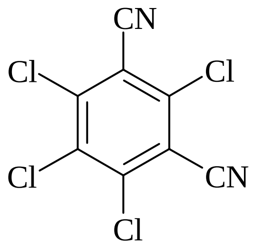
CHLOROTHALONIL
288



ISO common name	Chlorothalonil
Chemical name	Tetrachloroisophthalonitrile (IUPAC); 2,4,5,6-tetra-chloro-1,3-benzenedicarbonitrile (CA; *1897-45-6)*
Empirical formula	$C_8Cl_4N_2$
RMM	265.9
m.p.	252.1 °C
v.p.	7.6×10^{-5} Pa at 25 °C
Solubility	In water: 81 mg/l; acetone: 20 g/l; cyclohexanone: 30 g/l; dimethylformamide: 30 g/l; dimethyl sulfoxide: 20g/l; xylene: 80 g/l, all at 25 °C
Description	Colourless, odourless crystals
Stability	Stable under normal conditions; slow hydrolysis at pH >9
Formulations	Wettable powders, water dispersible granules and suspension concentrates

CHLOROTHALONIL TECHNICAL
[*]**288/**TC/(M)/-

1 Sampling. Take at least 100 g.

2 Identity tests

2.1 GLC. Use the GLC method below. The retention time of chlorothalonil peak of the sample solution should not deviate by more than 2 % from that of the calibration solution. The UV spectrum of this peak should match that of the one in the calibration solution.

2.2 Infrared. Prepare potassium bromide discs from the sample and the standard chlorothalonil. Scan the discs from 4000 to 400 cm^{-1}. The spectrum obtained from the sample should not differ significantly from that of the standard.

3 Chlorothalonil

OUTLINE OF METHOD Chlorothalonil and the impurity HCB are determined by capillary gas chromatography using flame ionisation detection.

REAGENTS

Methanol
Toluene
n-Butyl phthalate internal standard
Chlorothalonil standard of known purity. Check the HCB content prior to using. The HCB content should be less than 25 mg/kg.
Hexachlorobenzene (HCB), standard of known purity
Phosphoric acid 85 %
Solvent mixture methanol – toluene, 1 + 1 (v/v)
Internal standard solution. Weigh 2.0 ± 0.01 g *n*-butyl phthalate into a volumetric flask (1000 ml), dissolve in and fill to the mark with toluene (Solution IS).
Calibration diluent. Weigh in duplicate (to the nearest 0.1 mg) 30 ± 3 mg HCB standard (s_{HI} and s_{HII} mg) into separate volumetric flasks (100 ml). Fill to the mark with internal standard solution and mix until all the HCB has dissolved. Transfer by pipette 2.0 ml of each solution to separate volumetric flasks (100 ml), dilute to volume with internal standard solution and mix well (Solutions D_1 and D_2).

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[*] Provisional AOAC-CIPAC method 2000

Calibration solution. Weigh in duplicate (to the nearest 0.1 mg) 1.0 ± 0.01 g chlorothalonil standard (s_{CI} and s_{CII} mg) into separate ground glass stoppered flasks (100 ml). Transfer by pipette 50.0 ml of solution D_1 to the first flask and of solution D_2 to the second one. Place the flasks in an ultrasonic bath for 10 min. Allow to cool to room temperature (Solutions C_1 and C_2). Carry out the equilibration check (See *(b) System suitability (iii)* below). If the response factors meet the criteria, combine the solutions C_1 and C_2 by transferring by pipette 40.0 ml of each solution to a 150 ml ground glass stoppered flask (solution C_M). Use as mass for this solution the average of the masses for the two compounds for each of the two standards (s_C and s_H mg respectively). This solution is stable for seven days. Filter the solution through a 0.45 µm filter prior to injection.

APPARATUS

Gas chromatograph equipped with flame ionisation detector and split/splitless injector

Column fused silica, 30 m × 0.25 mm (i.d.), coated with crosslinked 50 % phenyl, 50 % dimethyl polysiloxane, film thickness 0.5 µm

Electronic integrator or *data system*

Disposable syringe

Disposable filters PFTE, pore diameter 0.45 µm

Mortar and *pestle*

Ultrasonic bath

PROCEDURE

(a) Chromatographic conditions (typical):

Column	Fused silica, 30 m × 0.25 mm (i.d.), coated with crosslinked 50 % phenyl, 50 % dimethyl polysiloxane, film thickness 0.5 µm
Injection system	
Injector	Split/splitless with fused silica liner, single taper with glass wool (taper DOWN) and high temperature septum
Split flow	approximately 140 ml/min
Injection volume	1 µl
Temperatures	
Column oven	205 °C
Injection port	330 °C
Detector	300 °C

Gas flow rates

Hydrogen (carrier gas)	linear velocity at 175 kPa: approximately 74 cm/sec
Nitrogen (make up)	approximately 30 ml/min
Hydrogen (detector)	as recommended for instrument
Air	as recommended for instrument
Retention times	chlorothalonil: about 6.0 min HCB: about 3.4 min internal standard: about 7.0 min

(b) System suitability check

(i) Optimisation of GC conditions. Adjust the GC conditions and ensure that the chlorothalonil peak does not overload the integrator or the detector. A slight column overload may be observed as a leading edge asymmetrical peak, but must be endured to ensure enough sensitivity for HCB. Adjust the split flow and initially bring the chlorothalonil peak on scale. Examine the apex of the peak to ensure that the peak is not "clipped." Optimise the split flow and examine the peak apex for a round rather than a flat apex (See fig. 6).

(ii) Determination of column efficiency. Determine the column efficiency by injecting a 1 µl portion of calibration solution C_1 followed by an injection of butane. Butane can be obtained from a disposable cigarette lighter using a 10 µl syringe. Open the valve (without lighting) and insert the syringe needle into the lighter jet. Fill and expel the gas several times, then draw back the syringe plunger to three or four microliters. Inject the gas in the same way as with liquids. Measure the retention times and calculate the number of effective theoretical plates (N) using the following formula:

$$N = 5.545 \times \left(\frac{t_C - t_B}{W} \right)^2$$

where:

N = number of effective theoretical plates
t_C = retention time of chlorothalonil, HCB or *n*-dibutyl phthalate
t_B = retention time of butane
W = peak width at half height

The column efficiency is acceptable if N is:

1560 theoretical plates per meter for HCB,
700 theoretical plates per meter for chlorothalonil and
1800 theoretical plates per meter for *n*-dibutyl phthalate.

All peaks of interest must be base line resolved. The resolution for the HCB and chlorothalonil peaks must be better than 1.5, and for the chlorothalonil and *n*-dibutyl phthalate peaks better then 3.

(iii) Equilibration. Inject 1 µl portions of the calibration solutions C_1 and C_2 and determine the relative response factors for chlorothalonil and HCB (*f*) based on duplicate injections. The factors should agree within ± 1 % for chlorothalonil and ± 10 % for HCB.

(c) Preparation of sample. Grind the sample with a mortar and pestle. Weigh (to the nearest 0.1 mg) sufficient sample to contain 1.0 ± 0.01 g chlorothalonil standard (*w* mg) into a ground glass stoppered flask (100 ml). Transfer by pipette 50.0 ml internal standard solution (Solution IS). Place the flasks in an ultrasonic bath in approximately 2.5 cm water for 20 min or add a stirring bar and place the solution on a magnetic stirrer for 20 min. Allow to cool to room temperature (Solution S). Some solids present in the technical material may not dissolve in the internal standard solution (e.g. carbon black, inherent to the technical material) and may give a dark grey hue to the solution. Allow standing the solution until any carbon black insoluble material has settled. Filter the sample with a 0.45 µm filter and a disposable syringe to which the filter is attached.

(d) Determination. Inject in duplicate 1 µl portions of calibration solution C_M and the sample solutions in the following sequence:

$$C_{MA}, C_{MB}, S_{1A}, S_{1B}, S_{2A}\ S_{2B}, S_{3A}\ S_{3B}, C_{MA}, C_{MB}\ \ldots\text{etc.}$$

Determine the peak area of the chlorothalonil and HCB peaks and calculate the mean response factor (*f*) of the calibration solution injections bracketing the injections of the sample solutions.

(e) Calculation

$$f = \frac{I_r \times s_C \times P}{H_s}$$

$$\text{Chlorothalonil content} = \frac{H_w \times f}{I_q \times w}\ \text{g/kg}$$

where:

f = mean response factor
H_s = peak area of chlorothalonil in the calibration solution
H_w = peak area of chlorothalonil in the sample solution
I_r = peak area of internal standard in the calibration solution
I_q = peak area of internal standard in the sample solution
s_C = mass of chlorothalonil in the calibration solution (mg)
w = mass of chlorothalonil in the sample solution (mg)
P = purity of chlorothalonil standard (g/kg)

Repeatability r = 13 g/kg at 980 g/kg active ingredient content
Reproducibility R = 28 g/kg at 980 g/kg active ingredient content

$$f_H = \frac{I_{rH} \times s_H \times P_H}{H_{sH}}$$

$$\text{HCB content} = \frac{H_{wH} \times f_H \times 1000}{I_{qH} \times w_H \times 100} \text{ mg/kg}$$

where:
f_H = mean response factor
H_{sH} = peak area of HCB in the calibration solution
H_{wH} = peak area of HCB in the sample solution
I_{rH} = peak area of internal standard in the calibration solution
I_{qH} = peak area of internal standard in the sample solution
s_H = mass of HCB in the calibration diluent solution (mg)
w_H = mass of HCB in the sample solution (mg)
P_H = purity of HCB standard (g/kg)

Repeatability r = 20 mg/kg at a HCB content of 194 mg/kg
Reproducibility R = 34 mg/kg at a HCB content of 194 mg/kg

CHLOROTHALONIL WETTABLE POWDERS

[*]**288**/WP/(M)/-

1 Sampling. Take at least 500 g.

2 Identity tests

2.1 HPLC. As for chlorothalonil technical **288**/TC/(M)/2.1.

2.2 Infrared. Extract the sample with dichloromethane, filter and evaporate the solvent. Proceed as for chlorothalonil technical **288**/TC/(M)/2.2.

3 Chlorothalonil. As for chlorothalonil technical **288**/TC/(M)/3.

Repeatability r = 14 g/kg at 756 g/kg active ingredient content
Reproducibility R = 14 g/kg at 756 g/kg active ingredient content

[*] Provisional AOAC-CIPAC method 2000

Repeatability r = 28 mg/kg at a HCB content of 210 mg/kg
Reproducibility R = 127 mg/kg at a HCB content of 210 mg/kg

4 Suspensibility (Draft method)

REAGENTS AND APPARATUS As for **288**/TC/(M)/3 and MT 15.

PROCEDURE

(a) Preparation of suspension. MT 15 *(i).*
(b) Determination of sedimentation. MT 15 *(ii).*
(c) Determination of chlorothalonil in the bottom 25 ml of suspension. After removal of the top 225 ml of suspension transfer the bottom 25 ml quantitatively with water to a round-bottomed flask (500 ml). Evaporate to dryness at 60 °C. Transfer by pipette 200.0 ml internal standard solution (Solution IS). Add a stirring bar and place the solution on a magnetic stirrer for 20 min. Centrifuge or filter an aliquot of the sample solution and inject this clear solution. Determine the mass of chlorothalonil (Q g) by **288**/TC/(M)/3 using a calibration solution with the appropriate concentration of chlorothalonil standard.

(d) Calculation

$$\text{Suspensibility} = \frac{111(c - Q)}{c}\,\%$$

where:

c = mass of chlorothalonil in the sample taken for the preparation of the suspension (g)
Q = mass of chlorothalonil in the bottom 25 ml of suspension (g)

CHLOROTHALONIL WATER DISPERSIBLE GRANULES

[*]**288**/WG/(M)/-

1 Sampling. Take at least 500 g.

2 Identity tests

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[*] Provisional AOAC-CIPAC method 2000

2.1 HPLC. As for chlorothalonil technical **288**/TC/(M)/2.1.
2.2 Infrared. As for chlorothalonil wettable powders **288**/WP/(M)/2.2.

3 Chlorothalonil. As for chlorothalonil technical **288**/TC/(M)/3.

Repeatability r = 8.4 g/kg at 903 g/kg active ingredient content
Reproducibility R = 14 g/kg at 903 g/kg active ingredient content

Repeatability r = 53 mg/kg at a HCB content of 363 mg/kg
Reproducibility R = 120 mg/kg at a HCB content of 363 mg/kg

4 Suspensibility (Draft method)

REAGENTS AND APPARATUS As for **288**/TC/(M)/3 and MT 168.

PROCEDURE

(a) Preparation of suspension and determination of sedimentation. MT 168
(b) Determination of chlorothalonil in the bottom 25 ml of suspension. As for chlorothalonil wettable powders **288**/WP/(M)/4*(c)*.
(c) Calculation. As for chlorothalonil wettable powders **288**/WP/(M)/4*(d)*.

CHLOROTHALONIL SUSPENSION CONCENTRATES

[*]**288**/SC/(M)/-

1 Sampling. Take at least 500 g.

2 Identity tests
2.1 HPLC. As for chlorothalonil technical **288**/TC/(M)/2.1.
2.2 Infrared. As for chlorothalonil wettable powders **288**/WP/(M)/2.2.

3 Chlorothalonil. As for chlorothalonil technical **288**/TC/(M)/3, except:

REAGENTS
Internal standard solution. Weigh 2.0 ± 0.01 g *n*-butyl phthalate into a volumetric flask (1000 ml), dissolve in solvent mixture and add four to six drops of phosphoric acid. Fill to the mark with solvent mixture and mix well (Solution SI).

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[*] Provisional AOAC-CIPAC method 2000

Use this solution instead of toluene for the preparation of the *Calibration diluent* (Solutions D_1 and D_2), the *Calibration solution* (Solution C_M) and the *Sample solution* (Solution S).

and

(b) Preparation of sample. Homogenise the sample by shaking it by hand for 3 min. Weigh (to the nearest 0.1 mg) sufficient sample to contain 1.0 ± 0.01 g chlorothalonil standard (*w* mg) into a ground glass stoppered flask (100 ml). Transfer by pipette 50.0 ml internal standard solution (Solution IS). Place the flasks in an ultrasonic bath in approximately 2.5 cm water for at least 20 min, or add a stirring bar and place the solution on a magnetic stirrer for at least 20 min. Allow enough time to ensure that there are no large clumps of non-extracted formulation present and take care that the sample is completely extracted. Allow to cool to room temperature (Solution S). Filter the sample with a 0.45 µm filter and a disposable syringe to which the filter is attached.

Repeatability r = 18 g/kg at 526 g/kg active ingredient content
Reproducibility R = 38 g/kg at 526 g/kg active ingredient content

Repeatability r = 17 mg/kg at a HCB content of 178 mg/kg
Reproducibility R = 68 mg/kg at a HCB content of 178 mg/kg

4 Suspensibility (Draft method)

REAGENTS AND APPARATUS As for **288**/TC/(M)/3 and MT 161.

PROCEDURE

(a) Preparation of suspension and determination of sedimentation. MT 161.

(b) Determination of chlorothalonil in the bottom 25 ml of suspension. As for **288**/WP/(M)/4 *(c).*

(c) Calculation

As for **288**/WP/(M)/4 *(d).*

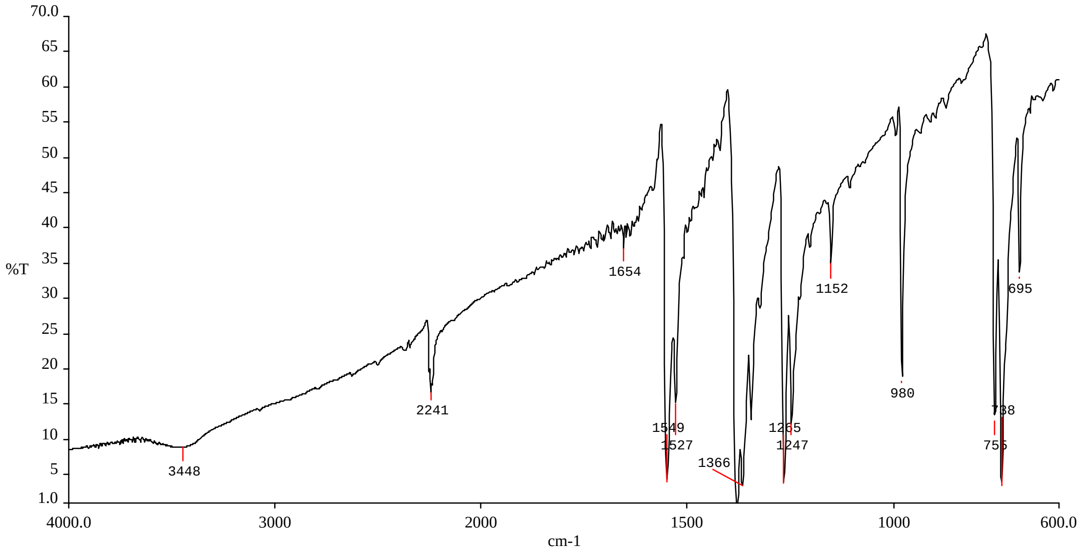

Fig. 5 IR spectrum of chlorothalonil in KBr

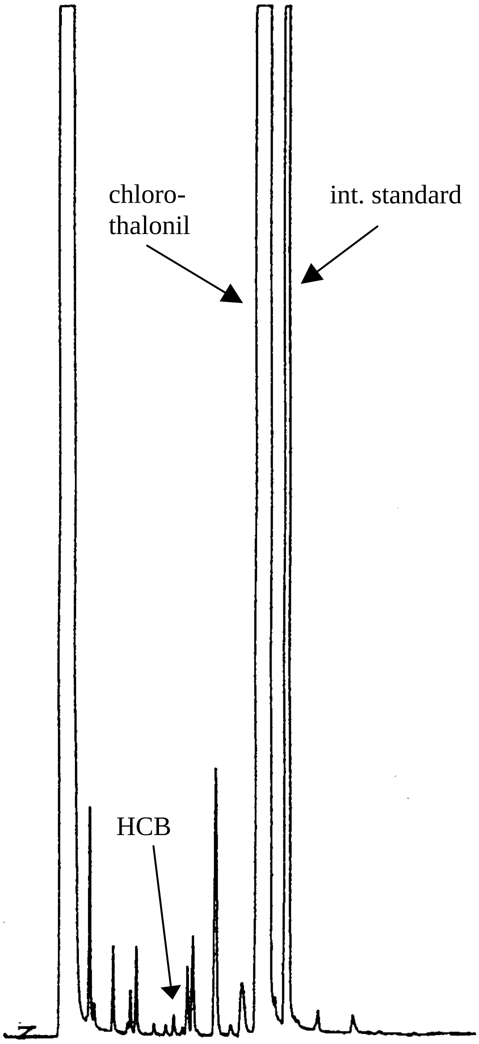

Fig. 6 Chromatogram of technical chlorothalonil