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**[[1]](#footnote-1)\*MT 190.2 DETERMINATION OF RELEASE PROPERTIES OF PIRIMIPHOS-METHYL CS FORMULATIONS**

SCOPE

The method is intended for use only with pirimiphos-methyl CS formulations for public health applications.

OUTLINE OF METHOD A known quantity of the capsule suspension is transferred to a glass bottle and is then subjected to a rolling movement with a specified amount of a hexane/ethanol mixture containing an internal standard. After rolling for ~~three specified periods~~ 15 min., the amount of pirimiphos-methyl in the solvent layer is determined by capillary gas chromatography.

REAGENTS

*Water* conforming to ASTM Type II.

APPARATUS

*Horizontal roller*, capable of rolling 150 ml bottles at 50 rpm (number of revolutions of the bottles, not of the roller. Typically, the roller will need to reach 70-80 rpm). (e.g. Finemech RM10V-W 10-80, Finemech Inc., 35 Kiowa Court, Portola Valley, CA 94028, U.S.A.). Do not use orbital shakers or similar equipment (see Fig. xx).

*Bottles* 150 ml glass, with an internal diameter of about 4.5 cm, with a solvent-resistant plastic cap and liner

*Timer* capable of measuring to the nearest second

***(1) Extraction of pirimiphos-methyl***

Prepare solutions in duplicate for each sample. Weigh (to the nearest 0.1 mg) sufficient sample to contain 52 - 62 mg (*w* mg) of total pirimiphos-methyl into a bottle (150 ml). Add water (5 ml) and cap the bottle. Swirl well by hand until the formulation is thoroughly dispersed (*i.e.* none of the formulation is stuck to the walls of the bottle). Using a dispenser, add internal standard solution (100 ml) (See section ***(2*)**). Cap the bottle and immediately place it on the roller (see Fig. xx), set to roll the bottle horizontally (*not* end-over end) at 50 rpm (i.e. the number of revolutions of the bottle, not of the roller). Simultaneously start the timer. After 15 min, remove the bottle from the roller, stand it vertically on a flat surface and allow to stand for 1 min. Transfer 1 ml from the top of the solution (taking care not to draw up any of the formulation with the solvent) into an autosampler vial (solutions SA and SB). ~~Replace the cap on the bottle and return the bottle to the roller immediately. Repeat this procedure when the timer reaches 60 min and 180 min.~~

***(2) Determination of pirimiphos-methyl***

REAGENTS

*Pirimiphos-methyl* standard of known purity. Even 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, it must be ensured 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.

*Ethanol* absolute

*Hexane* HPLC grade. Hexane is harmful by inhalation and prolonged exposure may cause serious health damage. Always handle and use this material, with the appropriate PPE, within a well ventilated area.

*Dicyclohexyl phthalate* Internal standard. Must not contain impurities with the same retention time as pirimiphos-methyl.

*Internal standard solution*. Dissolve dicyclohexyl phthalate (0.025 g) in a mixture of hexane (900 ml) and ethanol (100 ml). It is extremely important that the solvent mixture is made up accurately in the correct ratio. Prepare sufficient solution for the calibration solutions and all samples to be analysed.

*Calibration solution.* 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) 52 - 62 mg (*s* mg) of pirimiphos-methyl standard into a conical flask (150 ml). Using a dispenser, add internal standard solution (100 ml) and place the flask in an ultrasonic bath for 5 min. Allow to cool to room temperature. Mix thoroughly (solutions CA and CB).

APPARATUS

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

*Capillary column* fused silica, length 15 m ×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

*(a) Gas chromatographic conditions* (typical):

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

*Injection system*

Injector split injection

Injection volume 1 μl

Split ratio 50:1

*Detector* flame ionisation

*Temperatures*

Injection port 170 ºC

Detector 310 ºC

Oven programme temp 1: 60 ºC, hold 0 min, ramp rate 25 ºC/min

 temp 2: 100 ºC, hold 0 min, ramp rate

 40 ºC/min

 temp 3: 280 ºC, hold 1 min

*Gas flow rates*

Helium (carrier) 2 ml/min (typically 86 kPa 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 4.8 min

 internal standard: about 6.1 min

*(b) 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 the solution CB. *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 approximate values quoted, then the flow rate may be adjusted accordingly.

*(c) Determination.* Inject in duplicate 1 μl portions of each sample solution bracketing them with injections of the calibration solutions as follows: e.g. calibration solution CA, calibration solution CB, calibration solution CA, sample solution SA-1, sample solution SA-2, calibration solution CA, sample solution SB-1, sample solution SB-2, 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.

*(d) Calculation.* Calculate the mean value of each pair of response factors bracketing the two injections of a sample and use this value for calculating the pirimiphos-methyl content of the bracketed sample injections.



 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)

*Qt* = content of pirimiphos-methyl released at time *t* = 15 min. (g/kg)

*t* = rolling time

*c* = content of total pirimiphos-methyl (g/kg), determined by method **239**/CS/(M)/3

*Rt* = percentage of pirimiphos-methyl released at time *t* = 15 min. relative to the total pirimiphos-methyl content (%)

*Fig See MT 189.2*



**Fig xx** Typical chromatogram of pirimiphos-methyl after extraction of the CS formulation

1. \* CIPAC method2012. Prepared by the Swiss and German PAC. based on a method supplied by Syngenta
Crop Protection Münchwilen AG, Switzerland. [↑](#footnote-ref-1)