Determination of hexachlorobenzene and decachlorobiphenyl in technical and formulated chlorothalonil[*]

Outline of method

The sample of is dissolved in toluene and hexachlorobenzene (HCB) and decachlorobiphenyl (DCB),are determined by capillary gas chromatography using a mass selective detector (MSD). The single ion detection (SID) mode is used for HCB; multiple ion detection (MID) is used for DCB. The amount of HCB and DCB is quantified from a multi-level calibration curve, using three independently prepared calibration solutions. The use of standard commercially available office software programmes is recommended for the calculations.

Reagents

Toluene.

Acetone.

Methanol.

Hexachlorobenzene, standard of known purity.

Decachlorobiphenyl, standard of known purity.

Calibration Solutions

Preparation of stock calibration solutions

Weigh (to the nearest 0.1 mg) 5.0 $\pm$ 0.5 mg HCB standard (s_{HI} , s_{HII} , s_{HIII} mg) into each of three separate volumetric flasks (50 ml).

Weigh (to the nearest 0.1 mg) 5.0 $\pm$ 0.5 mg DCB standard (s_{DI}, s_{DII}, s_{DIII} mg) into the same three flasks. Fill to the mark with toluene and mix well until all the HCB and DCB has dissolved (call these solutions C1A, C2A and C3A). The solutions contain approximately 100 µg/ml of each analyte.

Preparation of intermediate calibration dilutions

Transfer by pipette 5.0 ml of the three solutions, C1A, C2A and C3A, to separate volumetric flasks (50 ml), fill to the mark with toluene and mix well (call these solutions C1B, C2B and C3B). The solutions contain approximately 10 µg/ml of each analyte.

Transfer by pipette 5.0 ml of the three solutions, C1B, C2B and C3B, to separate volumetric flasks (50 ml), fill to the mark with toluene and mix well (call these solutions C1C, C2C and C3C). The solutions contain approximately 1 µg/ml of each analyte.

Preparation of calibration solutions for injection

Transfer by pipette 2.5 ml of the solution C1C to a volumetric flask (50 ml), fill to the mark with toluene and mix well - call this solution C1D. The solution contains approximately 0.05 µg/ml of each analyte.

---

[*] Adapted from document 4377m, presented by Syngenta to the CIPAC meeting in Brno, June 2004.

Transfer by pipette 5.0 ml of the solution C2C to a volumetric flask (50 ml), fill to the mark with toluene and mix well - call this solution C2D. The solution contains approximately 0.1 µg/ml of each analyte.

Transfer by pipette 15.0 ml of the solution C3C to a volumetric flask (50 ml), fill to the mark with toluene and mix well - call this solution C3D. The solution contains approximately 0.3 µg/ml of each analyte.

These three diluted solutions C1D, C2D and C3D are to be injected for the analysis and correspond, nominally, to levels of 5 mg/kg, 10 mg/kg and 30 mg/kg of each impurity, relative to the amount of chlorothalonil in the sample, if the samples are prepared as described as described below.

All solutions are stable for at least 120 hours if kept at laboratory ambient temperature and out of direct sunlight.

Apparatus

Gas chromatograph equipped with a mass selective detector (MSD) and a facility for constant flow of carrier gas; an automatic injector and a split/splitless injection system with a deactivated glass splitless liner, operated in the splitless mode[*].

Column fused silica, 30 m x 0.25 mm (i.d.), coated with crosslinked 5% phenyl, 95% dimethyl polysiloxane, film thickness 0.25 µm.

Electronic integrator or *data system.*

Procedure

(a) Chromatographic conditions (typical)

Injection volume	1 µl (use a 10 µl syringe)
Column oven temperature programme	1 min at 120°C 120°C to 320°C at 20°C/min 3 min at 320°C
Injection port temperature	300 °C

MSD conditions

Transfer line temperature:	320°C
Source temperature:	230°C
Quadrupole temperature:	150°C
Solvent delay:	2 min
Group 1 ion:	286 amu
Group 1 start time:	2 min
Group 2 ions:	496, 498, 500, and 502 amu
Group 2 start time:	7 min

Helium carrier gas flow rate	1.1 ml/min
Retention times	HCB approximately 5.3 min DCB approximately 10.5 min

(b) Equilibration. Inject portions of solution C2D until the response factors for both HCB and DCB obtained from two consecutive injections differ by less than 10% of

---

[*] If split mode operation is preferred, it may be necessary to increase the injection volume, or even change the preparation of the calibration and sample solutions, in order to perform the analysis with sufficient sensitivity. A split ratio greater than 25:1 is not recommended.

the lower value. Then inject portions of the C1D and C3D solutions. The response factors for both HCB and DCB from these solutions should not deviate by more than 20% from the average obtained from calibration solution C2D; otherwise prepare new calibration solutions.

(c) Preparation of sample solution. Weigh (to the nearest 0.1 mg) in duplicate an amount of sample containing approximately 500 mg chlorothalonil (*w* mg) into separate volumetric flasks (50 ml). Add 5 ml acetone and 5 ml methanol and shake gently to disperse the contents. Treat the mixture for 10 minutes in an ultrasonic bath. Re-equilibrate to ambient temperature, fill to the mark with toluene and mix well (sample solutions S1 and S2).

(c) Determination. Inject each sample solution in duplicate and bracket a series of sample solution injections by duplicate injections of the three calibration solutions, in the following sequence:

<div align="center">C1D C2D C3D S1 S2 C1D C2D C3D …</div>

Integrate peaks areas for the ions monitored. In the case of DCB, sum the peak areas obtained from the 4 ions.

Typical ion chromatograms obtained from a calibration and sample solutions are given in Figures 1 and 2.

Calculation for HCB

Calculate average peak areas (H_{CH}) for HCB at each of the three levels from the calibration solutions which bracket the injections of the two sample solutions.

Calculate the nominal concentration of HCB (expressed relative to the amount of chlorothalonil in the sample, assuming that the sample solution contains 10 mg/ml chlorothalonil) using the following equations:

C1D, nominal HCB concentration relative to chlorothalonil $= \dfrac{s_{HI} \times P_H}{1000}$ mg/kg

C2D, nominal HCB concentration relative to chlorothalonil $= \dfrac{2 \times s_{HII} \times P_H}{1000}$ mg/kg

C3D, nominal HCB concentration relative to chlorothalonil $= \dfrac{6 \times s_{HIII} \times P_H}{1000}$ mg/kg

Where: s_{HI} , s_{HII} , s_{HIII} = mg HCB weighed into the stock solutions C1A, C2A and C3A, respectively;
P_H = purity of HCB standard, g/kg;
2 and 6   = concentration factors of solutions C2D and C3D, relative to C1D;
1000   = 1000 g, converts the value of P_H to a fraction.

Prepare a calibration curve for HCB by plotting, for each of the three levels, the average of the bracketing HCB peak area versus the nominal concentration (mg/kg) of HCB in that standard. Use the method of least squares to calculate the equation for a straight line through the three points that best fits the responses obtained and record the values for slope and intercept . The correlation coefficient (r^2) of the fit should be ≥0.95. If not, repeat the GC analysis sequence.

Calculate, by interpolation, the content of HCB (relative to the amount of chlorothalonil in the sample) of a bracketed sample solution injection using the following equation:

Content of HCB (relative to chlorothalonil) $= \dfrac{(H_{SH} - b) \times 500000}{a \times w \times T}$ mg/kg

where:
a = slope of calibration curve for HCB;
b = intercept of calibration curve for HCB;
H_{SH} = peak area of HCB;
w = mass of sample taken (mg);
T = chlorothalonil content of the sample (in g/kg);
500000 = 500 x 1000, where 500 = mg chlorothalonil assumed to be present in the sample when calculating the nominal HCB concentration relative to chlorothalonil in the calibration standards (see above) and where 1000 = 1000 g, which converts the value of T to a fraction.

Using the results obtained from the duplicate sample solutions, calculate the average value for mg HCB/kg chorothalonil, in the material tested.

Calculation for DCB

The calculation for DCB is analogous to that for HCB, using the corresponding data.

Figure 1. Typical chromatogram obtained from a reference solution at the 10 mg/kg
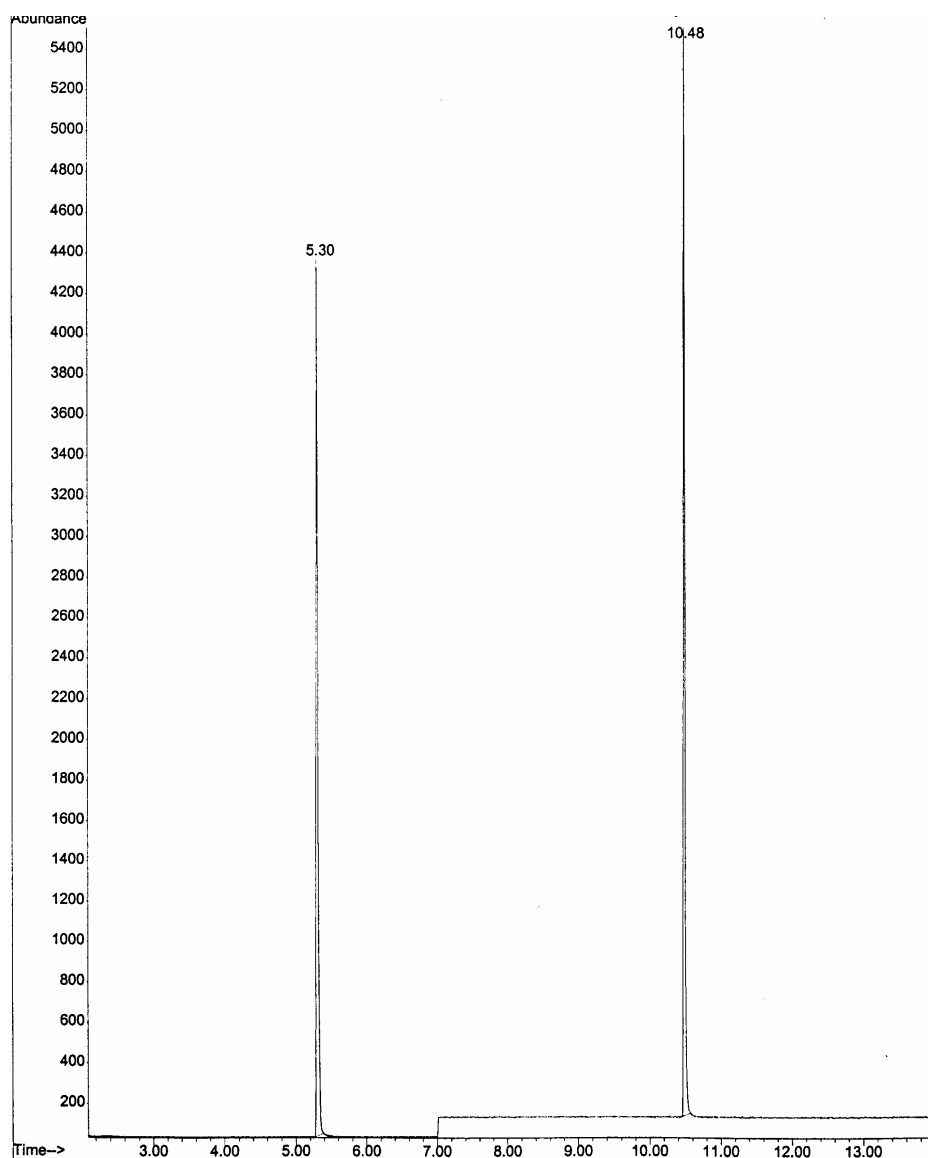level of HCB and DCB

Figure 2. Typical chromatogram obtained from a chlorothalonil formulation