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Clethodim

HPLC method

CIPAC Full Scale Collaborative Trial

5396/m

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Presented at the CIPAC meeting in Wageningen, The Netherlands

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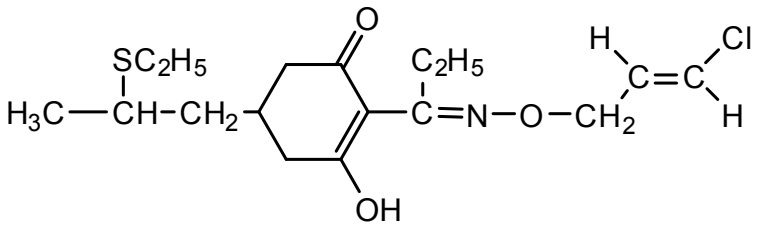
June, 2024

CLETHODIM



ISO common name	Clethodim
Chemical name	(5*RS*)-2-[(1*EZ*)-1-{[(2*E*)-(3-chloroallyl)oxy]imino}propyl]-5-[(2*RS*)-2-ethylthio)propyl]-3-hydroxycyclohex-2-en-1-one (IUPAC) 2-[1-[[[(2*E*)-3-chloro-2-propen-1-yl]oxy]imino]propyl]-5-[2-(ethylthio)propyl]-3-hydroxy-2-cyclohexen-1-one (CA, 99129-21-2)
Empirical formula	$C_{17}H_{26}ClNO_3S$
RMM	359.9
m.p.	Decomposition
v.p.	$<$0.01 mPa at 20°C
Solubility	Soluble in most solvents
Stability	Aqueous hydrolysis DT50 28 d (pH 5), 300 d (pH 7), 310 d (pH 9). Aqueous photolytic DT50 (sterile buffers, pH 5, 7 and 9), 1.7-9.6 d (without photosensitiser), 0.5-1.2 d (with photosensitiser).
Description	The pure material is clear, amber liquid.
Formulation	Emulsifiable concentrates (EC)

CLETHODIM TECHNICAL

1 Sampling. Take at least 100 g.

2. Identity test

2.1 HPLC. Use the normal phase HPLC method below. The relative retention time of the Clethodim peak in the sample solution should not deviate by more than 1.5% from that of the calibration solution.

2.2 Infrared. Prepare potassium bromide discs for the technical sample and Clethodim lithium reference substance. A typical potassium bromide disc should contain a sample prepared in the 0.15-0.35% by weight range. Scan the discs from 4000 to 400 cm^{-1}. The spectrum of the sample should not differ significantly from that of the reference substance.

3 Clethodim

OUTLINE OF METHOD Clethodim is determined by normal phase high performance liquid chromatography using UV detection at 254 nm and external standardisation.

REAGENTS

n-Hexane HPLC grade
Ethyl acetate HPLC grade
Acetic acid Analytically pure
Clethodim lithium reference standard of known content. Store refrigerated.

Calibration solutions. Weigh in duplicate about 50 mg (to the nearest 0.1 mg) of clethodim lithium reference standard (s mg) into separate volumetric flasks (50ml). Add acetic acid (about 0.6 mL) and mobile phase (about 5 ml), shake to dissolve it and fill to the mark with mobile phase. Mix thoroughly. (calibration solutions C_A and C_B).

APPARATUS

High performance liquid chromatograph equipped with a detector suitable for operation at 254 nm (UV-detection) and an injection system capable of injecting 5 µl.

Liquid chromatographic column stainless steel, 250 × 4.6 mm (i.d.), Agilent ZORBAX RX-SIL, 5µm, or equivalent with the same selectivity.

Electronic integrator or data system

PROCEDURE

(a) *Chromatographic conditions* (typical)

Column temperature	room temperature (The temperature change should not be more than 2°C
Flow rate	1.2 ml/min
Detector wavelength	254 nm
Injection volume	5 µl
Mobile phase	n-hexane + ethyl acetate +acetic acid, 940 + 40+20 (v/v)
Retention time	Clethodim approximately 12.6 min

(b) *Equilibration of the system.* Pump sufficient mobile phase through the column to equilibrate the system. Inject 5 µl portion of calibration solution C_A until the response obtained from two consecutive injections deviate by less than 1.5%. Then inject 5 µl portion of calibration solution C_B. The response factor for this solution should not deviate by more than 1.5% from that for calibration solution C_A, otherwise prepare new calibration solutions.

(c) *Preparation of clethodim TC sample.* Prepare sample solutions in duplicate for each sample. Weigh (to the nearest 0.1 mg) sufficient sample (*w* mg) to contain about 50 mg of clethodim into separate volumetric flasks (50 ml). Add acetic acid (about 0.6 mL) and mobile phase (about 5 ml), shake to dissolve it and fill to the mark with mobile phase. Mix thoroughly. (sample solutions S_1 and S_2).

(d) *Determination.* Inject in duplicate 5 µl portions of each sample solution bracketing them by injections of the calibration solutions as follows: calibration solution C_A, sample solution S_1, sample solution S_1, calibration solution C_B, sample solution S_2, sample solution S_2, calibration solution C_A, and so on. Measure the relevant peak areas. Average the values of the duplicate sample injections. Calculate the mean values of the response factors of the calibration solution bracketing two sample solutions and use this value to calculate the clethodim content of the bracketed samples.

(e) *Calculation.* Determine the peak area of Clethodim and calculate the mean value of response factors from the calibration solutions bracketing the injections of the sample solutions and use this value for calculating the Clethodim content of the bracketed sample solutions. The Clethodim content is the mean value of two sample solutions.

$$f_i = \frac{s \times P}{H_s}$$

$$\text{Clethodim content} = \frac{f \times w}{w} \times \frac{H}{359.0} \times \frac{}{365.8} \text{ g/kg}$$

where:

f_i = individual response factor
f = mean response factor
H_s = peak area of Clethodim in the calibration solution

H_w = peak area of Clethodim in the sample solution
s = mass of Clethodim lithium reference standard in the calibration solution (mg)
w = mass of sample taken (mg)
P = purity of Clethodim lithium reference standard (g/kg)

CLETHODIM TECHNICAL CONCENTRATES
/TK/M/-

1 Sampling. Take at least 100 g.

2. Identity test

2.1 HPLC. As for Clethodim technical /TC/M/2.1

3 Clethodim

As for Clethodim technical /TC/M/3.

CLETHODIM EMULSIFIABLE CONCENTRATES
/EC/M/-

1 Sampling. Take at least 200 ml.

2. Identity test

2.1 HPLC. As for Clethodim technical /TC/M/2.1

3 Clethodim

As for Clethodim technical /TC/M/3.

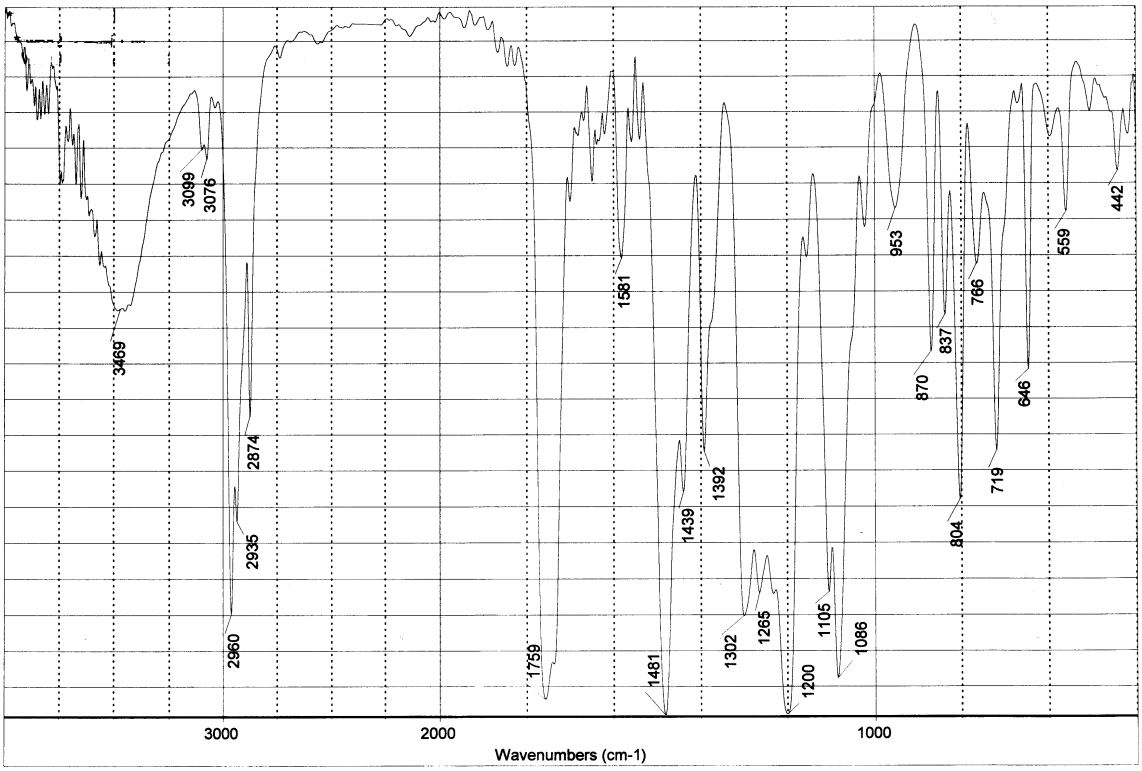


Fig.1 Infrared spectrum of Clethodim

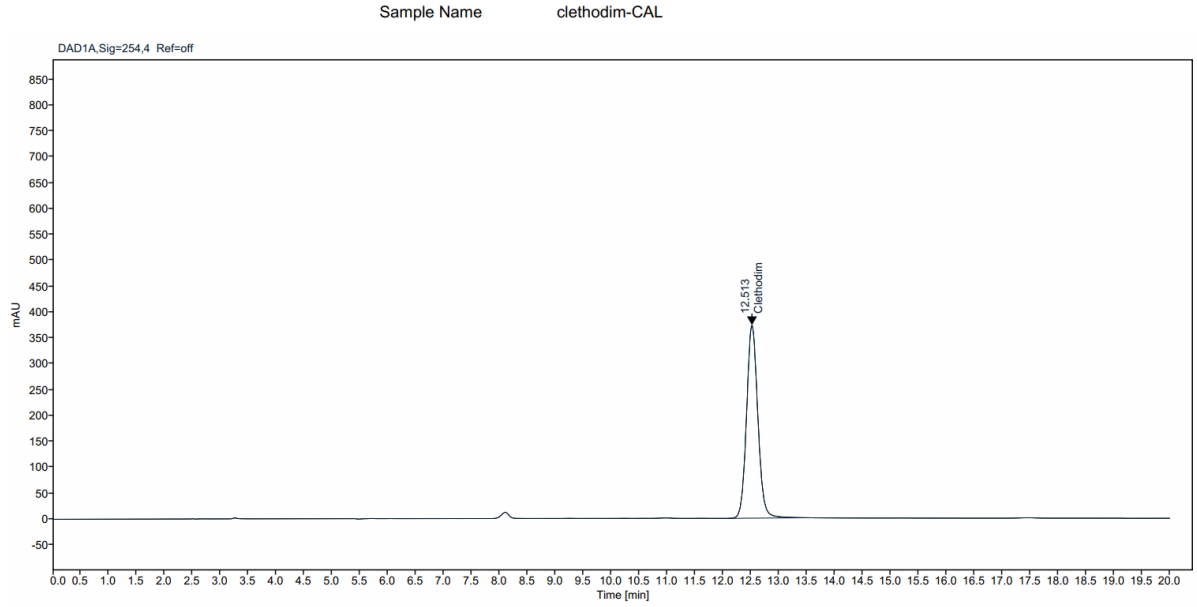


Fig.2 HPLC chromatogram of Clethodim lithium standard

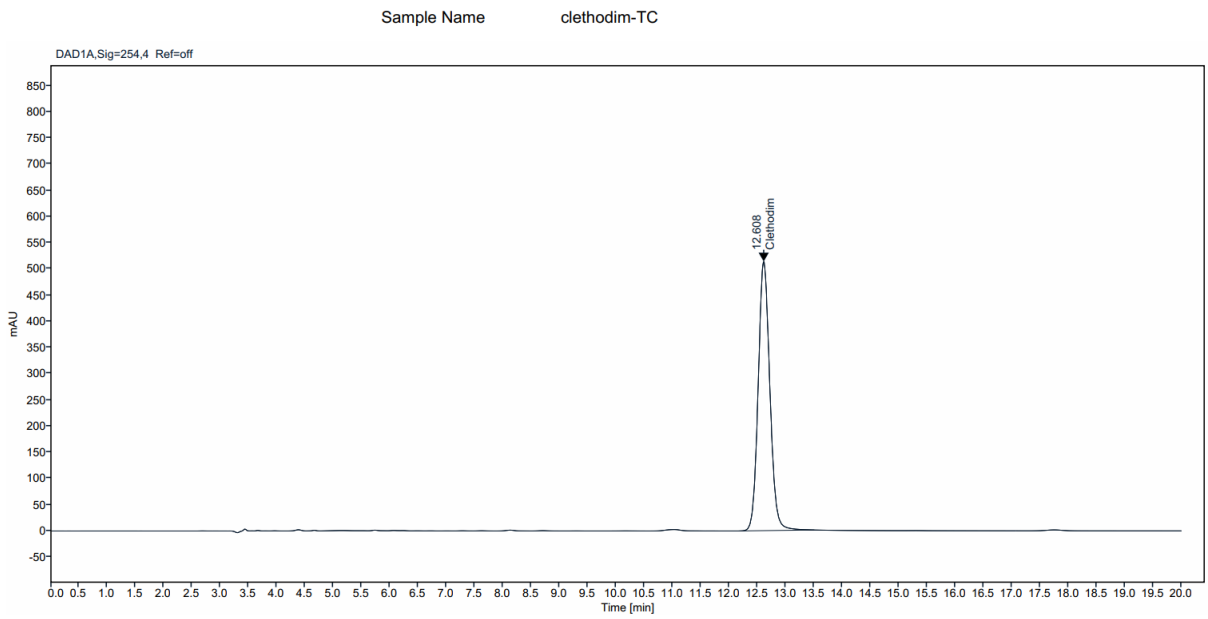


Fig.3 HPLC chromatogram of Clethodim TC

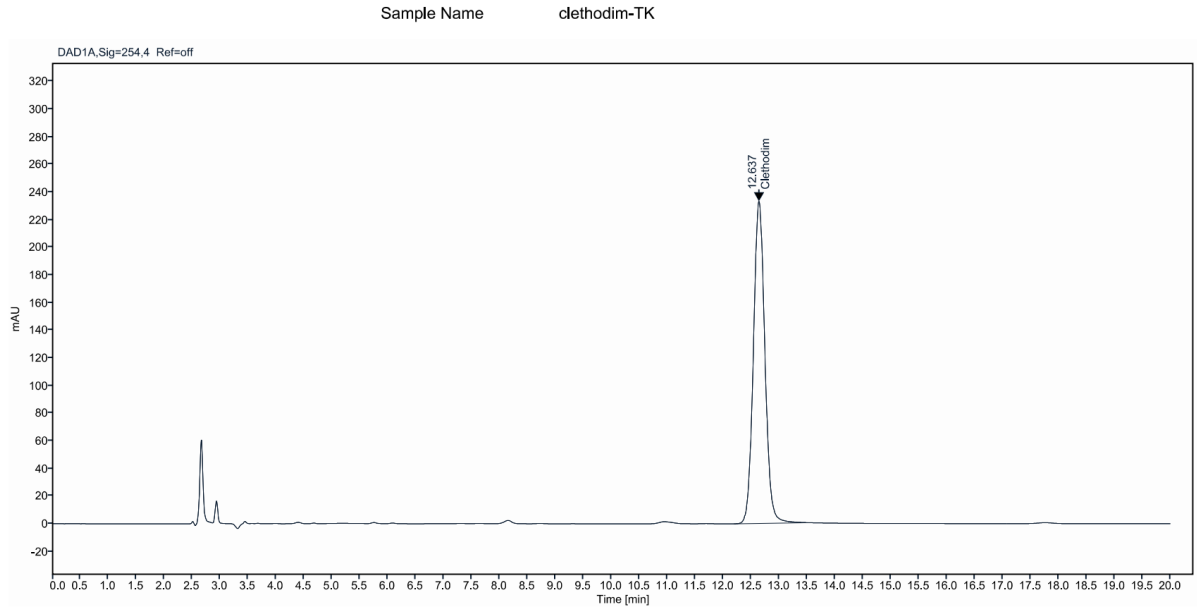


Fig.4 HPLC chromatogram of Clethodim TK

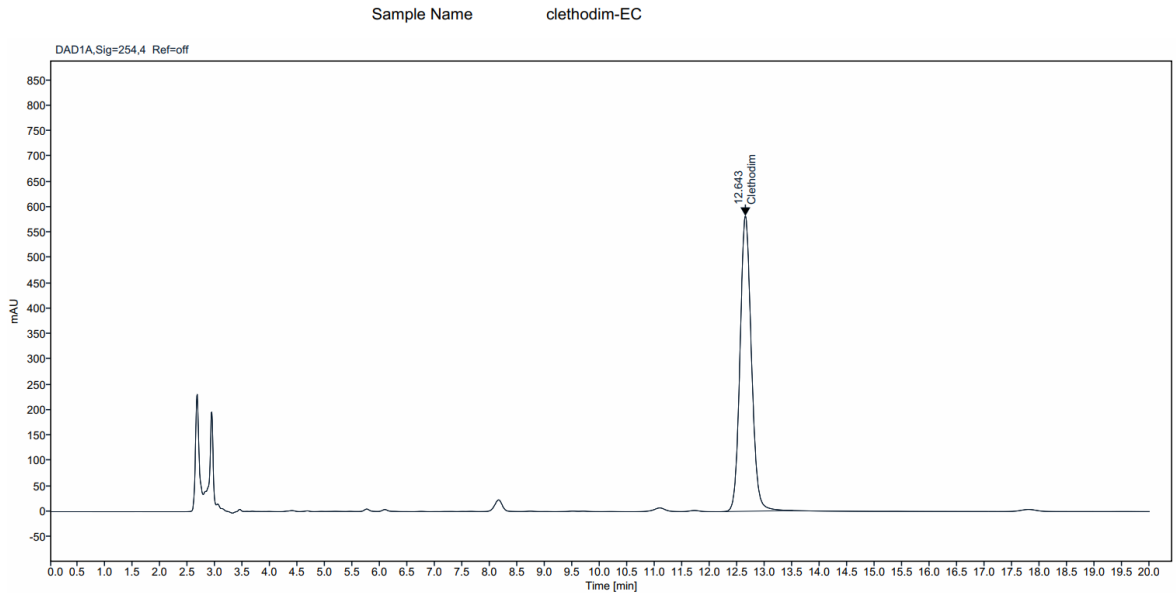


Fig.5 HPLC chromatogram of Clethodim EC