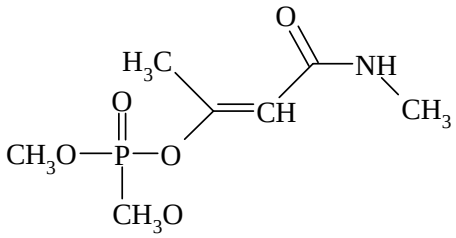
MONOCROTOPHOS
287



ISO common name	Monocrotophos
Chemical name	Dimethyl (*E*)-1-methyl-2-(methylcarbamoyl)vinyl phosphate (IUPAC); dimethyl (*E*)-1-methyl-3-(methylamino)-3-oxo-1-propenyl phosphate (CA; *6923-22-4*)
Empirical formula	$C_7H_{14}NO_5P$
RMM	223.2
Description	Pure monocrotophos forms colourless, hygroscopic crystals, the technical material is a reddish-brown semi-solid mass, containing more than 74% monocrotophos
m.p.	54-55 °C (pure) 25-35 °C (technical)
v.p.	0.29 mPa at 20 °C (pure)
Solubility	In water 1 kg/kg; acetone 700 g/kg; dichloromethane 800 g/kg; methanol 1 kg/kg; octan-1-ol 250 g/kg; toluene 60 g/kg
Stability	Unstable at elevated temperature and in solution in short-chain alcohols
Formulations	Technical concentrates, soluble liquids and ULV formulations

MONOCROTOPHOS TECHNICAL
*287/TC/M/-

1 Sampling. Homogenize the sample by heating in an oven at 40-45 °C before sub-sampling for analysis. Ensure that the heating time is restricted to the minimum necessary to render the sample a homogeneous liquid.

2 Identity tests.

2.1 HPLC. Use the HPLC method below. The relative retention time of monocrotophos with respect to the internal standard for the sample solution should not deviate by more than 1% from that for the calibration solution.

2.2 IR. Smear a portion of the material between two KCl discs and scan from 4000-400 cm^{-1} (2.5-25 µm). The spectrum produced from the sample should not differ significantly from that of the reference grade material.

3 Monocrotophos

OUTLINE OF METHOD The sample is dissolved in methanol and the monocrotophos content is determined by reversed phase liquid chromatography with ultra-violet detection.

REAGENTS

Methanol HPLC grade

Acetonitrile HPLC grade

Distilled water

Mobile phase water-acetonitrile-methanol, 80+10+10 (v/v). Mix 800 ml water, 100 ml acetonitrile and 100 ml methanol, filter and degas. Allow to stabilise at room temperature.

Monocrotophos standard of known purity. Store the standard in a cool dry place, in a desiccator. Allow standard to reach room temperature before removing from desiccator.

Calibration solutions. Into 100 ml volumetric flasks weigh (to the nearest 0.1 mg) 0.040, 0.060, 0.080 and 0.100 g of standard monocrotophos. Dilute each to volume with methanol and mix thoroughly, to give calibration solutions S_A, S_B, S_C and S_D.

* CIPAC method 1990. Prepared by the monocrotophos panel of PAC-GB. Chairman: Mr B L Mathews (Shell Research Ltd.). Based on a method prepared by shell Research Ltd., U.K.

APPARATUS

Liquid chromatograph fitted with an ultra-violet spectrophotometric detector capable of operating at 230 nm, a pulse-free pump and an injection valve e.g. Rheodyne 7125. The injection system should be capable of operating against a pressure of about 6 MPa

HPLC column An unused 0.25 m × 4.6 mm ID stainless steel column packed with Lichrosorb RP 18 (10 µm).

HPLC guard column A 20 mm × 2.0 mm ID stainless steel guard column dry packed with Pellicular ODS chemically bonded to 37-53 m glass beads.

Electronic integrator compatible with the liquid chromatograph.

Volumetric flasks 100 ml

PROCEDURE

(a) HPLC operating conditions

Column	
Material	Stainless steel
Length × i.d.	0.25 m × 4.6 mm
Packing	Lichrosorb RP18
Typical No. of theoretical plates	1300
Guard column	
Material	Stainless steel
Length × i.d.	20 m × 2.0 mm
Packing	Pellicular ODS
Injection volume	10 µl
Detector system	
Type	UV detector operated at 230 nm. Operation of UV detector in the range 220-240 nm is acceptable
Sensitivity	No special requirements
O.D. range	0.1 AUFS
Temperature	
Column, Mobile phase, Injection valve, Detector	Ambient, with maximum variation of 2 °C during the analysis

Mobile phase	Water-acetonitrile-methanol, 80+10+10 (v/v), degassed before use.
Flow rate	1.5 ml min-1. Constant flow is essential for repeatable results.
Calibration	External. Response factor peak area measurement.
Retention time	Monocrotophos. Typically 5.8 min.

(b) Equilibration of the system/linearity check. Set up the liquid chromatographic system in accordance with the parameters given under *(a)*. Inject the calibration solution containing about 1.00 g monocrotophos/l (S_D) and adjust the instrument controls so that the maximum of the monocrotophos peak gives a recorder deflection of 80-90% full scale. Inject each of the calibration solutions in duplicate and determine the areas of the monocrotophos peaks either by integration (preferably) or from the product of the peak height and width at half peak height. Construct a calibration graph relating the mean peak areas *(I_o)* to the concentration of monocrotophos (g/l) in the solutions injected. Calibrate the instrument as described at least once daily.

(c) Sample preparation. Homogenize the material by warming the sealed bottle of monocrotophos technical material at between 40 °C and 50 °C until no crystals remain and hehn shake the bottle. Weigh, in triplicate (to the nearest 0.1 mg), 0.10 g (*w* g) of sample into separate 100 ml volumetric flasks. Dilute each to volume with methanol and mix thoroughly.

(d) Sample analysis. Having calibrated the instrument as described in section *(b)*, inject each sample solution in duplicate. Bracket each group of four sample injections between injections of the calibration solutions closest in concentration to the samples, e.g. calibration solution SB; sample injections 1, 2, 3, and 4; calibration solution S_C. Determine the areas of the monocrotophos peaks produced as described in section *(b)*. For each injection of the calibration solutions calculate a calibration correction factor *(f)* as follows:

$$f = \frac{I_o}{I_m}$$

where:

I_o = initial peak area (section (b))
I_m = new peak area

Calculate the values f_B and f_C for each pair of calibration solutions bracketing a group of four sample injections. For each group of four sample injections, multiply the areas of the monocrotophos peaks by the appropriate mean calibration correction factor 0.5 (f_B + f_C) and read from the calibration graph (section (*b*)), the concentration of monocrotophos (g/l) present in the sample solutions.
If the calibration correction factors f_B and f_C of each pair of calibration solutions differ by more than 2%, then repeat both calibration and sample solution injections. If the mean calibration correction factor 0.5 (f_B + f_C) falls outside the range 0.95 to 1.05, stabilize the operating conditions and re-calibrate (section (*b*)) before proceeding with the analysis.

(e) Calculation.

where:

C = concentration of monocrotophos in sample solution (g/l)
w = mass of sample taken (g)
P = purity of the standard monocrotophos (g/kg)
V = total volume containing the sample (ml)

Repeatability r = 38 g/kg at 750 g/kg active ingredient content
Reproducibility R = 38 g/kg at 750 g/kg active ingredient content

Based on a study with 13 participants and 78 values.

MONOCROTOPHOS TECHNICAL CONCENTRATES
[*]**287**/TK/M/-

1 Sampling. Take at least 500 ml.

2 Identity tests. Isolate the active ingredient then proceed as for **287**/TC/M/2.

3 Monocrotophos. As for **287**/TC/M/3 except:

(c) Sample preparation. Weigh in triplicate (to the nearest 0.1 mg) into separate 100 ml volumetric flasks, amounts of formulation excepted to contain 0.08 g monocrotophos (*w* g). Dilute to volume with methanol and mix thoroughly.

[*] CIPAC method 1990. Prepared by the monocrotophos panel of PAC-GB. Chairman: Mr B L Mathews (Shell Research Ltd.). Based on a method prepared by shell Research Ltd., U.K.

Repeatability r = 16 g/kg at 486 g/kg active ingredient content
Reproducibility R = 16 g/kg at 486 g/kg active ingredient content

Based on a study with 13 paticipants and 78 values.

MONOCROTOPHOS SOLUBLE LIQUID FORMULATIONS
[*]**287**/SL/M/-

1 Sampling. Take at least 500 ml.

2 Identity tests. Isolate the active ingredient then proceed as for **287**/TC/M/2.

3 Monocrotophos. As for **287**/TC/M/3 except:

(c) Sample preparation. Weigh in duplicate (to the nearest 0.1 mg) into separate 100 ml volumetric flasks, amounts of formulation excepted to contain 0.08 g monocrotophos (*w* g). Dilute to volume with methanol and mix thoroughly. Formulations containing acetone should be weighed into stoppered flasks to limit solvent loss through evaporation.

Repeatability r = 12 g/kg at 373 g/kg active ingredient content
6 g/kg at 154 g/kg active ingredient content
Reproducibility R = 12 g/kg at 373 g/kg active ingredient content
6 g/kg at 154 g/kg active ingredient content

Based on a study with 13 participants and 78 values.

[*] CIPAC method 1990. Prepared by the monocrotophos panel of PAC-GB. Chairman: Mr B L Mathews (Shell Research Ltd.). Based on a method prepared by shell Research Ltd., U.K.