CIPAC

COLLABORATIVE INTERNATIONAL PESTICIDES ANALYTICAL COUNCIL LIMITED

Commission Internationale des Méthodes d'Analyse des Pesticides (CIMAP)

CIPAC Free relevant impurities methods:

Methods for relevant impurities becoming more and more important in the quality control of TK/TC and FAO-specifications. In order to meet an urgent need for methods to characterize TK/TC in a.i. and formulations, CIPAC provides selected methods as a download. By downloading these methods, you accept the following conditions of use.

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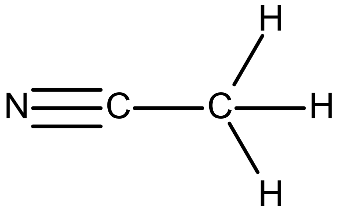
CHLORANTRANILIPROLE

794

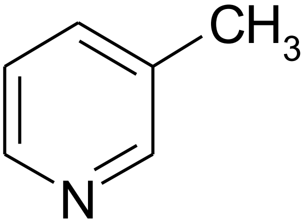
See CIPAC Handbook P, *p* 28.

relevant impurity ACETONITRILE



ISO Common name	Acetonitrile
Chemical name	Acetonitrile (IUPAC and CAS), cyanomethane
CAS No.	75-05-8
Empirical formula	CH_3CN
Molecular mass	41.053 g/mol
b.p.	80-82ºC.
Description	Colorless liquid.
Solubility	*Miscible with water*
Stability	Stable

relevant impurity 3-PICOLINE



Common name	3-Picoline
Chemical name	3-methylpyridine (IUPAC); Pyridine, 3-methyl
CAS No.	108-99-6
Empirical formula	C_6H_7N
Molecular Weight	93.13 g/ml
b.p.	144°C
Solubility 20°C	Water soluble
Description	Colorless liquid; Weak base, with a pKa of 5.63

CHLORANTRANILIPROLE TECHNICAL

*794/TC/M/-

1 Sampling. As received**.**

2 Identity tests

2.1 GC-MS. Using the GC method described below. The relative retention time of the 3-picoline and acetonitrile peaks in the sample solution should not deviate by more than 5% from that of the standard solution. The mass spectrum measured from these peaks should match that obtained from the standard substance as shown in the example mass spectra below.

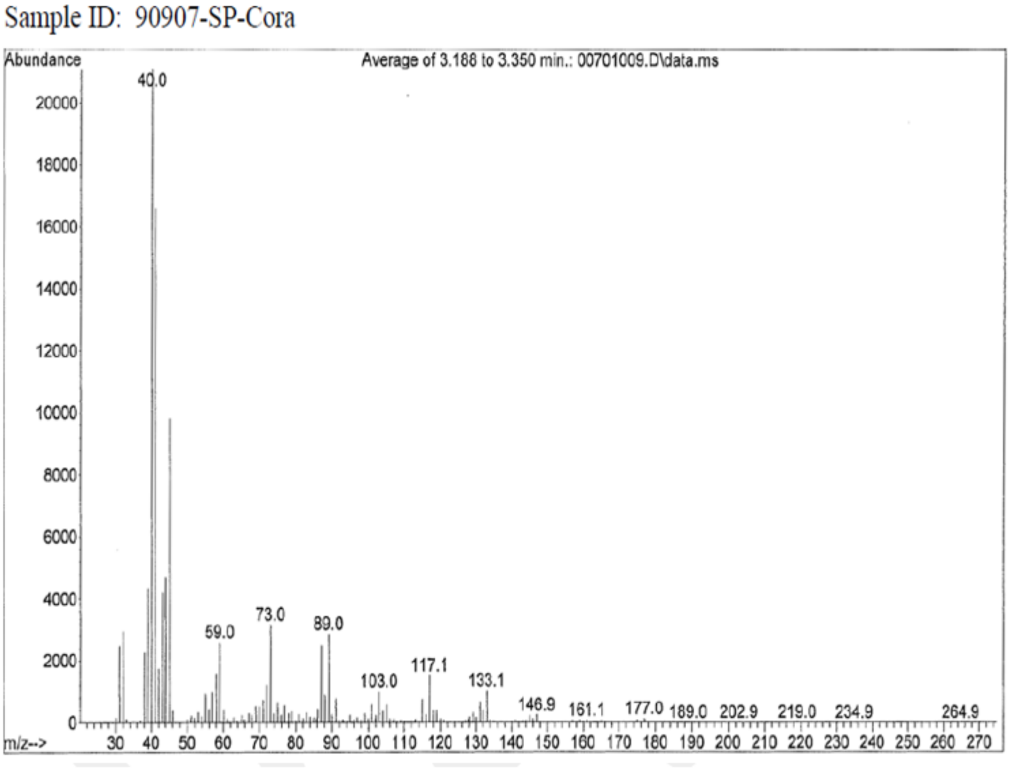


Fig. 1 Mass spectrum of acetonitrile in 200 SC formulation

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[*] CIPAC method 2024. Based on a method supplied by FMC, USA

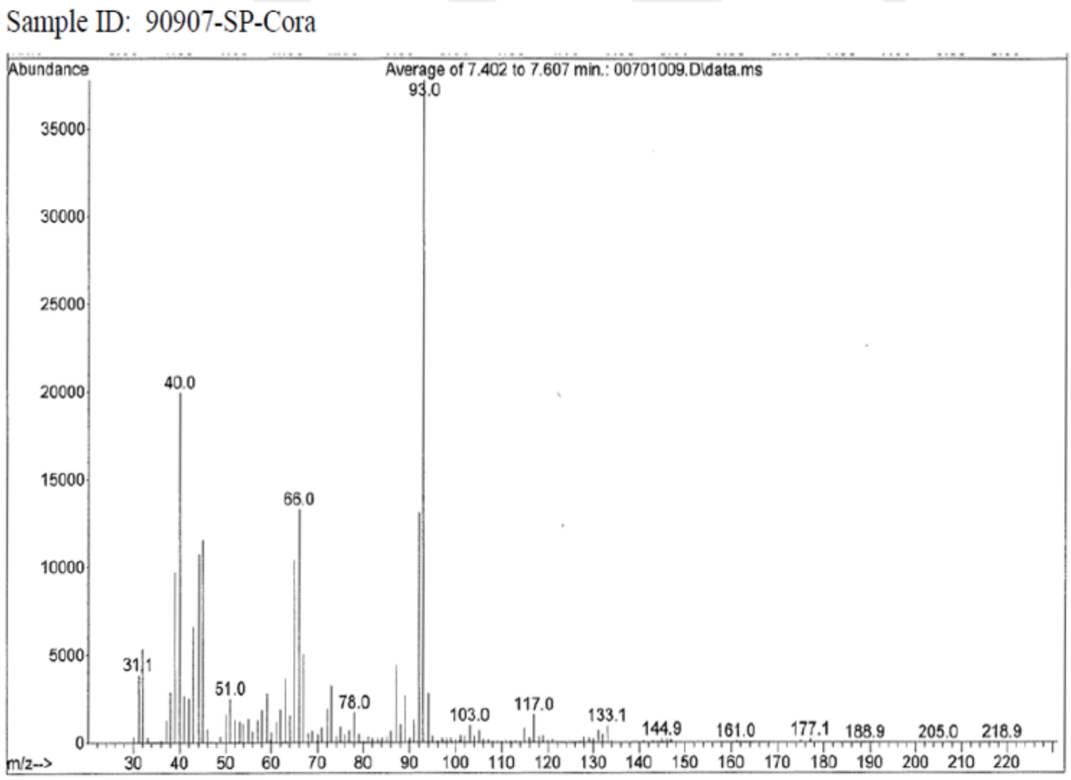

Fig. 2 Mass spectrum of 3-picoline in 200 SC formulation

2.2 Infrared (IR). Attenuated Total Reflectance (ATR) was used to determine the FT-IR spectra of the standard material of acetonitrile and 3-picoline. The ATR diamond is cleaned with a wipe or cotton swab immersed in water, then either ethanol, methanol, or isopropanol, followed by acetone. The background is collected before each sample, then with a pipette the sample is transferred directly to cover the diamond ATR crystal.

The sample is scanned using the following conditions and saved:

Range: 4000-650 cm^{-1} Scan Number: 32
Units: Absorbance Resolution: 4.00 cm^{-1}

The expected levels of acetonitrile and 3-picoline are not visible in the technical material or formulated products of chlorantraniliprole by ATR.

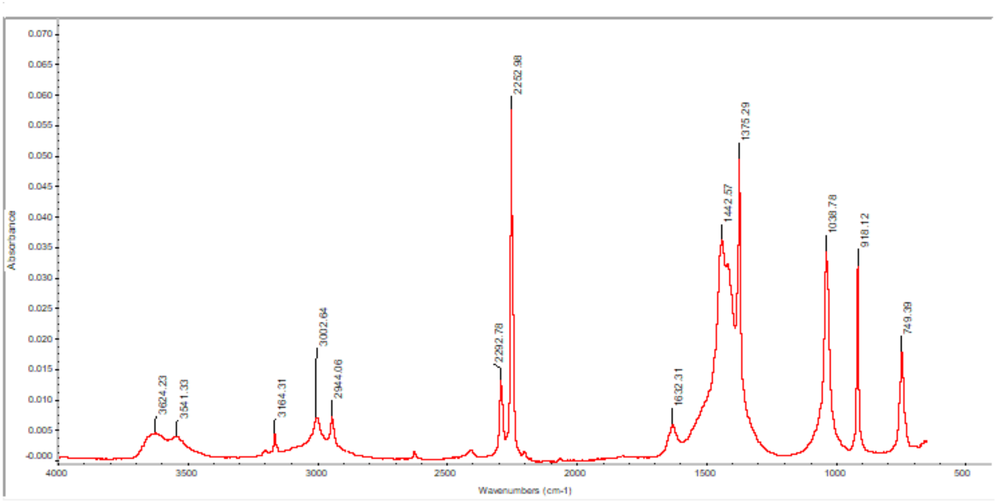

Fig. 3 Infrared spectrum of acetonitrile standard

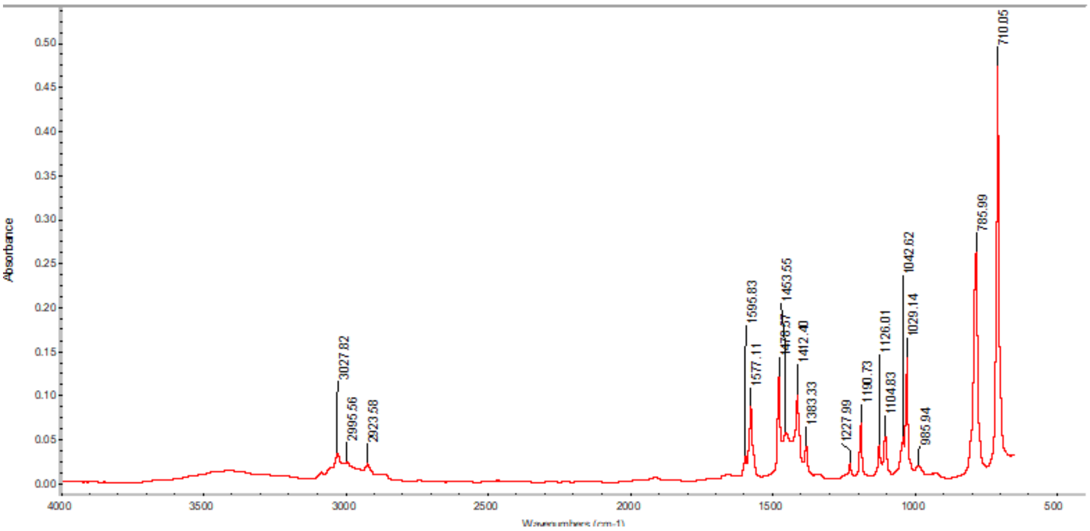

Fig. 4 Infrared spectrum of 3-picoline standard

5 Acetonitrile and 3-picoline

OUTLINE OF GC METHOD

A solution of the sample in N,N-dimethylacetamide (DMAC) is separated by capillary gas chromatography. Acetonitrile and 3-picoline are detected with a flame ionization detector (FID). The weight percent of acetonitrile and 3-picoline in the chlorantraniliprole technical and formulated samples are determined by comparing the peak area with a calibration curve (peak area vs. concentration) prepared from the analysis of standard solutions.

The method is applicable to the determination of acetonitrile and 3-picoline in chlorantraniliprole technical samples and end-use products. The applicable concentration range for acetonitrile is approximately 0.004% - 1.65% by weight and for 3-picoline is 0.004% - 1.64% by weight for a 35.0 mg/ml sample solution of technical material. The range can be extended by modifying the standard or sample concentrations.

REAGENTS

Acetonitrile: HPLC-GC grade, purity > 99.99%

3-Picoline: Analytical standard, purity > 99.50%

N,N-Dimethylacetamide: HPLC-GC grade

Calibration solutions. Seven standards are prepared to demonstrate linearity. For routine analyses once an acceptable 7-point calibration is produced, it is acceptable to use a three-point calibration that covers the range of analyte concentration in the samples to be analyzed.

Weigh 60 mg (± 10 mg) of acetonitrile standard solvent into a 100-ml volumetric flask prefilled with 40 ml of *N,N*-Dimethylacetamide (DMAC). Tare the flask and weigh 55 mg (± 10 mg) of 3-picoline. Dilute to volume with DMAC. This will be the stock standard. The nominal concentrations for acetonitrile and 3-picoline in this solution will be approximately 0.60 and 0.55 mg/ml, respectively.

Make the following dilutions into separate volumetric flasks. Dilute to volume with DMAC.

The volumetric glassware used should be type "Class A" glassware.

	Preparation	**ACN concentration, mg/ml**	**3-Picoline concentration, mg/ml**
Standard 1	Standard Stock Solution	0.600	0.550
Standard 2	25 ml Stock into 50 ml	0.300	0.275
Standard 3	15 ml Stock into 50 ml	0.180	0.165
Standard 4	10 ml Stock into 50 ml	0.120	0.110
Standard 5	5 ml Stock into 50 ml	0.060	0.055
Standard 6	3.5 ml Stock into 50 ml	0.042	0.039
Standard 7	2 ml Stock into 50 ml	0.024	0.022

APPARATUS

Gas chromatograph: Gas chromatograph capable of capillary column installation and equipped with a split/splitless inlet, an automated sample injector capable of injecting a 1-µl aliquot, constant temperature oven with temperature programming capability, flame ionization detector (FID), and integrator/ recorder or some other data handling system.

GC Column: Agilent DB Wax (30 m × 0.250 mm) × 0.50 µm film thickness (P/N: 122-7033)

Ultrasonic bath

Filters PTFE: 0.20 µm

Class A volumetric flasks with stoppers

Class A analytical pipets

Analytical balance: capable of measuring ± 0.1 mg.

PROCEDURE

(a) Operating Conditions (typical)

Oven

Initial Temp:	60 °C
Initial Hold Time:	3.0 minutes
Program Rate 1:	15.0 °C/minute
Final Temperature 1:	160 °C
Intermediate Hold Time:	0.0 minute
Program Rate 2:	25 °C/minute
Final Temperature 2:	240 °C
Final Hold Time:	3.0 minutes
Total Run Time:	15.9 minutes

Inlet Conditions

Mode:	Split
Inlet Temperature:	150 °C
Pressure:	19.9 psi
Split Ratio:	10:1
Carrier Gas Type:	Hydrogen
Injection Volume:	1.0 µl

The boiling points of acetonitrile and 3-picoline are 81-82 and 144 °C, respectively. The injector temperature is set at 150 °C to ensure volatilization and to minimize interferences.

The split flow determines the percentage of sample loaded onto the column. The split ratio is the ratio of split flow to column flow. A ratio of 20 is required to obtain optimum detector sensitivity from the FID detector. Adjust this as needed to optimize the instrument, since instrument performance varies.

Column Conditions

Column:	Agilent DB Wax (30 m × 0.250 mm) × 0.50 µm film thickness
Mode:	Constant Pressure
Initial Flow:	5.0 ml/min
Nominal Initial Pressure:	19.9 psi

Flame Ionization Detector Conditions

Temperature:	240 °C
Hydrogen Flow:	33 ml/min
Air Flow:	300 ml/min
Mode:	Constant makeup flow
Makeup Flow:	30 ml/minute

Makeup Gas: Nitrogen

Approximate Retention Times: *Acetonitrile – 4.1 minutes*
3-Picoline – 8.4 minutes

Peakwidth (response time):* > 0.03 min (0.5 sec)

*The peakwidth parameter may be instrument-specific. Ensure a data collection rate that permits at least 50 collected points across each peak.

Analysis Stop Time 16.0 minutes

(b) Sample preparation. Before sub-sampling liquid samples, mix thoroughly by swirling for approximately 1 to 2 minutes. For solid samples, grind and mix all samples thoroughly before weighing the test portions for analysis. Refer to the table below and accurately weigh (to at least 0.1 mg precision) the amount of sample indicated into a 10 or 50 ml volumetric flask.

Sample	**Nominal Amount**	**Volume**
Chlorantraniliprole Technical	350 ± 10 mg	10 ml
Chlorantraniliprole 200 g/L Suspension Concentrate (SC)	5000 ± 50 mg	50 ml
Chlorantraniliprole 600 g/L Suspension Concentrate (SC)	1750 ± 20 mg	50 ml

Dilute each flask to volume with DMAC and ultrasonicate for ten minutes.

Not all formulation inert ingredients will completely dissolve. Swirling during the final 5 minutes of ultrasonication aids the dissolution.

Allow the solution(s) to equilibrate to room temperature and syringe filter the sample into a GC sample vial and inject into the GC.

(c) Preparation of Calibration Curve(s). Equilibrate the instrument and column for one hour at the initial temperature. Cycle the oven one time through the temperature program prior to analysis. After the baseline has stabilized, inject an assay and impurity analytical standard solution to verify the retention times of each component.

Inject 1 µl of each standard and sample solution. For quantitative determinations, duplicate injections of standards and duplicate weighing of samples and duplicate injections of each weighing are recommended.

Prepare a calibration curve for each component by plotting the average peak area vs. concentration (mg/ml), corrected for purity, for each standard solution.

Using the method of least squares, calculate the equation for the best line fit for each component. Typically, the correlation coefficient of a least squares' equation is 0.999 or better. A computer data system, with least squares reduction capability, is recommended to generate calibration curves (i.e., y = mx + b) and the statistical analyses of the curves (i.e., correlation coefficients).

(d) Determination. Equilibrate the column until a stable baseline is obtained. Inject, in duplicate,1 µL each of a solvent blank (DMAC), standards, and samples, bracketing the samples with standard solutions.

(e) Calculation. Determine the analyte (i.e., acetonitrile and/or 3-picoline) concentration (mg/ml) from the peak area of the analyte using the equation from respective calibration curve, y = mx + b.

$$\text{Analyte concentration (x)} = \frac{y-(b)}{m}\ (mg/ml)$$

where:

x = analyte concentration (mg/ml) individual response factor

y = analyte peak area

b = intercept

m = slope

The analyte weight % can be calculated as follows:

$$\text{Weight \% analyte} = \frac{analyte\ [mg/ml]\ \times\ final\ volume\ [ml]}{sampleweight\ [mg]} \times 100$$

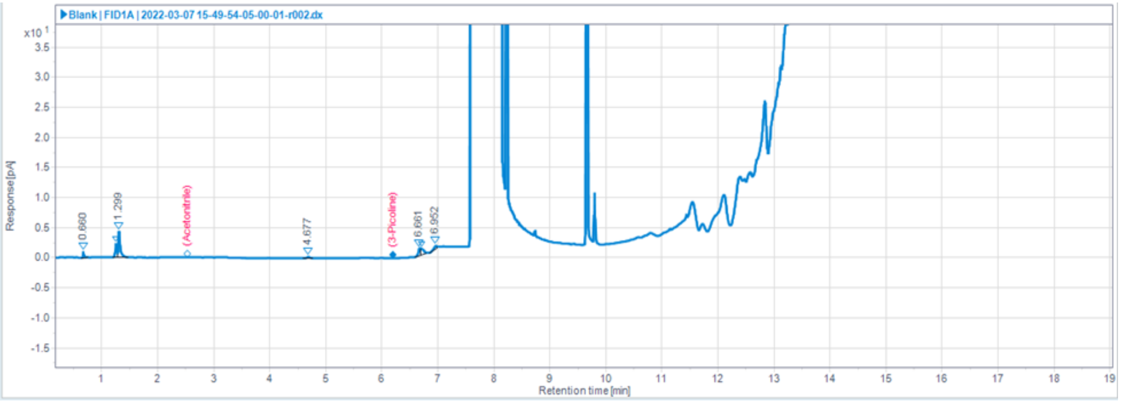

Fig. 5 Chromatogram of a blank DMAC solution

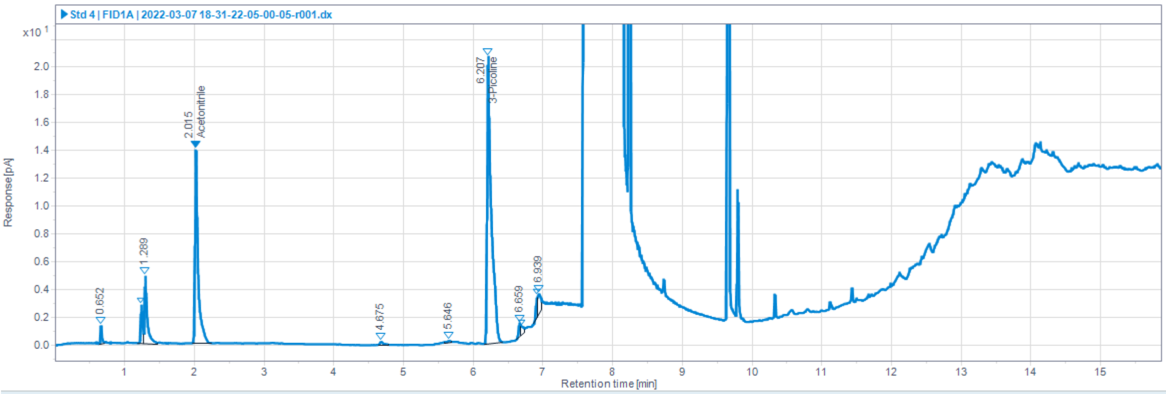

Fig. 6 Chromatogram of standard solution containing 0.043 mg/ml of acetonitrile and 0.045 mg/ml of 3-picoline in DMAC

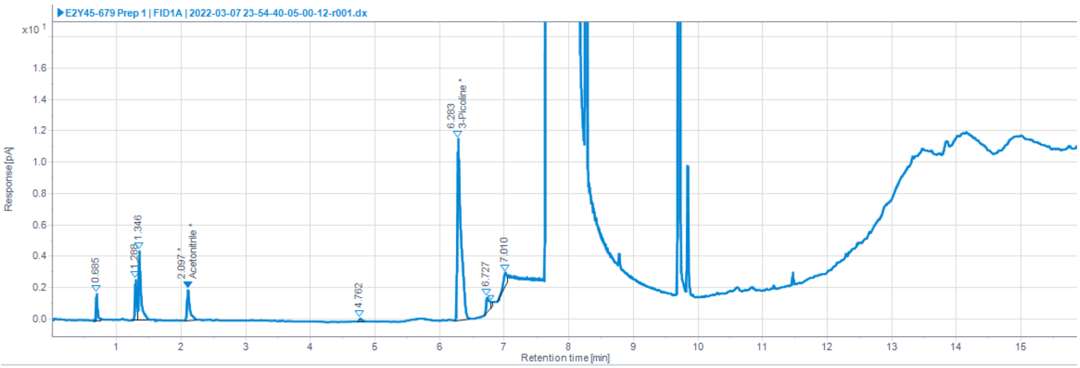

Fig. 7 Chromatogram of chlorantraniliprole technical sample containing 35.12 mg/ml technical a.i. in DMAC

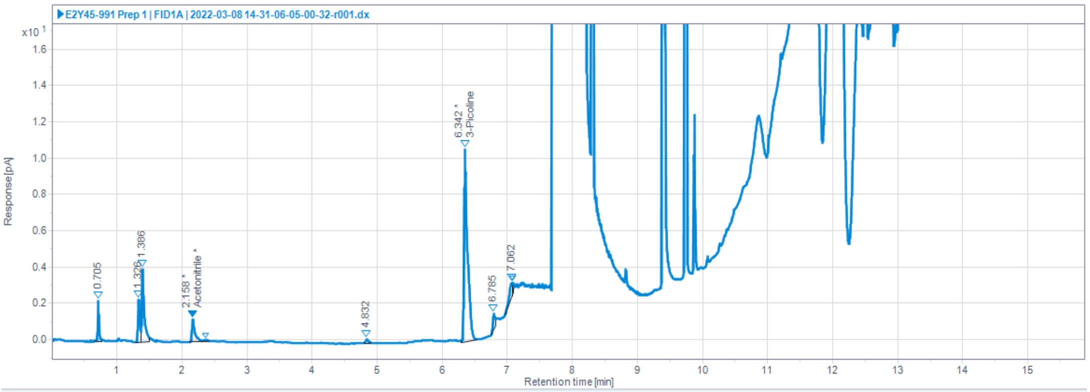

Fig. 8 Chromatogram of chlorantraniliprole 600 SC formulation sample containing 16.77 mg/mL of technical a.i. in DMAC.

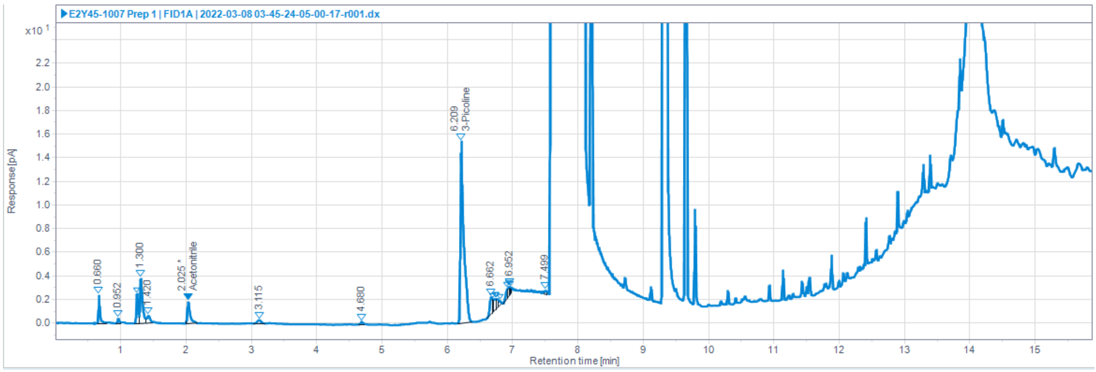

Fig. 9 Chromatogram of chlorantraniliprole 200 SC formulation sample, containing 18.39 mg/ml technical a.i. in DMAC