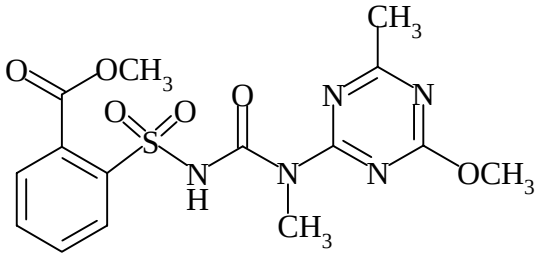
TRIBENURON METHYL
546



ISO Common name	Tribenuron methyl
Chemical name	Methyl 2-[4-methoxy-6-methyl-1,3,5-triazin-2-yl(methyl)-carbamoylsulfamoyl]benzoate (IUPAC); methyl 2-[[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)methylamino] carbonyl]-amino]sulfonyl]benzoate (CA; *101200-48-0*)
Empirical formula	$C_{15}H_{17}N_5O_6S$
RMM	395.4
m.p	141 °C
v.p.	5.2×10^{-8} Pa at 25 °C
Solubility	In water: 48 mg/l (pH 5) and 2.04 g/l (pH 7); acetone: 39.1 g/l; acetonitrile: 46.4 g/l; dichloromethane: >250 g/kg; ether acetate: 16.3 g/l; n-heptane: 20.8 mg/l; methanol: 2.59 g/l; xylene: 13.1 g/l (all at 25 °C)
Description	White powder
Stability	Aqueous hydrolysis, DT50 0.01 days (pH 5), 13.2 days (pH 7), 222.6 days (pH 9)
*Formulation*s	Water dispersible granules

TRIBENURON-METHYL TECHNICAL
*546/TC/(M)/-

1 Sampling. Take at least 100 g.

2 Identity tests

2.1 HPLC. Use the HPLC method below. The relative retention time of the tribenuron methyl peak in the sample solution should not deviate by more than 5% from that of the calibration solution and the UV spectrum measured from this peak should match that obtained from the calibration substance.

2.2 Infrared. Prepare potassium bromide discs for the technical sample and tribenuron-methyl reference substance. The spectra obtained from the samples should not differ significantly from that of the reference substance.

3 Tribenuron methyl

OUTLINE OF METHOD Tribenuron-methyl is determined by reversed phase high performance liquid chromatography using a 100 × 4.6 mm (i.d.) Whatman Partisil® ODS-3 RAC II column, UV detection at 254 nm and internal standardisation (3-methyl-1,1-diphenylurea; DPMU). The active ingredient content is quantified using a calibration curve.

REAGENTS:

Acetonitrile HPLC grade
Water HPLC grade
Phosphoric acid HPLC grade, 85%
Tribenuron methyl analytical standard of known purity
3-Methyl-1,1-diphenylurea (DPMU) internal standard
Mobile phase. Adjust 600 ml of HPLC grade water to pH 2.2 with phosphoric acid, using a pH meter standardised at pH 7.0 and pH 2.0. Add acetonitrile (400 ml) and mix. Mixing of the mobile phase may also be accomplished using a binary solvent HPLC pump. Filter and degas the mobile phase prior to use.
Internal standard solution. Weigh 3-methyl-1,1-diphenylurea (DPMU) (3 g) into a volumetric flask (1000 ml). Add acetonitrile (700 ml) and place the flask in an ultrasonic bath until the solid has dissolved. Allow to cool to room temperature and dilute to volume with acetonitrile.

* Provisional CIPAC method 2002. Prepared by a committee chaired by D E Brennan. Based on a method supplied by DuPont de Nemours, USA.

Note: A lesser total volume of internal standard solution, at the same concentration, can be prepared, based on the specific number of standard and samples solutions to be analysed, e.g., 0.75 g per 250 ml total volume.

Calibration solutions Weigh (to the nearest 0.1 mg) 90, 100 and 110 mg (± 5 mg) of tribenuron-methyl standard into separate bottles (125 ml) or volumetric flasks (100 ml). Pipette internal standard solution (10.0 ml) into each bottle or flask. Add acetonitrile (90 ml) to each bottle or dilute each flask to volume and place the bottle or flask in an ultrasonic bath until the solids are dissolved (1-3 min). Allow the bottle or flask to cool to room temperature. Filter a portion of each standard solution through a 0.2 µm filter prior to HPLC analysis and inject immediately**.**

Note: Due to the instability of tribenuron-methyl in solution, one standard solution should be prepared and injected before preparing the next one.

APPARATUS

High performance liquid chromatograph equipped with a constant-flow pump, constant-temperature column compartment, a sample injector capable of injecting 10 µl aliquots, a UV detector (254 nm) and digital integrator or other data-handling capability. A chilled autosampler should be used, if available (but is not required).

HPLC column Whatman Partisil® ODS-3 RAC II, 100 × 4.6 mm (i.d.), 5 µm particle size with in-line filter with replaceable frit. Column substitution is not recommended. Substitution of alternate columns should be accompanied by data demonstrating equivalency and/or method revalidation. The filter frit should be Upchurch Scientific, Inc. model A-102X, A-318 or equivalent (0.5 µm frit).

Filtering apparatus (for sample and standards solutions) disposable plastic syringes (3 ml) fitted with 0.2 µm Acrodisc-CR filters

Ultrasonic bath

pH meter

PROCEDURE:

(a) Operating conditions (typical)

Column	100 × 4.6 mm (i.d.), packed with Whatman Partisil® ODS-3 RAC II, particle size 5 µm
Mobile phase	acetonitrile- water (adjusted to pH 2.2 with phosphoric acid), 40 + 60 (v/v)
Column temperature	40 °C
Flow rate	2.0 ml/min

Injection volume	10 µl
Detector wavelength	254 nm (band width 4 nm)
Reference wavelength	400 nm (band width 80 nm)
Run time	approximately 5 min
Retention time	tribenuron-methyl: approximately 3.5 min
	DPMU: approximately 1.95 min

Note: The pH of the aqueous portion of the mobile phase is adjusted to 2.2 to protonate the tribenuron-methyl and to maintain separation between tribenuron-methyl, DPMU and potential impurities. Maintain the pH within $\pm$ 0.1 pH units of this value.

(b) Sample preparation. Mill or grind all samples thoroughly prior to weighing. Weigh (to the nearest 0.1 mg) into a bottle (125 ml) or volumetric flask (100 ml) sufficient sample (*w* mg) to contain about 100 mg tribenuron-methyl. Pipet internal standard solution (10.0 ml) into each bottle or flask. Add acetonitrile (90 ml) to each bottle or dilute each flask to volume and place the bottle flask in an ultrasonic bath for 1 to 3 min. Allow the bottle or flask to cool to room temperature. Filter a portion of the sample solution through a 0.2 µm filter prior to HPLC analysis and inject immediately**.**
Note: Due to the instability of tribenuron-methyl in solution, one sample solution should be prepared and injected before preparing the next one.

(c) Determination. Equilibrate the column with mobile phase until a stable baseline is obtained. Inject, **singly**, 10 µl each of a solvent blank (acetonitrile), standards, and samples. The run time for each injection is 5 minutes. Calculate the tribenuron-methyl to DMPU peak area ratio.

(d) Calculation. Prepare a calibration curve for tribenuron-methyl by plotting the tribenuron-methyl to DMPU peak area ratios versus the mass of the standards (mg). Using the method of least squares, calculate the equation for the straight line that best fits the experimental data. The correlation coefficient should be 0.999 or better. If not, repeat the calibration
Determine the concentration of tribenuron methyl for each sample injection using the following equation:

$$\text{Tribenuron-methyl content} = \frac{(R - b)\ x\ P}{a\ x\ w}\ \text{g/kg}$$

where:
R = tribenuron-methyl to DMPU peak area ratio in the sample solutions
a = slope of calibration curve
b = intercept of calibration curve
P = purity of the tribenuron-methyl standard (g/kg)
w = mass of the sample taken (mg)

Repeatability r = 10 - 15 g/kg at 989 g/kg active ingredient content
Reproducibility R = 19 - 21 g/kg at 989 g/kg active ingredient content

TRIBENURON-METHYL WATER DISPERSIBLE GRANULES
[*]**546**/WG/(M)/-

1 Sampling. Take at least 500 g.

2 Identity tests
2.1 HPLC. As for tribenuron technical **546**/TC/(M)/2.1.
2.2 Infrared. Add 80 mg of sample to acetonitrile (5-10 ml), mix well, and filter. Evaporate the filtrate to dryness and continue as for tribenuron-methyl technical **546**/TC/(M)/2.2.

3 Tribenuron-methyl. As for technical **546**/TC/(M)/3, except add under REAGENTS:
Ammonium hydroxide solution 30 %
Ammonium hydroxide solution $c(NH_4OH)$ = 0.01 mol/l. Add 30% ammonium hydroxide (0.6 ml) to HPLC grade water (1000 ml) and mix well.
Sample solvent acetonitrile - ammonium hydroxide solution ($c(NH_4OH)$ = 0.01 mol/l), 50 +50 (v/v). Add acetonitrile (500 ml) and ammonium hydroxide solution, $c(NH_4OH)$ = 0.01 mol/l (500 ml) to a flask (1000) ml and mix well.

and substitute *(b) Sample preparation* for:
(b) Sample preparation. Mill or grind all samples thoroughly prior to weighing. Weigh (to the nearest 0.1 mg) into a bottle (125 ml) or volumetric flask (100 ml) sufficient sample (*w* mg) to contain about 100 mg tribenuron-methyl. Pipet internal

[*] Provisional CIPAC method 2002. Prepared by a committee chaired by D E Brennan. Based on a method supplied by DuPont de Nemours, USA.

standard solution (10.0 ml) into each bottle or flask. Add sample solvent (90 ml) to each bottle or dilute each flask to volume and place the bottle or flask in an ultrasonic bath for 5 min. Allow to cool the bottle or flask to room temperature. Filter a portion of the sample solution through a 0.2 µm filter prior to HPLC analysis and inject immediately**.**
Note: Due to the instability of tribenuron-methyl in solution, one sample solution should be prepared and injected before preparing the next one.

Repeatability r	=	5.1 – 8.0 g/kg at 752 g/kg active ingredient content
		4.4 – 5.7 g/kg at 748 g/kg active ingredient content
Reproducibility R	=	14.9 – 16.6 g/kg at 752 g/kg active ingredient content
		15.4 – 19.1 g/kg at 748 g/kg active ingredient content

4 Suspensibility

REAGENTS and APPARATUS as for MT 168 and **546**/WG/(M)/3, except: add at
Calibration solutions: Prepare standard solutions at other concentrations in the same way, if needed. Filter a small portion of each solution through a 0.2-µm (or 0.45 µm) PTFE filter prior to analysis.

PROCEDURE
(a) Preparation of suspension and determination of sedimentation. MT 168.

(b) Determination of tribenuron methyl in the bottom 25 ml of suspension. After removal of the top 225 ml of suspension, add 25 ml of acetonitrile to the remaining 25 ml. Place the cylinder in an ultrasonic bath for 5 minutes. Allow to cool to room temperature, mix well by inverting the cylinder several times, then take a suitable aliquot of the solution for the determination of the mass of tribenuron-methyl (*Q* g).

(c) Calculation

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

where:

c = mass of tribenuron-methyl in the sample taken for the preparation of the suspension (g)

Q = mass of tribenuron-methyl in the bottom 25 ml of suspension (g)

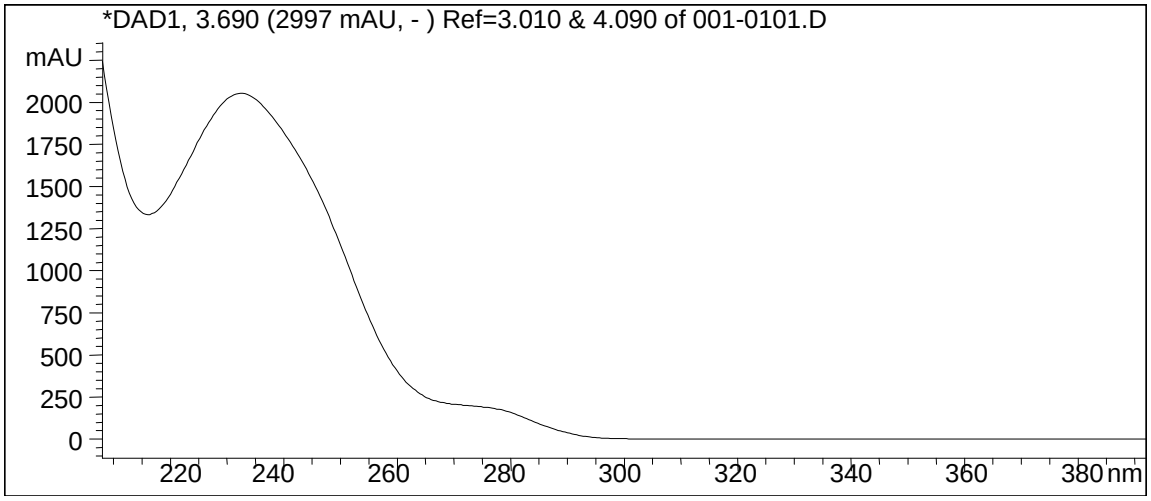


Fig. 45 UV spectrum of tribenuron-methyl

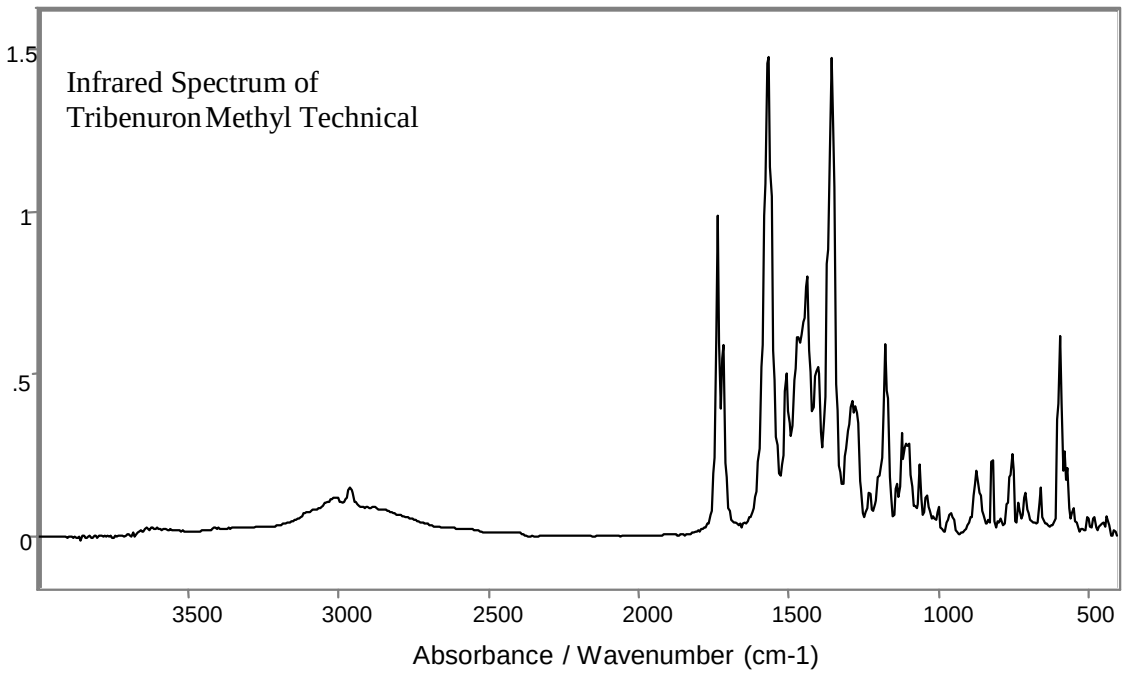


Fig. 46 Infrared spectrum of tribenuron-methyl technical

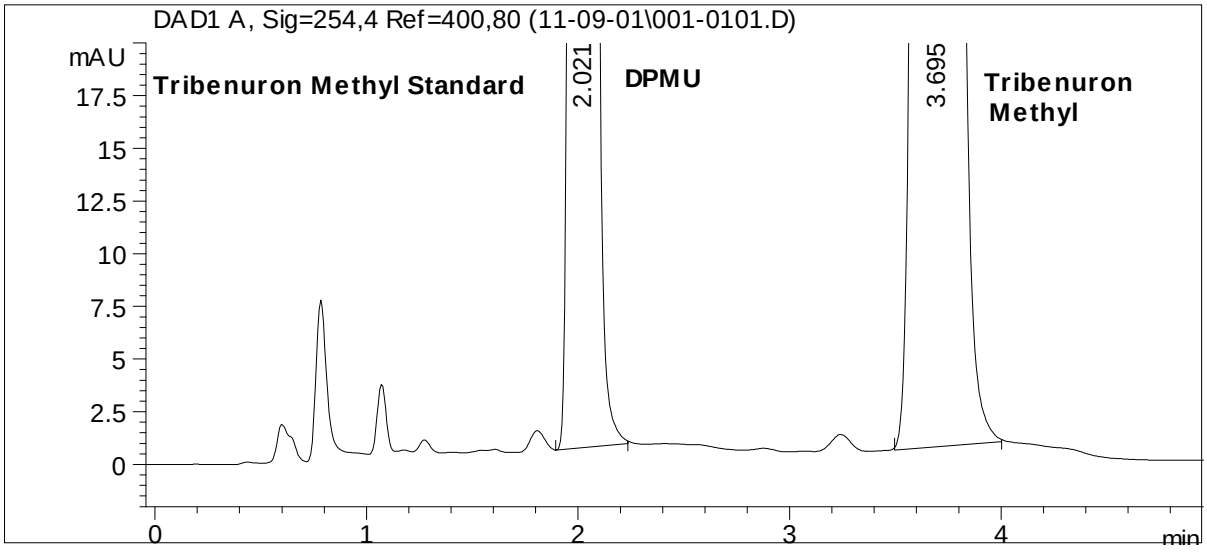


Fig. 47 Chromatogram of tribenuron-methyl technical

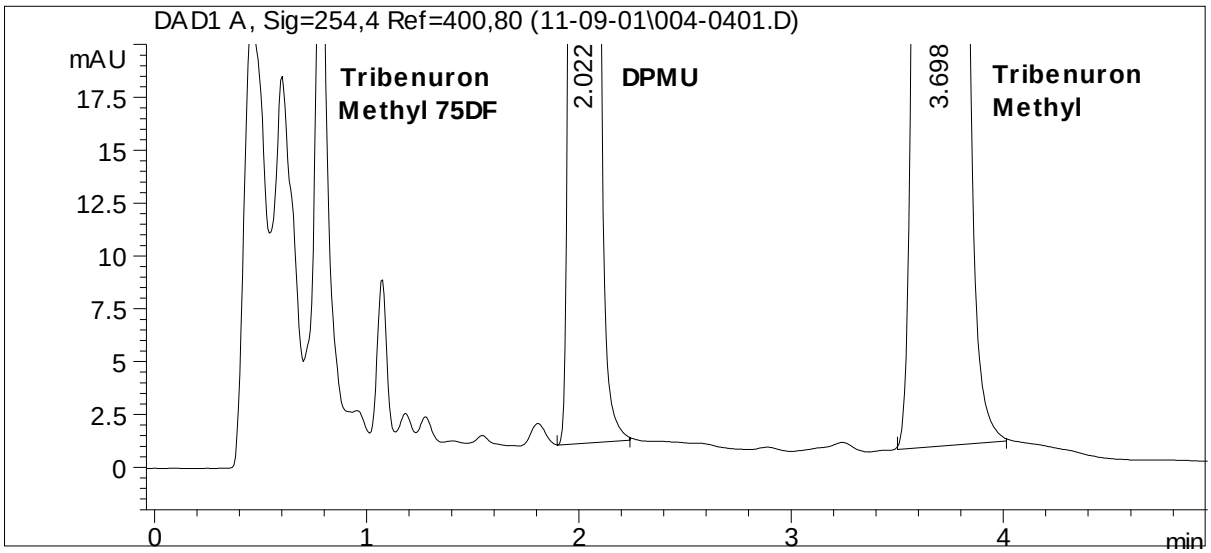


Fig. 48 Chromatogram of tribenuron-methyl WG