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On

d-Tetramethrin

Small scale collaborative trial
for
the determination of d-Tetramethrin's content and isomer fraction percentage

Apir 2016

Contents

1. Participants

National Pesticide Quality Control Test Center	Address: No 22 Building, Maizidian Street, Chaoyang District, Beijing, 100125, China
Laprode (Zhejiang) Analysis Co., Ltd	Level 5, West Wing, Building 7, Huaye High-Tech Industrial Park, 1180 Bin'an Road, Binjiang District,Hangzhou, Zhejiang, P.R. China
Nutrichem Laboratory Co., Ltd.	D-1, Dongsheng Science Park, 66 Xixiaokou Road, Haidian District, Beijing 100192, P. R. China

Participants are listed in alphabetical order whereas laboratory numbers are assigned on the basis of the order in which results were submitted.

2. Active ingredient, general information

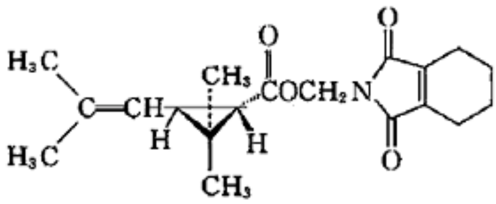
ISO common name: Not available

Other names: d-tetramethrin

Chemical name: (1,3,4,5,6,7-Hexahydro-1,3-dioxo-2H-isoindol-2-yl)methyl (1R-trans)-2,2-dimethyl-3-(2-methylprop-1-enyl)cyclopropanecarboxylate

CAS No. 1166-46-7

Structure



Molecular mass: 331.42

Molecular Formula: $C_{19}H_{25}NO_4$

Note: d-tetramethrin is a mixture of the isomers (1R-*trans*, *R*), (1R-*trans*, *S*), (1R-*cis*, *R*) and (1R-*cis*, *S*) of tetramethrin in an approximate ratio of 4:4:1:1. In practice the trans isomer range is 75-85 % and the cis isomer range is 15-25 %

3. Samples

Three technical materials were sent to the participants, these are listed below. Participants in the trial also received an analytical standard with a purity of 99.9%.

1. Technical material A
2. Technical material B
3. Technical material C

4. Method

4.1 Scope

Determine of the active ingredient content and isomer ratio of the enantiomers of d-tetramethrin in technical grade active ingredients.

4.2 Principle

d-tetramethrin is determined by Gas chromatograph with internal standardization and the isomer ratio of the enantiomers is determined by normal phase High performance liquid chromatograph.

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4.3 Procedure

See attached method for details.

Fig 1a d-Tetramethrin Technical material.

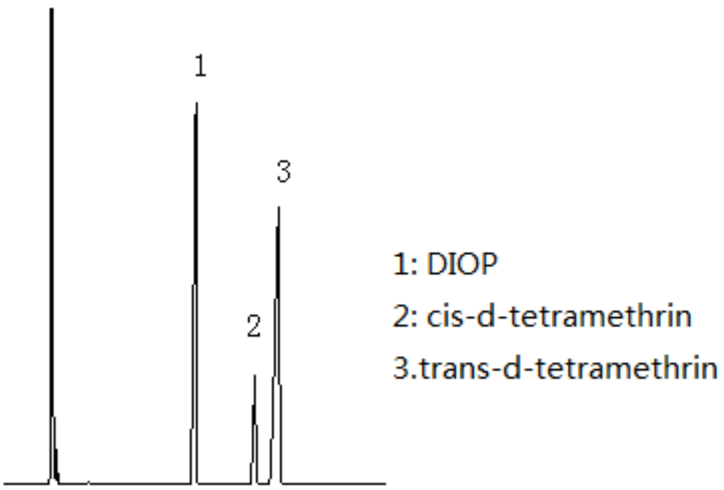
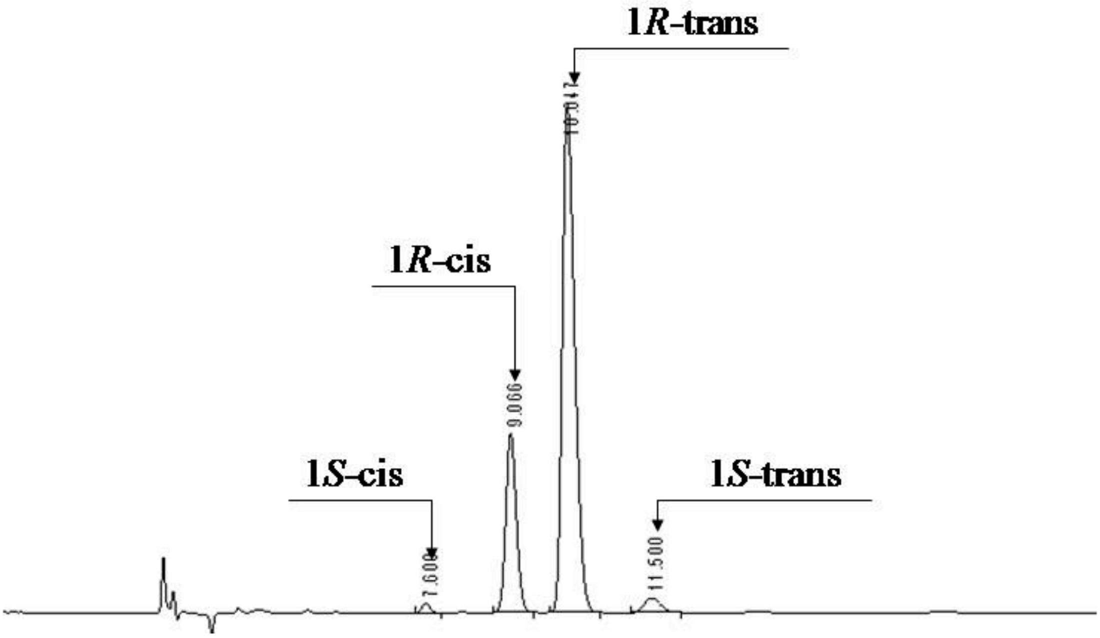


Fig 1 b Enantiomeric purity of d-Tetramethrin



5. Comments from the Participants.

The following comments were received from the study participants.

Laboratory 1 No comments

Laboratory 2 No comments

Laboratory 3 No comments

6. Evaluation and Discussion

6.1 Screening for valid data

The statistical evaluation was carried out according to the guidelines in the CIPAC document "Guideline for CIPAC collaborative studies Procedure for Assessment of Performance of Analytical Methods. The data was tested for outliers firstly using Cochran's test on the within laboratory variance and then using Grubbs test on laboratory means to test the between laboratory variance. The tests were carried out at the alpha level of 0.01 for outliers and 0.05 for stragglers.

6.2 Determination of active ingredient content.

The results obtained for laboratories 1 – 3 are given in Tables 1-3 and Fig's 2 – 4.

All technical materials meet the Horowitz criteria.

Data

Table 1: Test Data for All Materials-GC(d-teramethrin(%))

Material	Test Number	Laboratory 1	Laboratory 2	Laboratory 3
A	Day 1	945.7/943.4	943.4/949.1	940.0/943.3
	Day 2	946.2/946.2	938.8/938.4	941.9/942.7
B	Day 1	947.2/946.1	943.9/947.6	943.4/945.7
	Day 2	945.6/949.4	945.4/949.4	946.2/944.9
C	Day 1	947.7/943.8	937.1/946.1	941.9/945.2
	Day 2	943.7/952.0	948.9/951.1	940.1/942.2

Table 1.1. Initial Preparation of Test Result Data for Material A

Laboratory Number	Test Results, n=4					
	Day 1	Day 2	Yi	$(Yi)^2$	Si	$(Si)^2$
1	945.7	946.2	945.38	893743.34	1.34	1.80
	943.4	946.2				
2	943.4	938.8	942.43	888174.30	4.99	24.9
	949.1	938.4				
3	940.0	941.9	941.98	887326.32	1.44	2.06
	943.3	942.7				

Cochran's test (p=3,n=4)

$C=Si^2max/S3$ = 0.865 > 0.798 (p=3,n=4, 5%),---- a Cochrans' straggler

Grubb's test (p=95%,n=3)

Lower = ［Y –Yi(min)］/S = 0.49 < 1.15 (p=95%,n=3)

Upper = ［Yi(max)-Y］/S= 0.82<1.15 (p=95%,n=3)

Table 1.2. Initial Preparation of Test Result Data for Material B

Laboratory Number	Test Results, n=4					
	Day 1	Day 2	Yi	$(Yi)^2$	Si	$(Si)^2$
1	947.2	945.6	947.08	896960.53	1.69	2.85
	946.1	949.4				
2	943.9	945.4	946.58	896013.70	2.42	5.86
	947.6	949.4				
3	943.4	946.2	945.05	893119.50	1.22	1.50
	945.7	944.9				

Cochran's test (p=3,n=4)

$C=Si^2max/S3$ = 0.57 < 0.798 (p=3,n=4, 5%)

Grubb's test (p=95%,n=3)

Lower = ［Y –Yi(min)］/S = 0.67 < 1.15 (p=95%,n=3)

Upper = ［Yi(max)-Y］/S=0.47 <1.15 (p=95%,n=3)

Table 1.3. Initial Preparation of Test Result Data for Material C

Laboratory Number	Test Results, n=4					
	Day 1	Day 2	Yi	$(Yi)^2$	Si	$(Si)^2$

1	947.7	943.8	946.80	896430.24	3.94	15.49
	943.7	952.0				
2	937.1	948.9	945.80	894537.64	6.15	37.83
	946.1	951.1				
3	941.9	940.1	942.35	888023.52	2.11	4.47
	945.2	942.2				

Cochran's test (p=3, n=4)
C=Si^2max/S3 = 0.655 ＜ 0.798 (p=3,n=4, 5%)
Grubb's test (p=95%,n=3)
Lower = ［Y –Yi(min)］/S = 0.646 ＜ 1.15 (p=95%,n=3)
Upper = ［Yi(max)-Y］/S=0.447 ＜1.15 (p=95%,n=3)

Table 2: Test Data for Trans isomer fraction percentage-LC (trans isomer (%))

Material	A	B	C
Laboratory 1	80.59, 80.43	80.31, 80.34	80.70, 80.07
Mean	**80.51**	**80.32**	**80.38**
Laboratory 2	80.13, 81.91	80.86, 80.19	79.88, 82.79
Mean	**81.02**	**80.52**	**81.33**
Laboratory 3	80.05, 80.10	80.12, 80.08	79.91, 79.90
Mean	**80.07**	**80.10**	**79.90**
Si	**0.47**	**0.21**	**0.73**
Yi	**80.53**	**80.31**	**80.54**

Grubb's test (p=95%,n=6) For Material A
Lower = ［Y –Yi(min)］/S = 0.98 < 1.15 (p=95%,n=3)
Upper = ［Yi(max)-Y］/S= 1.04 < 1.15 (p=95%,n=3)

Grubb's test (p=95%,n=6) For Material B
Lower = ［Y –Yi(min)］/S = 1.00 < 1.15 (p=95%,n=3)
Upper = ［Yi(max)-Y］/S= 1.00 < 1.15 (p=95%,n=3)

Grubb's test (p=95%,n=6) For Material C
Lower = ［Y –Yi(min)］/S = 0.88 < 1.15 (p=95%,n=3)
Upper = ［Yi(max)-Y］/S= 1.08 < 1.15 (p=99%,n=3)

Table 3: Test Data for 1R isomer fraction percentage –LC (**1R isomer %**)

Material	A	B	C
Laboratory 1	96.42, 96.06	96.36, 96.34	96.35, 96.20
Mean	**96.24**	**96.35**	**96.27**
Laboratory 2	97.15, 96.87	96.95, 95.78	97.03, 96.89
Mean	**97.01**	**96.36**	**96.96**
Laboratory 3	96.48, 96.67	96.54, 96.58	96.60, 96.74
Mean	**96.57**	**96.56**	**96.67**
Si	**0.39**	**0.12**	**0.35**
Yi	**96.61**	**96.43**	**96.63**

Grubb's test (p=95%,n=6) For Material A

Lower = ［Y –Yi(min)］/S = 0.95 ＜ 1.15 (p=95%,n=3)
Upper = ［Yi(max)-Y］/S= 1.02 <1.15 (p=95%,n=3)

Grubb's test (p=95%,n=6) For Material B
Lower = ［Y –Yi(min)］/S = 0.67 ＜ 1.15 (p=95%,n=3)
Upper = ［Yi(max)-Y］/S= 1.08 <1.15 (p=95%,n=3)

Grubb's test (p=95%,n=6) For Material C
Lower = ［Y –Yi(min)］/S = 1.03＜ 1.15 (p=95%,n=3)
Upper = ［Yi(max)-Y］/S= 0.94 <1.15 (p=95%,n=3)

Fig. 2 Summary of Statistic Evaluation of d-teramethrin Small Scale Collaborative Study

	Sample A	**Sample B**	**Sample C**
X(g/Kg)	**943.3**	**946.2**	**945.0**
L	**3**	**3**	**3**
S_r	**3.10**	**1.84**	**4.39**
S_L	**1.00**	**0.52**	**0.79**
S_R	**3.26**	**1.91**	**4.46**
RSD_r	**0.33**	**0.19**	**0.46**
RSD_R	**0.35**	**0.20**	**0.47**
r	**8.68**	**5.15**	**12.29**
R	**9.13**	**5.35**	**12.49**
RSD_R(Hor)	**2.002**	**2.002**	**2.002**

Where:

x = average
L = number of laboratories
s_r = repeatability standard deviation
s_L = "pure" between laboratory standard variation
s_R = reproducibility standard deviation = $\sqrt{(s_r^2 + s_L^2)}$
RSD_r = repeatability relative standard deviation (s_r/x*100)
RSD_R = reproducibility relative standard deviation (s_R/x*100)
r = repeatability (s_r*2.8)
R = reproducibility (s_R*2.8)
RSD_R(Hor) = Horwitz value calculated from: $2^{(1 - 0.5\log c)}$
where c = the concentration of the analyte as a decimal fraction

NB Where appropriate values should be given in units of g/kg !

7. Conclusion

Three laboratories received three samples for this collaborative trial and all of these laboratories submitted results. After the initial evaluation the calculated Reproducibility Standard Deviation (RSD_R) meets the Horowitz criteria for both Technical materials. Although one straggler occurred using Cochrans' Test (TC, Laboratory 2), it cannot prove the error of the method, and we need more laboratories to validate the method.

On the basis of these results, we propose proceeding to a large scale collaborative study (a full scale trial).