CIPAC

COLLABORATIVE INTERNATIONAL PESTICIDES ANALYTICAL COUNCIL LIMITED

Commission Internationale des Méthodes d'Analyse des Pesticides (CIMAP)

Minutes of the 68th Annual meeting

The 68th meeting was held on Wednesday 19th June in Wageningen, The Netherlands

Those attending

- Items 1 to 7: members, correspondents, observers and expert witnesses.
- Items 8 to 12: members, correspondents and observers (representatives of industry and commercial laboratories, by special invitation only)

1. Welcome and introductory remarks

The chair, Mr R. Hänel, opened the 68th CIPAC meeting, and welcomed all the participants.

2. Apologies

Apologies were received from: Mr L. Benke, Mr V. Chmil, Ms V. Kmecl, Ms O. Nováková, Ms A. Santilio.

3. Adoption of the agenda

The agenda was adopted. Ms Xu Rong replaces Ms Yue Wang at item 4.8 and 4.9.

4. Reports of expert witnesses on collaborative trials

4.1 4-(trifluoromethyl)-nicotinamide by Mr Christian Mink (5368, 5369)

Mr Christian Mink presented the results of a small scale collaborative trial of 4-(trifluoromethyl)-nicotinamide of five TC samples in which five DAPA laboratories participated. Two Syngenta laboratories analysed and reported results twice which totalled to seven available results for statistical review. Unfortunately, sample E was lost at a laboratory, so for sample E only six results were available. The analysis was performed by RP-HPLC using UV detection at 265 nm and external standardization. A Kinetex Polar C18 column was used (Phenomenex, 150 × 4.6 mm, 2.6 µm) at 30°C and an acetonitril/water + 0.5% H_3PO_4 gradient was applied. Five results were obtained with the prescribed HPLC column, two results were obtained with a comparable HPLC column and all laboratories returned results in due time. During statistical evaluation no stragglers or outliers were identified. The HorRat values of the five TC samples were between 0.2 and 0.3 therefore fulfilling the test criteria.

Mr Christian Mink recommended to go for a full scale CIPAC collaborative trial.

Questions and remarks from the meeting.

No comments were given or questions were asked by the meeting.

4.2 Abamectin by Ms Yue Wang (5384, 5385)

Ms Yue Wang presented the results of a small scale collaborative trial of abamectin in three TC samples in which four Chinese laboratories participated. The analysis was performed by high performance liquid chromatography on a reversed phase column (C18, no brand indicated, 250 × 4.6 mm, 5.0 µm) at 30°C ± 2°C with UV detection at 245 nm and external standardization. The eluent was methanol : acetonitrile : water, 55:30:15 (v/v/v) at a flow rate of 0.8 ml/min. The four laboratories used different HPLC columns each but did not change the prescribed method. 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. Testing for outliers/stragglers was not performed. The HorRat values of abamectin (B_{1a} + B_{1b}) of the three TC samples were between 0.3 and 0.5. All samples were fulfilling the test criteria.

Ms Yue Wang finalised her presentation by stating that CHIPAC considered the method for abamectin in TC to be suitable validated and recommended a full scale CIPAC collaborative trial.

Questions and remarks from the meeting.

- The total run time is 35 minutes which is long, abamectin B_{1a} and B_{1b} are widely separated, approximately 5 minutes. Why is not tried to go for a shorter retention time?
    - In samples more interfering peaks might be present.
- Why only TC samples have been analysed?
    - This is a first set-up. Formulations will be added to the full scale trial.

4.3 Broflanilide by Ms Laetitia Leroy (5388, 5389)

Ms Laetitia Leroy presented (on behalf of Carlos Moncada) a method extension of the CIPAC method for broflanilide TC to a UL formulation (994/TC/M/3) in which two laboratories participated. The broflanilide content was determined by reversed phase HPLC (Waters XSelect CSH C18 (or eq.), 250 × 4.6 mm, 5.0 µm) at 40°C with UV detection at 254 nm and external standardization. The eluent was acetonitrile : water, 65:35 (v/v) at a flow rate of 1.0 ml/min. During the performance of the method it appeared that dilution of the sample with eluent resulted in a bi-phase system which resulted in inadequate quantification. Changing the dilution solvent from eluent to neat acetonitrile solved this problem and quantitation was possible. Changing the dilution solvent was assessed to be a minor change as the retention time of broflanilide did not deviate by more than 2% from that of the calibration solution. The results of the two laboratories were combined and resulted in a HorRat value of 0.5.

Ms Laetitia Leroy considered the result fully acceptable and proposed acceptance of the extension.

Questions and remarks from the meeting.

No comments were given or questions were asked by the meeting.

4.4 Bifenthrin, chlorfenapyr and PBO by Ms Marie Baes (5390, 5391)

Ms Marie Baes presented (in collaboration with Sara Rathinam & Anand Samiappan) a full scale collaborative trial for the determination of bifenthrin, chlorfenapyr and piperonyl butoxide in Long-Lasting Insecticide treated net formulations (LN). Five LN samples were investigated by 16 laboratories which resulted in 12 sets of results. The original method was changed by weighing a larger amount of calibration substances (resulting in a smaller response variation from 1.0% to 0.4%), by using dioctyl phthalate as internal standard instead of dicyclohexyl phthalate and by the observation that heating during the extraction is a critical step. The extraction temperature should be 90°C (max 95°C) instead of 80°C and ultra sonication could be omitted. The timeframe was 2 hrs at 90°C followed by 15 hrs at room temperature. After filtration the analysis was performed by GC-FID on a DB-210 or equivalent (50% (trifluoropropyl)-methylpolysiloxane) GC column (30 m × 0.25 mm, 0.25 µm), a temperature gradient of 110°C to 240°C, helium as carrier gas and internal

standardization. Baseline separation was achieved for the three analytes and the internal standard. Several comments from the participating laboratories were discussed. The statistical evaluation was performed according the CIPAC guidelines.

For bifenthrin one Cochran's straggler was identified in LN1. Including the straggler, the HorRat values for bifenthrin ranged from 0.62 to 0.73. For chlorfenapyr a Grubbs' straggler was identified in LN1, one Cochran's outlier was identified in LN1, two Cochran's outliers were identified in LN2 and one Cochran's outlier was identified in LN3. Including all results the HorRat values for chlorfenapyr ranged from 0.60-0.82. For piperonyl butoxide a Cochran's straggler and a Grubbs' outlier were identified in LN1, a Grubbs' outlier was identified in LN2, a Grubbs' outlier was identified in LN3, a Cochran's outlier and a Grubbs' outlier were identified in LN4, and a Cochran's outlier and a Grubbs' outlier were identified in LN5. Including all data, the HorRat values for piperonyl butoxide ranged from 1.09 to 1.45. As laboratory two was a consequent Grubbs' outlier for piperonyl butoxide the data from laboratory two were removed from the dataset resulting in HorRat values of 0.57-1.10. A HorRat value between 1.0 and 2.0 is acceptable if a reasonable explanation can be given. Ms Marie Baes mentioned that LN are inhomogeneous samples and that the reduced dataset still contained a Cochran's outlier. After removing this outlier from the dataset the HorRat value for the LN4 sample was 0.61.

Ms Marie Baes recommended this method to be accepted as a provisional CIPAC method for the determination of bifenthrin, chlorfenapyr and piperonyl butoxide in in LN formulations.

Questions and remarks from the meeting.

- Is there a tolerance for the water bath temperature?
    - The range is 85-93°C and boiling is not allowed.
- A 2% retention time tolerance seems to be high when compared to the calibration solutions.
- Please specify exactly which dioctyl phthalate was used as internal standard as more options are possible.

The five-point calibration curve is too irregularly distributed and should be more evenly distributed.

Piperonyl butoxide as reference material is a viscous liquid which makes weighing difficult. Please add a remark to the method how to deal with this.

- The Cochran's test was performed on duplicate results which is not allowed
    - We just followed the CIPAC guidelines.
- Is a longer standing time than 15 hrs allowed?
    - It should not be shorter but longer is allowed.

4.5 Chlorantraniliprole relevant impurity by Ms M.E. McNally (5376, 5377)

Ms Mary Ellen McNally presented the results of a full scale collaborative trial of two relevant impurities (acetonitrile and 3-picoline) in two chlorantraniliprole SCs and one chlorantraniliprole TC. Fifteen laboratories participated and returned 15 results for the TC and 14 results for both SCs. The analysis was performed by GC-FID on a DB-Wax GC column (30 m × 0.250 mm, 0.50 µm), a temperature gradient of 60°C to 240°C, helium or hydrogen as carrier gas and internal standardization. Baseline separation was achieved for the two analytes and the internal standard. Several comments from the participating laboratories were discussed. However, none of them were assessed as critical. For 3-picoline the results were as follows: in the TC two Grubbs' outliers and stragglers were identified as were two Cochran's outliers and stragglers. In the 200 SC sample two Grubbs' outliers and stragglers were identified as were two Cochran's stragglers. In the 600 SC sample two Grubbs' outliers and stragglers were identified as were two Cochran's outliers and stragglers. After removing the Grubbs' outliers and stragglers HorRat values of 1.4 (TC) and 0.6-0.7 (SCs) were calculated. For acetonitrile the results were as follows: in the TC three Cochran's outliers and stragglers were identified. In the 200 SC sample two Cochran's outliers and stragglers were identified. And finally in the 600 SC sample one Cochran's outlier and straggler were

identified. The accompanying HorRat values were 1.23 (TC) and 1.27 (200 SC) and 0.54 (600 SC) while no Cochran's outliers and stragglers were removed. The presence of the HorRat values 1.23 and 1.27 were explained as being caused by the low concentration of acetonitrile in the SC samples.

Ms Mary Ellen McNally recommended this method to be accepted as a provisional CIPAC method for the determination of acetonitrile and 3-picoline in chlorantraniliprole TC and SC.

Questions and remarks from the meeting.

- Two laboratories reported performed the analysis after dilution with *N*,*N*-dimethylformamide instead of the prescribed *N*, *N'*-dimethyl acetamide as solvent. Were these results excluded?
    - The statistical evaluation was performed with and without the results of both laboratories. There was no difference between both ways of calculation.
- The rel. 5% retention time deviation is too large if it is encountered within a measurement series. It is acceptable between series. This should be clear in the text.
    - The description of the method will be updated.

4.6 Clethodim by Ms Haixia Wang (5396, 5397)

Ms Haixia Wang presented the results of a full scale collaborative trial of two clethodim TCs, two TK and four EC formulations by 13 laboratories mainly from China of which 11 returned results. The clethodim content was determined by normal phase HPLC (Agilent ZORBAX RX-SIL (or eq.), 250 × 4.6 mm, 5.0 µm) at room temperature (±2°C) with UV detection at 254 nm and external standardization. The eluent was *n*-hexane : ethyl acetate : acetic acid, 940:40:20 (v/v/v) at a flow rate of 1.2 ml/min. Also the infrared spectrum of clethodim was shown, however this was not part of the full scale collaborative trial. Remarks and deviations of the method were reported. However, none of them were assessed as significant. The statistical evaluation of the data was done following DIN ISO 5725 and the 'Guidelines for CIPAC Collaborative Study Procedure for Assessment of Performance of Analytical Methods'. No outliers or stragglers were encountered. The HorRat values ranged from 0.38 to 0.65.

Ms Haixia Wang proposed the analytical method for Clethodim in TC, and TK and EC formulations to become provisional.

Questions and remarks from the meeting.

- Is the mean value calculated per day and then combined or are the mean value results of both days combined across both measurement days?
    - Calculated per day and then combined.
- The mentioning of room temperature at the HPLC conditions is not acceptable as the room temperature differs across the globe and during the different seasons. It should be set at a certain temperature.
- The results for the EC formulations are reported as g/kg. They should be reported as g/l.
- Why have you chosen for normal phase chromatography?
    - Clethodim is not stable in solvents used for reversed phase chromatography.
- Hexane is considered to be toxic and should be replaced by less toxic solvents as iso-octane or heptane.
- Was clethodim or clethodim-lithium being used for standard preparations? This should be very clear in the method description.
    - The lithium salt is much more stable compared to the clethodim.

4.7 Coronatine by Ms Yue Wang (5382, 5383)

Ms Yue Wang presented the results of a full scale collaborative trial of coronatine in two TCs and three SL formulations by 18 participants which returned 18 sets of results. The analysis was performed by high performance liquid chromatography on a reversed phase column (C18, no brand

indicated, 250 × 4.6 mm, 5.0 µm) at 35°C with UV detection at 220 nm and external standardization. The eluent was acetonitrile : aqueous phosphoric acid, 30:70 (v/v) at a flow rate of 1.0 ml/min. Seventeen of the participating laboratories used a variety of HPLC columns with comparable reversed phases and one laboratory used a comparable reversed phase however with different dimensions. None of the deviations were assessed to be critical. 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. With the SL1 formulation two Grubbs' stragglers were identified, no further Grubbs' stragglers or outliers were encountered. HorRat values, calculated without elimination of the stragglers of 0.3-0.4 were identified for all samples.

Ms Yue Wang finalised her presentation by stating that CHIPAC considered the method for the analysis of coronatine in TC and SL formulation to be suitable validated and recommended to become provisional.

Questions and remarks from the meeting.

- The data of SL-1 and SL-2 seemed to be identical. Please check.
    - Probably a mistake was made. Data will be double checked.
- The target concentration for the SL formulations is missing. Please adjust the report.
    - In this case the sample preparation is different, as there was no dilution of the sample. The description of the method will be updated.
- Reversed phase chromatography was applied whereas coronatine theoretically has multiple isomers. Normal phase chromatography would be method of choice for distinguishing between the isomers.
    - Only one isomer is present in the coronatine material so normal phase chromatography was not needed. This will be clarified in the text of the method.

4.8 Emamectin benzoate by Ms Xu Rong (5386, 5387)

Ms Xu Rong presented the results of a small scale collaborative trial of emamectin benzoate in three TC samples by three Chinese participants. The analysis was performed by high performance liquid chromatography on a reversed phase column (C18, no brand indicated, 250 × 4.6 mm, 5.0 µm) at 30°C ± 2°C with UV detection at 245 nm and external standardization. The eluent was methanol : acetonitrile : ammonia solution, 25:55:20 (v/v/v) at a flow rate of 1.2 ml/min. The composition of the ammonia solution was not given. Each of the three participating laboratories used a different HPLC column and one laboratory had to adjust the flow rate to 1.0 ml/min accordingly. The deviations were assessed as minor. 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. Testing for outliers/stragglers of the participating laboratory mean values was not performed. The HorRat values of emamectin sum of B_{1a} and B_{1b} of the three TC samples were 0.5 each. The HorRat values of emamectin B_{1a} were in the range of 0.04 - 0.05. All results fulfilled the required criteria.

Ms Xu Rong finalised her presentation by stating that CHIPAC considered the method for the analysis of emamectin benzoate in TC material to be suitable validated and recommended a full scale CIPAC collaborative trial.

Questions and remarks from the meeting.

- It was remarked that where emamectin benzoate was mentioned, emamectin (without the counter ion) was analysed. This should be clearly clarified in the method. Emamectin benzoate is a derivative of the a.s. emamectin having the ISO common name.
- The ammonia concentration should be specified.
- The total run time is 35 minutes which is long. The chromatograms looks empty and the baseline separation between both abamectin B1a and B1b is approximately 5 minutes. Why is not tried to go for a shorter retention time?

    - In samples more interfering peaks might be present.
- In the table about analytical conditions the wavelength of laboratory three was given as 210 nm. This should probably be 245, in line with the method and both other laboratories.
- If photodegradation is rapid, then this should be highlighted in the text of the method by mentioning that special precautions are required.

4.9 Gibberellic acid by Ms Xu Rong (5378, 5379)

Ms Xu Rong presented the results of a full scale collaborative trial of gibberellic acid in three TC samples by 20 participants and 19 of them returned results. The analysis was performed by high performance liquid chromatography on a reversed phase column (Agilent SB-C18, 150 × 4.6 mm, 5.0 µm) at 33°C with UV detection at 210 nm and external standardization. The eluent was methanol : 0.05% phosphoric acid in water 33:67 (v/v) at a flow rate of 1.0 ml/min. Several participants reported deviations in the use of different brands of C-18 columns and two laboratories have set the column temperatures at 30°C instead of the prescribed 33°C. All changes were assessed as minor. 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. Testing for outliers/stragglers of the participating laboratory mean values was not performed. The HorRat values of the three TC samples ranged from 0.4-0.7 thus fulfilling the required criteria.

Ms Xu Rong finalised her presentation by stating that CHIPAC considered the method for the analysis of gibberellic acid in TC material to be suitable validated and recommended to become provisional.

Questions and remarks from the meeting.

No comments were given or questions were asked by the meeting.

4.10 Isocycloseram by Mr Christian Mink (5370, 5371)

Mr Christian Mink presented the results of an isocycloseram chiral method collaborative trial for TC and WP. Isocycloseram consists of four isomers with a defined composition: 5*S*,4*R* 87.5%, 5R,4*R* 5.5%, 5*S*,4*S* 3.0% and 5*R*,4*S* 0.1%. The chiral analysis was performed by high performance liquid chromatography on a Chiralpak IG-3 (Daicel, 150 × 4.6 mm, 3 µm) at 40°C with UV detection at 265 nm and external standardization. The eluent was water : acetonitrile : methanol 25:50:25 (v/v/v) at a flow rate of 1.0 ml/min. All peaks were baseline separated. Three TC and two WP materials were sent to seven laboratories and all laboratories reported results. Three minor deviations were reported which were of no significance for the results. Excluding stragglers and outliers both WP samples returned HorRat values ranging from 0.01 – 0.02 for the 5*S*,4*R* isomer, 0.45 – 0.46 for the 5*R*,4*R* isomer, and 0.73 – 0.88 for the 5*S*,4*S* isomer. The 5*R*,4*S* isomer content was below the detection limit of both WP formulations. The three TC samples returned HorRat values ranging from 0.02 – 0.05 for the 5*S*,4*R* isomer, 0.5 – 0.96 for the 5*R*,4*R* isomer, and 0.45 – 0.69 for the 5*S*,4*S* isomer. Only in one TC the 5*R*,4*S* isomer content was above the detection limit which resulted in a HorRat value of 1.81.

Mr Christian Mink concluded that with exception of one result for the isocycloseram 5*R*,4*S* isomer the method fulfilled all the requirements. As explanation of the 5*R*,4*S* isomer deviation it was highlighted that the 5*R*,4*S* isomer content was near or below the detection limit of the method.

Questions and remarks from the meeting.

- It was not clear what the aim of the method was as it was announced as an identification method but was reported as a quantitative method.
    - The method was validated as an identifying method as the composition of the isocycloseram is strictly defined by ISO. The identification of the composition was a

request of the CIPAC 2023 meeting in Braunschweig.

- Why did only seven labs participated as at least eight labs are required for a quantitative validation.
    - The method was intended as an identification method, not as a quantification method.
- Was the percentage set at 100% for the total isocycloseram content?
    - Yes
- Calculation of the relation between the different isomers based on their respective peak areas requires that the respective extinction coefficients are identical. Is this known?
    - They are equal, but it will be checked.

4.11 Metalaxyl by Mr Christian Mink (5372, 5373)

Mr Christian Mink presented the results of two small scale trials. First the results of a small scale trial of a GC method for the determination of the sum of the racemic mixture of the *R* and *S*-isomers were presented. And secondly the results of a small scale trial were presented of a HPLC method for the determination of the isomeric ratio *R* and *S*-isomers as present in metalaxyl-M based formulations. Both trials were performed with two TC materials (one racemic mixture and one enantiomerically enriched) and one SL, one ES and one WG formulation. Six laboratories participated and all returned results.

The total metalaxyl GC analysis was performed by GC-FID on a DB-5 MS (or equivalent) GC column (30 m × 0.25 mm, 0.25 µm), a temperature gradient of 160°C to 300°C, hydrogen as carrier gas and internal standardization. TBME was used as solvent for the TC and acetone was used for the formulated products. All participating laboratories used a DB-5 or equivalent column with two laboratories using GC-columns with a diameter of 0.32 mm. The changes were assessed as not relevant. HorRat values of 0.39 – 0.93 were obtained for metalaxyl (sum of isomers) in all samples.

Mr Christian Mink considered the GC method to be suitably validated and recommended to extent this to a full collaborative trial.

The chiral HPLC analysis was performed on a Chiralpak IB-3 (Daicel, 150 × 4.6 mm, 5 µm) at 40°C with UV detection at 220 nm and external standardization. The eluent was water : acetonitrile 65:35 (v/v) versus acetonitrile gradient at a flow rate of 0.8 ml/min. All laboratories used the same stationary phase but the column dimensions varied between laboratories. Four laboratories used the prescribed column whereas three laboratories used an HPLC column which was either longer or was of reduced diameter. As a result, flow rates and injection volumes were adjusted. However, all laboratories reported baseline separation between the *R*- and *S*-isomer. As the chiral method was intended for identification of metalaxyl-M only, the changes were assessed as not relevant. It was observed by the participants that the performance of the chiral column was determined by its age and history. Furthermore, it was observed that the WG extracts were not stable over a longer period and that the extracts should be made within 24 hours of the HPLC determination. Only the results of the *R*-isomer were reported and the HorRat values ranged from 0.09 – 0.28 in all samples.

Mr Christian Mink considered the chiral HPLC method to be suitably validated for the differentiation between the racemic metalaxyl and the enantiomerically enriched metalaxyl-M and recommended to extent this to a full collaborative trial.

Questions and remarks from the meeting.

No comments were given or questions were asked by the meeting for the GC method. However, comments were given or questions were asked by the meeting for the chiral HPLC method.

- Do not disclose the identity of the individual participants during the presentation.
- A column temperature of 40°C is rather high and an improved separation was achieved at lower column temperatures. Will a column temperature of 40°C also be prescribed for the full collaborative trial?
    - Yes, as it was validated at this temperature.

4.12 Pyroxasulfone by Ms Junhua Song (5392, 5393)

Ms Junhua Song presented the results of a small scale collaborative trial of pyroxasulfone in two TC samples, three SC samples and three WG samples in which three Chinese laboratories participated. The analysis was performed by high performance liquid chromatography on a reversed phase column (XBridge® C18, 150 × 4.6 mm, 5.0 µm, or equivalent) at 35°C with UV detection at 225 nm and external standardization. The eluent was acetonitrile : water, 45:55 (v/v) at a flow rate of 1.0 ml/min. Two laboratories used the prescribed HPLC column but the third laboratory used a C18 column of a different brand resulting in much longer retention times. This deviation was not assessed as critical. Including stragglers and outliers the HorRat values ranged between 0.13 and 0.54 for the two TC, three SC and three WG samples.

Ms Junhua Song recommended to extent this to a full collaborative trial.

Questions and remarks from the meeting.

- There was an error in the calculation formula, that should be corrected
- The filter was not mentioned in the description of the method.

4.13 S-Metolachlor by Ms Junhua Song (5394, 5395)

Ms Junhua Song presented the results of a small scale collaborative trial of S-metolachlor in two TC samples and three EC samples in which three Chinese laboratories participated. The analysis was performed by high performance liquid chromatography on a Daicel CHIRALPAK AY-H (250 mm × 4.6 mm × 5 µm or equivalent) at 30°C with UV detection at 230 nm and external standardization. The eluent was heptane : ethanol, 94:6 (v/v) at a flow rate of 0.6 ml/min. All laboratories used the same column. However, the retention times of the individual four isomers differed considerably. E.g. the retention time of the S1 isomer for lab 1 was 14.8 min (at a flowrate of 0.5 ml/min), for lab 2 was 12.9 min and for lab 3 was 16.6. Comparable differences for the other three isomers were obtained. No outliers were identified and HorRat values ranging from 0.25 – 0.28 for the sum of the two S-isomers were obtained for all samples.

Ms Junhua Song considered the method applicable for the determination of the S-isomer percentage in S-metolachlor TC material and EC formulation. A full scale collaborative trial was proposed.

Questions and remarks from the meeting.

- The formula of the S-metolachlor should be corrected
- Two different reference standards were used. Why?
    - Will be double checked after the CIPAC meeting
- The retention times of the different isomers differed considerably between the laboratories. Is an explanation available?
    - Will be answered after the CIPAC meeting
- The title of the presentation ('*5395/R Small scale collaborative trial for the determination of S-isomers ratio in S-metolachlor TC and EC*') is not correct as during the small scale collaborative trial the combined content of both S-metolachlor isomers was validated, not the ratio between the S-isomers.

4.14 Tebuconazole by Mr Terry Wang (5374, 5375)

Mr Terry Wang presented the results of a full scale collaborative trial of tebuconazole with 15 participating laboratories from Asia, America and Europe of which 14 reported results in time. Two TC, two EC, two EW, two WP and two SC formulations were investigated by GC on a HP-5 MS (or equivalent) GC column (30 m × 0.32 mm, 0.25 µm), helium or nitrogen as carrier gas and internal standardization and using dicyclohexyl phthalate as internal standard. No temperature program settings were reported and two laboratories reported a 1:1 split injection ratio instead of the prescribed 20:1 ratio. Four laboratories used a GC column with a comparable stationery phase but

from a different brand. The deviations were assessed as not to affect the analytical results. The results of laboratory eight were outliers or stragglers (no further details were presented about the type of outliers or stragglers was presented) in two TC, one EC, two EW, two WP and one SC samples. The result of laboratory three in one TC sample was also identified as outlier or straggler. After elimination of the outliers or stragglers the HorRat values for all samples ranged from 0.18 to 0.80 therefore fulfilling the required criteria.

Mr Terry Wang considered the method to be appropriate validated for the intended purpose and recommended accepting it as a provisional CIPAC method for the determination of tebuconazole in TC material as well as EC, EW, WP and SC formulated material.

Questions and remarks from the meeting.

- The detector was not mentioned (FID?)
    - It should be there
- The meeting disagreed with Mr Wang that the application of 1:1 split injection ratio was not relevant (two laboratories reported the use of a 1:1 split injection ratio whereas a 20:1 ratio was described). This is a fundamentally different way of injecting and as a consequence these data should not be used in the statistical evaluation. That the data of both laboratories were in line with the other laboratories is not relevant.
    - The data of both laboratories were in line with the other laboratories
- Laboratory eight is a clear straggler. Is a reason known why their performance is deviating from the other participants?
    - The lab was excluded because of the tests.

It appeared that language problems were fundamental to the answering of Mr Wang and it was decided to send him the questions after the meeting.

4.15 Tembotrione by Ms Yue Wang (5380, 5381)

Ms Yue Wang presented the results of a full scale collaborative trial of tembotrione in two TC samples, two SC and two OD formulations in which 21 laboratories participated and reported results. The analysis was performed by high performance liquid chromatography on a reversed phase column (C18, no brand indicated, 250 × 4.6 mm, 5.0 µm) at 30°C ± 2°C with UV detection at 284 nm and external standardization. The eluent was acetonitrile : 0.1% phosphoric acid in water 30:70 (v/v) at a flow rate of 1.0 ml/min. All participating laboratories applied the prescribed method with minor deviations in HPLC column brand or column dimensions. The deviations were assessed as not critical. Several laboratories reported difficulties in dissolving the sample material and the sample preparation procedure was adjusted. Laboratory seven analysed the samples for a third day as they realized that their performance in analysing the two TC sample were below standard and the organizers decided that the results of the third day were allowed in the statistical evaluation. Nevertheless, both TC results of laboratory seven were identified as outliers. Laboratory 19 reported one straggler and one outlier in the two TC samples and also one outlier with an OD sample. Without removing the outliers and stragglers both TC samples showed HorRat values of 1.3 and 1.6. The HorRat values of both OD and SC samples were between 0.5 and 0.9. After removing of the outliers and stragglers the HorRat values were 0.2 for both TC samples and between 0.5 and 0.9 for the two OD and SC samples thus fulfilling the required criteria.

Ms Yue Wang considered the method to be appropriate validated for the intended purpose and recommended accepting it as a provisional CIPAC method.

Questions and remarks from the meeting.

No comments were given or questions were asked by the meeting.

5. Reports of expert witnesses on other matters

5.1 MT 148.2 Pourability by Mr Burkhard Wiese (5355)

Mr Burkhard Wiese presented the results of eight years of investigations into CIPAC MT 148.2 Pourability. The objectivities were to consolidate MT 148 & MT 148.1, to improve the usability and to perform a general editorial revision. First was presented why this parameter should be investigated. The FAO/WHO manual formulates it as '*To ensure that formulations have characteristics that will enable them to be poured easily from containers. If required, a residue after rinsing with water can be determined*.' The method consists of a pouring and a rinsing step. Pourability needs to be demonstrated for dispersed liquid formulations like SC, FS, OD / SE / CS / EW / ZC, ZW, ZE…. Changes were proposed for the container types: the use of Kilner jars, ISO certified cylinders (500 ml) and commercial pesticide formulation containers. Kilner jars are not useful due their unspecified shape. The graduations on ISO certified cylinders are not relevant, however the required dimensions remain unchanged. Commercial pesticide formulation containers remain applicable as they are relevant due to their use in agricultural practice.

In the method an ullage of 20% is mentioned. This translates best in a laboratory by using a 500 ml measuring cylinder, with a headspace above the liquid of ~100 ml (= 20 %). The next parameter which was assessed was rinsing as it is defined in MT 148 but not in MT 148.1. It was concluded that in the new MT method a tiered approach is defined where rinsing is required only when pourability is above 5% (or specified limit). Rinsing can be repeated twice, if needed. Further minor adjustments were related to the pouring time (less than 60 seconds is allowed), the rinsed residue (cannot be 0%) and the text explaining the 'Reason for revision'. In MT 148 the standing time is 24 hours and this was assessed by users of the method as much too long. This was underlined by the outcome of a DAPF round robin trial in which ten laboratories participated. The results indicated that the standing time has no influence on the pourability. Therefore 30 min standing time is acceptable.

In the same trial also the influence of the use of glass cylinders or HDPE bottles (as used by the producers of plant protection products) was investigated and it was concluded that '*Cylinder shape has strongest impact on variability of results, but further standardization is a challenge*.' And '*The usage of commercial packaging is a valuable alternative.*'

Mr Burkhard Wiese concluded that the results obtained with the new MT 148.2 are equivalent to those obtained with MT 148 and MT 148.1 and recommended that MT 148.2 supersedes MT 148 and MT 148.1.

Questions and remarks from the meeting.

- Was the reduction of the volume investigated to use les product?
    - No changes were considered.
- The revised method had made many good scientific and technical modifications. Suggestion was made to change the rinsed residue limit from 0.2% to 0.5% because of the uncertainty of the method.
    - The limits shouldn't be part of the method, this is up to the FAO Manual to recommend limits.
- It was proposed to change the wording "if required".
- It was asked if it is not possible to exclude the use of the cylinder
    - For the quality control laboratories it is not possible to have these commercial packages as they are of different types
- It was asked if it wouldn't be beneficial to use a formulation of 5% for the test?

5.2 DAPF Statement according to the proposed new MT-method "Density of Solids and Liquids with Automated Systems" introduced at the 67th annual CIPAC meeting (5398)

A new method for the determination of the densities of solids and liquids with fully automated systems was introduced by DAPF at the 67th annual CIPAC meeting in Braunschweig. According to the minutes of the technical meeting doubts arose within CIPAC whether the handling of a fully automated system should be included in a CIPAC method since it could be judged as an endorsement of certain brand of equipment. CIPAC members also stressed the importance of performing an interlaboratory test as correct calibration of the system was vital for obtaining correct results.

DAPF prepared a statement document to answer the two main questions of the last year meeting: why should a fully automated method be registered as a CIPAC method and why is no collaborative trial needed.

DAPF is well aware, that the proposed new method is very simple and most of the described procedure is part of a fully automated system. Nevertheless, since some authorities insist on using CIPAC MT methods for data generation and the density is a data requirement for all liquid and in some parts of the world also for solid PPP´s, it seems adequate to describe the use of automated gas comparison pycnometers and oscillating density meters in an independent CIPAC MT method.

This agenda point was mistakenly put under agenda point 7 and no discussions were hold. It was proposed to circulate the document and the decision will be taken based on the comments.

6. Revision/update of CIPAC guidelines

6.1 CIPAC Guideline by Mr Dirk Wolffram (5254)

Mr Hänel explained that no final version was available so therefore it was decided before the meeting that a discussion based on a draft document was not useful. The annotated draft document will be circulated among the members for comment with a three months response time so that the final version can be discussed in the 2025 CIPAC meeting.

7. Replacement of obsolete methods, comments to existing methods, errata

It was asked who defines if a CIPAC method becomes obsolete. The answer was that if it is not in use or if it is a packed column GC method, it might become obsolete. In the previous years there was a programme of reviewing the older CIPAC methods and the PAC decided if it is obsolete or not.
There weren't reported any proposals for replacement of obsolete methods or comments to existing methods.

8. Minutes of the 67th meeting (5365/P)

The minutes were circulated to the participants by e-mail. After comments were received and agreed upon no further comments were sent, so as a conclusion, the minutes were accepted as a true record of the last year meeting.

9. Secretary's report (5366/P)

Mr Bura presented the Secretary's report. The report was previously circulated to members by e-mail. No comments were received. It was accepted.

10. Discussion of individual compounds

xxx S-methoprene

The normal phase HPLC method (CIPAC/5359) for the determination of S-methoprene in technical materials was accepted as **provisional** CIPAC method as after the elimination of the results of laboratory 9 the recalculated results were within the relevant criteria.

400 metolachlor

The capillary gas chromatographic method with FID, using internal standard chromatography with flame ionization detection, using dipentyl phthalate as internal standard (CIPAC/5335), for the determination of metolachlor in TC, EC and EW formulations was accepted as **full** CIPAC method with the remark that the new method supersedes the current method.

xxx isocycloseram

The reversed phase HPLC method (CIPAC/5349) for the determination of isocycloseram in TC and WP formulations was accepted as full CIPAC method.

33 PBO

The extension of the gas chromatographic method CIPAC 33/LN/(M)/3 (CIPAC/5343) to the determination of PBO in coated insecticidal nets in the presence of deltamethrin was accepted as **full** CIPAC method.

MT 185.1 Wet sieve test

The revision of methods MT 182 and MT 185 (CIPAC/5353) to combine into a single method for wet sieve test was accepted as **full** CIPAC method under the prerequisite that it supersedes both MT 182 and MT 185.

Active substances discussed this year:

4.1 4-(trifluoromethyl)-nicotinamide (5368, 5369)

No comments were given or questions were asked by the meeting. The method can proceed to full scale trial.

4.2 Abamectin (5384, 5385)

The comments and remarks were sufficiently answered during the open meeting. The method can proceed to full scale trial.

4.3 Broflanilide (5388, 5389)

No comments were given or questions were asked by the meeting. The method was accepted as **provisional** method.

4.4 Bifenthrin, chlorfenapyr and PBO (5390, 5391)

The comments and remarks were answered during the open meeting, the method was accepted as **provisional** CIPAC method considering the amendments in the description of the method.

4.5 Chlorantraniliprole relevant impurity (5376, 5377)

Some remarks were given by the meeting.

- The presence of two HorRat values of around 1.2 for the SC formulations is fully acceptable.
- This might be the case but it cannot be explained by stating that the low concentration is responsible for that as HorRat value incorporates the actual concentration of the analyte in its calculation formula. So further explanation is required.
- It was asked what is the maximum acceptable number of removed outliers? Max 20%.

- The relevant impurity methods validated through CIPAC are available free of charge.

Conclusion: after further clarification of the HorRat values between 1 and 2 the method was accepted as **relevant impurity method**, freely available from the CIPAC site.

4.6 Clethodim (5396, 5397)

Some remarks were given by the meeting.

- The vast majority of participating laboratories was from China. That intervenes with the CIPAC policy of a global coverage of participating laboratories in interlaboratory trials. However as this is not strictly stipulated in the CIPAC guidelines it cannot be requested from the organizers of this trial.
- A remark should be added to the method that hexane is considered to be a toxic solvent and it should be checked if hexane could be substituted with a less toxic compound like heptane or isooctane.

Conclusion: the method was accepted as **provisional** CIPAC method, with the remark that hexane is considered a toxic substance and with amendments of the used temperature.

4.7 Coronatine (5382, 5383)

Some remarks were given by the meeting.

- The datasets of SL1 and SL2 are identical and a further explanation/clarification by the presenter/company has to be given.

Conclusion: pending the clarification of the datasets of SL1 and SL2 the method can be accepted as **provisional** method.

4.8 Emamectin benzoate (5386, 5387)

Some remarks were given by the meeting.

- The remarks and questions during the open meeting were not fully satisfactory answered. The method should be adjusted before initiating the full scale trial

Conclusion: after adjustment of the method it can proceed as full scale trial.

4.9 Gibberellic acid (5378, 5379)

No comments were given or questions were asked by the meeting. The method was accepted as **provisional** method.

4.10 Isocycloseram (5370, 5371)

Some remarks were given by the meeting.

- Provide data to prove that the extinction coefficients of the different isomers are equal.
- An elaborate discussion emerged because of the dual aspect of the interlaboratory validation procedure. The method was notified as an identification method. However, the identification required quantification of the different isomers as the composition is defined by ISO. And as the quantification method is not capable of distinguishing between the different isomers, this method can only report the total isocycloseram concentration.

Conclusion: The methodwas accepted as chiral identity method with the need of clarification of the absorption coefficient of the isomers.

4.11 Metalaxyl (5372, 5373)

No comments were given or questions were asked by the meeting. The method can proceed to full scale trial.

4.12 Pyroxasulfone (5392, 5393)

No comments were given or questions were asked by the meeting. The method can proceed to full scale trial.

4.13 S-metolachlor (5394, 5395)

The comments and remarks were answered during the open meeting, however some clarifications remain. After the clarifications have been received the method can proceed to full scale trial.

4.14 Tebuconazole (5374, 5375)

The comments and remarks were answered during the open meeting, however some clarifications remain and will be sent in written to Mr Terry Wang.
The method was accepted as **provisional** CIPAC method pending on the clarifications concerning the split ratio used and the right number of eliminated laboratories, requiring possible recalculation of the statistics.

4.15 Tembotrione (5380, 5381)

No comments were given or questions were asked by the meeting. The method was accepted as **provisional** method.

5.1 MT 148.2 Pourability (5355)

No comments were given or questions were asked by the meeting. The method was accepted as **provisional** method.

6. CIPAC Guideline (5254)

The new version of the guideline will be circulated with the commenting table with a deadline to make any proposals, comments.

11. Matters related to FAO and WHO specifications

There were no matters related to FAO and WHO specifications.

12. Any other business

No remarks, comments or questions were received.

13. Closure

Mr Hänel thanked the organising team and the participants for their contribution to the success of the meeting and closed the meeting.

Ralf Hänel	László Bura	Theo de Rijk
Chairman	Secretary	Assist. secretary