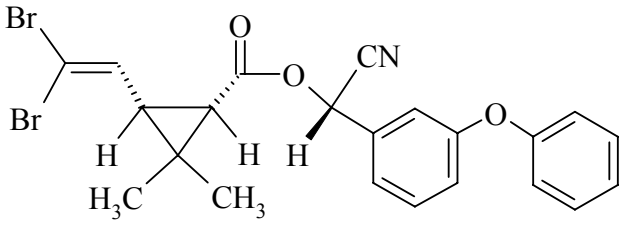
DELTAMETHRIN
333



ISO common name	Deltamethrin
Chemical name	(*S*)-α-cyano-3-phenoxybenzyl-(1*R*,3*R*)-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropanecarboxylate (IUPAC); (1*R*)[1α(*S**), 3α]-cyano(3-phenoxy-phenyl) methyl 3-(2,2-dibromoethyenyl)-2,2-dimethylcyclo-propanecarboxylate (CA; 52918-63-5)
Empirical formula	$C_{22}H_{19}Br_2NO_3$
RMM	505.2
Description	The technical product is a white, odourless crystalline and non corrosive powder
m.p.	100.4° C
v.p.	2.0×10^{-6} Pa at 25°C
Optical rotation [α]	+ 57° ± 1° (4% toluene)
Solubility	In water less than 0.1 mg/l; soluble in acetone: (450 g/l), tetrahydrofuran: (450 g/l), hexane: (2 g/l)
Formulations	Emulsifiable concentrates, ULV, wettable powders, dustable powder, suspension concentrates, and in mixtures with other pesticides

DELTAMETHRIN TECHNICAL
[*]**333**/TC/M2/-

1 Sampling. Take at least 100 g.

2 Identity tests
2.1 HPLC. Use the HPLC method below. The retention time of deltamethrin in the sample solution should not deviate by more than 15 s from that of the calibration solution.
2.2 Infrared. As for deltamethrin technical **333**/TC/M/2.3, CIPAC D, *p* 59.
2.3 NMR. As for deltamethrin technical **333**/TC/M/2.4, CIPAC D, *p* 59.
2.4 Mass spectrometry. As for deltamethrin technical **333**/TC/M/2.5, CIPAC D, *p* 59.

3 Deltamethrin

OUTLINE OF METHOD The sample is dissolved in a mixture of *iso*-octane and dioxane. The deltamethrin content is determined by normal phase high performance liquid chromatography using external standardisation and detection at 230 nm (See Fig. 17 - 23).

REAGENTS
1,4-dioxane (HPLC grade). Add 0.15% (v/v) water before use.
Iso-octane (HPLC grade)
Water (HPLC grade)
Diluting solvent iso-octane - 1,4-dioxane, 80 + 20 (v/v)
Eluent iso-octane - 1,4-dioxane (+ 0.15% water), 94 + 6 (v/v)
Deltamethrin standard of known purity
Calibration solution. Weight (to the nearest 0.1 mg) in duplicate about 50 mg (*s* mg) deltamethrin standard into volumetric flasks (50 ml). Dissolve in 1,4-dioxane (about 10 ml) and *iso*-octane (about 35 ml). Allow the solutions to attain ambient temperature and fill to the mark with *iso*-octane. Mix well. Transfer by pipette 5.0 ml of these solutions to separate volumetric flasks (50 ml) and dilute to the mark with diluting solvent. Mix well (solutions C_1 and C_2).

APPARATUS
High performance liquid chromatograph equipped with an automatic loop injector (20 µl) and an UV spectrophotometric detector capable to measure at 230 nm

[*] CIPAC method 2005. Prepared by the the German PAC (DAPA). Chairman: R.Hänel. Based on a method supplied by Bayer CropScience GmbH, Germany.

Column, stainless steel, 250 × 4 (i.d.) mm, packed with Nucleosil 100-5-CN 5 µm or equivalent material of the same type
Electronic integrator or *data system*
Disposable filter, e.g. Schleicher & Schuell; Spartan 30/0, 45 RC 0.45 µm brown rim L or equivalent

PROCEDURE
(a) Operating conditions (typical):

Column	250 × 4.0 (i.d.) mm, packed with Nucleosil 100-5-CN, 5µm
Mobile phase	*iso*-octane - 1,4-dioxane (+ 0.15% water), 94 + 6 (v/v)
Flow rate	1.5 ml/min
Column temperature	35 °C
Injection volume	20 µl
Detector wavelength	230 nm
Retention time	6 to 8 min

(b) Preparation of sample. Weigh (to the nearest 0.1 mg) in duplicate into separate volumetric flasks (50 ml) sufficient sample to contain about 50 mg (*w* mg) deltamethrin. Dissolve in 1,4-dioxane (about 10 ml) and *iso*-octane (about 35 ml). Allow the solutions to attain ambient temperature and fill to the mark with *iso*-octane. Mix well. Transfer by pipette 5.0 ml of these solutions into separate volumetric flasks (50 ml), dilute to the mark with diluting solvent and mix well (solutions S_1 and S_2).

(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 C_1, sample solution S_1 (double injection), calibration solution C_2, sample solution S_2 (double injection), calibration solution C_1 etc. Measure the relevant peak areas.
Calculate the mean value of each pair of response factors bracketing the injections of the two samples and use this value for calculating the deltamethrin contents of the bracketed sample solution injections.

(d) Calculation

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

$$\text{Deltamethrin content} = \frac{f \times H_w}{w} \text{ g/kg}$$

where:
f_i = individual response factor
f = mean response factor
H_s = peak area of deltamethrin in the calibration solution
H_w = peak area of deltamethrin in the sample solution
s = mass of deltamethrin in the calibration solution (mg
w = mass of sample taken (mg)
P = purity of deltamethrin analytical standard (g/kg)

Repeatability r = 13 g/kg at 998 g/kg active ingredient content
Reproducibility R = 17 g/kg at 998 g/kg active ingredient content

DELTAMETHRIN WATER DISPERSIBLE GRANULES
*333/WG/M/-

1 Sampling. Take at least 500 g.

2 Identity tests
2.1 HPLC. As for deltamethrin technical, **333/**TC/M2/2.1.
2.2 Infrared. As for deltamethrin technical **333/**TC/M/2.3, CIPAC D, *p* 59, but extract the deltamethrin with a suitable solvent. Evaporate the solvent using a stream of clean dry air.
2.3 NMR. As for deltamethrin technical **333/**TC/M/2.4, CIPAC D, *p* 59, but extract the deltamethrin with a suitable solvent. Evaporate the solvent using a stream of clean dry air.
2.4 Mass spectrometry. As for deltamethrin technical **333/**TC/M/2.5, CIPAC D, *p* 59, but extract the deltamethrin using a suitable solvent. Evaporate the solvent using a stream of clean dry air.

3 Deltamethrin. As for deltamethrin technical, **333/**TC/M2/3, except substitute the following:
(b) Preparation of sample. Weigh (to the nearest 0.1 mg) in duplicate into separate volumetric flasks (250 ml) sufficient sample to contain 250 mg (*w* mg) deltamethrin. Disperse with water (about 5 ml) and fill the flasks to below the mark with 1,4-dioxane. Place the flasks in an ultrasonic bath for about 15 min and allow to cool to ambient temperature. Fill to the mark with 1,4-dioxane. Transfer by pipette 5.0 ml of these solutions to separate volumetric flasks (50 ml) and add 1,4-dioxane (about 5 ml) and *iso*-octane (about 35 ml). Allow

* CIPAC method 2005. Prepared by the the German PAC (DAPA). Chairman: R.Hänel. Based on a method supplied by Bayer CropScience GmbH, Germany.

the solutions to attain ambient temperature and fill to the mark with *iso*-octane. Mix well (solutions S_1 and S_2). Filter the sample solutions through a disposable syringe-filter prior to injection.

and:

(d) Calculation

$$\text{Deltamethrin content} = \frac{f \times H_w \times 5}{w} \text{ g/kg}$$

Repeatability r = 5.5 g/kg at 244 g/kg active ingredient content
Reproducibility R = 10 g/kg at 244 g/kg active ingredient content

4 Suspensibility (Draft method)

REAGENTS AND APPARATUS as for **333**/TC/M2/3 and MT 184.

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

(b) Determination of deltamethrin in the bottom 25 ml of suspension. After removal of the top 225 ml of suspension transfer the remaining 25 ml to a 50 ml separatory funnel, add *iso*-octane (20 ml)and shake. Enhance the separation by centrifugation (approx. 3000 rpm, 5 min). After separation of the phases isolate the *iso*-octane phase, dry it with sodium sulphate and it to a graduated flask (50 ml). Repeat the extraction procedure of the water phase with another 20 ml portion of *iso*-octane and transfer the *iso*-octane phase to the graduated flask. Make up to the volume with dioxane. Transfer by pipette 5.0 ml (in case of a 1% dispersion, 1,0 ml in case of a 5% dispersion) of this solution to a volumetric flask (50 ml) and dilute to the mark with diluting solvent. Determine the mass of deltamethrin (Q g) by3**33**/TC/M2/3.

(c) Calculation

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

where:
c = mass of active ingredient in sample actually taken
Q = mass of active ingredient in the 25 ml remaining in the cylinder

DELTAMETHRIN WETTABLE POWDERS
*333/WP/(M)/-

1 Sampling. Take at least 500 g.

2 Identity tests. As for deltamethrin wettable granules, **333**/WG/M/2

3 Deltamethrin. As for deltamethrin wettable granules, **333**/WG/M/3 except substitute the following:
(b) Preparation of sample. Weigh (to the nearest 0.1 mg) in duplicate into separate volumetric flasks (250 ml) sufficient sample to contain 250 mg (*w* mg) deltamethrin. Disperse with water (about 5 ml in case of formulations with approximately 250 g/kg active ingredient content; in case of lower concentrations more water will be needed, e.g. 20 ml for a content of 25 g/kg) and fill the flasks to below the mark with 1,4-dioxane. Place the flasks in an ultrasonic bath for about 15 min. and allow to cool to ambient temperature. Fill to 250 ml with 1,4-dioxane. Transfer by pipette 5.0 ml of these solutions into separate volumetric flasks (50 ml), add 1,4-dioxane (about 5 ml) and *iso*-octane (about 35 ml). Allow the solutions to attain ambient temperature and fill to the mark with *iso*-octane. Mix well (solutions S_1, S_2).
Filter the sample solutions through a disposable syringe-filter prior to injection.

4 Suspensibility. As for deltamethrin wettable granules, **333**/WG/M/4.

DELTAMETHRIN EMULSIFIABLE CONCENTRATES
*333/EC/M2/-

1 Sampling. Take at least 500 ml.

2 Identity tests
2.1 HPLC. As for deltamethrin technical, **333**/TC/M2/2.1.
2.2 Infrared. As for deltamethrin technical **333**/TC/M/2.3, CIPAC D, *p* 59, but the deltamethrin must first be isolated by preparative liquid chromatography, preparative TLC or preparative HPLC.

* Provisional CIPAC method 2005. Prepared by the the German PAC (DAPA). Chairman: R.Hänel. Based on a method supplied by Bayer CropScience GmbH, Germany.

* CIPAC method 2005. Prepared by the the German PAC (DAPA). Chairman: R.Hänel. Based on a method supplied by Bayer CropScience GmbH, Germany.

2.3 NMR. As for deltamethrin technical **333/**TC/M/2.4, CIPAC D, *p* 59, but the deltamethrin must first be isolated by preparative liquid chromatography, preparative TLC or preparative HPLC.
2.4 Mass spectrometry. As for deltamethrin technical **333/**TC/M/2.5, CIPAC D, *p* 59, but the deltamethrin must first be isolated by preparative liquid chromatography, preparative TLC or preparative HPLC.

3 Deltamethrin. As for deltamethrin technical, **333/**TC/M2/3, except substitute the following:
(b) Preparation of sample. Weigh (to the nearest 0.1 mg) in duplicate into separate volumetric flasks (50 ml) sufficient sample to contain about 5 mg (*w* mg) deltamethrin. Dissolve in diluting solvent (about 45 ml) and place the flasks in an ultrasonic bath for about 15 min. Allow the solutions to cool to ambient temperature. Fill to the mark with diluting solvent and mix well (solutions S_1 and S_2). Filter the sample solutions through a disposable syringe-filter prior to injection.

and

(d) Calculation

$$\text{Deltamethrin content} = \frac{f \times H_w}{w \times 10} \text{ g/kg}$$

Repeatability r = 0.35 g/kg at 27.3 g/kg active ingredient content
Reproducibility R = 0.51 g/kg at 27.3 g/kg active ingredient content

DELTAMETHRIN SUSPENSION CONCENTRATES
[*]**333/**SC/M/-

1 Sampling. Take at least 500 ml.

2 Identity tests
2.1 HPLC. As for deltamethrin technical, **333/**TC/M2/2.1.
2.2 Infrared. As for deltamethrin technical **333/**TC/M/2.3, CIPAC D, *p* 59, but the deltamethrin must first be isolated by preparative liquid chromatography, preparative TLC or preparative HPLC.

[*] CIPAC method 2005. Prepared by the the German PAC (DAPA). Chairman: R.Hänel. Based on a method supplied by Bayer CropScience GmbH, Germany.

2.3 NMR. As for deltamethrin technical **333/**TC/M/2.4, CIPAC D, *p* 59, but the deltamethrin must first be isolated by preparative liquid chromatography, preparative TLC or preparative HPLC.
2.4 Mass spectrometry. As for deltamethrin technical **333/**TC/M/2.5, CIPAC D, *p* 59, but the deltamethrin must first be isolated by preparative liquid chromatography, preparative TLC or preparative HPLC.

3 Deltamethrin. As for deltamethrin technical, **333/**TC/M2/3, except substitute the following:
(b) Preparation of sample. Shake the sample to ensure an even distribution of deltamethrin. Weigh (to the nearest 0.1 mg) in duplicate into separate volumetric flasks (50 ml) sufficient sample to contain 25 mg (*w* mg) deltamethrin. Place the flasks in an ultrasonic bath for about 15 min. Allow the flasks to cool to ambient temperature and make up to volume with 1,4-dioxane. Transfer by pipette 10.0 ml of these solutions to separate volumetric flasks (50 ml), add *iso*-octane (about 35 ml) and place the flasks in an ultrasonic bath for about 15 min. Allow to cool to ambient temperature and fill to the mark with *iso*-octane. Mix well. (solutions S_1, S_2). Filter the sample solutions through a disposable syringe-filter prior to injection.

(d) Calculation

$$\text{Deltamethrin content} = \frac{f \times H_w \times 2}{w} \text{ g/kg}$$

Repeatability r = 0.73 g/kg at 25.5 g/kg active ingredient content
Reproducibility R = 2.3 g/kg at 25.5 g/kg active ingredient content

4 Suspensibility (Draft method)

As for deltamethrin water dispersible granules (333/WG/M/4).

DELTAMETHRIN DUSTABLE POWDERS
*333/DP/M2/-

1 Sampling. Take at least 500 g.

2 Identity tests

2.1 HPLC. As for deltamethrin technical, **333**/TC/M2/2.1.

2.2 Infrared. As for deltamethrin technical **333**/TC/M/2.3, CIPAC D, *p* 59, but extract the deltamethrin with a suitable solvent. Evaporate the solvent using a stream of clean dry air.

2.3 NMR. As for deltamethrin technical **333**/TC/M/2.4, CIPAC D, *p* 59, but extract the deltamethrin with a suitable solvent. Evaporate the solvent using a stream of clean dry air.

2.4 Mass spectrometry. As for deltamethrin technical **333**/TC/M/2.5, CIPAC D, *p* 59, but extract the deltamethrin using a suitable solvent. Evaporate the solvent using a stream of clean dry air.

3 Deltamethrin. As for deltamethrin technical, **333**/TC/M2/3, except substitute the following:

Calibration solution. Weigh (to the nearest 0.1 mg) in duplicate about 50 mg (*s* mg) deltamethrin analytical standard into volumetric flasks (50 ml). Dissolve in 1,4-dioxane (about 10 ml) and iso-octane (about 35 ml). Allow the solutions to attain ambient temperature and fill to the mark with *iso*-octane. Mix well. Transfer by pipette 1.0 ml of these solutions into separate volumetric flasks (100 ml) and dilute to the mark with diluting solvent. Mix well (solutions C_1 and C_2).

(b) Preparation of sample. Weigh (to the nearest 0.1 mg) in duplicate into separate volumetric flasks (50 ml) sufficient sample to contain about 0.5 mg (*w* mg) deltamethrin. Dissolve in 1,4-dioxane (about 10 ml) and place the flasks in an ultrasonic bath for about 15 min. Add *iso*-octane (about 35 ml), swirl and allow the solutions to cool to ambient temperature. Fill to the mark with *iso*-octane and mix well (solutions S_1 and S_2). Filter the sample solutions through a disposable syringe-filter prior to injection.

(d) Calculation

$$\text{Deltamethrin content} = \frac{f \times H_w}{w \times 100} \text{ g/kg}$$

Repeatability r = 0.07 g/kg at 0.44 g/kg active ingredient content
Reproducibility R = 0.07 g/kg at 0.44 g/kg active ingredient content

* CIPAC method 2005. Prepared by the the German PAC (DAPA). Chairman: R.Hänel. Based on a method supplied by Bayer CropScience GmbH, Germany.

DELTAMETHRIN WATER SOLUBLE TABLETS

[*] **333**/WT/m/-

1 Sampling. Take at least 500 g.

2 Identity tests

2.1 HPLC. As for deltamethrin technical, **333**/TC/M2/2.1.

2.2 Infrared. As for deltamethrin technical **333**/TC/M/2.3, CIPAC D, *p* 59, but extract the deltamethrin with a suitable solvent. Evaporate the solvent using a stream of clean dry air.

2.3 NMR. As for deltamethrin technical **333**/TC/M/2.4, CIPAC D, *p* 59, but extract the deltamethrin with a suitable solvent. Evaporate the solvent using a stream of clean dry air.

2.4 Mass spectrometry. As for deltamethrin technical **333**/TC/M/2.5, CIPAC D, *p* 59, but extract the deltamethrin using a suitable solvent. Evaporate the solvent using a stream of clean dry air.

3 Deltamethrin. As for deltamethrin technical, **333**/TC/M2/3, except substitute the following:

(b) Preparation of sample. Grind 5 tablets in a mortar with pestle. Weigh (to the nearest 0.1 mg) in duplicate into separate volumetric flasks (50 ml) sufficient sample to contain about 50 mg deltamethrin (*w* mg). Disperse with water (about 1 ml) and fill the flasks to below the mark with 1,4-dioxane. Place the suspensions in an ultrasonic bath for about 15 min. Allow to cool to ambient temperature and fill to the mark with 1,4-dioxane. Transfer by pipette 5.0 ml of these solutions to separate volumetric flasks (50 ml) and add 1,4-dioxane (about 5 ml) and *iso*-octane (about 35 ml). Allow the solutions to attain ambient temperature and fill to the mark with *iso*-octane. Mix well (solutions $S_1$and S_2). Filter the sample solutions through a disposable syringe-filter prior to injection.

Repeatability r = 12 g/kg at 240 g/kg active ingredient content
Reproducibility R = 21 g/kg at 240 g/kg active ingredient content

[*] Tentative CIPAC method 2004. Prepared by the the German PAC (DAPA). Chairman: R.Hänel. Based on a method supplied by Bayer CropScience GmbH, Germany.

DELTAMETHRIN EMULSIFIABLE GRANULES
*333/EG/(M)/-

1 Sampling. Take at least 500 g.

2 Identity tests. As for deltamethrin water dispersible granules **333**/WG/M/2.

3 Deltamethrin. As for deltamethrin technical, **333/**WG/M2/3, except substitute the following:
(b) Preparation of sample. Weigh (to the nearest 0.1 mg) in duplicate into separate volumetric flasks (250 ml) sufficient sample to contain 250 mg (*w* mg) deltamethrin. Disperse with water (about 5 ml) and fill the flasks to below the mark with 1,4-dioxane. Place the flasks in an ultrasonic bath for about 15 min and allow to cool to ambient temperature. Fill to the mark with 1,4-dioxane. Transfer by pipette 5.0 ml of these solutions to separate volumetric flasks (50 ml) and add 1,4-dioxane (about 5 ml) and *iso*-octane (about 35 ml). Allow the solutions to attain ambient temperature and fill to the mark with *iso*-octane. Mix well (solutions S_1 and S_2). Filter the sample solutions through a disposable syringe-filter prior to injection.

and:

(d) Calculation

$$\text{Deltamethrin content} = \frac{f \times H_w \times 5}{w} \text{ g/kg}$$

DELTAMETHRIN EMULSIONS, OIL IN WATER
*333/EW/(M)/-

1 Sampling. Take at least 500 ml.

2 Identity tests. As for deltamethrin suspension concentrates **333**/SC/M/2.

3 Deltamethrin. As for deltamethrin suspension concentrates **333**/SC/M/3.

* Provisional CIPAC method 2005. Prepared by the the German PAC (DAPA). Chairman: R.Hänel. Based on a method supplied by Bayer CropScience GmbH, Germany.

DELTAMETHRIN ULTRA LOW VOLUME LIQUIDS
*333/UL/(M2)/-

1 Sampling. Take at least 500 ml.

2 Identity tests
2.1 HPLC. As for deltamethrin technical, **333**/TC/M2/2.1.
2.2 Infrared. As for deltamethrin technical **333**/TC/M/2.3, CIPAC D, *p* 59, but extract the deltamethrin with a suitable solvent. Evaporate the solvent using a stream of clean dry air.
2.3 NMR. As for deltamethrin technical **333**/TC/M/2.4, CIPAC D, *p* 59, but extract the deltamethrin with a suitable solvent. Evaporate the solvent using a stream of clean dry air.

3 Deltamethrin. As for deltamethrin technical **333**/TC/M2/3 except substitute the following:
(a) Calibration solution. Weigh (to nearest 0.1mg) in duplicate about 50 mg (*s* mg) deltamethrin analytical standard into separate volumetric flasks (50 ml). Dissolve in 1,4-dioxane (about. 10 ml) and *iso*-octane (about 35 ml). Allow to cool to ambient temperature and fill to the mark with *iso*-octane. Mix well. Transfer by pipette 5.0 ml of these solutions into separate volumetric flasks (100 ml), dilute to the mark with diluting solvent. Mix well. (solutions C_1 and C_2).

(b) Preparation of sample. Weigh (to nearest 0.1 mg) in duplicate into separate volumetric flasks (100 ml) sufficient sample to contain about 5 mg (*w* mg) deltamethrin. Dissolve with diluting solvent and place the flasks in an ultrasonic bath for about 15 min. Allow to cool to attain ambient temperature and fill to the mark with diluting solvent (solutions S_1 and S_2).

(d) Calculation

$$\text{Deltamethrin content} = \frac{f \times H_w}{w \times 10} \text{ g/kg}$$

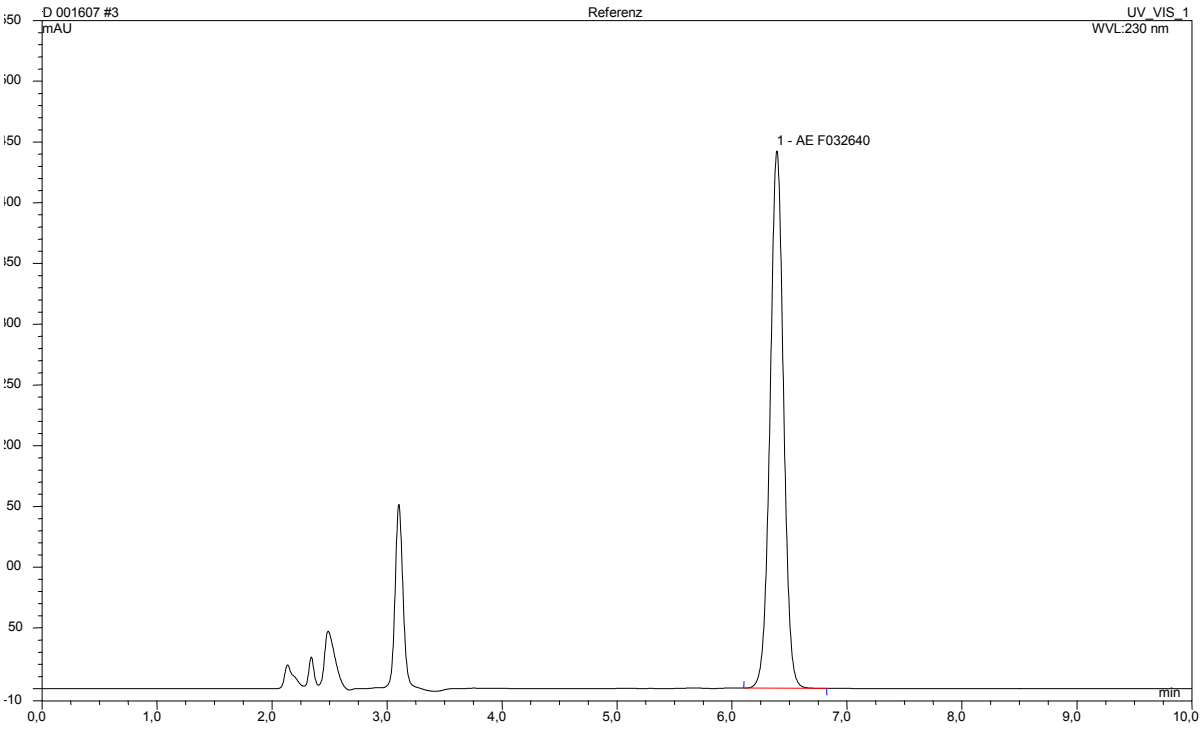


Fig. 17 Chromatogram of deltamethrin standard

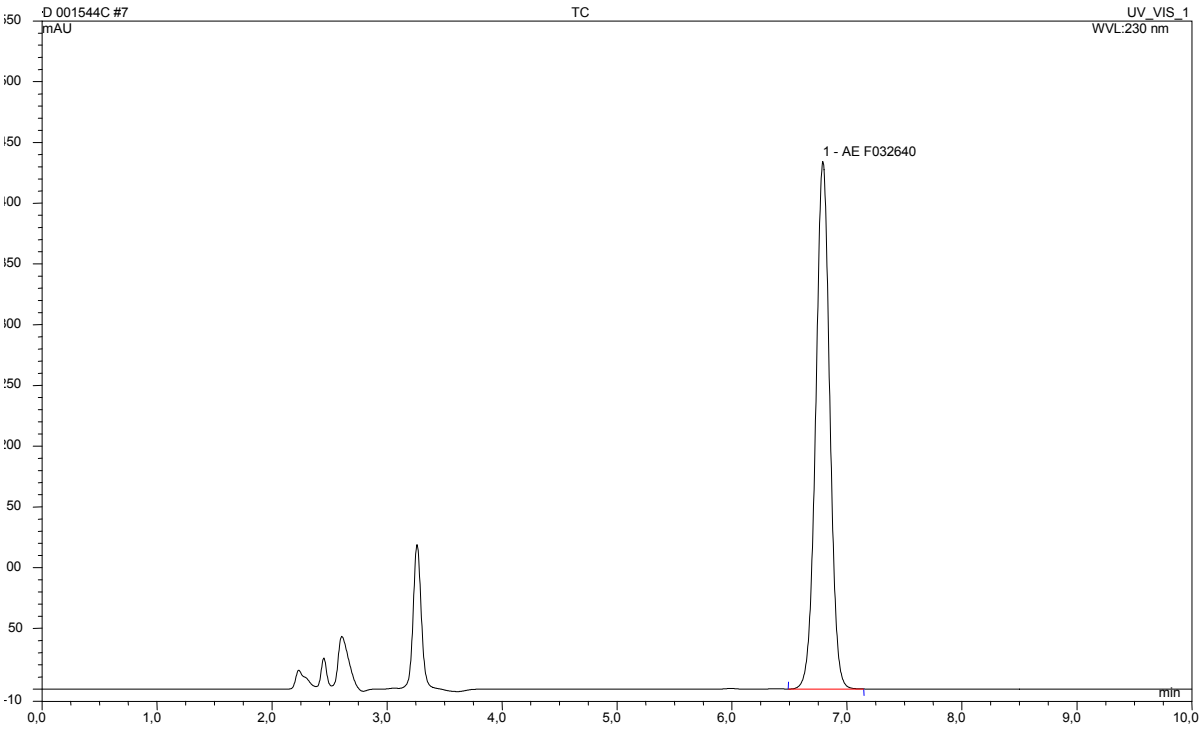


Fig. 18 Chromatogram of deltamethrin technical

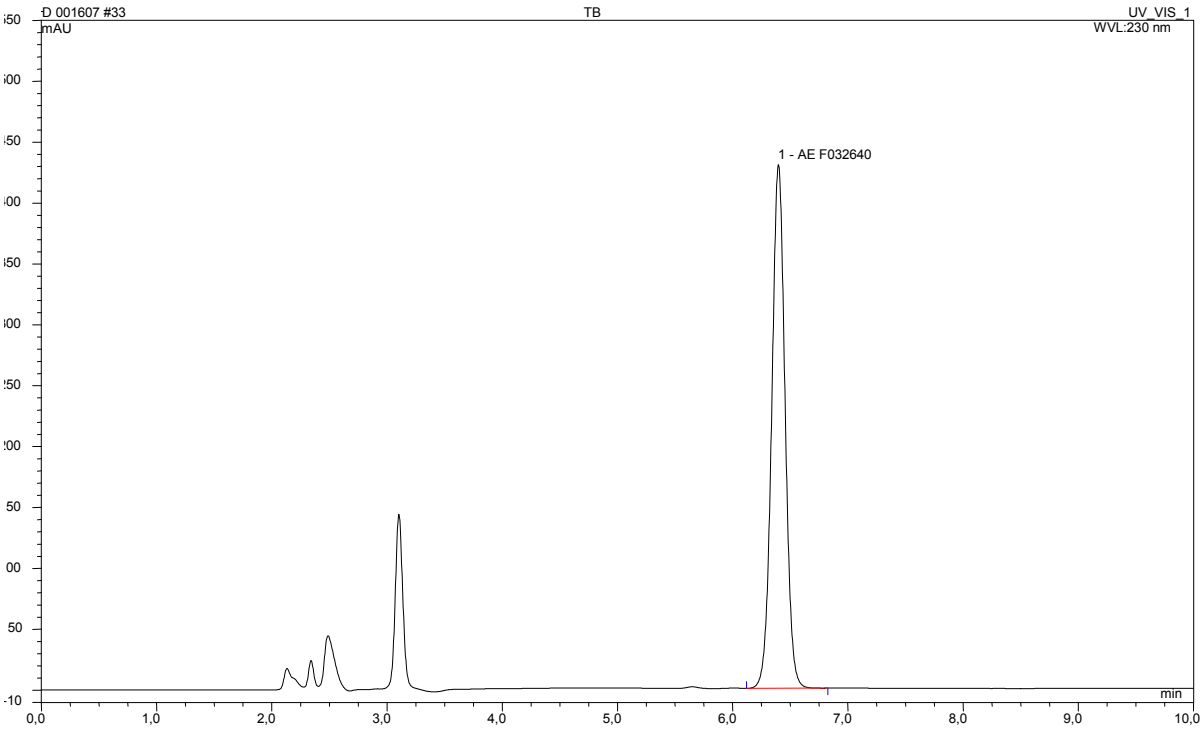


Fig. 19 Chromatogram of deltamethrin TB

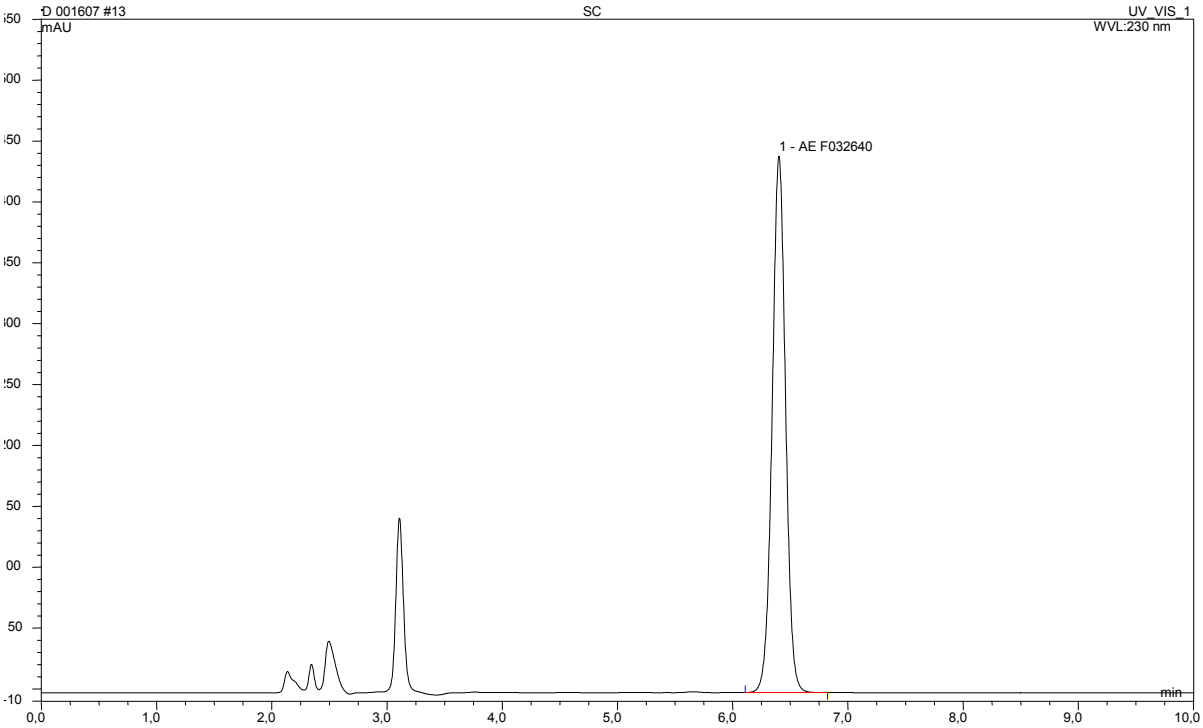


Fig. 20 Chromatogram of deltamethrin SC

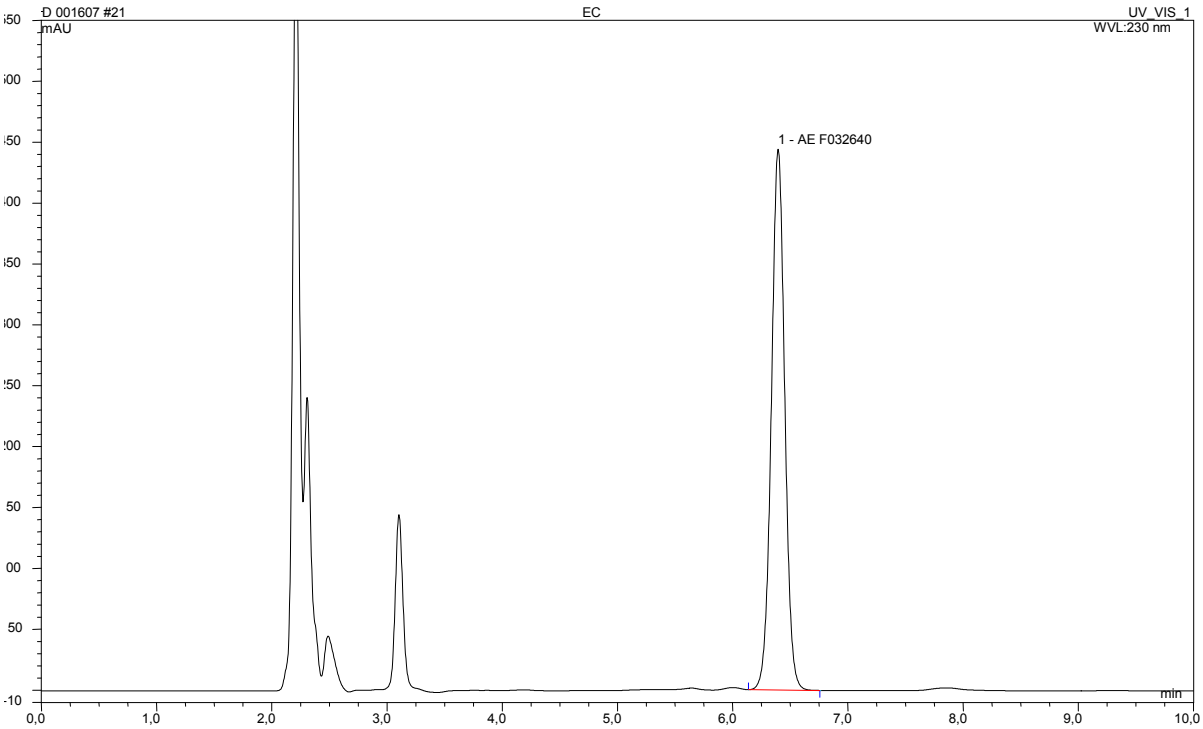


Fig. 21 Chromatogram of deltamethrin EC

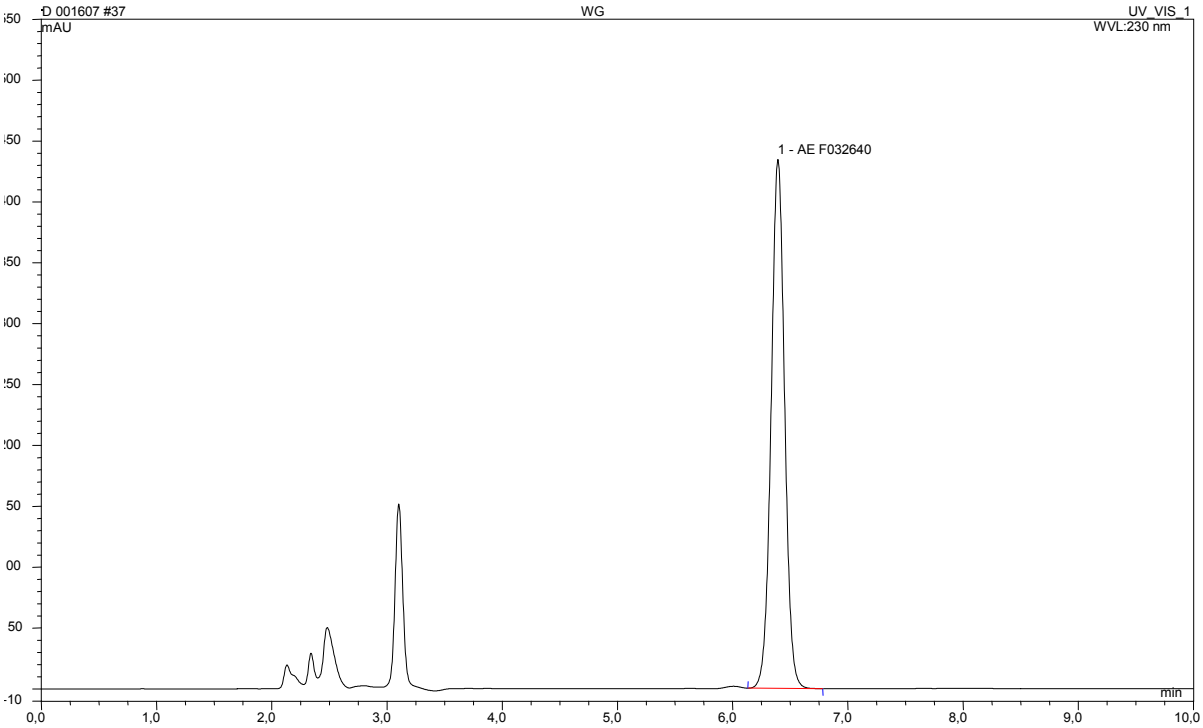


Fig. 22 Chromatogram of deltamethrin WG

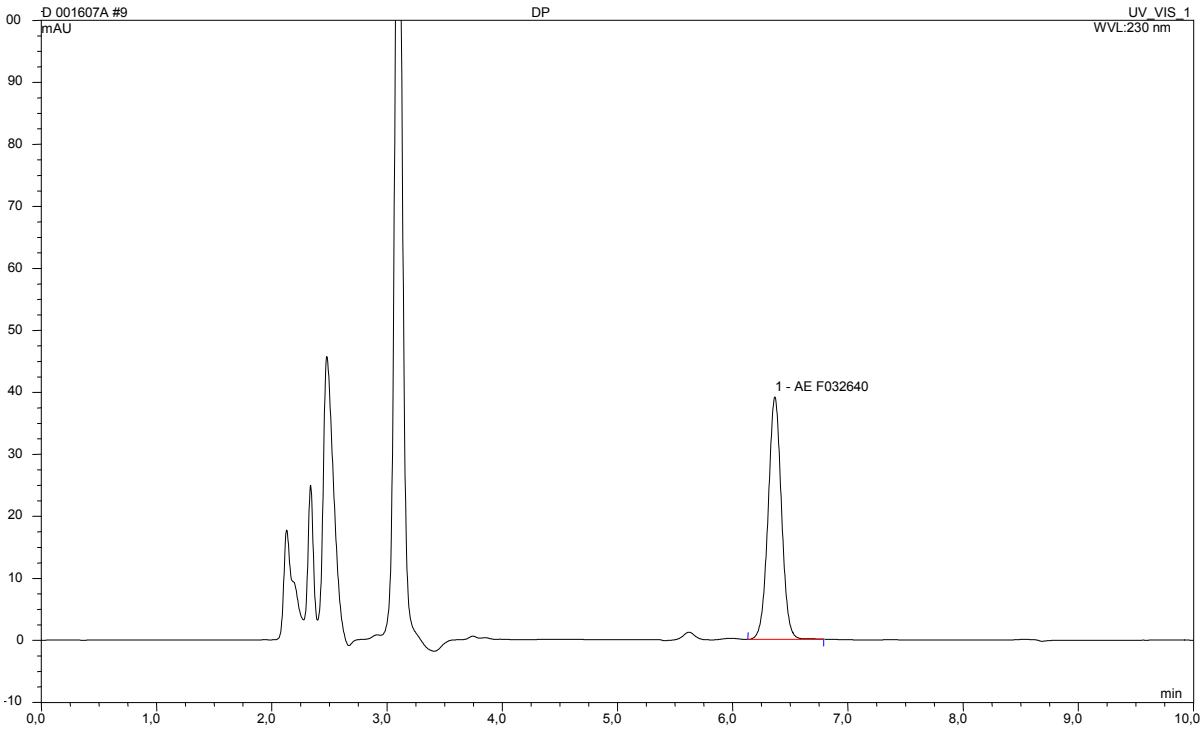


Fig. 23 Chromatogram of deltamethrin DP