

5310/R

**Methoprene
414**

Large Scale Collaborative Study for the
Determination of the Ratio of s-methoprene in TC

Report to CIPAC By

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Method developed by
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June 2023

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1. Participants

Large scale collaborative study for the determination of s-methoprene in TC by Normal HPLC was organized by Shenyang SYRICAL Testing Co., Ltd. 12 laboratories responded to participate in the collaborative trials via email. Among them, 9 laboratories completed the experiment and provided test data. One laboratory did not receive the samples, and two laboratories failed to provide the results and didn't report any reason.

9 Participating laboratories are listed in random order in the table below whereas lab numbers in the result tables were assigned, chronologically, based upon receipt of results.

No. Contact	Lab	Country
1 Vanessa Lecocq	Walloon Agricultural Research Centre (CRA-W)	Beigium
2 Wenzhuo Wang	National Center for Pesticide Quality Supervision and Inspection (Beijing) Institute for the Control of Agrochemicals Ministry of Agriculture and Rural Affairs, P. R. China	China
3 Javier García-Hierro Navas	Plant Protection Products Formulations Department Agri-Food Arbitration Laboratory Ministry of Agriculture, Fisheries and Food	Spain
4 Dr. Christian Mink	Analytical Development and Product Chemistry Syngenta Crop Protection AG	Switzerland
5 Hou Chunqing	SYRICIT	China
6 Aysel TAKKABULAN	Republic Of Turkiye Ministry of Agriculture And Forestry Pesticide Laboratory Quality Control Department Chemical Analysis Unit	Turkey
7 Zhiyu HE	Guizhou Jiande Technology Co.,Ltd.	China
8 Qu Tingsi	Vaster Testing Technology Co.,Ltd.	China
9 Dr. Jim Garvey	Department of Agriculture, Food and The Marine	Ireland

2. Active Ingredient: General Information

CAS Number: 65733-16-6

IUPAC name: iso-propyl (E, E)-(S)-11-methoxy-3,7,11-trimethyldodeca-2,4-dienoate

Chemical name: isopropyl (2E, 4E, 7S)-11-methoxy-3,7,11-trimethyl-2,4-dodecadienoate

Empirical formula: C₁₉H₃₄O₃

RMM: 310.5

B.p.: 279.9 °C at atmospheric pressure (97.2 kPa)

V.p.: 0.623 mPa (20 °C), 1.08 mPa (25 °C) (Knudsen effusion)

S.g./density: 0.924 (20 °C)

Description: a pale yellow liquid, with a fruity odour

Solubility: In water 6.85 ppm (20 °C).

Soluble in most organic solvents, in acetone and hexane >500, methanol >450 (all in g/l, 20±1 °C).

Stability: Stable in water, organic solvents, and in the presence of aqueous acids and alkalis. Sensitive to uv light.

Specific rotation [α] 20D +5.64°

3. Samples

3 batches of test samples and one batch of stereoisomer control standard were sent to the participants:

s-methoprene TC-1 Batch No. SCL20220260
s-methoprene TC-2 Batch No. SCL20220262
s-methoprene TC-3 Batch No. SCL20220265
methoprene stereoisomer Batch No: 20210324

4. Method

4.1 Scope

Determination of the ratio of s-methoprene to the sum of s-methoprene + R-methoprene in S-methoprene TC.

4.2 Principle

The sample is dissolved in n-hexane and the ratio of S-methoprene is determined by normal phase high performance liquid chromatography on a chiralpak AD-H silica column with detection at 254 nm.

4.3 Procedure

Each sample was analyzed using four independent determinations. The samples were analyzed on two different days, each day involving duplicate injections of duplicate weights. Both test and control solutions were freshly prepared on each day. Repeat the measurement of control sample solution (solution R) after a series of 4 sample runs and at the end of the sequence.

5. Remarks of the Participants

Analytical condition

Lab	Column	FR (mL/min)	CT (°C)	WL (nm)	Inj. vol. (µL)	Mobile Phase
1	Phenomenex Lux Amylose-1, 5 µm, 250 x 4.6 mm i.d.	0.5	25	254.8	10	n-hexane/2-propanol, 100/0.5 (v/v)
2	250 × 4.6 mm (i.d.) packed with CHIRALPAK AD-H SILICA	0.5	25	254	10	n-hexane/2-propanol, 100/0.5 (v/v)
3	250 × 4.6 mm (i.d.) packed with CHIRALPAK AD-H SILICA	0.5	25	254	10	n-hexane/2-propanol, 100/0.5 (v/v)
4	250 × 4.6 mm (i.d.) packed with CHIRALPAK AD-H SILICA	0.5	25	254	10	n-hexane/2-propanol, 100/0.5 (v/v)
5	CHIRALCEL AD-H, 5 µm, 250 x 4.6 mm i.d.	0.5	25	254	10	n-hexane/2-propanol, 100/0.5 (v/v)
6	250 × 4.6 mm (i.d.) packed with CHIRALPAK AD-H SILICA	0.5	25	254	10	n-hexane/2-propanol, 100/0.5 (v/v)
7	250 × 4.6 mm (i.d.) packed with CHIRALPAK AD-H SILICA	0.5	25	254	10	n-hexane/2-propanol, 100/0.5 (v/v)
8	250 × 4.6 mm (i.d.) packed with CHIRALPAK AD-H SILICA	0.5	25	254	10	n-hexane/2-propanol, 100/0.5 (v/v)
9						

Remarks

1 Other column was used with the same separation

Phenomenex Lux Amylose-1, 5 µm, 250 x 4.6 mm i.d. This chromatogram shows that a column Phenomenex Lux Amylose-1, 5 µm, 250 x 4.6 mm i.d. can also be used and provides a good separation and similar retention times of the stereoisomers

2 Note: We have also determined the content of S-Methoprene TC using the CIPAC 414/TC/(M), if these data are also needed, please contact us to provide.

5 Other column was used with the same separation, CHIRALCEL AD-H, 5 µm, 250 x 4.6 mm i.d.

6 The method submitted was applied exactly. In the R solution, while the stereoisomers were separated as in the representative chromatogram, 2 peaks were observed in the technical material samples, unlike the representative chromatogram. In subsequent injections, the retention time for S-Methoprene was about 9.5 and 10.7

9 I could not get resolution of the peaks – both cis isomers were co-eluting, and both trans isomers were co-eluting. The Retention times were drifting throughout the run.

6. Evaluation and Discussion

6.1 Data Review

The data obtained from each laboratory was visually reviewed to determine if there were any significant chromatography differences, from what was expected, which might affect the analytical results.

The report below contains statistical evaluations from 9 participating laboratories.

6.2 Statistical results

The statistical evaluation of the data was accomplished following the “Guidelines for CIPAC Collaborative Study Procedures for Assessment of Performance of Analytical Methods”, according to DIN ISO 5725. The testing for outliers/stragglers was not performed.

The Horwitz Ratio (HorRat) was found within the range of 0.47-0.55

All results are given in %.

Table 1 Results of TC1

	Day 1	Day 2	Mean	STD		
Lab 1	965.29	965.32	963.98	962.69	964.32	1.2521
Lab 2	968.70	969.67	970.66	969.98	969.75	0.8144
Lab 3	965.15	965.05	965.23	964.91	965.08	0.1422
Lab 4	966.90	967.31	966.88	966.97	967.01	0.1980
Lab 5	952.19	953.31	953.57	958.91	954.49	3.0065
Lab 6	980.82	982.63	982.24	982.34	982.01	0.8090
Lab 7	970.28	972.37	969.77	969.92	970.58	1.2121
Lab 8	969.59	968.44	968.65	968.29	968.74	0.5810
Lab 9	984.23	984.09	985.76	985.68	984.94	0.9035

Table 2 Results of TC 2

	Day 1	Day 2	Mean	STD		
Lab 1	965.21	964.49	964.92	964.27	964.72	0.4210
Lab 2	951.62	953.42	963.25	964.71	958.25	6.6837
Lab 3	964.20	964.31	965.44	965.23	964.80	0.6299
Lab 4	966.83	966.93	965.87	966.78	966.60	0.4925
Lab 5	953.04	952.92	952.65	953.78	953.10	0.4809
Lab 6	982.35	982.38	982.15	982.22	982.28	0.1102
Lab 7	971.10	972.50	969.76	970.32	970.92	1.1878
Lab 8	968.71	968.77	956.28	968.10	965.47	6.1290
Lab 9	984.06	984.38	986.38	987.16	985.50	1.5131

Table 3 Results of TC 3

	Day 1	Day 2	Mean	STD
Lab 1	964.91	964.91	963.60	961.68
Lab 2	955.78	969.11	957.71	953.56
Lab 3	963.51	963.68	965.29	966.54
Lab 4	967.19	966.89	966.29	966.41
Lab 5	956.96	953.09	956.27	956.89
Lab 6	982.41	982.47	982.26	982.24
Lab 7	971.56	971.09	969.35	969.90
Lab 8	968.65	968.56	968.53	968.44
Lab 9	986.02	986.05	987.66	988.32

Table 4 Mean Values of 3 labs

	s-methproene ratio TC-1	s-methproene ratio TC-2	s-methproene ratio TC-3
Lab 1	964.32	964.72	963.77
Lab 2	969.75	958.25	959.04
Lab 3	965.08	964.80	964.76
Lab 4	967.01	966.60	966.70
Lab 5	954.49	953.10	955.80
Lab 6	982.01	982.28	982.34
Lab 7	970.58	970.92	970.47
Lab 8	968.74	965.47	968.55
Lab 9	984.9	985.5	984.9

Table 5 Summary of the statistical evaluation

	s-methproene ratio TC-1	s-methproene ratio TC-2	s-methproene ratio TC-3
x_m [g/kg]	969.66	967.96	968.49
x_m [%]	96.966	96.796	96.849
L	9	9	9
S_r	1.2740	3.1091	2.5331
S_R	9.2451	10.7407	9.9664
RSD_R	0.9534	1.1096	1.0291
$RSD_{R(Hor)}$	2.0093	2.0098	2.0097
HorRat	0.4745	0.5521	0.5121

x_m = total mean value

L = number of laboratories

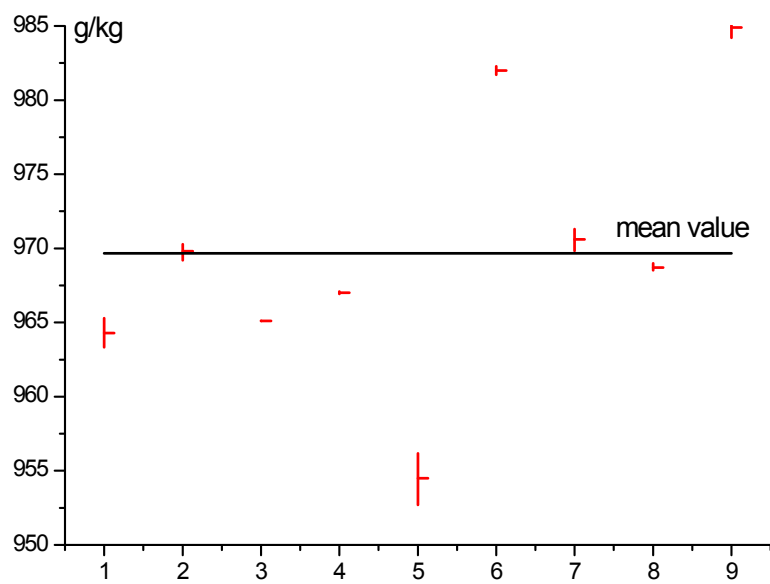
s_r = repeatability standard deviation

s_R = reproducibility standard deviation

RSD_R = relative standard deviation of reproducibility

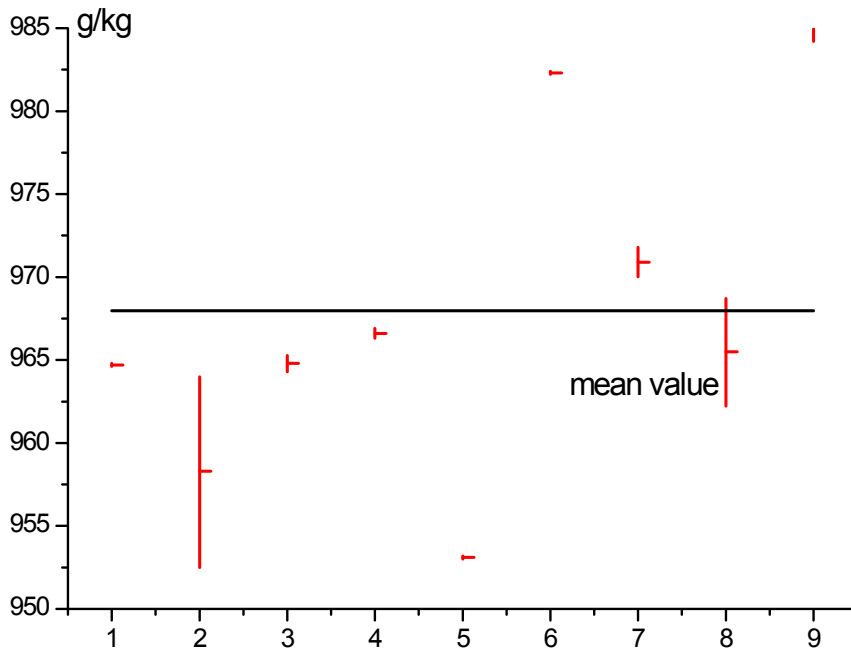
$RSD_{R(Hor)}$ = Horwitz Value according to Horwitz equation

HorRat = Horwitz Ratio ($RSD_R / RSD_{R(Hor)}$)



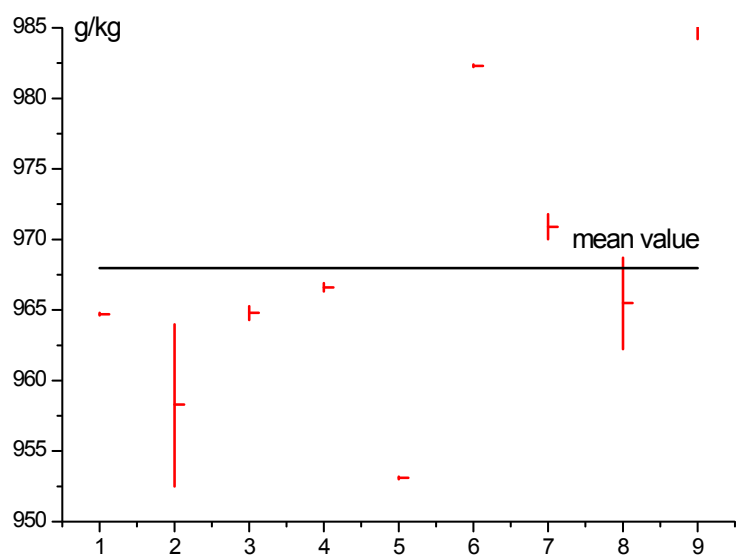
Mean value: 96.966%
 S_r : 1.2740
 S_R : 9.2451
 RSD_R : 0.9534
 $RSD_{R(Hor)}$: 2.0093
 HorRat: 0.4745

Fig. 2 TC- 2



Mean value: 96.796%
 Sr: 3.1091
 S_R : 10.7407
 RSD_R : 1.1096
 $RSD_{R(Hor)}$: 2.0098
 HorRat: 0.5521

Fig. 3 TC- 3



Mean value: 96.849
 Sr: 2.5331
 S_R : 9.9664
 RSD_R : 1.0291
 $RSDR$ (Hor) : 2.0097
 HorRat: 0.5121

7. Conclusions

The data presented in the statistical summary show that this method led to HorRat values falling within the range of 0.3-1. The method could be accepted as CIPAC provisional method.