |
| Sample solution A-2  | 174.14365 | 120.16515 | 507.6 | 　 | 173.536965 | 119.14029 |
| Sample solution A-2  | 172.93028 | 118.11543 | 　 |
| Calibration solution CA | 176.58194 | 111.50954 | × | 16466.96  | × | × |

|  |  |
| --- | --- |
| Average response factor f | 16536.66  |
| Pirimiphos-methyl content in subsampleA-1(g/kg) | 10.02  |
| Pirimiphos-methyl content in subsampleA-2(g/kg) | 9.49  |

Sample B:

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Sample B | peak area of pirimiphos-methyl | peak area of 4,4'-dimethoxybenzophenone |  weight of subsamples(mg) | individual response factor fi | average peak area of pirimiphos-methyl in sample solutions | average peak area of 4,4'-dimethoxybenzophenone in sample solutions |
| Calibration solution CA | 176.58194 | 111.50954 | × | 16466.96  | × | × |
| Sample solution B-1  | 189.02397  | 113.11663  | 522.1 | 　 | 188.95723 | 113.251955 |
| Sample solution B-1  | 188.89049  | 113.38728  | 　 |
| Calibration solution CA | 174.42876  | 111.71622  | × | 16701.13  | × | × |
| Sample solution B-2 | 195.05658  | 117.95132  | 523.1 | 　 | 195.664955 | 118.67149 |
| Sample solution B-2  | 196.27333  | 119.39166  | 　 |
| Calibration solution CA | 175.62668  | 112.11619  | × | 16646.60  | × | × |

|  |  |
| --- | --- |
| Average response factor f | 16604.89  |
| Pirimiphos-methyl content in subsampleB-1(g/kg) | 10.61  |
| Pirimiphos-methyl content in subsampleB-2(g/kg) | 10.47  |

Sample C:

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Sample C | peak area of pirimiphos-methyl | peak area of 4,4'-dimethoxybenzophenone |  weight of subsamples(mg) | individual response factor fi | average peak area of pirimiphos-methyl in sample solutions | average peak area of 4,4'-dimethoxybenzophenone in sample solutions |
| Calibration solution CA | 175.62668  | 112.11619  | × | 16646.60  | × | × |
| Sample solution C-1  | 167.41685 | 112.67695 | 494.1  | 　 | 166.89626 | 112.586455 |
| Sample solution C-1  | 166.37567 | 112.49596 | 　 |
| Calibration solution CA | 171.65598 | 110.77972 | × | 16828.64  | × | × |
| Sample solution C-2 | 175.82483 | 112.21394 | 508.3 | 　 | 175.82374 | 112.79308 |
| Sample solution C-2  | 175.82265 | 113.37222 | 　 |
| Calibration solution CA | 177.57922 | 113.96183 | × | 16734.58  | × | × |

|  |  |
| --- | --- |
| Average response factor f | 16736.61  |
| Pirimiphos-methyl content in subsampleC-1(g/kg) | 10.04  |
| Pirimiphos-methyl content in subsampleC-2(g/kg) | 10.27  |

Sample D:

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Sample D | peak area of pirimiphos-methyl | peak area of 4,4'-dimethoxybenzophenone |  weight of subsamples(mg) | individual response factor fi | average peak area of pirimiphos-methyl in sample solutions | average peak area of 4,4'-dimethoxybenzophenone in sample solutions |
| Calibration solution CA | 177.57922 | 113.96183 | × | 16734.58  | × | × |
| Sample solution D-1  | 183.14008 | 113.30664 | 492.5 | 　 | 183.893765 | 113.630685 |
| Sample solution D-1  | 184.64745 | 113.95473 | 　 |
| Calibration solution CA | 174.75919 | 112.89019 | × | 16844.72  | × | × |
| Sample solution D-2 | 193.02127 | 116.93018 | 491.8 | 　 | 192.360565 | 116.894295 |
| Sample solution D-2  | 191.69986 | 116.85841 | 　 |
| Calibration solution CA | 178.48085 | 113.96491 | × | 16650.50  | × | × |

|  |  |
| --- | --- |
| Average response factor f | 16743.27  |
| Pirimiphos-methyl content in subsampleD-1(g/kg) | 11.00  |
| Pirimiphos-methyl content in subsampleD-2(g/kg) | 11.20  |

Sample E:

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Sample E | peak area of pirimiphos-methyl | peak area of 4,4'-dimethoxybenzophenone |  weight of subsamples(mg) | individual response factor fi | average peak area of pirimiphos-methyl in sample solutions | average peak area of 4,4'-dimethoxybenzophenone in sample solutions |
| Calibration solution CA | 178.48085 | 113.96491 | × | 16650.50  | × | × |
| Sample solution E-1  | 177.55739 | 113.2831 | 491.3  | 　 | 176.24318 | 112.566585 |
| Sample solution E-1  | 174.92897 | 111.85007 | 　 |
| Calibration solution CA | 174.72026 | 112.9757 | × | 16861.24  | × | × |
| Sample solution E-2 | 187.31955 | 115.64451 | 508.0  | 　 | 186.564215 | 114.86046 |
| Sample solution E-2  | 185.80888 | 114.07641 | 　 |
| Calibration solution CA | 180.50789 | 113.78806 | × | 16437.97  | × | × |

|  |  |
| --- | --- |
| Average response factor f | 16649.90  |
| Pirimiphos-methyl content in subsampleE-1(g/kg) | 10.61  |
| Pirimiphos-methyl content in subsampleE-2(g/kg) | 10.65  |

Day 2 results from *Test Center for Chemical Products of Zhejiang Chemical Industry Research Institute*

Sample A:

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Sample A | peak area of pirimiphos-methyl | peak area of 4,4'-dimethoxybenzophenone |  weight of subsamples(mg) | individual response factor fi | average peak area of pirimiphos-methyl in sample solutions | average peak area of 4,4'-dimethoxybenzophenone in sample solutions |
| Calibration solution CA | 190.93498  | 113.39183 | × | 17104.12  | × | × |
| Sample solution A-1  | 167.93919 | 117.99675 | 500.1 | 　 | 167.911275 | 117.889025 |
| Sample solution A-1  | 167.88336 | 117.78130 | 　 |
| Calibration solution CA | 190.45580 | 113.45358 | × | 17156.49  | × | × |
| Sample solution A-2  | 157.21127  | 115.74509 | 475.8 | 　 | 157.700095 | 116.194175 |
| Sample solution A-2  | 158.18892  | 116.64326 | 　 |
| Calibration solution CA | 191.18004 | 114.00919  | × | 17175.20  | × | × |

|  |  |
| --- | --- |
| Average response factor f | 17145.27  |
| Pirimiphos-methyl content in subsampleA-1(g/kg) | 9.77  |
| Pirimiphos-methyl content in subsampleA-2(g/kg) | 9.78  |

Sample B:

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Sample B | peak area of pirimiphos-methyl | peak area of 4,4'-dimethoxybenzophenone |  weight of subsamples(mg) | individual response factor fi | average peak area of pirimiphos-methyl in sample solutions | average peak area of 4,4'-dimethoxybenzophenone in sample solutions |
| Calibration solution CA | 191.18004 | 114.00919  | × | 17175.20  | × | × |
| Sample solution B-1  | 184.23752  | 119.36330 | 501.1 | 　 | 183.527695 | 119.193375 |
| Sample solution B-1  | 182.81787 | 119.02345 | 　 |
| Calibration solution CA | 191.32333  | 114.16342 | × | 17185.56  | × | × |
| Sample solution B-2 | 171.74458 | 115.80752 | 499.5 | 　 | 171.75569 | 116.055705 |
| Sample solution B-2  | 171.7668 | 116.30389 | 　 |
| Calibration solution CA | 192.45450  | 114.91430  | × | 17196.92  | × | × |

|  |  |
| --- | --- |
| Average response factor f | 17185.89  |
| Pirimiphos-methyl content in subsampleB-1(g/kg) | 10.56  |
| Pirimiphos-methyl content in subsampleB-2(g/kg) | 10.18  |

Sample C:

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Sample C | peak area of pirimiphos-methyl | peak area of 4,4'-dimethoxybenzophenone |  weight of subsamples(mg) | individual response factor fi | average peak area of pirimiphos-methyl in sample solutions | average peak area of 4,4'-dimethoxybenzophenone in sample solutions |
| Calibration solution CA | 192.45450  | 114.91430  | × | 17196.92  | × | × |
| Sample solution C-1  | 179.00790 | 124.93880 | 497.2 | 　 | 177.63134 | 123.90511 |
| Sample solution C-1  | 176.25478 | 122.87142 | 　 |
| Calibration solution CA | 192.68925 | 114.96367 | × | 17183.34  | × | × |
| Sample solution C-2 | 193.94156 | 129.22905 | 506.9 | 　 | 195.0884 | 129.893295 |
| Sample solution C-2  | 196.23524  | 130.55754 | 　 |
| Calibration solution CA | 193.07222 | 115.31122 | × | 17201.10  | × | × |

|  |  |
| --- | --- |
| Average response factor f | 17193.79  |
| Pirimiphos-methyl content in subsampleC-1(g/kg) | 9.92  |
| Pirimiphos-methyl content in subsampleC-2(g/kg) | 10.19  |

Sample D:

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Sample D | peak area of pirimiphos-methyl | peak area of 4,4'-dimethoxybenzophenone |  weight of subsamples(mg) | individual response factor fi | average peak area of pirimiphos-methyl in sample solutions | average peak area of 4,4'-dimethoxybenzophenone in sample solutions |
| Calibration solution CA | 193.07222 | 115.31122 | × | 17201.10  | × | × |
| Sample solution D-1  | 212.50520 | 135.37244 | 498.9 | 　 | 211.907185 | 135.222805 |
| Sample solution D-1  | 211.30917  | 135.07317 | 　 |
| Calibration solution CA | 194.94493 | 116.45521 | × | 17204.88  | × | × |
| Sample solution D-2 | 193.85980  | 119.68283 | 515.2 | 　 | 193.68788 | 119.731595 |
| Sample solution D-2  | 193.51596 | 119.78036 | 　 |
| Calibration solution CA | 192.13301  | 114.79537 | × | 17207.86  | × | × |

|  |  |
| --- | --- |
| Average response factor f | 17204.61  |
| Pirimiphos-methyl content in subsampleD-1(g/kg) | 10.81  |
| Pirimiphos-methyl content in subsampleD-2(g/kg) | 10.80  |

Sample E:

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Sample E | peak area of pirimiphos-methyl | peak area of 4,4'-dimethoxybenzophenone |  weight of subsamples(mg) | individual response factor fi | average peak area of pirimiphos-methyl in sample solutions | average peak area of 4,4'-dimethoxybenzophenone in sample solutions |
| Calibration solution CA | 192.13301  | 114.79537 | × | 17207.86  | × | × |
| Sample solution E-1  | 197.24648 | 123.54248 | 508.90  | 　 | 195.8009 | 122.714215 |
| Sample solution E-1  | 194.35532 | 121.88595 | 　 |
| Calibration solution CA | 194.37234 | 116.12966 | × | 17207.32  | × | × |
| Sample solution E-2 | 186.91327 | 119.04614  | 498.1 | 　 | 186.05771 | 118.48254 |
| Sample solution E-2  | 185.20215 | 117.91894 | 　 |
| Calibration solution CA | 193.51843  | 115.84441 | × | 17240.80  | × | × |

|  |  |
| --- | --- |
| Average response factor f | 17218.66  |
| Pirimiphos-methyl content in subsampleE-1(g/kg) | 10.80  |
| Pirimiphos-methyl content in subsampleE-2(g/kg) | 10.86  |

Day 1 results from *Tianjin Yorkool International Trading Co., Ltd.*

Sample A:

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Sample A | peak area of pirimiphos-methyl | peak area of 4,4'-dimethoxybenzophenone | weight of subsamples(mg) | individual response factor fi | average peak area of pirimiphos-methyl in sample solutions | average peak area of 4,4'-dimethoxybenzophenone in sample solutions |
| Calibration solution CA | 148.694 | 114.548 | × | 19053.84 | × | × |
| Sample solution A-1 | 172.726 | 115.511 | 551.2 |  | 171.2755 | 114.726 |
| Sample solution A-1 | 169.825 | 113.941 |  |
| Calibration solution CA | 149.064 | 114.449 | × | 18990.12 | × | × |
| Sample solution A-2 | 169.134 | 116.502 | 550.3 |  | 170.9485 | 117.6145 |
| Sample solution A-2 | 172.763 | 118.727 |  |
| Calibration solution CA | 150.785 | 115.66 | × | 18972.01 | × | × |

|  |  |
| --- | --- |
| Average response factor f | 19005.32  |
| Pirimiphos-methyl content in subsampleA-1(g/kg) | 10.30 |
| Pirimiphos-methyl content in subsampleA-2(g/kg) | 10.04 |

Sample B:

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Sample B | peak area of pirimiphos-methyl | peak area of 4,4'-dimethoxybenzophenone |  weight of subsamples(mg) | individual response factor fi | average peak area of pirimiphos-methyl in sample solutions | average peak area of 4,4'-dimethoxybenzophenone in sample solutions |
| Calibration solution CA | 150.785 | 115.66 | × | 18972.01 | × | × |
| Sample solution B-1  | 180.560 | 116.074 | 555.7 |  | 180.3065 | 115.9245 |
| Sample solution B-1  | 180.053 | 115.775 |  |
| Calibration solution CA | 151.409 | 115.569 | × | 18878.96 | × | × |
| Sample solution B-2 | 176.198 | 115.194 | 548.2 |  | 175.389 | 114.716 |
| Sample solution B-2  | 174.580 | 114.238 |  |
| Calibration solution CA | 152.424 | 116.454 | × | 18896.85 | × | × |

|  |  |
| --- | --- |
| Average response factor f | 18915.94  |
| Pirimiphos-methyl content in subsampleB-1(g/kg) | 10.59 |
| Pirimiphos-methyl content in subsampleB-2(g/kg) | 10.55 |

Sample C:

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Sample C | peak area of pirimiphos-methyl | peak area of 4,4'-dimethoxybenzophenone |  weight of subsamples(mg) | individual response factor fi | average peak area of pirimiphos-methyl in sample solutions | average peak area of 4,4'-dimethoxybenzophenone in sample solutions |
| Calibration solution CA | 152.424  | 116.454  | × | 18896.85  | × | × |
| Sample solution C-1  | 158.806 | 116.925 | 502.6  | 　 | 158.609 | 116.868 |
| Sample solution C-1  | 158.412 | 116.811 | 　 |
| Calibration solution CA | 152.335 | 116.496 | × | 18914.71  | × | × |
| Sample solution C-2 | 158.658 | 116.618 | 501.2 | 　 | 158.7335 | 116.627 |
| Sample solution C-2  | 158.809 | 116.636 | 　 |
| Calibration solution CA | 151.982 | 116.071 | × | 18889.48  | × | × |

|  |  |
| --- | --- |
| Average response factor f | 18900.35  |
| Pirimiphos-methyl content in subsampleC-1(g/kg) | 10.21 |
| Pirimiphos-methyl content in subsampleC-2(g/kg) | 10.26 |

Sample D:

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Sample D | peak area of pirimiphos-methyl | peak area of 4,4'-dimethoxybenzophenone |  weight of subsamples(mg) | individual response factor fi | average peak area of pirimiphos-methyl in sample solutions | average peak area of 4,4'-dimethoxybenzophenone in sample solutions |
| Calibration solution CA | 151.982 | 116.071 | × | 18889.48  | × | × |
| Sample solution D-1  | 182.131 | 117.098 | 526.4 | 　 | 182.507 | 117.2995 |
| Sample solution D-1  | 182.883 | 117.501 | 　 |
| Calibration solution CA | 152.774 | 116.511 | × | 18862.79  | × | × |
| Sample solution D-2 | 181.476 | 117.497 | 523.7 | 　 | 181.239 | 117.354 |
| Sample solution D-2  | 181.002 | 117.211 | 　 |
| Calibration solution CA | 149.221 | 113.986 | × | 18893.39  | × | × |

|  |  |
| --- | --- |
| Average response factor f | 18881.89  |
| Pirimiphos-methyl content in subsampleD-1(g/kg) | 11.16 |
| Pirimiphos-methyl content in subsampleD-2(g/kg) | 11.14 |

Sample E:

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Sample E | peak area of pirimiphos-methyl | peak area of 4,4'-dimethoxybenzophenone |  weight of subsamples(mg) | individual response factor fi | average peak area of pirimiphos-methyl in sample solutions | average peak area of 4,4'-dimethoxybenzophenone in sample solutions |
| Calibration solution CA | 149.221 | 113.986 | × | 18893.39  | × | × |
| Sample solution E-1  | 181.022 | 117.109 | 520.2  | 　 | 180.55 | 116.8465 |
| Sample solution E-1  | 180.078 | 116.584 | 　 |
| Calibration solution CA | 152.806 | 116.398 | × | 18840.55  | × | × |
| Sample solution E-2 | 175.306 | 117.89 | 521.9  | 　 | 178.877 | 119.896 |
| Sample solution E-2  | 182.448 | 121.902 | 　 |
| Calibration solution CA | 159.49 | 120.703 | × | 18718.58  | × | × |

|  |  |
| --- | --- |
| Average response factor f | 18817.51  |
| Pirimiphos-methyl content in subsampleE-1(g/kg) | 11.18 |
| Pirimiphos-methyl content in subsampleE-2(g/kg) | 10.76 |

Day 2 results from *Tianjin Yorkool International Trading Co., Ltd.*

Sample A:

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Sample A | peak area of pirimiphos-methyl | peak area of 4,4'-dimethoxybenzophenone |  weight of subsamples(mg) | individual response factor fi | average peak area of pirimiphos-methyl in sample solutions | average peak area of 4,4'-dimethoxybenzophenone in sample solutions |
| Calibration solution CA | 153.267 | 111.803 | × | 18042.35  | × | × |
| Sample solution A-1  | 158.218 | 112.148 | 518 | 　 | 158.164 | 112.2985 |
| Sample solution A-1  | 158.11 | 112.449 | 　 |
| Calibration solution CA | 153.529 | 112.167 | × | 18070.20  | × | × |
| Sample solution A-2  | 157.495 | 112.278 | 516.1 | 　 | 157.9045 | 112.5485 |
| Sample solution A-2  | 158.314 | 112.819 | 　 |
| Calibration solution CA | 154.454 | 113.564  | × | 18185.70  | × | × |

|  |  |
| --- | --- |
| Average response factor f | 18099.42  |
| Pirimiphos-methyl content in subsampleA-1(g/kg) | 9.84 |
| Pirimiphos-methyl content in subsampleA-2(g/kg) | 9.84 |

Sample B:

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Sample B | peak area of pirimiphos-methyl | peak area of 4,4'-dimethoxybenzophenone |  weight of subsamples(mg) | individual response factor fi | average peak area of pirimiphos-methyl in sample solutions | average peak area of 4,4'-dimethoxybenzophenone in sample solutions |
| Calibration solution CA | 154.454 | 113.564  | × | 18185.70  | × | × |
| Sample solution B-1  | 170.588 | 116.806 | 510.5 | 　 | 170.846 | 116.8345 |
| Sample solution B-1  | 171.104 | 116.863 | 　 |
| Calibration solution CA | 154.7 | 112.972 | × | 18062.13  | × | × |
| Sample solution B-2 | 245.082 | 176.959 | 500.2 | 　 | 209.193 | 147.9585 |
| Sample solution B-2  | 173.304 | 118.958 | 　 |
| Calibration solution CA | 155.406 | 114.193 | × | 18174.40  | × | × |

|  |  |
| --- | --- |
| Average response factor f | 18140.74  |
| Pirimiphos-methyl content in subsampleB-1(g/kg) | 10.39 |
| Pirimiphos-methyl content in subsampleB-2(g/kg) | 10.26 |

Sample C:

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Sample C | peak area of pirimiphos-methyl | peak area of 4,4'-dimethoxybenzophenone |  weight of subsamples(mg) | individual response factor fi | average peak area of pirimiphos-methyl in sample solutions | average peak area of 4,4'-dimethoxybenzophenone in sample solutions |
| Calibration solution CA | 155.406 | 114.193 | × | 18174.40  | × | × |
| Sample solution C-1  | 165.467 | 116.99 | 503.1 | 　 | 165.164 | 116.8135 |
| Sample solution C-1  | 164.861 | 116.637 | 　 |
| Calibration solution CA | 155.128 | 113.381 | × | 18077.50  | × | × |
| Sample solution C-2 | 167.538 | 118.301 | 506.3 | 　 | 167.217 | 118.093 |
| Sample solution C-2  | 166.896 | 117.885 | 　 |
| Calibration solution CA | 155.953 | 114.137 | × | 18101.77  | × | × |

|  |  |
| --- | --- |
| Average response factor f | 18117.89  |
| Pirimiphos-methyl content in subsampleC-1(g/kg) | 10.18 |
| Pirimiphos-methyl content in subsampleC-2(g/kg) | 10.13 |

Sample D:

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Sample D | peak area of pirimiphos-methyl | peak area of 4,4'-dimethoxybenzophenone |  weight of subsamples(mg) | individual response factor fi | average peak area of pirimiphos-methyl in sample solutions | average peak area of 4,4'-dimethoxybenzophenone in sample solutions |
| Calibration solution CA | 155.953 | 114.137 | × | 18101.77  | × | × |
| Sample solution D-1  | 190.807 | 118.051 | 510.4 | 　 | 191.35 | 118.222 |
| Sample solution D-1  | 191.893 | 118.393 | 　 |
| Calibration solution CA | 156.198 | 114.271 | × | 18094.60  | × | × |
| Sample solution D-2 | 185.191 | 114.599 | 513.9 | 　 | 187.509 | 115.7765 |
| Sample solution D-2  | 189.827 | 116.954 | 　 |
| Calibration solution CA | 156.333 | 113.931 | × | 18025.18  | × | × |
|  |  |
| Average response factor f | 18073.85  |
| Pirimiphos-methyl content in subsampleD-1(g/kg) | 11.46 |
| Pirimiphos-methyl content in subsampleD-2(g/kg) | 11.39 |

Sample E:

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Sample E | peak area of pirimiphos-methyl | peak area of 4,4'-dimethoxybenzophenone |  weight of subsamples(mg) | individual response factor fi | average peak area of pirimiphos-methyl in sample solutions | average peak area of 4,4'-dimethoxybenzophenone in sample solutions |
| Calibration solution CA | 156.333 | 113.931 | × | 18025.18  | × | × |
| Sample solution E-1  | 186.294 | 122.302 | 508.9  | 　 | 189.427 | 124.344 |
| Sample solution E-1  | 192.56 | 126.386 | 　 |
| Calibration solution CA | 156.087 | 113.263 | × | 17947.74  | × | × |
| Sample solution E-2 | 183.417 | 120.163  | 505 | 　 | 181.249 | 118.658 |
| Sample solution E-2  | 179.081 | 117.153 | 　 |
| Calibration solution CA | 156.661  | 114.007 | × | 17999.44  | × | × |

|  |  |
| --- | --- |
| Average response factor f | 17990.79  |
| Pirimiphos-methyl content in subsampleE-1(g/kg) | 10.77 |
| Pirimiphos-methyl content in subsampleE-2(g/kg) | 10.88 |

**Summary of the results of two laboratories**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | sample A | sample B | sample C | sample D | Sample E |
| x | 9.88 | 10.45 | 10.15 | 11.12 | 10.81 |
| L | 2 | 2 | 2 | 2 | 2 |
| sr | 0.22 | 0.17 | 0.12 | 0.18 | 0.16 |
| sL | 0.13 | 0.00 | 0.03 | 0.22 | 0.09 |
| sR | 0.25 | 0.15 | 0.12 | 0.28 | 0.18 |
| RSDr | 2.19 | 1.66 | 1.15 | 1.60 | 1.49 |
| RSDR | 2.55 | 1.44 | 1.19 | 2.53 | 1.70 |
| r | 0.61 | 0.49 | 0.33 | 0.50 | 0.45 |
| R | 0.71 | 0.42 | 0.34 | 0.79 | 0.52 |
| RSDR(Hor) | 4.01 | 3.97 | 3.99 | 3.94 | 3.95 |
| HorRat | 0.64 | 0.36 | 0.30 | 0.64 | 0.43 |
| Where: |  |  |  |  |
| X | = average |  |  |  |
| L | = number of laboratories |  |  |
| sr | = repeatability standard deviation |  |
| sL | = "pure" between laboratory standard variation |
| sR | = reproducibility standard deviation= √(sr2 +sL2) |
| RSDr | = repeatability relative standard deviation (sr/x\*100) |
| RSDR |  = reproducibility relative standard deviation (sR/x\*100) |
| r | = repeatability (sr\*2.8) |  |  |
| R | = reproducibility (sR\*2.8) |  |  |
| RSDR(Hor) |  = Horwitz value calculated from: 2(1-0.5logc) |  |
|  where c = the concentration of the analyte as a decimal fraction |

HorRat = RSDR/RSDR(Hor)

**Conclusion**

In order to demonstrate modified CIPAC 239/TC/M/3 suitable for determining pirimiphos-methyl in coated insecticidal nets in the presence of deltamethrin. Validation tests were conducted in two laboratories.

In addition to the known criteria the use of the HorRat value could be an additional criterion.

 0.3 ≤ HorRat ≤ 1 => fully acceptable

 HorRat < 0.3 or 1 < HorRat ≤ 2 => Acceptable, but reasonable explanation required!

 HorRat > 2 => not acceptable

The two laboratories data shown all sample’s HorRat is between 0.3 and 1, so

it demonstrates that the method is accuracy and repeatability, modified CIPAC 239/TC/M/3 can be extended in coated pirimiphos-methyl insecticidal nets.