

Propineb

Collaborative Study

Small Scale Collaborative Study for the
Determination of Propineb TC and WP formulation by HPLC

Report to CIPAC

by

LIMIN CHEMICAL CO., LTD.

Economic Development Zone, Xinyi, Jiangsu, China

Method developed by Jiangsu Limin

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1. Participants

Small Scale Collaborative Study for the determination of propineb TC and WP formulation by HPLC was organized by Limin Chemical Co., Ltd., and participated by 5 labs. All of the 5 laboratories provided their results, which are presented in the following sections.

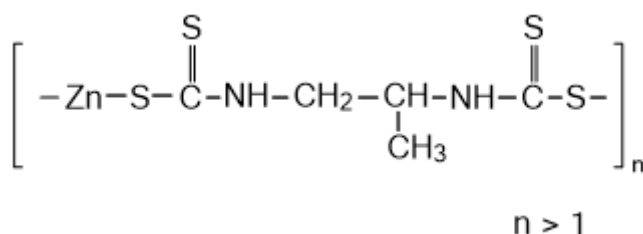
Chronologically, based upon receipt of results.

Contact	Lab
Haisheng Miao	Zhejiang KBchem Testing Co., Ltd. Building 3, No. 1233, Quyuan Road, Fuxi Sub-district, Deqing Country, Huzhou City, Zhejiang, China, 313200
Tang Huimin	Jiangsu Agricultural Product Quality Inspection and Testing Center 124 Caochangmen Dajie, Nanjing City, Jiangsu Province, China
Mei Baogui	Pesticides Test Laboratory of Shenyang Research No.8, Shenliao East Road, Tie xi District, Shenyang 110021, China
Jing Gao	Nutrichem Laboratory Co., Ltd No. 27, Life Science Park Road, Changping Dist., Beijing 102206, P. R. China
Xu Mei	Limin Chemical Co., Ltd. Economic Development Zone, Xinyi Jiangsu, China

2. Active Ingredient: General Information

ISO common name: Propineb

CAS-No.: 12071-83-9



Structure:

Molecular mass: 289.8 g/mol

Empirical formula: $(\text{C}_5\text{H}_8\text{N}_2\text{S}_4\text{Zn})_x$

Activity: fungicide

3. Samples

Five test samples and Propineb analytical standard were sent to the participants:

1. Propineb tech. sample (TC-1) (batch No. 202003001)
 2. Propineb tech. sample (TC-2) (batch No. 202003002)
 3. Propineb WP sample (WP-1) (batch No. 202003003)
 4. Propineb WP sample (WP-2) (batch No. 202003004)
 5. Propineb WP sample (WP-3) (batch No. 202003005)
- Propineb, reference standard (purity 90.0 %w/w)

4. Method

4.1 Scope

The determination of Propineb active ingredient content in technical grade material (TC) and WP formulation.

4.2 Principle

Propineb is determined by reversed phase high performance liquid chromatography using UV detection at 280 nm and external standardization.

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 reference solutions were freshly prepared on each day. The four injections of each test solution were bracketed by double injections of the calibration solution. The average response factor, used to calculate the amount of Propineb in the test solution, was calculated using the injection before and after the test injections.

5. Remarks of the Participants

Lab	Instrument	Column	Flow Rate	Column Temp. °C	Wavelength	Injection Volume	Mobile phase (V/V)
1	Agilent 1260- II	Agilent Extent C18 (4.6×150mm, 5µm)	1.0	20	280	5	Solution A- Methanol =65:35 (V/V)
2	Agilent 1260- II	Agilent Extent C18 (4.6×150mm, 5µm)	1.0	20	280	5	Solution A- Methanol =65:35 (V/V)
3	Agilent 1260- II	Agilent Extent C18 (4.6×150mm, 5µm)	1.0	20	280	5	Solution A- Methanol =65:35 (V/V)

4	Agilent 1260- II	Agilent Extent C18 (4.6×150mm, 5µm)	1.0	20	280	5	Solution A-Methanol =65:35 (V/V)
5	Agilent 1260- II	Agilent Extent C18 (4.6×150mm, 5µm)	1.0	20	280	5	Solution A-Methanol =65:35 (V/V)

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.

In summary it can be stated that the method deviations, noted by the participants, were deemed not to affect the analytical results significantly and therefore all data sets were included within the statistical assessment.

Therefore, the report below contains statistical evaluations with the full set of 5 participating laboratories.

6.2 Determination of Propineb

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 of the laboratory mean values were performed according to Grubbs test on a 1%/5% significance level, respectively.

In the tables 1-3 and figures 1-5, respectively, the full set of all laboratories (5 participants) are reported. No outliers and stragglers have been found. The Horwitz Ratio (HorRat) was found within the desired range (≥ 0.3 but ≤ 1.0).

Determination of Propineb –5 labs

All results are given in g/kg

Table 1 Results

	Propineb TC-1		Propineb TC-2		Propineb WP-1		Propineb WP-2		Propineb WP-3	
	Day 1	Day 2	Day 1	Day 2	Day 1	Day 2	Day 1	Day 2	Day 1	Day 2
Lab 1	895.07	894.46	893.48	887.14	696.05	699.57	695.95	701.74	693.09	696.57
Lab 2	893.71	895.04	893.72	892.95	706.98	700.64	705.89	697.84	706.07	699.65
Lab 3	901.41	899.07	900.27	894.98	706.38	707.42	711.89	713.86	710.80	710.17
Lab 4	900.66	901.17	902.00	902.78	711.07	708.88	710.30	707.53	709.54	709.00
Lab 5	899.80	901.83	898.31	900.82	707.40	704.19	705.30	706.26	704.12	706.26

Table 2 Mean values

	Propineb TC-1	Propineb TC-2	Propineb WP-1	Propineb WP-2	Propineb WP-3
Lab 1	894.77	890.31	697.81	698.85	694.83
Lab 2	894.38	893.34	703.81	701.87	702.86
Lab 3	900.24	897.63	706.90	712.88	710.49
Lab 4	900.92	902.39	709.98	708.92	709.27
Lab 5	900.82	899.57	705.80	705.78	705.19

Table 3 Summary of the statistical evaluation

	Propineb TC-1	Propineb TC-2	Propineb WP-1	Propineb WP-2	Propineb WP-3
xm [g/kg]	898.2	896.6	704.9	705.7	704.5
xm [% w/w]	89.82	89.66	70.49	70.57	70.45
L	5	5	5	5	5
Sr	2.45	3.17	3.48	3.19	2.88
SR	3.96	5.56	5.44	6.21	6.71
r	6.94	8.96	9.85	9.03	8.15
R	11.10	15.74	15.39	17.56	18.99
RSDR	0.44	0.62	0.77	0.88	0.95
RSDR (Hor)	2.03	2.03	2.11	2.11	2.11
HorRat	0.217	0.305	0.366	0.417	0.452

x_m = total mean value

L = number of laboratories

s_r = repeatability standard deviation

s_R = reproducibility standard deviation

r = repeatability limit

R = reproducibility limit

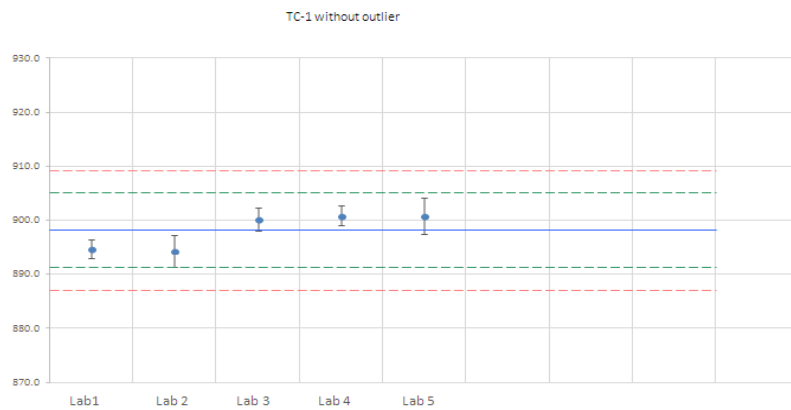
RSD_R = relative standard deviation of reproducibility

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

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

Full set of 5 participants:

Fig. 1 Propineb tech. sample 1



Mean value: 898.2 g/kg

S_r : 2.45

S_R : 3.96

RSD_R : 0.44

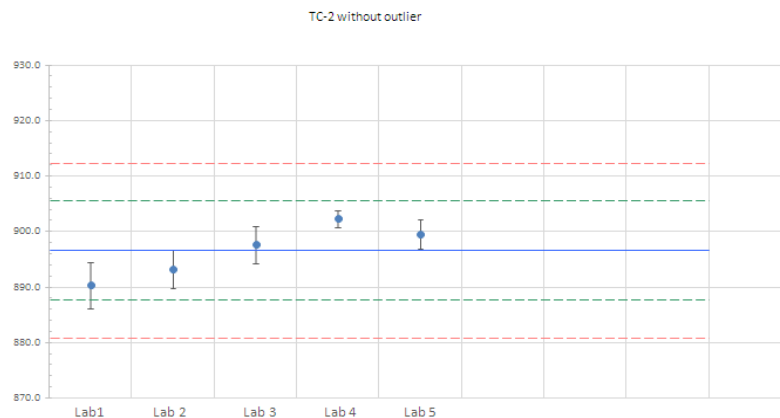
$RSD_{R(Hor)}$: 2.03

HorRat: 0.217

Outlier (Grubbs): none

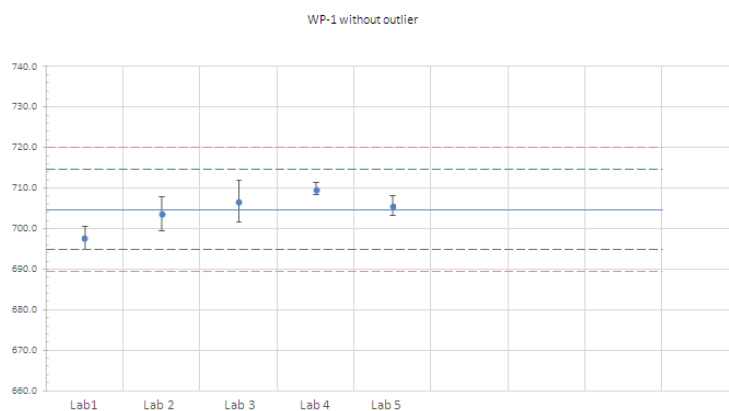
Straggler (Grubbs): none

Fig. 2 Propineb tech. sample 2



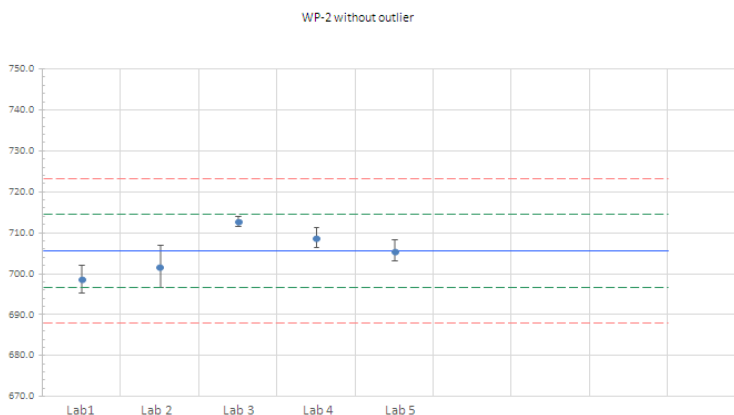
Mean value: 896.6 g/kg
 S_r : 3.17
 S_R : 5.56
 RSD_R : 0.62
 RSD_R (Hor): 2.03
 HorRat: 0.305
 Outlier (Grubbs): none
 Straggler (Grubbs): none

Fig. 3 Propineb WP sample 1



Mean value: 704.9 g/kg
 S_r : 3.48
 S_R : 5.44
 RSD_R : 0.77
 RSD_R (Hor): 2.11
 HorRat: 0.366
 Outlier (Grubbs): none
 Straggler (Grubbs): none

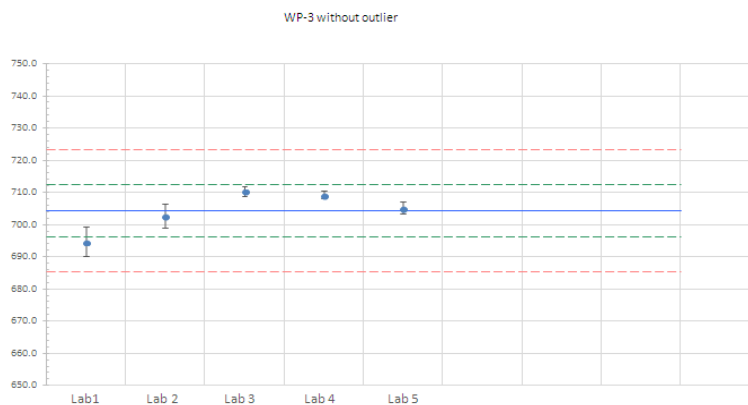
Fig. 4 Propineb WP sample 2



Mean value: 705.7 g/kg
 S_r : 3.19

S_R : 6.21
 RSD_R : 0.88
 $RSD_{R(Hor)}$: 2.11
HorRat: 0.417
Outlier (Grubbs): none
Straggler (Grubbs): none

Fig. 5 Propineb WP sample 3



Mean value: 704.5 g/kg
 S_r : 2.88
 S_R : 6.71
 RSD_R : 0.95
 $RSD_{R(Hor)}$: 2.11
HorRat: 0.452
Outlier (Grubbs): none
Straggler (Grubbs): none

7. Conclusions

A total of 5 laboratories have participated in the small scale collaborative study.

The data presented in the statistical summary show that this method led to HorRat values all within the required range. That is evidence for the fact that the present HPLC method is acceptable and suitable to produce reproducible results.

Recommends for performing large-scale collaborative trials.