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Chlorfenapyr 570

HPLC-Method

CIPAC 4825/m

by

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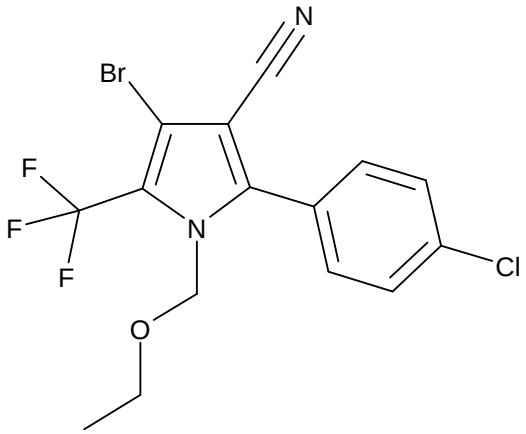
Number of Pages: 12

Chlorfenapyr
570



ISO common name	Chlorfenapyr
Chemical name	4-bromo-2-(4-chlorophenyl)-1-(ethoxymethyl)-5-(trifluoromethyl)pyrrole-3-carbonitrile (IUPAC)
CAS.No.	122453-73-0
Empirical formula	$C_{15}H_{11}BrClF_3N_2O$
RMM	407.6
m.p.	100 °C - 101°C
Solubilty	in water: 0.12 mg/l
Octanol / H_2O partition coefficient	log K_{ow} = 4.83
Appearance	off white to light brown powder with a halide odour
Formulations	suspension concentrates

CHLORFENAPYR TECHNICAL
***570**/TC/(M)/-

1 Sampling. Take at least 5 g.

2 Identity tests
2.1 HPLC. Use the HPLC method below. The relative retention time of the chlorfenapyr peak in the sample solution should not deviate by more than 2% from that of the calibration solution.

2.2 Infrared. Prepare pure chlorfenapyr using some mg material, e. g. tip of a small spatula and place it into the sampler of the IR spectrometer. Prepare potassium bromide disk if necessary (about 1 mg material and 350 mg potassium bromide). Scan the sample from 4000 cm^{-1} to 550 cm^{-1}. The spectrum obtained from the sample should not differ significantly from that of the standard.

3 Chlorfenapyr

OUTLINE OF METHOD. Chlorfenapyr is determined by high performance liquid chromatography on a reversed phase column (isocratic elution with flush gradient) with UV-detection using the external standard method.

REAGENTS

Chlorfenapyr reference standard of known purity
Water deionized, HPLC grade
Acetonitrile HPLC grade
Acetic acid p. a.

Calibration solution. Weigh in duplicate (to the nearest 0.1 mg) about 25 mg of the chlorfenapyr standard (*s* mg) into separate volumetric flasks (50 ml). Add approximately 30 ml acetonitrile into each flask, place the flasks in an ultrasonic bath and sonicate for approximately 10 minutes (max. ambient temperature, usually achieved by cooling with ice). Add acetonitrile close to the calibration mark. After temperature equilibrium dilute to volume with acetonitrile and mix thoroughly.

APPARATUS

High performance liquid chromatograph equipped with a constant flow pump, an automatic injector, a column oven and an UV detector capable of measuring 300 nm

Electronic integrator or data system

Column stainless steel, HALO C18 (2.7 µm), 50 mm x 4.6 mm (i. d.) or equivalent material with the same selectivity.
Note: A list of analytical columns used by the participants in the CIPAC collaborative trial is given in the REMARKS.

Ultrasonic bath with cooling equipment, e. g. ice bath

PROCEDURE
(a) Chromatographic conditions (typical)

Flow rate of the mobile phase:	2 ml/min
Column temperature :	ambient
Injection volume :	5 µl
Detection mode :	UV
Measuring wavelength:	300 nm[1]
Retention time :	about 2.6 minutes
Run time:	10 minutes

Gradient:

time [min]	A [% v/v]	B [% v/v]
0	40	60
3.5	40	60
3.6	10	90
6.0	10	90
6.1	40	60
10.0	40	60

with A: 0.5 ml/L acetic acid in water
B*:* 0.5 ml/L acetic acid in acetonitrile

Note: Isocratic conditions are applied in the separation step of the chromatographic run.
To avoid interferences of formulants a gradient is applied for column clean up.

(b) Preparation of sample. Weigh (to the nearest 0.1 mg) about 25 mg ± 5 mg technical chlorfenapyr into a volumetric flask (50 ml). Add approximately 30 ml acetonitrile, place the flask in an ultrasonic bath and sonicate for approximately 10 minutes (max. ambient temperature). Add acetonitrile close to the calibration mark. After temperature equilibrium dilute to volume with acetonitrile (solution S). Filter through a 0.2 µm PTFE-Filter if necessary.

(c) Determination. Inject each sample solution in duplicate and bracket a series of sample solution injections by injections of the calibration solutions as follows: calibration solution, sample solution S_A (double injection), calibration solution, sample solution S_B (double injection), calibration solution and so on. Measure the relevant peak areas and calculate the individual response factors of the calibration solutions (f_i). Calculate the mean (f) of each pair of response factors bracketing the injections. Use this value for calculating the chlorfenapyr content of the bracketed sample solutions.
The response factors and retention times for the successive injections should agree within 1 %.

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

$$\text{Content of chlorfenapyr} = \frac{f \times H_w}{w} \text{ g/kg}$$

[1] To minimize the influence of coelution of formulants with chlorfenapyr a wavelength of 300 nm was choosen.

where:

f_i = single response factor
$\bar{f}$ = mean response factor
s = mass of chlorfenapyr standard in the calibration solution (mg)
P = purity of chlorfenapyr standard (g/kg)
H_s = area of the chlorfenapyr peak in the calibration solution
H_w = area of the chlorfenapyr peak in the sample solution
w = mass of sample (mg)

REMARKS

List of analytical HPLC columns used by participants of the CIPAC collaborative trial:

Halo C18, 50 mm x 4.6 mm (2.7 μm), recommended by the organizer

Synergi 4mm Fusion-RP80A, 50 mm x 4.6 mm (4 μm)

Kintex XB C18, 100 mm x 4.6 (2.6 μm)

Poroshell 120 EC-C18, 50 mm x 4.6 mm (2.7 μm)

Halo C8, 50 mm x 2.1 mm (2.7 μm)

BDS Hypersil C18, 50 mm x 4.6 mm (2.4 μm)

Poroshell 120 SB-C18, 50 mm x 4.6 mm (2.7 μm)

Symmetry C18, 50 mm x 4.6 mm (2.7 μm)

Zorbax SB-C18, 30 mm x 2.1 mm (3.5 μm)

LiChrosorb RP-18

Zorbax Eclipse XDB-C18, 250 mm x 4.6 mm

CHLORFENAPYR SUSPENSION CONCENTRATES
***570**/SC/(M)/-

1 Sampling. Take at least 50 ml.

2 Identity test
2.1 HPLC. As for 570/TC/(M)/2.1.
2.2 UV spectrometry. Use a diode array detector and measure the top of the chlorfenapyr peak, wavelength 190 – 400 nm. The spectra of the sample and the reference have to be identical.

3 Chlorfenapyr. As for 570/TC/(M)/3 except:

PROCEDURE
Calibration solution: Weigh in duplicate (to the nearest 0.1 mg) about 25 mg of the chlorfenapyr standard (*s* mg) into separate volumetric flasks (50 ml). Add approximately 30 ml acetonitrile into each flask, place the flasks in an ultrasonic bath and sonicate for approximately 10 minutes (max. ambient temperature). Add 5 ml water and add acetonitrile close to the calibration mark. After temperature equilibrium dilute to volume with acetonitrile and mix thoroughly.

(c) Preparation of sample: Weigh (to the nearest 0.1 mg) sufficient sample to contain about 25 mg chlorfenapyr into a volumetric flask (50 ml). Add about 5 ml water and shake slightly. Add 30 ml acetonitrile, place the flask in an ultrasonic bath and sonicate for approximately 10 minutes (max. ambient temperature). Add acetonitrile close to the calibration mark. After temperature equilibrium dilute to volume with acetonitrile, mix thoroughly and filter through a 0.2 µm PTFE-Filter if necessary.

4 Suspensibility

OUTLINE OF THE METHOD
The suspensibility is determined using a solution of known concentration in CIPAC Standard water. The solution is placed inside a measuring cylinder at constant temperature and allowed to remain undisturbed for a specific time, e. g. 30 minutes. 9/10 th are dropped off and the remaining 1/10 th is used for chemical assay of the active ingredient with subsequent calculation of suspensibility.

REAGENTS AND APPARATUS as for 570/SC/(M)/- and as for MT 184.

PROCEDURE

(a) Preparation of suspension and determination of sedimentation. MT 184.

(b) Determination of chlorfenapyr in the bottom 25 ml of suspension. Remove the top 225 ml of the suspension and take the remaining 25 ml inside the cylinder. Transfer it to a graduated flask, volume e. g. 250 ml. Flush the cylinder several times with small portions of acetonitrile. Collect solutions from flushing procedure in the same volumetric flask. Fill up to approx. 200 ml. Place the flask in an ultrasonic bath, sonicate for approximately 10 minutes (max. ambient temperature), add 40 ml of acetonitrile, equilibrate to room temperature dilute to volume with acetonitrile. Mix thoroughly and filter if necessary.

(c) *Determination*. Take an aliquot of each solution and determine the mass of chlorfenapyr (*Q* g) by **570**/TC/M/-.

(d) Calculation

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

where:

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

Typical chromatograms of chlorfenapyr

Figure 1 Analytical standard chlorfenapyr

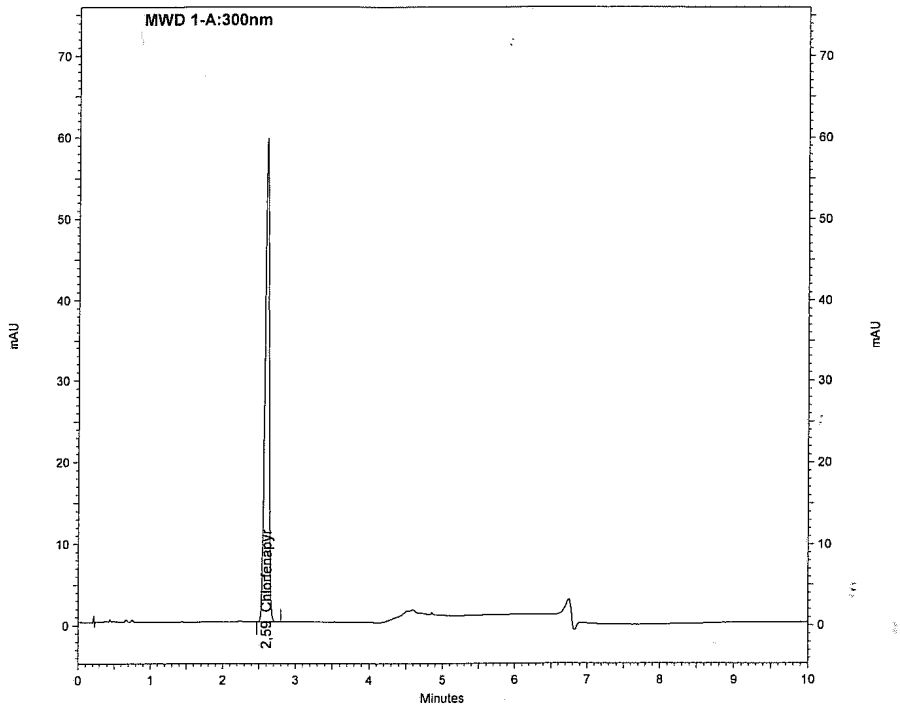


Figure 2 Technical material TC I

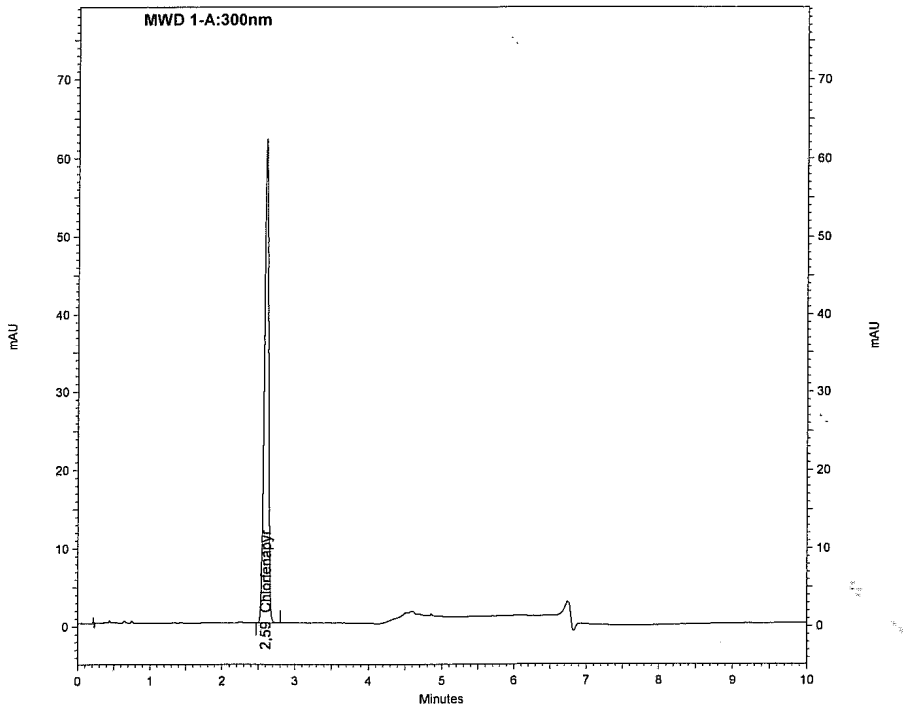


Figure 3 Technical material TC II

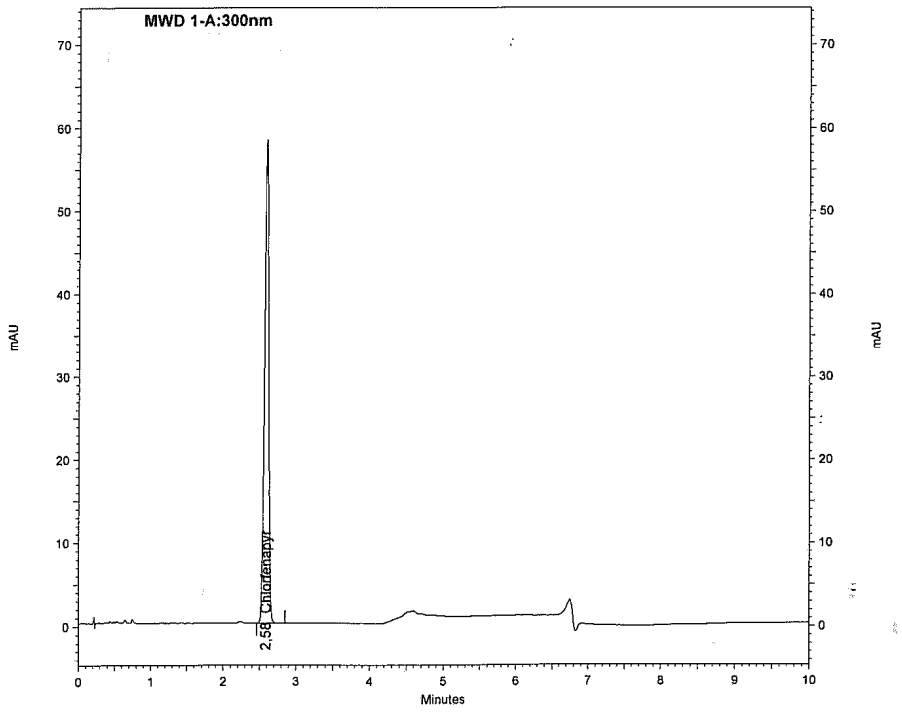


Figure 4 Suspension concentrate SC I

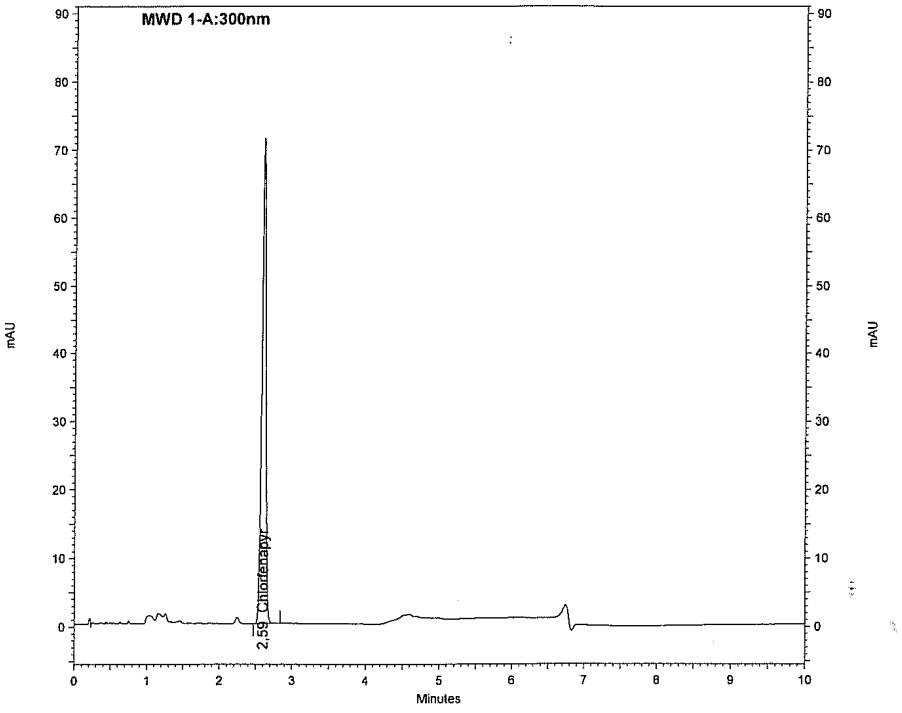


Figure 5 Suspension concentrate SC I (blank formulation)

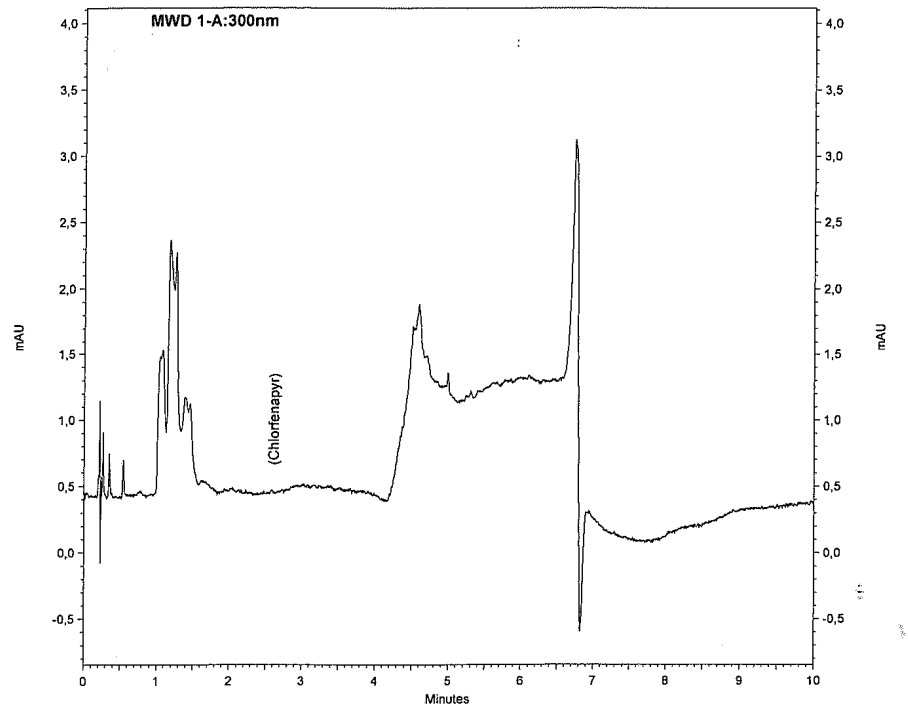


Figure 6 Suspension concentrate SC II

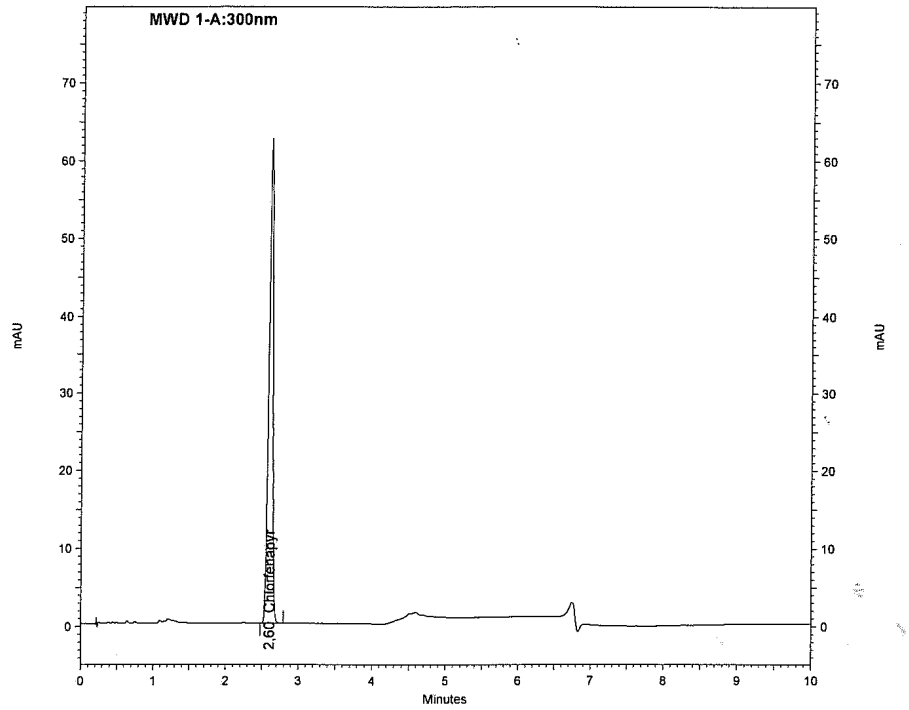


Figure 7 Suspension concentrate SC II (blank formulation)

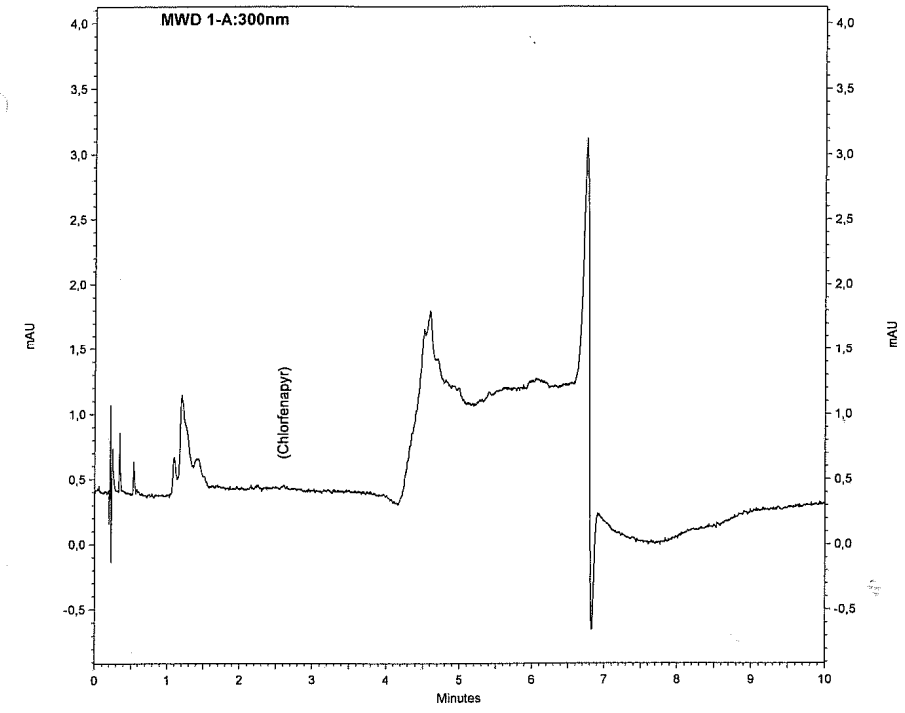


Figure 8 UV spectrum of chlorfenapyr analytical standard

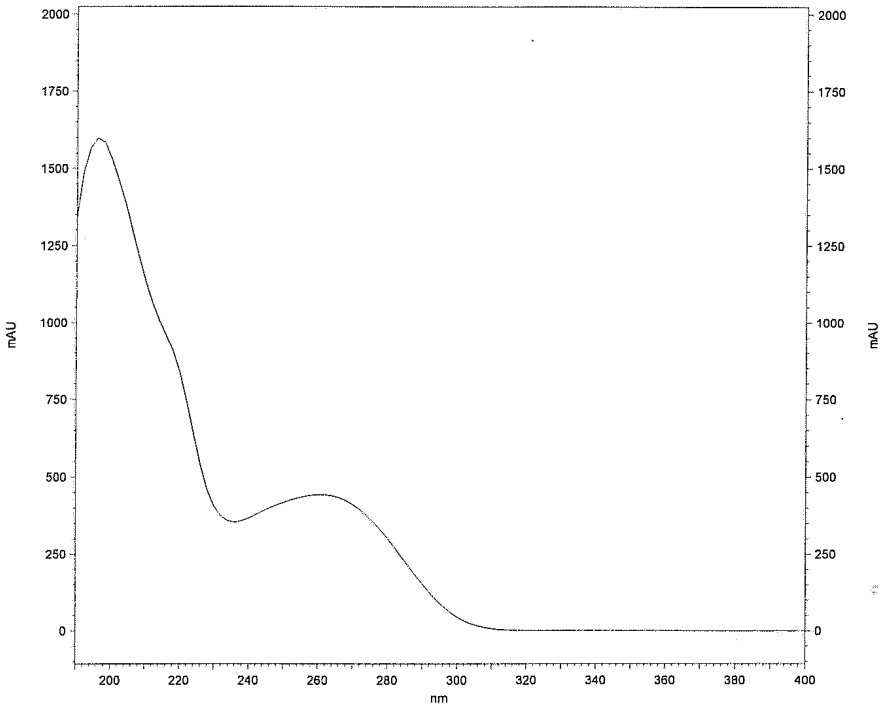


Figure 9 Infrared spectrum of chlorfenapyr analytical standard