ICS 65.100.10

G25

GB

National Standards of the People's Republic of China

GB XXXX----XXXX

d-allethrin technical material

(Draft)

Published XX – XX – XXXX Effective as of XX – XX – XXXX

Issued by the

General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China (AQSIQ) and

the Standardisation Administration of the People's Republic of China (SAC)

Foreword

Chapter 3 and 5 of these standards are mandatory. The rest are recommendations.

These standards are drafted in accordance with the rules stipulated in GB/T 1.1-2009.

These standards are proposed by China Petroleum and Chemical Industry Federation (CPCIF).

The compilation of these standards was managed by the National Standardisation Technical Committee on Pesticides.

These standards were drafted by Jiangsu Yangnong Chemical Co. Ltd with contributions by Aestar (Zhongshan) Co. Ltd and LIBY Group Co. Ltd.

Main persons responsible for drafting these standards: Weirong Liu, Weilian Shi, Bin Lin, Shen Ruan and Zuoyi Yang.

d-allethrin compound

1. Scope of these standards

These standards stipulate the requirements relating to testing methods, marking, labelling, packaging, storing and transport for d-allethrin.

These standards are used for d-allethrin which consists of d-allethrin with related manufacturing impurities.

Note: Please refer to Appendix A for the structural formula, information and other names of d-allethrin.

2. Reference documents

The following documents are essential to the application of these standards. For reference documents which are dated, only the dated versions are applicable to these standards. For reference documents which are not dated, the latest versions (including all amendments) are applicable to these standards.

GB/T 601 Chemical reagent – preparations of standard volumetric solutions

GB/T 1600 Testing method of water in pesticides

GB/T 1604 Regulation concerning acceptance checks for commercial pesticides

GB/T 1605-2001 Sampling method for commodity pesticides

GB 3796 General rule for packing of pesticides

GB/T 6682-2008 Water for analytical laboratory use – specification and test methods

GB/T 8170-2008 Rules of rounding off for numerical values & expression and judgement of limiting values

3. Requirements

3.1 Composition and appearance

The material consists of d-allethrin with related manufacturing impurities. It is a yellowish-brown, oil-like liquid.

3.2 d-allethrin should meet the requirements set out in Table 1.

Table 1 d-allethrin, value of indicators

Item	Value
Allethrin content / % ≥	95.0

Dextrorotatory ratio / % ≥	95.0
Cis/trans isomerism of acid	(20 ± 5) / (80 ± 5)
Acidity (measured by H2SO4) / % ≤	0.3
Water content / % ≤	0.3

4. Testing methods

4.1 General rules

Unless otherwise stated, the reagent and water referred to in these standards are the analytical reagent (AR) and the third grade water described in GB/T 6682-2008.

Unless otherwise stated, the standard volumetric solution used in this test should be prepared and calibrated in accordance with GB/T 601. All results should be rounded and analysed in accordance with 4.3.3 of GB/T 8170-2008.

4.2 Sampling

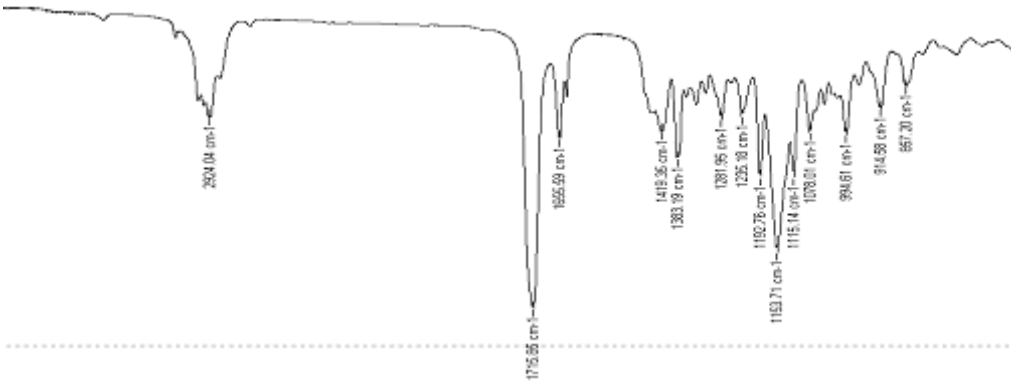
Sampling should be conducted in accordance with the method described under "sampling for commodity compound" in GB/T 1605 – 2001. The number of packages sampled should be determined by the "random rule" and the volume sampled should be no less than 100g.

4.3 Tests

Both tests below are valid. Either test can be chosen to identify the compound. If it is not possible to produce a conclusive result with one test, the other test should also be conducted in order to confirm the result.

Gas chromatography. This test can be carried out together with the allethrin content test. Under the same conditions, the difference between the retention time peaks for the sample and the retention time peaks for the reference standard (allethrin) should not exceed 1.5%.

Infrared spectrometry. In the region of 4000 cm^{-1} ~ 400 cm^{-1}, the absorption spectrums between the sample and the d-allethrin reference standard should be very similar. Please see graph 1 for the infrared spectrum of the d-allethrin reference standard.



Graph 1 Infrared spectrum of d-allethrin reference standard

4.4 Allethrin content test

4.4.1 Method

Dissolve the sample in ethyl acetate; use dibutyl phthalate as the internal standard; use a 30 m x 0.32 mm HP-1 capillary column and flame ionization detector; separate and analyse the sample using gas chromatography.

4.4.2 Reagents and solutions

Allethrin reference standard: known allethrin content, $\omega \geq 98.0\%$;

Dibutyl phthalate;

Ethyl acetate;

Internal standard solution: dissolve 0.7 g of dibutyl phthalate with ethyl acetate in a 100 mL volumetric flask and shake well.

4.4.3 Instruments

Gas chromatograph: with flame ionization detector;

Gas chromatograph data processing machine or software;

Column: 30 m x 0.32 mm (i.d.) quartz capillary column, with HP-1 (100% dimethylpolysiloxane) applied to the inner wall at a thickness of 0.25 μm.

4.4.4 Conditions

Temperature (℃): column 200, inlet 250, detector 250.

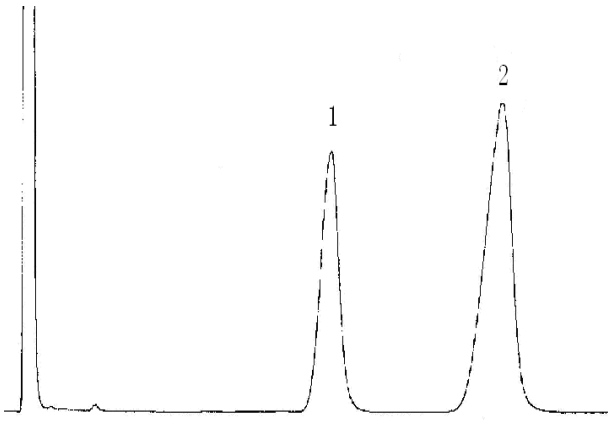
Flow rate (mL/min): carrier gas (N_2) 1.6, hydrogen 30, atmosphere 400;

Split rate: 30:1;

Amount injected: 0.6 μL;

Retention time (min): internal standard 2.9 approximately, allethrin 4.4 approximately;

The above standard parameters can be adjusted when using different instruments in order to achieve the best results. Please see graph 2 for the standard gas chromatograph spectrum of allethrin.



1 – Internal standard;

2 – Allethrin.

Graph 2 Gas chromatograph spectrum of allethrin compound and internal standard

4.4.5 Steps

4.4.5.1 Preparation of reference standard

Add 0.10 ~ 0.12g (accurate to 0.0002 g) of allethrin to a clean, dry 15 mL bottle (with a cap). Use a pipette to add 10 mL of internal standard solution and shake well.

4.4.5.2 Preparation of sample

Add 0.10 ~ 0.12g of allethrin (accurate to 0.0002 g) to a clean, dry 15 mL bottle (with a cap). Use the same pipette as in 4.4.5.1 to add 10 mL of internal standard solution and shake well.

4.4.5.3 Analysis

Under the conditions specified above and when the instrument is stabilised, continuously inject the sample into the chromatograph. The analysis can be carried out when the difference in peak area ratio (allethrin: internal standard) between two injections is below 1.2%. The analysis should be conducted in the following order: reference standard, sample, sample and reference standard.

4.4.6 Calculation

Calculate the average the peak area ratio (allethrin: internal standard) of two injections of the sample; then calculate the average of two injections of reference standard before and after the injection of the sample; the allethrin content in the sample can then be calculated based on formula (1):

$$\omega_1 = \frac{r_2 \times m_1 \times \omega}{r_1 \times m_2} \qquad \text{……...…….(1)}$$

Where:

ω_1 = Mass/presence of allethrin in sample (%)

r_2 = The average peak retention time of the allethrin sample and the internal standard.

r_1 = The average peak retention time of the reference standard and the internal standard.

m_1 = The mass of allethrin in the reference sample (g)

m_2 = The mass of the allethrin test sample (g)

ω = The proportional content of allethrin in the reference standard (%)

4.4.7 Tolerance

The parallel allethrin content readings should have a discrepancy of less than 1.2%. Take the calculated average as the final result.

4.5 Dextro-isomer ratio and the determination of isomer and trans-isomer composition

4.5.1 Overview of the method

After the sample has undergone saponification and acidulation treatment, separate and determine the acidified product using a β DEX-120 coated quartz capillary column, split injection device and flame ionization detector (FID). Then use this reading to calculate the amount of displaced chrysanthemic acid.

4.5.2 Reagents and solutions

Sodium hydroxide methanol solution: ω (NaOH) =10%

Hydrochloric acid: ω(HCI) =10%

Diethyl ether

4.5.3 Instruments

Gas chromatograph (GC): with flame ionization detector (FID);

Capillary column: 30 m × 0.25mm (i.d) fused silica column, with an internal coating of β DEX-120, to a thickness of 0.2μm;

Sample injector apparatus: split silica lined

Conical flask: 100ml

Separating funnel: 60ml

Spherical condenser: 200mm

4.5.4 Operating conditions

Temp (ºC): Column 150; vaporising chamber 250; detection chamber 250;

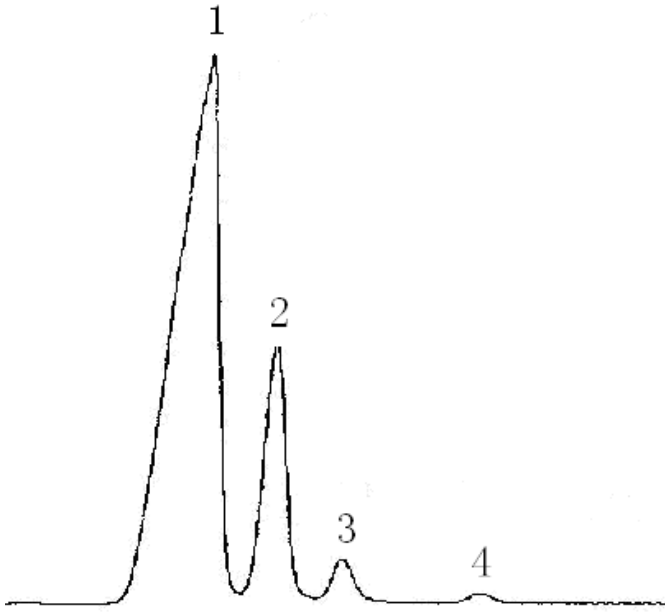
Gas flow volume (mL/min): carrier gas (He) 1.6, Hydrogen 30, Atmosphere 400;

Flow ratio: 30:1;

Sample volume: 0.6 μL;

Retention time (min): 1R, trans; 1R chrysanthemic acid 9.2; 1R,cis; 1R chrysanthemic acid 9.5; 1R, trans; 1S chrysanthemic acid 9.7; 101R, cis; 1S chrysanthemic acid 10.0;

The above guidelines produce the standard reference results. Small adjustments can be made according to the specific requirements of certain instruments in order to achieve the most accurate results. Figure 3 shows a standard chromatograph for dextro-chrysanthemic acid.



1. + *trans* chrysanthemic acid

2. + *cis* chrysanthemic acid

3. – *trans* chrysanthemic acid

4. + *cis* chrysanthemic acid

Chart 3 Chromatograph for dextro-chrysanthemic acid

4.5.5 Method for determination

4.5.5.1 Preparing the sample solution

Take approximately 0.4g of the sample and place in a conical flask. Add 10ml of Sodium Hydroxide methanol solution (10% concentration) and place in a water-bath at 50-60ºC to saponify. Add a further 10ml of water and dissolve, then extract twice using diethyl ether. Use 10ml of diethyl each time. Extract the lower layer twice and then add together. Then add a solution of hydrochloric acid (concentration of 10%) to bring the water layer to pH3-4. At this point add a further 10ml of diethyl ether and extract once again before extracting the upper layer of dextro-chrysanthemic acid which is now ready to use.

4.5.5.2 Determination

Set up the GC according to the directions above, wait for the instrument to stabilise and then add the sample solution.

4.5.6 Calculations

Dextro-isomer composition is calculated using the formula $\acute{\omega}_2$ (2):

$$\omega_2 = \frac{A_1 + A_2}{A_1 + A_2 + A_3 + A_4} \times 100 \quad \text{.....(2)}$$

Where:

A_1 = + *trans* chrysanthemic acid peak retention;

A_2 = + *cis* chrysanthemic acid peak retention;

A_3 = – *trans* chrysanthemic acid peak retention;

A_4 = + *cis* chrysanthemic peak retention.

4.5.7 Determination of acid cis-isomer and trans-isomer composition

The determination of acid cis-isomer and trans-isomer composition and that of the acid 1R isomer can be carried out at the same time.

The composition of cis-isomers and trans-isomers can be calculated using formula *a* (3):

$$a = \frac{\dfrac{A_2 + A_4}{A_1 + A_2 + A_3 + A_4} \times 100}{\dfrac{A_1 + A_3}{A_1 + A_2 + A_3 + A_4} \times 100} \quad \text{.....(3)}$$

Where:

A_1 = + *trans* chrysanthemic acid peak retention;

A_2 = + *cis* chrysanthemic acid peak retention;

A_3 = – *trans* chrysanthemic acid peak retention;

A_4 = + *cis* chrysanthemic peak retention.

Determination of acidity levels

4.6.1 Chemical reagent/solution

Pure ethanol;

Sodium hydroxide titrate solution: c (NaOH) = 0.01 mol/L;

Methyl red: 1g/L ethanol solution;

Bromocresol green: 1g/L ethanol solution;

Compound indicator: Mix together 2ml of methyl red solution and 10ml of bromocresol green solution.

4.6.2 Procedure

Place 2g of a-allethrin (accurate to 0.0002g) in a 250ml laboratory beaker and add 50 ml of pure ethanol and shake until evenly diluted; add 6 drops of compound indicator, and then add sodium hydroxide titrate solution (concentration of 0.01 mol/L) until the solution changes from red to green; carry out a blank determination at the same time.

4.6.3 Calculations

Use the following formula (4) to calculate the acidity of the sample - ω_3:

$$\omega_3 = \frac{c \times (V_1 - V_0) \times M}{1000m} \times 100 \quad \text{.....(4)}$$

Where:

ω_3 =the mass percentage of the sample's acid content expressed as a %:

c =*the concentration of the sodium hydroxide titrate solution (mol/L)*

V_1 = *the amount of titrate consumed during the assay (mL)*

V_0 = *the amount of titrate consumed during the blank assay (mL)*

m = mass of the sample (g)

M = hydrochloric molar mass (g/moL), [M ___ H_2SO_4]=49.04].

4.7 Determination of water content

Using the GB/T1600 Karl Fischer technique facilitates the use of highly precise moisture measurement instruments.

4.8 Testing and required tolerances

Carry out using the GB/T 1604 parameters.

5 Labelling, marking, packaging, transit, storage, safety and certification period

5.1 Labelling, marking and packaging

The labelling, marking and packaging of d-allethrin should conform to the requirements stipulated in general rule GB 3796. It should be contained in plastic coated metal containers, each weighing between 20-50kg. It can be packaged in a different manner according to user's requirements but the packaging must conform to GB 3796.

5.2 Storage and shipping

Containers of d-allethrin should be stored in a suitable dry, ventilated room; during shipping, care must be taken to ensure the containers are protected from moisture and sunlight. The containers should not be shipped together with foodstuffs, seeds or animal feed and should not come into contact with skin or eyes. Take measures to ensure none of the contents are ingested orally or inhaled.

5.3 Safety

D-allethrin is classified as a low-toxicity insecticide. Protective clothing should be worn when using this product and users should wash with soap after handling. This product has no particular and effective antidote. The main form of treatment is thoroughly rinsing off any trace and treating on a case by case basis.

5.4 Effective inspection period

The effective inspection period of d-allethrin is one month. Quality inspections which test for conformity with relevant standards should be carried out within one month of receipt.

Annex A

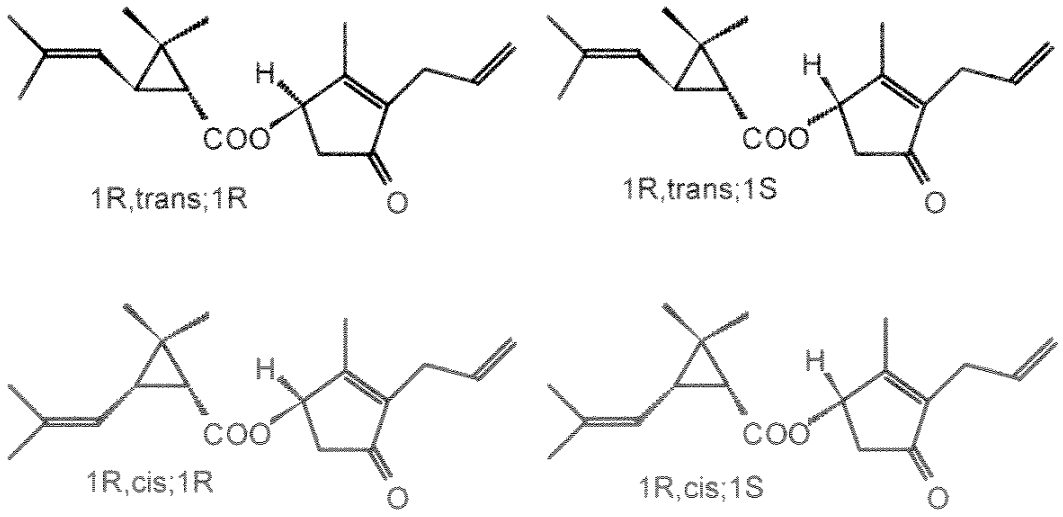
(Informative annex)

Alternative names for d-allethrin, structural formula and basic material statistics

The chemical name, common name, structural formula and basic material statistics of d-allethrin are as follows:

ISO common name:	d-allethrin
CIPAC reference code:	742
CASE registry No:	584-79-2
Chemical name:	(RS)-3-allyl-2-methyl-4-oxocyclopent-2-enyl (1R)-cis, transchrysanthemate

Structural formula:



d-allethrin consists of [1R,trans;1R] + [1R,trans;1S] +[1R,cis;1R] + [1R,cis;1S] in an approximate ratio of 4:4:1:1

Molecular formula:	$C_{19}H_{26}O_3$
Relative molecular mass:	302.41 (according to 2007 international relative atomic mass)
Bioactivity:	Pesticide
Vapour pressure (21.6ºC):	1.65×10^{-4}Pa
Solubility	Not soluble in water. Miscible with most other organic solvents including acetone, dimethylbenzene, chloroform and ethanol.

Stability:	Stable in the presence of weak-mild acidity; easily breaks down in the presence of an alkali; becomes instable if exposed to sunlight.