

# **221 CHLORPYRIFOS**

## **Collaborative Study**

Full Scale Collaborative Study for the  
Determination of Chlorpyrifos in TC and EC formulation by HPLC

Report to CIPAC

by

Shenyang SYRICI Testing Co., Ltd.

No.8, Shenliao East Road,

Tiexi District Shenyang 110021, P.R. China

May 2021

## **Content**

|  |          |
|--|----------|
| <b>1. PARTICIPANTS</b>                           |          |
| <b>2. ACTIVE INGREDIENT: GENERAL INFORMATION</b> | <b>5</b> |
| <b>3. SAMPLES</b>                                | <b>6</b> |
| <b>4. METHOD</b>                                 | <b>6</b> |
| 4.1 Scope  | 6        |
| 4.2 Principle                                    | 6        |
| 4.3 Procedure                                    | 6        |
| <b>5. REMARKS OF THE PARTICIPANTS</b>            | <b>7</b> |
| <b>6. EVALUATION AND DISCUSSION</b>              | <b>9</b> |
| 6.1 Data Review                                  | 9        |
| 6.2 Determination of Chlorpyrifos                | 9        |
| <b>7. CONCLUSIONS</b>                            |          |

## 1. Participants

In September 2020, Information Sheet No. 327 was sent out by the CIPAC Secretary inviting members to participate in a large-scale collaborative study on the determination of Chlorpyrifos in TC and EC formulation by HPLC. 20 laboratories participated in the trial.

By the end of March 2021, all of the 20 selected laboratories provided their results. One participant provided results by Gas Chromatography instead of HPLC. Therefore, the results of the rest 19 participants are presented in the following sections.

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

| Contact                  | Lab   |
|--------------------------|---|
| Cornel Grecu             | Alchimex SA - Quality Control Lab<br>Bucharest-1<br>Alexandru Constantinescu nr. 63, Romania  |
| Huang Liang              | Anhui Fengle Agrochemical Co., Ltd.<br>Hefei Circular Economy Demonstration Park, Feidong County, Hefei City,<br>Anhui Province 231600, China |
| Liu Lihong               | Analysis Center of Lier Chemical Co., Ltd<br>Lier Chemical Co., Ltd Add.<br>Economic and Technical Development Zone, Mianyang Sichuan, China  |
| Hien Nguyen T            | Bioytrics Vietnam Co., Ltd. Lab<br>No. 15B, Alley 1, Lane 34, Au Co str.,<br>Tay Ho dist., Ha Noi, Vietnam                                    |
| Dr. Michael<br>Haustein  | Currenta GmbH & Co. OHG - Thio Labor (DOR)<br>41538 Dormagen   Gebäude A559, BÜRO 11,5m<br>Germany  |
| Ms.Woramon<br>Suriyachan | Department of Medical Sciences (DMSc),<br>Bureau of Cosmetics and Hazardous Substances<br>Tivanon rd. , Muang, Nonthaburi<br>11000            |
| Mr. He Zhiyu             | Guizhou JAD technology co., Ltd.<br>Baijin road No.3491, Baiyun district, Guiyang, P. R. China  |
| Leonardo Bravo           | Instituto Colombiano Agropecuario - ICA<br>Laboratorio Nacional de Insumos Agrícolas - LANIA. C.I Tibaitata,<br>Km 14 Vía Bogotá – Mosquera   |
| Dr Claudia Vinke         | Labor für Formulierungschemie<br>Messeweg 11/12<br>D-38104 Braunschweig, Germany  |

|                     |   |
|---------------------|---|
| Eva Jacobsen        | Lab for Chemistry and Microbiology<br>Danish Technological Institute<br>Kongsvang Allé 29, DK-8000 Aarhus, Denmark  |
| Volodymyr Mykhaylov | Lab of pesticides analytical chemistry of<br>L.I. Medved's Research Center of Preventive Toxicology, Food and<br>Chemical Safety, Ministry of Health, Ukraine<br>6, Heroiv Oborony st., Kiev, Ukraine, 03680  |
| Peng Wu             | National Center for Pesticide Quality Supervision and Inspection (Beijing),<br>Institute for the Control of Agrochemicals,<br>Ministry of Agriculture and Rural Affairs , P. R. China<br>Address: Maizidian road No.22, Chaoyang district, Beijing, P. R. China |
| Florentina Ciotea   | National Phytosanitary Lab<br>National Phytosanitary Authority Voluntari Bvd. No. 11, Voluntari Town, Ilfov<br>County, Romania  |
| Agus Salim          | PT Agriculture Construction (AGRICON)<br>Jl. Siliwangi No. 68 Bogor 16134 West Java, Indonesia  |
| Hou Chungqing       | Pesticides Test Lab of Shenyang SYRICI Testing Co., Ltd.<br>No.8, Shenliao East Road, Tiexi District Shenyang 110021, P.R. China  |
| Shirish Bondre      | Quality Assurance Dept., Gharda Chemicals Ltd.<br>D-1/2, MIDC, Lote Parshuram, Taluka Khed<br>District: Ratnagari 415722, Maharashtra India   |
| Lynn                | Shandong Sino-Agri United Biotechnology Co., Ltd. Testing Center<br>NO.28, Sangyuan Road, Jinan City, Shandong, China   |
| Judy                | Shandong Binnong Technology Co., Ltd.<br>No.518, Yongxin Road, Binbei Town, Binzhou, Shandong, China  |
| Maureen Tian        | Test Center of Shandong Weifang Rainbow Chemical Co., Ltd.<br>Binhai Economic Development Area, Weifang, Shandong, China  |
| Vanessa Lecocq      | Walloon Agricultural Research Centre (CRA-W)<br>Batiment Rachel Carson Rue du Bordia,115030 Gembloux Belgique<br>Belgium  |

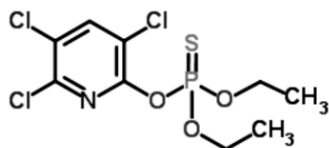
## 2. Active Ingredient: General Information

Chemical name: *O, O-diethyl O-3,5,6-trichloro-2-pyridyl phosphorothioate(IUPAC)*

*O, O-diethyl O-(3,5,6-trichloro-2-pyridyl) phosphorothioate(CA; 2912-88-2)*

ISO common name: Chlorpyrifos

CAS-No.: 2921-88-2



Structure:

Molecular mass: 350.6 g/mol

Empirical formula: C<sub>9</sub>H<sub>11</sub>Cl<sub>3</sub>NO<sub>3</sub>PS

Activity: Insecticide

### 3. Samples

The following 5 test samples and analytical standard were sent to the participants:

1. Chlorpyrifos tech. sample 1 (Chlorpyrifos TC-1, Batch Number: 2020092263)
  2. Chlorpyrifos tech. sample 2 (Chlorpyrifos TC-2, Batch Number: 2020092161)
  3. Chlorpyrifos tech. sample 3 (Chlorpyrifos TC-3, Batch Number: 2020092365)
  4. Chlorpyrifos 40 % EC sample 4 (Chlorpyrifos EC-1, Batch Number: 20200710)
  5. Chlorpyrifos 40 % EC sample 5 (Chlorpyrifos EC-2, Batch Number: 20200705)
- Chlorpyrifos, reference standard (purity 99.2 %w/w)

### 4. Method

#### 4.1 Scope

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

#### 4.2 Principle

Chlorpyrifos is determined by reversed phase high performance liquid chromatography using UV detection at 290 nm and external standardisation.

#### 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 Chlorpyrifos in the test solution, was calculated using the injection before and after the test injections.

## 5. Analytical Condition and Remarks of the Participants

| Lab | Instrument                                    | Column   | Flow Rate | Column Temp. °C | Wave length | Injection Volume | Mobile phase   |
|-----|---|--|-----------|-----------------|-------------|------------------|--|
| 1   | Thermo Ultimate 3000                          | Agilent Extend-C18<br>5um 250 x 4.6mm                        | 1.0       | 30              | 290         | 5                | Acetonitrile/Water/Glacial acetic acid(820/175/5, v/v/v) |
| 2   | Agilent 1260                                  | ZORBAX SB-C18<br>5um 250 x 4.6mm                             | 1.0       | 25              | 290         | 5                | Acetonitrile/Water/Glacial acetic acid(820/175/5, v/v/v) |
| 3   | Agilent 1260                                  | TC-C18(2), 5um 250 x 4.6mm                                   | 1.0       | 25              | 290         | 5                | Acetonitrile/Water/Glacial acetic acid(820/175/5, v/v/v) |
| 4   | Agilent 1100                                  | Phenomenex Lunar®<br>5um C18(2) 100Å                         | 1.2       | 25              | 290         | 5                | Acetonitrile/Water/Glacial acetic acid(820/175/5, v/v/v) |
| 5   | Agilent 1260 Infinity II                      | Agilent Zorbax<br>Extend-C18 / 5um<br>250 x 3.0mm            | 1.0       | 25              | 290         | 5                | Acetonitrile/Water/Glacial acetic acid(820/175/5, v/v/v) |
| 6   | Waters , Model Alliance e2695 , Detector 2998 | Xterra RP18 with 5um<br>250 x 4.6mm, 123 oA<br>pore diameter | 1.0       | 25              | 290         | 5                | Acetonitrile/Water/Glacial acetic acid(820/175/5, v/v/v) |
| 7   | SHIMADZU LC-2030C 3D Plus                     | ZORBAX Extend-C18,<br>5um 250 x 4.6mm                        | 1.0       | 25              | 290         | 5                | Acetonitrile/Water/Glacial acetic acid(820/175/5, v/v/v) |
| 8   | Agilent 1200 Series                           | Zorbax Extend- C18,<br>5um 250 x 4.6mm                       | 1.0       | 25              | 290         | 5                | Acetonitrile/Water/Glacial acetic acid(820/175/5, v/v/v) |
| 9   | Agilent HPLC-DAD 1260 Infinity                | Luna C18(2) 100A,<br>5um 250 x 4.6mm                         | 1.0       | 25              | 290         | 5                | Acetonitrile/Water/Glacial acetic acid(820/175/5, v/v/v) |
| 10  | Shimadzu Nexera XR with SPD-20A               | Zorbax Extend C18<br>5um 250 x 4.6mm<br>with precolumn       | 1.0       | 25              | 290         | 5                | Acetonitrile/Water/Glacial acetic acid(820/175/5, v/v/v) |
| 11  | YQ-1-35                                       | Agilent Extend-C18,<br>5um 250 x 4.6mm                       | 1.0       | 25              | 290         | 5                | Acetonitrile/Water/Glacial acetic acid(820/175/5, v/v/v) |
| 12  | Dionex UltiMate 3000                          | Agilent - Zorbax<br>Eclipse XDB-C18 ,<br>5um 250 x 4.6mm     | 1.0       | 25              | 290         | 5                | Acetonitrile/Water/Glacial acetic acid(820/175/5, v/v/v) |

|    |  |  |     |    |     |   |  |
|----|--|--|-----|----|-----|---|--|
| 13 | Shimadzu 20 AD                                       | Phenomenex Luna C-18, 5um 250 x 4.6mm      | 1.0 | 25 | 290 | 5 | Acetonitrile/Water/Glacial acetic acid(820/175/5, v/v/v) |
| 14 | Themro, Dionex UltiMate 3000 HPLC                    | Agilent Extend C18, 5um 250 x 4.6mm        | 1.0 | 25 | 290 | 5 | Acetonitrile/Water/Glacial acetic acid(820/175/5, v/v/v) |
| 15 | Thermo Scientific Ultimate-3000                      | Cosmosil C-18, 5um 250 x 4.6mm             | 1.0 | 25 | 290 | 5 | Acetonitrile/Water/Glacial acetic acid(820/175/5, v/v/v) |
| 16 | Agilent  | Agilent Extend-C18, 5um 250 x 4.6mm        | 1.0 | 35 | 290 | 5 | Acetonitrile/Water/Glacial acetic acid(820/175/5, v/v/v) |
| 17 | Agilent Technologies Pte. Ltd DAD: DEAEK00202/G7117C | WondaSil C18 Superb 5um 250 x 4.6mm        | 1.0 | 35 | 290 | 5 | Acetonitrile/Water/Glacial acetic acid(820/175/5, v/v/v) |
| 18 | Agilent 1260 Infinity II                             | Agilent Eclipse XDB-C18, 5um 250 x 4.6mm   | 1.0 | 35 | 290 | 5 | Acetonitrile/Water/Glacial acetic acid(820/175/5, v/v/v) |
| 19 | Agilent 1100 Series                                  | Agilent Zorbax Extend-C18, 5um 250 x 4.6mm | 1.0 | 25 | 290 | 5 | Acetonitrile/Water/Glacial acetic acid(820/175/5, v/v/v) |
| 20 | GC   |  |     |    |     |   |  |

Several participants provided comments about the method performance and also made a note of any deviations from the method:

| Lab No. | Comments   |
|---------|--|
| Lab 6   | The preparation of TC samples is deviated from the method specified by adding only 80 ml of acetonitrile before being placed in an ultrasonic bath for 5 min, allow to cool at ambient temperature and then fill acetonitrile to the mark.   |
| Lab 8   | Each TC sample was one cluster in the container. To weight the required amount the sample has to be scraped with a spatula. The labeling of the samples was not clearly. For identification the charge numbers must be compared (from container and from the report).For the Day2-Z sheet the formulae were missing. Sheet Day1-Z was duplicated and re-named. |
| Lab 17  | DAY1-Z: The test/reference items were injected into HPLC system on 2021-01-12. The data was analyzed on 2021-01-13.<br>DAY2-Z: The test/reference items were injected into HPLC system on 2021-01-13. The data was analyzed on 2021-01-14.   |
| Lab 18  | 1 Approximately weigh 50mg of Chlorpyrifos standard respectively into 50ml volumetric flask. 2 Approximately weigh containing Chlorpyrifos 50mg of Chlorpyrifos TC or EC into 50ml volumetric flask.   |

## 6. Evaluation and Discussion

### 6.1 Data Review

The data obtained from each Lab 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 from 19 participating laboratories were included within the statistical assessment, except the one using GC method.

### 6.2 Determination of Chlorpyrifos

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 Lab 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, 19 laboratories are reported. Lab 9 three times was identified as outliers of TC-1, TC-2 and TC-3 according to Grubbs test. In the tables 4-6 and figures 6-8, TC-1, TC-2 and TC-3 of 18 laboratories (without lab 9) are reported. Lab 6 one time was identified as outlier of TC-3. In the tables 7-9 and figures 9, TC-3 of 17 laboratories (without lab 9 and 6) are reported. No outliers or stragglers are included. The Horwitz Ratio (HorRat) was found within the desired range ( $\geq 0.3$  but  $\leq 1.0$ ).

All results are given in g/kg

**Table 1 Results of 19 labs**

|              | Chlorpyrifos TC-1 |       | Chlorpyrifos TC-2 |       | Chlorpyrifos TC-3 |       | Chlorpyrifos EC-1 |       | Chlorpyrifos EC-2 |       |
|--------------|-------------------|-------|-------------------|-------|-------------------|-------|-------------------|-------|-------------------|-------|
|              | Day 1             | Day 2 | Day 1             | Day 2 | Day 1             | Day 2 | Day 1             | Day 2 | Day 1             | Day 2 |
| <b>Lab 1</b> | 977.9             | 975.3 | 977.2             | 980.6 | 979.9             | 978.1 | 406.3             | 406.7 | 405.1             | 406.5 |
| <b>Lab 2</b> | 978.4             | 977.0 | 979.0             | 978.2 | 979.6             | 980.2 | 403.6             | 403.2 | 403.2             | 402.8 |
| <b>Lab 3</b> | 975.4             | 977.4 | 975.9             | 978.3 | 979.1             | 977.9 | 404.6             | 403.7 | 403.4             | 403.2 |
| <b>Lab 4</b> | 976.7             | 976.4 | 979.3             | 977.4 | 979.1             | 971.2 | 400.6             | 406.8 | 400.8             | 402.7 |
| <b>Lab 5</b> | 982.8             | 981.0 | 978.9             | 978.0 | 984.0             | 975.2 | 407.7             | 407.9 | 407.0             | 407.6 |
| <b>Lab 6</b> | 963.4             | 973.6 | 960.6             | 971.5 | 953.4             | 962.0 | 397.8             | 397.4 | 398.3             | 399.2 |
| <b>Lab 7</b> | 982.4             | 985.6 | 982.8             | 984.8 | 982.1             | 983.8 | 406.4             | 406.7 | 405.5             | 405.8 |
| <b>Lab 8</b> | 978.9             | 973.3 | 983.2             | 972.7 | 983.0             | 966.2 | 403.3             | 398.1 | 402.4             | 399.9 |
| <b>Lab 9</b> | 935.2             | 954.6 | 924.2             | 963.5 | 936.5             | 945.3 | 395.6             | 400.8 | 395.7             | 400.0 |



|        |       |       |       |       |       |       |       |       |       |       |
|--------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Lab 10 | 985.7 | 980.1 | 989.3 | 977.3 | 991.2 | 977.8 | 408.5 | 405.8 | 410.5 | 407.4 |
| Lab 11 | 971.5 | 971.3 | 975.4 | 974.8 | 980.3 | 980.8 | 404.3 | 405.7 | 401.3 | 402.7 |
| Lab 12 | 976.8 | 976.1 | 979.4 | 979.6 | 981.6 | 981.9 | 402.9 | 403.3 | 403.4 | 403.9 |
| Lab 13 | 977.5 | 973.7 | 979.8 | 974.8 | 969.3 | 970.5 | 403.2 | 399.5 | 399.3 | 398.6 |
| Lab 14 | 979.9 | 980.7 | 978.6 | 980.1 | 977.7 | 976.5 | 405.0 | 405.6 | 406.0 | 405.3 |
| Lab 15 | 977.2 | 977.5 | 980.4 | 975.7 | 974.4 | 977.4 | 406.6 | 407.1 | 405.7 | 410.2 |
| Lab 16 | 980.0 | 977.6 | 978.1 | 976.1 | 980.2 | 979.6 | 405.8 | 404.2 | 406.3 | 404.2 |
| Lab 17 | 983.8 | 978.2 | 982.6 | 984.0 | 983.7 | 979.2 | 405.5 | 403.5 | 405.3 | 402.5 |
| Lab 18 | 981.4 | 978.1 | 982.7 | 981.9 | 980.6 | 982.1 | 403.8 | 404.6 | 405.4 | 405.5 |
| Lab 19 | 982.6 | 978.6 | 962.3 | 970.3 | 973.2 | 965.0 | 404.1 | 406.1 | 404.0 | 405.7 |

**Table 2 Mean values**

|        | Chlorpyrifos<br>TC-1 | Chlorpyrifos<br>TC-2 | Chlorpyrifos<br>TC-3 | Chlorpyrifos<br>EC-1 | Chlorpyrifos<br>EC-2 |
|--------|----------------------|----------------------|----------------------|----------------------|----------------------|
| Lab 1  | 976.6                | 978.9                | 979.0                | 406.5                | 405.8                |
| Lab 2  | 977.7                | 978.6                | 979.9                | 403.4                | 403.0                |
| Lab 3  | 976.4                | 977.1                | 978.5                | 404.2                | 403.3                |
| Lab 4  | 976.5                | 978.3                | 975.1                | 403.7                | 401.8                |
| Lab 5  | 981.9                | 978.4                | 979.6                | 407.8                | 407.3                |
| Lab 6  | 968.5                | 966.0                | 957.7                | 397.6                | 398.7                |
| Lab 7  | 984.0                | 983.8                | 983.0                | 406.6                | 405.7                |
| Lab 8  | 976.1                | 978.0                | 974.6                | 400.7                | 401.2                |
| Lab 9  | 944.9                | 943.9                | 940.9                | 398.2                | 397.8                |
| Lab 10 | 982.9                | 983.3                | 984.5                | 407.1                | 408.9                |
| Lab 11 | 971.4                | 975.1                | 980.6                | 405.0                | 402.0                |
| Lab 12 | 976.5                | 979.5                | 981.8                | 403.1                | 403.6                |
| Lab 13 | 975.6                | 977.3                | 969.9                | 401.4                | 398.9                |
| Lab 14 | 980.3                | 979.4                | 977.1                | 405.3                | 405.7                |
| Lab 15 | 977.4                | 978.1                | 975.9                | 406.9                | 408.0                |
| Lab 16 | 978.8                | 977.1                | 979.9                | 405.0                | 405.2                |
| Lab 17 | 981.0                | 983.3                | 981.5                | 404.5                | 403.9                |
| Lab 18 | 979.8                | 982.3                | 981.4                | 404.2                | 405.5                |
| Lab 19 | 980.6                | 966.3                | 969.1                | 405.1                | 404.9                |

**Table 3 Summary of the statistical evaluation (19 Labs included)**

|                | Chlorpyrifos<br>TC-1 | Chlorpyrifos<br>TC-2 | Chlorpyrifos<br>TC-3 | Chlorpyrifos<br>EC-1 | Chlorpyrifos<br>EC-2 |
|----------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| $x_m$ [g/kg]   | 976.15               | 976.02               | 974.89               | 404.01               | 403.75               |
| $x_m$ [% w/w]  | 97.62                | 97.60                | 97.49                | 40.40                | 40.38                |
| L              | 19                   | 19                   | 19                   | 19                   | 19                   |
| $S_r$          | 4.31                 | 6.68                 | 4.82                 | 2.06                 | 1.57                 |
| $S_R$          | 9.24                 | 10.79                | 11.30                | 3.35                 | 3.39                 |
| r              | 12.07                | 18.70                | 13.51                | 5.76                 | 4.38                 |
| R              | 25.86                | 30.22                | 31.65                | 9.37                 | 9.50                 |
| $RSD_R$        | 0.95                 | 1.11                 | 1.16                 | 0.83                 | 0.84                 |
| $RSD_{R(Hor)}$ | 1.42                 | 1.42                 | 1.42                 | 1.62                 | 1.62                 |
| HorRat         | 0.67                 | 0.78                 | 0.82                 | 0.51                 | 0.52                 |

$x_m$  = total mean value

L = number of laboratories

$s_r$  = repeatability standard deviation

$s_R$  = reproducibility standard deviation

r = repeatability limit

R = reproducibility limit

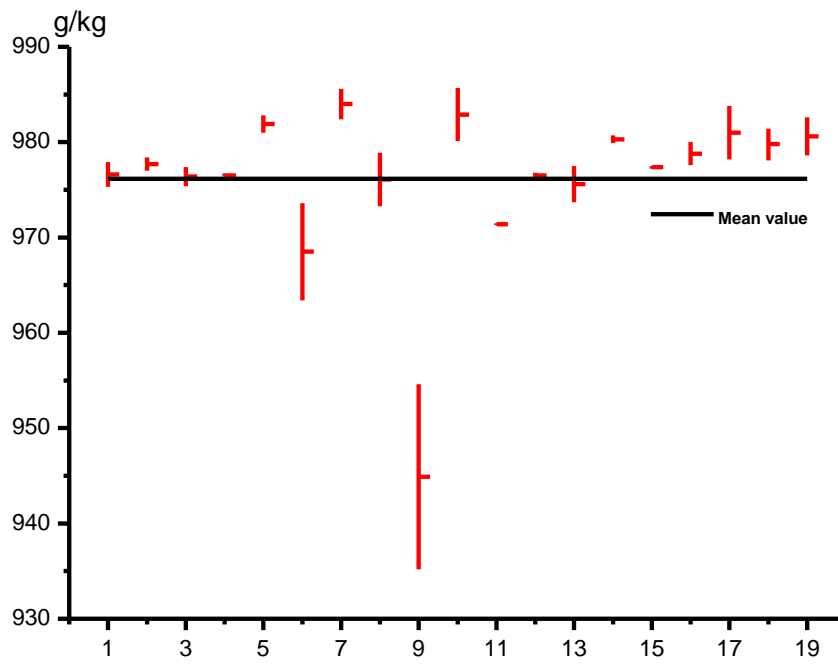
$RSD_R$  = relative standard deviation of reproducibility

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

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

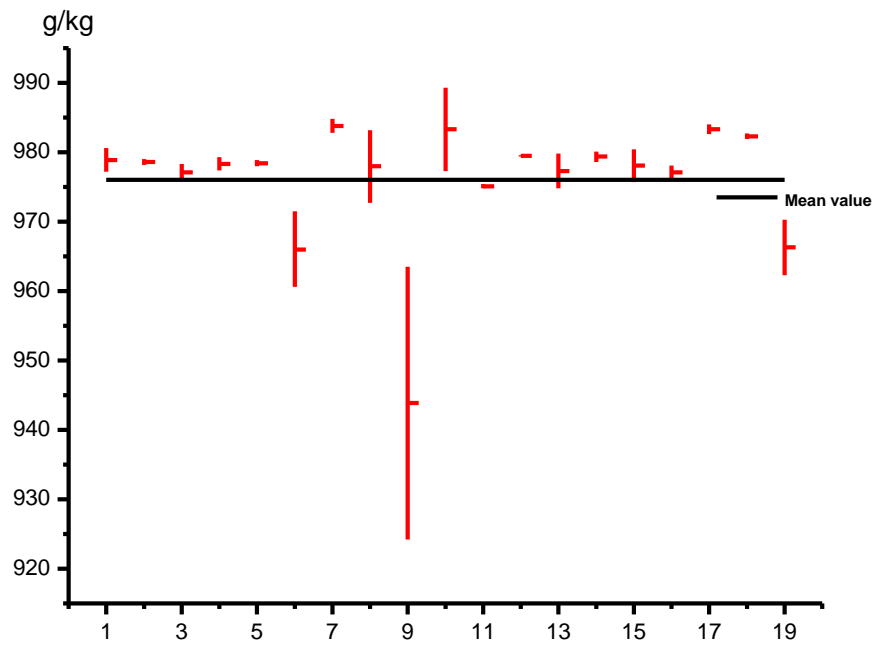
19 participants:

Fig. 1 Chlorpyrifos tech. sample - 1 (19 labs included)



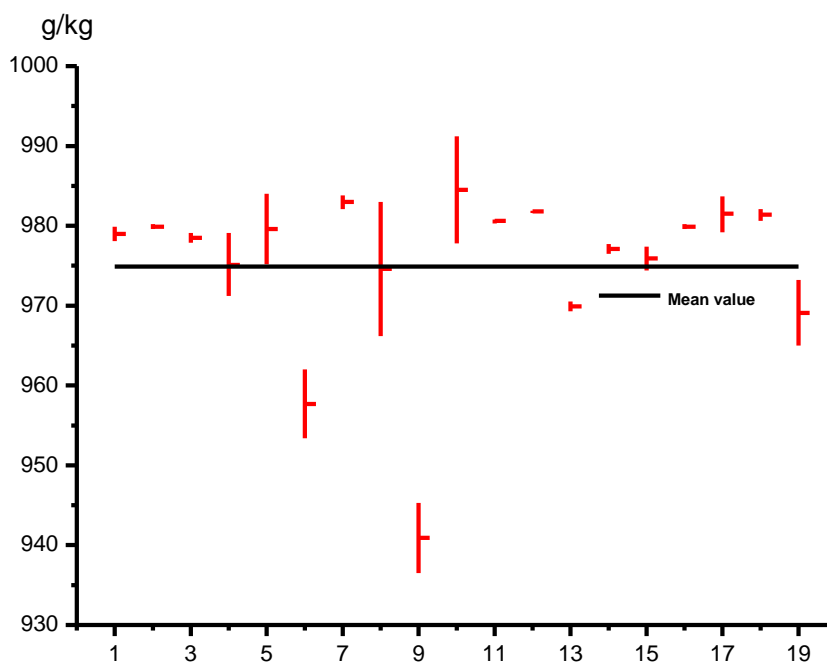
Mean value: 976.15 g/kg  
 $S_r$ : 4.31  
 $S_R$ : 9.24  
 $RSD_R$ : 0.95  
 $RSD_{R(Hor)}$ : 1.42  
 HorRat: 0.67  
 Outlier (Grubbs): lab 9

Fig. 2 Chlorpyrifos tech. sample - 2 (19 labs included)



Mean value: 976.02 g/kg  
 $S_r$ : 6.68  
 $S_R$ : 10.79  
 $RSD_R$ : 1.11  
 $RSD_{R(Hor)}$ : 1.42  
 HorRat: 0.78  
 Outlier (Grubbs): lab 9

Fig. 3 Chlorpyrifos tech. sample - 3 (19 labs included)



Mean value: 974.89 g/kg

$S_r$ : 4.82

$S_R$ : 11.30

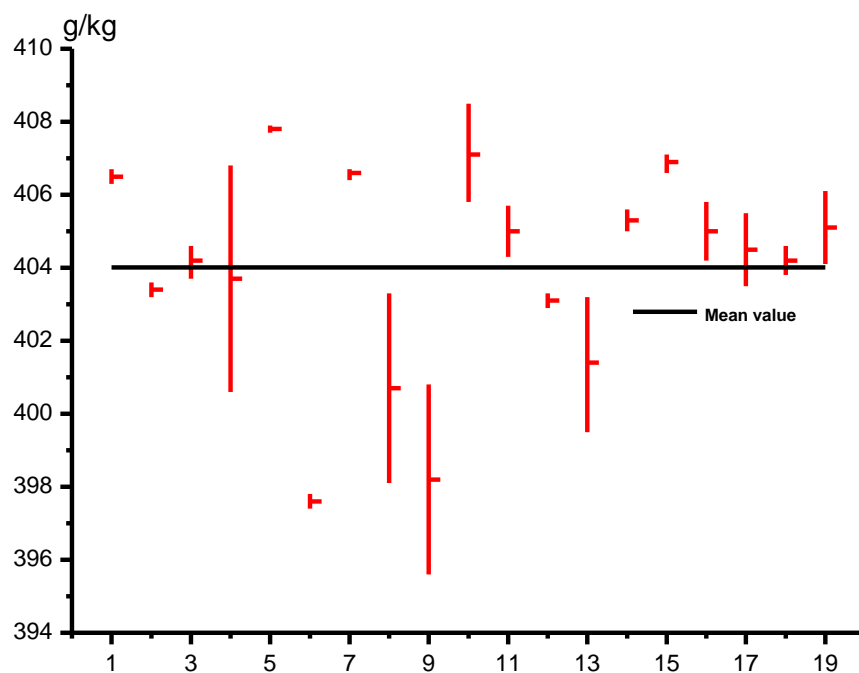
$RSD_R$ : 1.16

$RSD_{R(Hor)}$ : 1.42

HorRat: 0.82

Outlier (Grubbs): lab 9

Fig. 4 Chlorpyrifos EC sample - 1 (19 labs included)



Mean value: 404.01 g/kg

$S_r$ : 2.06

$S_R$ : 3.35

$RSD_R$ : 0.83

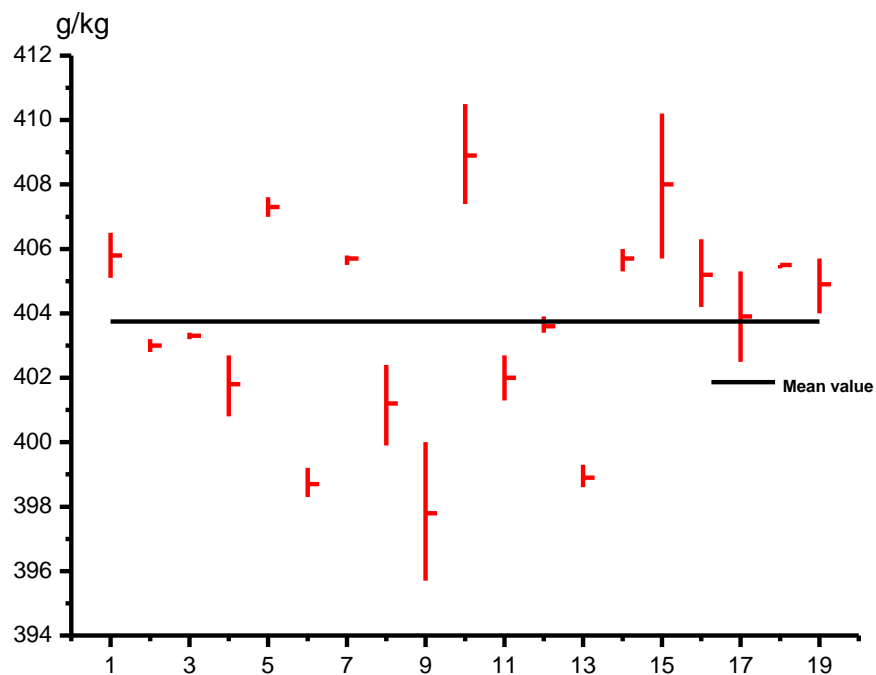
$RSD_{R(Hor)}$ : 1.62

**HorRat: 0.51**

Outlier (Grubbs): none

Straggler (Grubbs): none

Fig. 5 Chlorpyrifos EC sample - 2 (19 labs included)



Mean value: 403.75 g/kg

$S_r$ : 1.57

$S_R$ : 3.39

$RSD_R$ : 0.84

$RSD_{R(Hor)}$ : 1.62

HorRat: 0.52

Outlier (Grubbs): none

Straggler (Grubbs): none

Table 4 Results (without lab 9)

|       | Chlorpyrifos TC-1 |       | Chlorpyrifos TC-2 |       | Chlorpyrifos TC-3 |       |
|-------|-------------------|-------|-------------------|-------|-------------------|-------|
|       | Day 1             | Day 2 | Day 1             | Day 2 | Day 1             | Day 2 |
| Lab 1 | 977.9             | 975.3 | 977.2             | 980.6 | 979.9             | 978.1 |
| Lab 2 | 978.4             | 977.0 | 979.0             | 978.2 | 979.6             | 980.2 |
| Lab 3 | 975.4             | 977.4 | 975.9             | 978.3 | 979.1             | 977.9 |
| Lab 4 | 976.7             | 976.4 | 979.3             | 977.4 | 979.1             | 971.2 |
| Lab 5 | 982.8             | 981.0 | 978.9             | 978.0 | 984.0             | 975.2 |
| Lab 6 | 963.4             | 973.6 | 960.6             | 971.5 | 953.4             | 962.0 |

|        |       |       |       |       |       |       |
|--------|-------|-------|-------|-------|-------|-------|
| Lab 7  | 982.4 | 985.6 | 982.8 | 984.8 | 982.1 | 983.8 |
| Lab 8  | 978.9 | 973.3 | 983.2 | 972.7 | 983.0 | 966.2 |
| Lab 10 | 985.7 | 980.1 | 989.3 | 977.3 | 991.2 | 977.8 |
| Lab 11 | 971.5 | 971.3 | 975.4 | 974.8 | 980.3 | 980.8 |
| Lab 12 | 976.8 | 976.1 | 979.4 | 979.6 | 981.6 | 981.9 |
| Lab 13 | 977.5 | 973.7 | 979.8 | 974.8 | 969.3 | 970.5 |
| Lab 14 | 979.9 | 980.7 | 978.6 | 980.1 | 977.7 | 976.5 |
| Lab 15 | 977.2 | 977.5 | 980.4 | 975.7 | 974.4 | 977.4 |
| Lab 16 | 980.0 | 977.6 | 978.1 | 976.1 | 980.2 | 979.6 |
| Lab 17 | 983.8 | 978.2 | 982.6 | 984.0 | 983.7 | 979.2 |
| Lab 18 | 981.4 | 978.1 | 982.7 | 981.9 | 980.6 | 982.1 |
| Lab 19 | 982.6 | 978.6 | 962.3 | 970.3 | 973.2 | 965.0 |

**Table 5 Mean values (without lab 9)**

|        | Chlorpyrifos<br>TC-1 | Chlorpyrifos<br>TC-2 | Chlorpyrifos<br>TC-3 |
|--------|----------------------|----------------------|----------------------|
| Lab 1  | 976.6                | 978.9                | 979.0                |
| Lab 2  | 977.7                | 978.6                | 979.9                |
| Lab 3  | 976.4                | 977.1                | 978.5                |
| Lab 4  | 976.5                | 978.3                | 975.1                |
| Lab 5  | 981.9                | 978.4                | 979.6                |
| Lab 6  | 968.5                | 966.0                | 957.7                |
| Lab 7  | 984.0                | 983.8                | 983.0                |
| Lab 8  | 976.1                | 978.0                | 974.6                |
| Lab 10 | 982.9                | 983.3                | 984.5                |
| Lab 11 | 971.4                | 975.1                | 980.6                |
| Lab 12 | 976.5                | 979.5                | 981.8                |
| Lab 13 | 975.6                | 977.3                | 969.9                |
| Lab 14 | 980.3                | 979.4                | 977.1                |
| Lab 15 | 977.4                | 978.1                | 975.9                |
| Lab 16 | 978.8                | 977.1                | 979.9                |
| Lab 17 | 981.0                | 983.3                | 981.5                |
| Lab 18 | 979.8                | 982.3                | 981.4                |
| Lab 19 | 980.6                | 966.3                | 969.1                |



**Table 6 Summary of the statistical evaluation (without lab 9)**

|                | <b>Chlorpyrifos<br/>TC-1</b> | <b>Chlorpyrifos<br/>TC-2</b> | <b>Chlorpyrifos<br/>TC-3</b> |
|----------------|------------------------------|------------------------------|------------------------------|
| $x_m$ [g/kg]   | 977.89                       | 977.81                       | 974.89                       |
| $x_m$ [% w/w]  | 97.79                        | 97.78                        | 97.68                        |
| L              | 18                           | 18                           | 18                           |
| $S_r$          | 3.56                         | 4.10                         | 4.66                         |
| $S_R$          | 4.94                         | 6.03                         | 7.83                         |
| r              | 9.96                         | 11.47                        | 13.06                        |
| R              | 13.83                        | 16.88                        | 21.93                        |
| $RSD_R$        | 0.51                         | 0.62                         | 0.80                         |
| $RSD_{R(Hor)}$ | 1.42                         | 1.42                         | 1.42                         |
| <b>HorRat</b>  | <b>0.36</b>                  | <b>0.43</b>                  | <b>0.57</b>                  |

$x_m$  = total mean value

L = number of laboratories

$s_r$  = repeatability standard deviation

$s_R$  = reproducibility standard deviation

r = repeatability limit

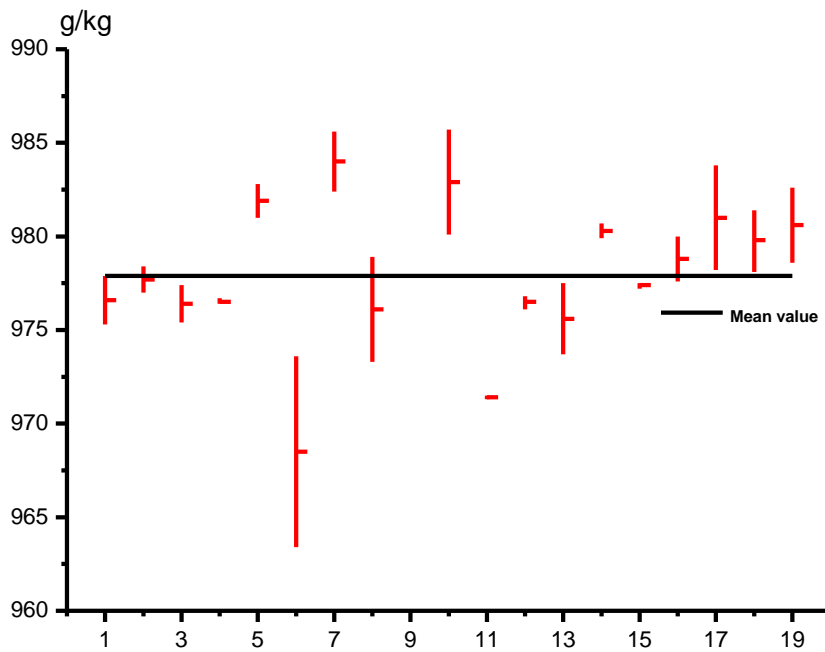
R = reproducibility limit

$RSD_R$  = relative standard deviation of reproducibility

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

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

Fig. 6 Chlorpyrifos tech. sample - 1 (without lab 9)



Mean value: 977.89 g/kg

$S_r$ : 3.56

$S_R$ : 4.94

$RSD_R$ : 0.51

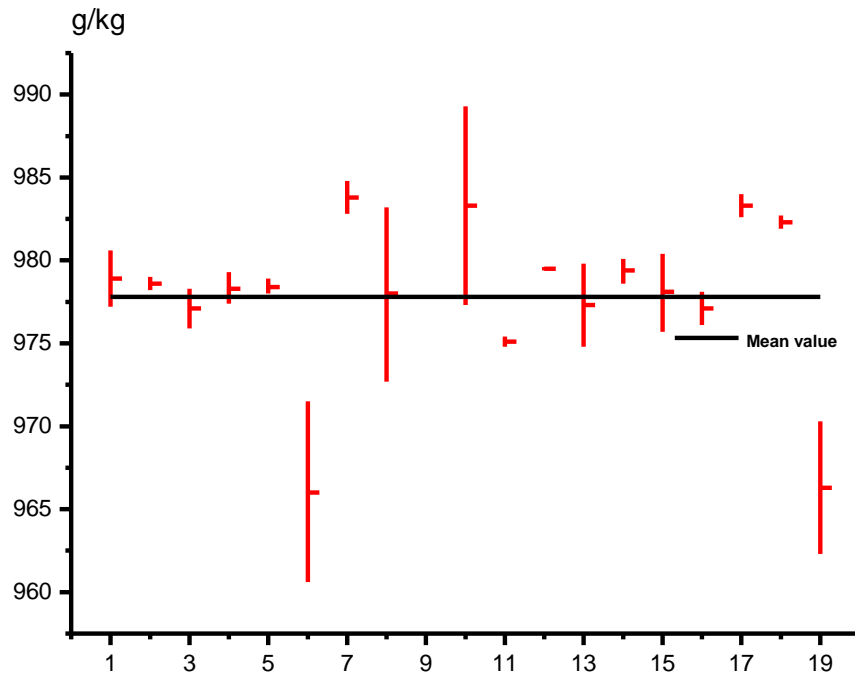
$RSD_R (Hor)$ : 1.42

**HorRat: 0.36**

Outlier (Grubbs): none

Straggler (Grubbs): none

Fig. 7 Chlorpyrifos tech. sample - 2 (without lab 9)



Mean value: 977.81 g/kg

$S_r$ : 4.10

$S_R$ : 6.03

$RSD_R$ : 0.62

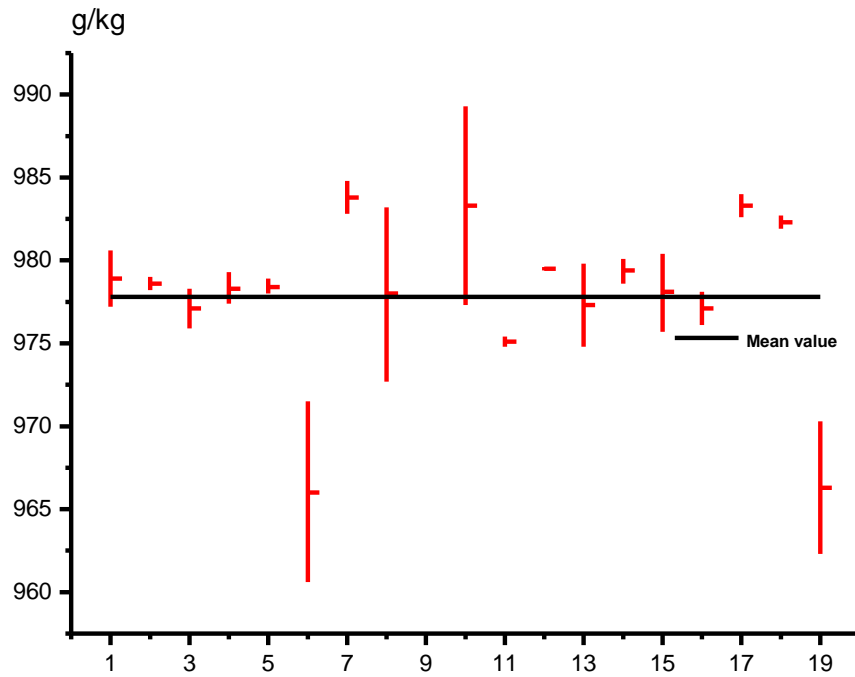
$RSD_{R(Hor)}$ : 1.42

**HorRat: 0.43**

Outlier (Grubbs): none

Straggler (Grubbs): none

Fig. 8 Chlorpyrifos tech. sample - 3 (without lab 9)



Mean value: 974.89 g/kg

$S_r$ : 4.66

$S_R$ : 7.83

$RSD_R$ : 0.80

$RSD_{R(Hor)}$ : 1.42

**HorRat: 0.57**

Outlier (Grubbs): lab 6

**Table 7 Results (without lab 9 and 6)**

|               | Chlorpyrifos TC-3 |       |
|---------------|-------------------|-------|
|               | Day 1             | Day 2 |
| <b>Lab 1</b>  | 979.9             | 978.1 |
| <b>Lab 2</b>  | 979.6             | 980.2 |
| <b>Lab 3</b>  | 979.1             | 977.9 |
| <b>Lab 4</b>  | 979.1             | 971.2 |
| <b>Lab 5</b>  | 984.0             | 975.2 |
| <b>Lab 7</b>  | 982.1             | 983.8 |
| <b>Lab 8</b>  | 983.0             | 966.2 |
| <b>Lab 10</b> | 991.2             | 977.8 |
| <b>Lab 11</b> | 980.3             | 980.8 |

|        |       |       |
|--------|-------|-------|
| Lab 12 | 981.6 | 981.9 |
| Lab 13 | 969.3 | 970.5 |
| Lab 14 | 977.7 | 976.5 |
| Lab 15 | 974.4 | 977.4 |
| Lab 16 | 980.2 | 979.6 |
| Lab 17 | 983.7 | 979.2 |
| Lab 18 | 980.6 | 982.1 |
| Lab 19 | 973.2 | 965.0 |

**Table 8 Mean values(without lab 9 and 6)**

|        | Chlorpyrifos TC-3 |
|--------|-------------------|
| Lab 1  | 979.0             |
| Lab 2  | 979.9             |
| Lab 3  | 978.5             |
| Lab 4  | 975.1             |
| Lab 5  | 979.6             |
| Lab 7  | 983.0             |
| Lab 8  | 974.6             |
| Lab 10 | 984.5             |
| Lab 11 | 980.6             |
| Lab 12 | 981.8             |
| Lab 13 | 969.9             |
| Lab 14 | 977.1             |
| Lab 15 | 975.9             |
| Lab 16 | 979.9             |
| Lab 17 | 981.5             |
| Lab 18 | 981.4             |
| Lab 19 | 969.1             |

**Table 9 Summary of the statistical evaluation (without lab 9 and 6)**

|  | Chlorpyrifos TC-3 |
|--|-------------------|
|  |                   |

|                |             |
|----------------|-------------|
| $x_m$ [g/kg]   | 977.9       |
| $x_m$ [% w/w]  | 97.79       |
| L              | 17          |
| $S_r$          | 4.58        |
| $S_R$          | 6.29        |
| r              | 12.82       |
| R              | 17.62       |
| $RSD_R$        | 0.64        |
| $RSD_{R(Hor)}$ | 1.42        |
| <b>HorRat</b>  | <b>0.45</b> |

$x_m$  = total mean value

L = number of laboratories

$s_r$  = repeatability standard deviation

$s_R$  = reproducibility standard deviation

r = repeatability limit

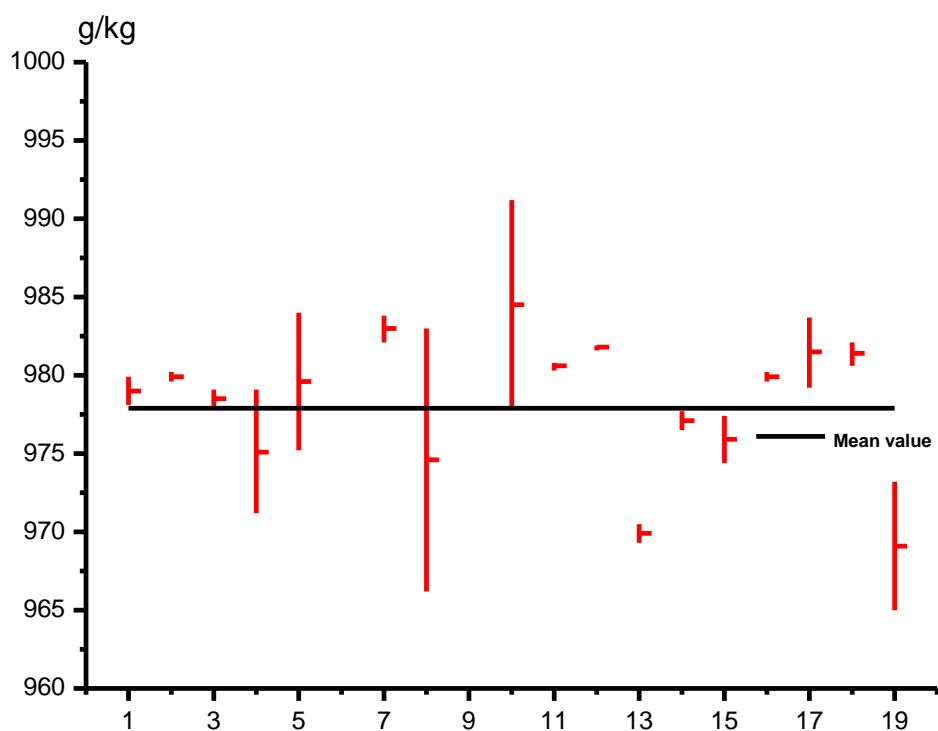
R = reproducibility limit

$RSD_R$  = relative standard deviation of reproducibility

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

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

Fig. 9 Chlorpyrifos tech. sample - 3 (without lab 9 and 6)



Mean value: 977.9 g/kg

$S_r$ : 4.58

$S_R$ : 6.29

$RSD_R$ : 0.64

$RSD_{R(Hor)}$ : 1.42

HorRat: 0.45

Outlier (Grubbs): none

Straggler (Grubbs): none

## 7. Conclusions

A total of 20 laboratories have participated in this full scale collaborative study. And data from 19 participants have been included in the final data statistical. The excluded one used GC method instead of HPLC.

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 LC method is acceptable and suitable to produce reproducible results.

SYRICIT consider this method to be suitable for the intended purpose, without further changes, and recommend accepting it as a provisional CIPAC method for the determination of Chlorpyrifos in technical grade material and in EC formulation.