

Metribuzin

GLC Method

CIPAC Collaborative Trial according to CIPAC Information Sheet No 321

By

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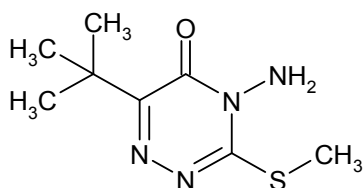
METRIBUZIN**283**

Chemical name: 4-amino-6-tert-butyl-4,5-dihydro-3-methylthio-1,2,4-triazin-5-one

ISO common name: metribuzin

CAS-No.: 21087-64-9

Structure:



Molecular mass: 214.3 g/mol

Empirical formula: C₈ H₁₄ N₄ O S

m.p.: 125.9 °C

b.p.: not applicable

Solubility: In water 1.05 g/L at 20°C; soluble in n-Heptane 0.84 g/L

Xylene 60 g/L

Dichloromethane > 250 g/L

2-Propanol > 250 g/L

1-Octanol 54 g/L

Polyethyleneglycol > 250 g/L

Acetone > 250 g/L

Ethylacetate > 250 g/L

Acetonitrile > 250 g/L

Dimethylsulfoxide > 250 g/L

all at 20 °C

Description: white fine needles, with weak, not characteristic odour

METRIBUZIN
283/TC/M/-

1 Sampling. Take at least 100 g.

2 Identity tests

2.1 GLC. Use the GLC method described below. The relative retention time of metribuzin in the sample solution should not deviate by more than 2% from that of the calibration solution.

2.2 GC-MS. Obtain a mass spectrum from the sample by coupled gas chromatography-mass spectrometry and compare it with the GC-MS spectrum of the metribuzin standard. (Fig. 1)

3 metribuzin

OUTLINE OF THE METHOD.

The content of metribuzin (g/kg) is determined by capillary gas chromatography with split injection, using dipentylphthalate as internal standard.

3.1 Determination of metribuzin by gas chromatography

REAGENTS

Metribuzin reference standard of known content

Dipentylphthalate

Dimethylacetamide

Internal standard solution. Dissolve 0.75g (to the nearest 0.01 g) *dipentylphthalate* in *dimethylacetamide* in a volumetric flask (250 ml) and make up to the mark with the same solvent.

Calibration solutions C1 and C2. Weigh in duplicate (to the nearest 0.01 mg) approximately 50 mg (*s* in mg) of the metribuzin reference standard into separate suitable vessels. Add by pipette internal standard solution (10 ml). Mix thoroughly. (calibration solutions C1, C2, chromatogram of C1 see Fig. 2).

APPARATUS

Capillary gas chromatograph equipped with a flame ionization detector and a split injector capable to inject 0.2 μL .

Capillary column, fused silica, 30 m x 0.32 (i.d.) mm, with a DB-5 bounded phase and a film thickness of 0.25 μm , or equivalent with the same selectivity.

Electronic integrator or data system

Ultrasonic bath

PROCEDURE

(a) *Operating conditions (typical):*

<i>Injector type</i>	split injection
<i>Split Ratio</i>	1:20
<i>Injection volume</i>	0.2 μL
<i>Injector temperature</i>	250 $^{\circ}\text{C}$
<i>Detector type</i>	flame ionisation
<i>Detector temperature</i>	300 $^{\circ}\text{C}$
<i>Oven temperature</i>	220 $^{\circ}\text{C}$ (isothermal)
<i>Flow rates</i>	
<i>carrier gas</i>	helium: 2.5 mL/min
<i>make-up gas</i>	helium: 30 mL/min
<i>air</i>	400 mL/min
<i>hydrogen</i>	30 mL/min
<i>Running time</i>	10 minutes
<i>Retention time</i>	metribuzin: approx. 2.3 min dipentylphthalate: approx. 3.8 min

(b) *System equilibration.* Pump sufficient carrier gas through the column to equilibrate the system. Inject 0.2 μL portions of the calibration solution C1 (see below) and repeat the injections until retention times and peak areas deviate by less than $\pm 1\%$ from the mean for three successive injections.

(c) *Preparation of sample solution.* Prepare sample solutions in duplicate for each sample. Weigh (to the nearest 0.01 mg) sufficient sample (w in mg) (containing approximately 50 mg of metribuzin) into separate suitable vessels. Add by pipette internal standard solution (10 ml). Mix thoroughly. (sample solutions S1, S2, chromatogram of S1 see Fig. 3)

(d) *Determination.* Inject in duplicate each sample solution and bracket a series of sample solution injections by injections of the calibration solution as follows: calibration solution C1, calibration solution C2, calibration solution C1, sample solution S1, sample solution S1, sample solution S2, sample solution S2, calibration solution C1 ... (C1, C2, C1, S1, S1, S2, S2, C1, ...)

Determine the peak areas of metribuzin and dipentylphthalate.

(e) *Calculation.* Calculate the peak area ratios (metribuzin / dipentylphthalate) from the calibration solutions bracketing the injections of the sample solutions. Average the peak area ratios of the calibration solutions preceding and following the sample solution injections (R). They must not deviate by more than ± 1 % of the average, otherwise repeat the determination. Average the peak area ratios of the sample injections (R') and calculate the content of the sample solutions as follows:

$$\text{metribuzin content (g/kg)} = \frac{R' \times s \times P}{R \times w}$$

Where:

- R' = average peak area ratio of metribuzin to internal standard in the sample solution
R = average peak area ratio of metribuzin to internal standard in the calibration solution
s = mass of metribuzin in the calibration solution (mg)
w = mass of sample taken (mg)
P = purity of metribuzin reference substance (g/kg)

**METRIBUZIN WATER-DISPERSIBLE GRANULE
283/WG/M/-**

1 Sampling. Take at least 100 g. Grind the sample thoroughly in a mortar.

2 Identity tests.

2.1 GLC. As for metribuzin 283/TC/M/-

2.2 UV spectrometry. As for metribuzin 283/TC/M/-

3 metribuzin.

Same approach as for metribuzin 283/TC/M/-

3.1 Determination of metribuzin by gas chromatography

As for metribuzin 283/TC/M/- in addition:

APPARATUS

Centrifuge

(c) Preparation of sample solution. Prepare sample solutions in duplicate for each sample. Weigh (to the nearest 0.01 mg) sufficient sample (w in mg) (containing approximately 50 mg of metribuzin) into separate suitable vessels. Add by pipette internal standard solution (10 ml). Mix thoroughly. Clarify a part of the solution by centrifugation or filtration prior to analysis. (Sample solutions S3, S4, chromatogram of S3 see Fig. 4)

METRIBUZIN SUSPENSION CONCENTRATE
283/SC/M/-

1 Sampling. Take at least 500 mL. Shake the sample well before weighing.

2 Identity tests.

2.1 GLC. As for metribuzin 283/TC/M/-

2.2 UV spectrometry. As for metribuzin 283/TC/M/-

3 metribuzin.

Same approach as for metribuzin 283/TC/M/-

3.1 Determination of metribuzin by gas chromatography

As for metribuzin 283/TC/M/- in addition:

REAGENTS

Purified water [RE 130]

PROCEDURE

(c) Preparation of sample solution. Prepare sample solutions in duplicate for each sample. Weigh (to the nearest 0.01 mg) sufficient sample (w in mg) (containing approximately 50 mg of metribuzin) into separate suitable vessels. Suspend in 0.5 mL purified water and add by pipette internal standard solution (10 ml). Mix thoroughly. (sample solutions S5, S6, chromatogram of S5 see Fig. 5).

METRIBUZIN Wettable powder
283/WP/M/-

1 Sampling. Take at least 100 g.

2 Identity tests.

2.1 GLC. As for metribuzin 283/TC/M/-

2.2 UV spectrometry. As for metribuzin 283/TC/M/-

3 metribuzin.

Same approach as for metribuzin 283/TC/M/-

3.1 Determination of metribuzin by gas chromatography

As for metribuzin 283/TC/M/- in addition:

REAGENTS

PROCEDURE

(c) Preparation of sample solution. Prepare sample solutions in duplicate for each sample. Weigh (to the nearest 0.01 mg) sufficient sample (w in mg) (containing approximately 50 mg of metribuzin) into separate suitable vessels. Add by pipette internal standard solution (10 ml). Mix thoroughly. Clarify a part of the solution by centrifugation or filtration prior to analysis. (sample solutions S7, S8, chromatogram of S7 see Fig. 6).

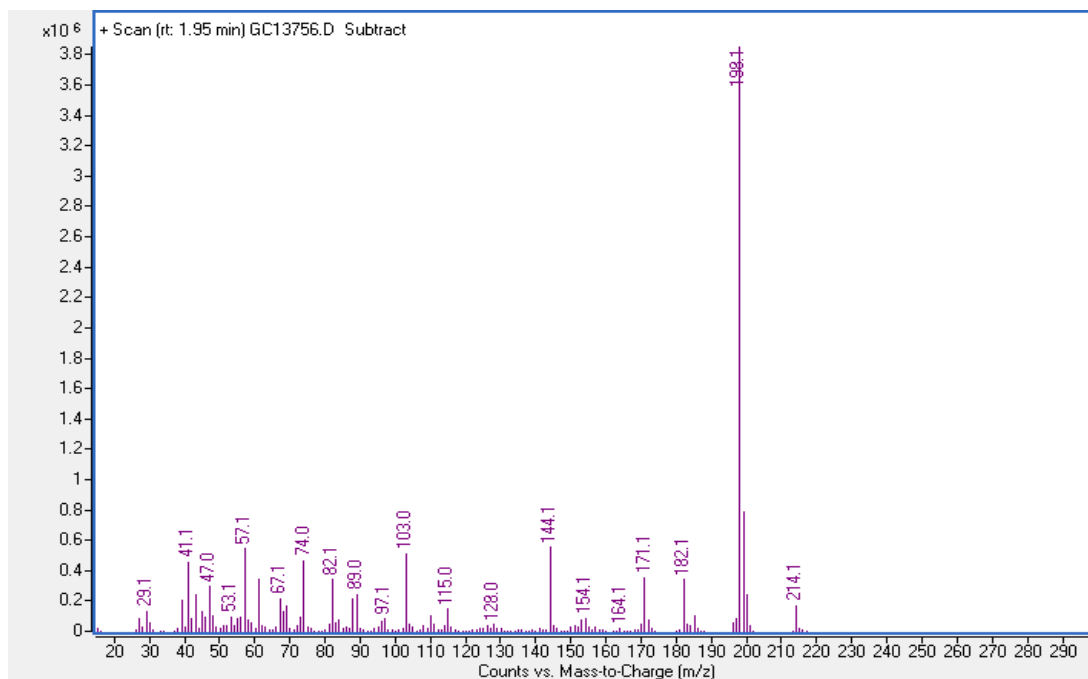
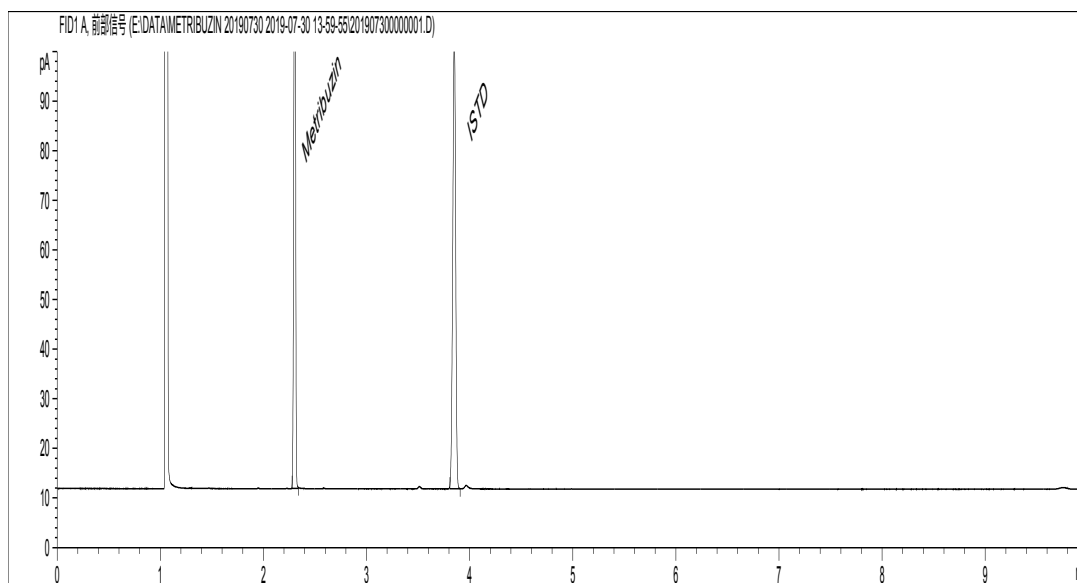
Fig. 1 Mass Spectrum of metribuzin**Fig. 2** Analytical Standard metribuzin (C1)

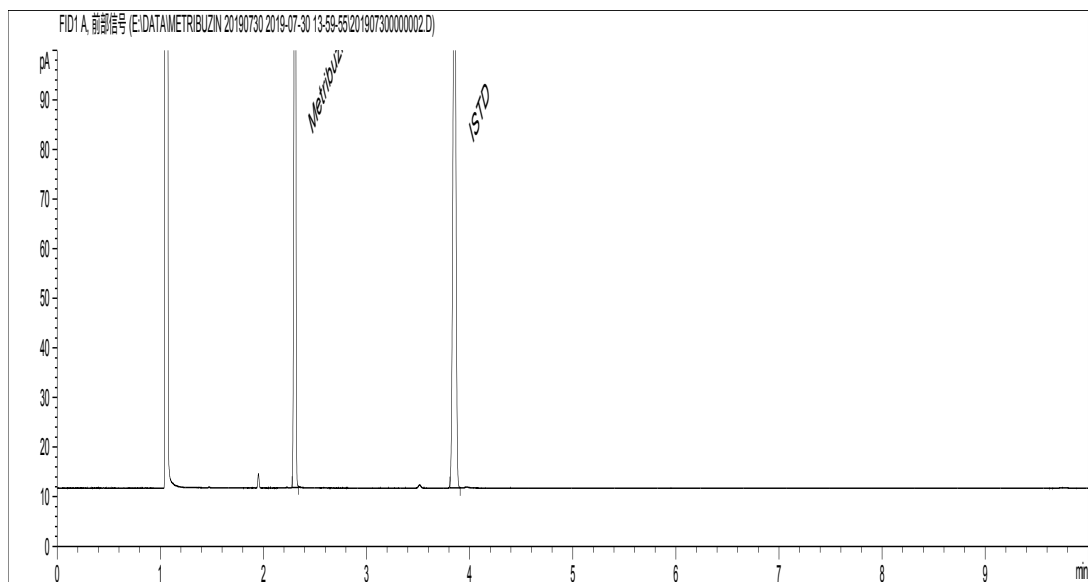
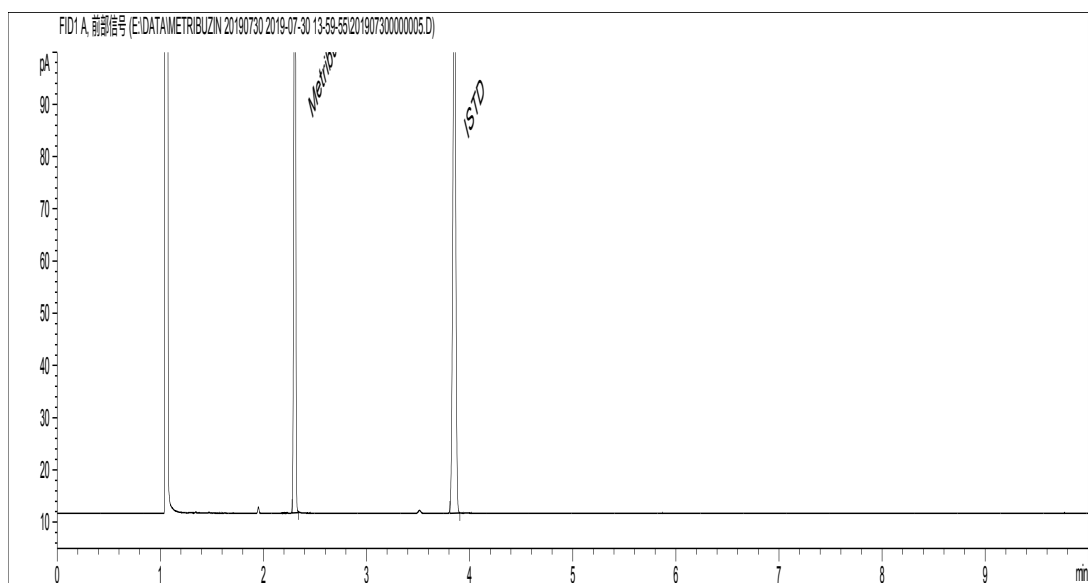
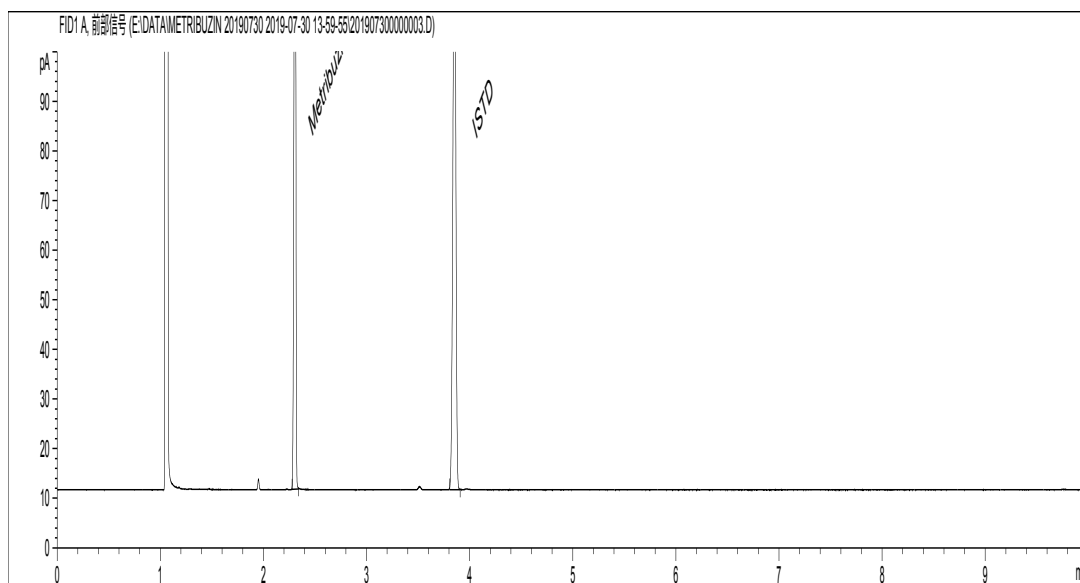
Fig. 3 Technical Material TC (S1)**Fig. 4** Water-dispersible Granule WG (S3)

Fig. 5 Suspension Concentrate SC (S5)**Fig. 6** Wettable powder WP (S7)