CIPAC

COLLABORATIVE INTERNATIONAL PESTICIDES ANALYTICAL COUNCIL LIMITED

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

Minutes of the 62nd Annual meeting

The 62nd meeting was held on Wednesday 13th June 2018 at the Sheraton Grand Panamá Hotel, Panamá City, Panamá.

Those attending
- Items 1 to 7 on 13th June: members, correspondents, observers and expert witnesses.
- Items 8 to 12 on 13th June: members, correspondents and observers (representatives of industry and commercial laboratories, by special invitation only)

1. Welcome and introductory remarks by the Chairman
The chair, Mr R. Hänel, opened the 62nd CIPAC meeting, and welcomed all the participants. Mr T. De Rijk acted as assistant secretary during the meeting.

2. Apologies
Apologies were received from: Mr L. Benke, Mr W. Bergermayer, Mrs E. Jacobsen, Mrs S. Marais, Mr A. Martijn, Mrs F. Mathieu, Mr A. Plumb, Mr F. Sánchez-Rasero, Ms A. Santilio and Mrs J. Schlosserova

3. Adoption of the agenda
No amendments were made to the agenda.

4. Reports of expert witnesses on collaborative trials

4.1 Acephate by Mr Rajendra Petkar (5139, 5140)
As Mr Rajendra Petkar was not present and as no report or other data were received, the item could not be discussed.

4.2 Broflanilide by Mr Takeo Okochi (5157, 5158)
Mr Takeo Okochi presented the results of a **small scale** collaborative trial on the determination of the active ingredient broflanilide in two technical materials and three wettable powders.
Broflanilide was determined by reversed phase HPLC using UV detection at 254 nm and external standardization. Elution was performed with acetonitrile-water (65-35 (v/v)) on an XSelect CSH C18, 250 x 4.6 mm (i.d.), 5 µm reversed phase column with a flow rate of 1.0 ml/min. The retention time of broflanilide was approx. 11.5 min.
Three Japanese laboratories participated in the trial and reported results. Laboratory 3 reported technical problems with the analysis on day 2. However as no scientific reasons could be identified the data of day 2 were accepted and statistically evaluated.
After statistical evaluation one Cochran's outlier was identified for technical material 2 (lab 3). However as the reproducibility relative standard deviation (RSD_R) of all five samples was well within the calculated Horwitz values (even including the Cochran's outlier) all results were

accepted.
The organizers recommended that the broflanilide method should progress to a full scale collaborative study.
The following comments were received from the meeting:

- Mr Ramesh asked whether dissolution was complete or whether precipitation occurred. Mr Okochi answered that the duplicate results showed excellent agreement this was considered to be not relevant.
- A second question related to the large difference in flow rate between the labs. Mr Okochi answered that no influence of the differences in flow rate on the results was expected and this was done to adjust the RT to approx. 5 min.

4.3 Etpyrafen by Ms Haixia Wang (5141, 5142)
Ms Haixia Wang presented the results of a **small scale** collaborative trial on the determination of the active ingredient etpyrafen in one technical material (TC-1) and two suspension concentrates (SC-1 and SC-2).
Etpyrafen was determined by reversed phase HPLC using UV detection at 230 nm and external standardization. Elution was performed with acetonitrile-0.05% phosphoric acid in water (80-20 (v/v)) on an Agilent ZORBAX SB C18, 150 x 4.6 mm (i.d.), 5µm, reversed phase column with a flow rate of 1.0 ml/min. The retention time of etpyrafen was approx. 8.4 min.
Proposed identity tests were based on Infrared (for TC-1) and LC-MS (for SC-1 and SC-2). However the identity test was not part of the small scale trial.
Seven Chinese laboratories participated in the trial and reported results. Deviations of the proposed method were mentioned by several participants, mainly related to the use of different reversed phase columns (four times). One laboratory reported that they used a column temperature of 40°C whereas the method prescribed a column temperature of 30°C.
Statistical evaluation of the data was performed following DIN ISO 5725 and "Guidelines for CIPAC Collaborative Study Procedure for Assessment of Performance of Analytical Methods". No Cochran's or Grubb's stragglers or outliers were identified and the Horwitz criteria were met for all three samples. HorRat values of 0.16, 0.31, and 0.38 were reported for TC-1, SC-1, and SC-2 respectively.
The organizers recommended that the etpyrafen method should progress to a full scale collaborative study.
The following comments were received from the meeting:

- Mr Hänel expressed his sincere gratitude for calculating and reporting the HorRat value.
- Mr Ramesh asked whether any difference in the isomer ratio has been noticed in the case of the laboratory using 40ºC? The answer was that the *E* isomer separation was not influenced by this increase of temperature.
- Mrs Nováková asked whether brown glassware (as described in the method) was necessary. Ms Wang answered that etpyrafen is photosensitive and that brown glassware had to be used.
- Mrs Nováková asked whether the LC-MS identity test for the SC formulation could also be performed by FTIR. Ms Wang answered that the SC formulation composition was complex and that therefore FTIR was less suited for the identification of etpyrafen.
- Mr Garvey asked whether additional identification methods for the SC formulation could be tested, for example UV, as LC-MS equipment was not widely available in testing laboratories. Ms Wang answered that this will be checked. It was also recommended to show a chromatogram of the separation of the two isomers.
- Mrs Saravia asked why two different HPLC eluents were used for the identity test and the active ingredient determination. Ms Wang explained that this was needed because of the used ionisation mode in MS with the remark that phosphoric acid based eluents cannot be used in LC-MS equipment.

4.4 Mancozeb by Mr Li Linhu (5146, 5147)

Mr Li Linhu presented the results of an **additional** CIPAC collaborative trial for mancozeb in two technical materials and three wettable powders. The additional trial was the result of method improvement suggestions made at the 61st CIPAC annual meeting (Rome, 2017). The original analytical method was modified with respect to environmental control (not controlled changed to 17±1°C), the length of the HPLC column (250 changed to 150 mm), HPLC column temperature (30 °C changed to 15 °C), pH of the mobile phase (9.5 changed to 10), composition of solution B (1 g/l sodium sulfite and 10 mM EDTA, pH 10.8 changed to 3 g/l sodium sulfite and 20 mM EDTA, pH 11.0), and the weight of the sample (100 mg changed to 40 mg).

Four laboratories participated in the trial, three from China and one from Europe. Three participants used the recommended conditions during the trial and reported no deviations or comments. However the fourth laboratory struggled with the method and had to repeat the experiments for six days.

The organizers decided to exclude the data of the fourth laboratory from the statistical data evaluation according to DIN ISO 5725. No Cochran's or Grubb's stragglers or outliers were identified and the Horwitz criteria were met for all three samples. HorRat values of 0.14, 0.11, 0.14, 0.26 and 0.24 were reported for TC-1, TC-2, WP-1, WP-2 and WP-3 respectively.

The organizers recommended that the method should be accepted as a provisional CIPAC method.

The following comments were received from the meeting:

- Mr Haustein remarked that the key issue is the temperature of the column and that of the laboratory and an environmental temperature of 17±1°C is very difficult to maintain for the average pesticide control laboratories.
- Mr Garvey remarked that at an environmental temperature of >20 °C the EDTA complex is breaking down, resulting in clogging of the HPLC system.
- Mr Ramesh proposed to cool the samples to lower temperatures before the analysis in a cooling chamber.
- Mrs Bos remarked that it is needed to use the same purity reference standard as the samples for solubility reasons, otherwise the results will be not correct.
- Mrs Bos asked whether the analysis would provide reliable answers when other WP concentrations than the tested concentration of 81% had to be determined. She expressed her concern of the correctness of the results if a 90% pure analytical standard is used to analyse a 50 % sample, for example. Mr Linhu answered that this was possible but again doubts remained about the validity of the answer.
- Mr Garvey remarked that the chromatographic peak resulted from an EDTA complex and not as such from mancozeb. Therefore the retention time was not a reliable identification parameter. This was seconded by Mrs Bos and Mr Pigeon as they stated that other dithiocarbamates (e.g. maneb) would elute at exactly the same retention time. Mr Hänel remarked that FTIR could be used as identity test. Mr Garvey and Mr Haustein suggested to use LC-MS for identification. Mr Haustein also suggested to use the identification method which is prescribed when using the current titration based method for mancozeb. From the audience came also the remark that the identity might also be proven by using the UV-absorbance spectrum. Mr Linhu answered that mancozeb is not amenable for LC-MS analysis, this is why they use IR.
- Mr Hänel concluded that many questions still existed and that the answers were not always sufficient to satisfy the audience. He proposed to try to analyse a sample of for example 50% purity with a standard of higher purity, also using the cooling chamber proposed and see if this works.

4.5 Propiconazole by Mr Simon Baker (5150, 5151)

Mr Simon Baker presented the results of a **full** scale CIPAC collaborative study for propiconazole in three emulsifiable concentrates (EC-A, B, and C) and two technical concentrates (TC-D and E). The TCs were tested for propiconazole content and *cis*/*trans* isomer ratio, whereas the ECs were

tested for propiconazole content only. Samples were dissolved in methyl isobutyl ketone (MIBK) containing an internal standard (docosane), and the diastereomer concentration was determined by capillary gas chromatography on a fused silica DB-5 (15 m x 0.32 mm i.d., d_f 1.0 µm) GC column using a 20:1 split injection, H_2 carrier gas (2 ml/min) and flame ionisation detection.
Out of 32 respondents 26 were selected and 21 participants from Asia, Europe and America sent back results in time. The reported method deviations were regarded as not significant and the data of all participants were subjected to statistical evaluation. Mandel's outliers were identified in EC-A (one k and one h outlier), EC-B (one k and two h outliers), EC-C (one k and two h outliers), TC-D (one k and one h+k outlier), and TC-E (one k and one h+k outlier). Incorporating all outliers the samples fulfilled the Horwitz criteria, with even better results after elimination of the outliers.
The proposed analytical method was also tested for the determination of the *cis*/*trans* isomer ratio in TC-D and E. The method showed excellent agreement with relative standard deviation of less than 2%.The organizers recommended that the method should be accepted as a provisional CIPAC method.
The following comments were received from the meeting:

- Mrs Nováková asked why MIBK was used as solvent whereas acetone also could be used. Mr Baker replied that MIBK was in the original method but that acetone also could be accepted as solvent.
- Mr Manso reported that his laboratory also used acetone.
- Mrs Saravia asked if the standards had the same isomer ratio as the samples, which was confirmed.

4.6 Prothioconazole by Mr Friedhelm Schulz (5159, 5160)
Mr Friedhelm Schulz presented the results of a **full** scale collaborative trial for prothioconazole in one TC and four different formulation samples: one emulsifiable concentrate (EC 250), two flowable concentrates for seed treatment (FS 100 and FS 258), and one suspension concentrate (SC 480) with 20 participants from America, Asia, and Europe.
The samples were dissolved in an acetonitrile/water solvent mixture followed by active ingredient determination using HPLC based chromatography on an Agilent Zorbax Extend C18, 50 mm x 4.6 mm, particle size 3,5 µm HPLC-column, a 10 mM phosphoric acid in water/acetonitrile-tetrahydrofuran-methanol (50-25-25) gradient, UV detection at 254 nm and external standard calibration.
The participants reported several deviations, mainly related to the use of different reversed phase HPLC columns. Also deviations of the prescribed flow rate, injection volume and the use of filtration instead of centrifugation were reported.
Statistical evaluation revealed one Grubb's outlier in FS 100, one in FS 258, and one in SC 480. Horwitz criteria were met for all five samples when the outliers were removed. However incorporating the outlier data resulted in RSD_R values which were above the Horwitz criteria for FS 100, FS 258, and SC 480. After removal of outlier data HorRat values of 0.43, 0.56, 0.74, 0.65, and 0.74 were reported for TC, EC 250, FS 100, FS 258, and SC 480 respectively.
The organizers recommended that the method should be accepted as a provisional CIPAC method in technical samples as well as EC-, FS- and SC-formulations.
The following comments were received from the meeting:

- Mr Manso asked how many potential participants have reacted and how many labs were selected. Mr Schulz replied that 40 potential participants have reacted, that 25 were selected for participation and that results of 20 participants were received. The selection of participants was based on a "first come-first served" procedure.
  Mr Hänel added that CIPAC has no guideline for the selection of participants in CIPAC trials. However a proposal from DAPA regarding this subject is on the agenda of this meeting at 6.3.
- Mr Garvey asked whether the outliers could be traced back to deviations from the method. The answer was that the outliers had deviations from the method.

4.7 Spirodiclofen by Ms Lyu Cong (5148, 5149)

Ms Lyu Cong presented the results of a **small** scale collaborative study for spirodiclofen in two technical samples (TC-1 and 2), three suspension concentrates (SC-1, 2, and 3), and four participants.

The method consisted of methanol extraction and reversed phase high performance liquid chromatography (C18, 250 mm x 4.6 mm; flow rate 1.0 ml/min), using UV detection at 260 nm and external standardization. The reported individual analytical conditions were assessed as "basically the same".

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. In SC-1 one Grubb's outlier was detected, but in the remaining formulations no outliers were established. Without elimination of the outlier all results complied fully to the Horwitz criteria.

The organizers recommended that the spirodiclofen method should progress to a full scale collaborative study.

No comments were received from the meeting.

5. Reports of expert witnesses on other matters

5.1 Determination of permethric acid anhydride (PAA) in transfluthrin TCs by Mr Michael Haustein (5105, 5106)

Mr Haustein presented the outcome of a peer validation study for a method for the determination of 1*R*-trans-permethric acid anhydride (PAA) impurity in technical transfluthrin.

The samples were dissolved in acetonitrile and the PAA content was analysed by use of a 0.01 M phosphoric acid in water/acetonitrile gradient, reversed phase high performance liquid chromatography (Zorbax SB C8, 1.8 µm, 100 mm x 4.6 mm at 70°C), UV detection at 210 nm and external standard calibration. The retention time of PAA was approx. 4.6 min.

The identity of PAA was confirmed by comparison of the UV-spectrum and retention time with the UV-spectrum and retention time of the certified reference material. The specificity of the analytical method for PAA was deemed sufficient as no interferences with known transfluthrin impurities were detected at the retention time of the analyte.

Initial validation with five samples spiked at 70 and 250 mg/kg under GLP conditions resulted in a proven linearity ranging from 53-530 mg/kg, and an acceptable precision and accuracy.

A peer validation followed with three participants in which the identity of PAA, the specificity of the method, and the linearity were confirmed by all participants. Each participant received three technical material samples (spiked at 70, 140, and 350 mg/kg respectively) and they were requested to analyse the samples in fourfold. The data presented in the statistical summary showed that the method is suitable to gain accurate and reproducible results for all test items tested.

The organizers recommend the acceptance of the proposed method for the determination of the relevant impurity 1*R*-trans-permethric acid anhydride in technical transfluthrin.

The following comments were received from the meeting:

- Mr di Loreto asked about the vulnerability of PAA in glass vials as the use polypropylene HPLC vials was recommended whereas all other vials used in the preparation of calibration solutions and extracts were made of glass. Mr Haustein replied that degradation of PAA was encountered once; however it was not encountered again in later experiments.

5.2 Peer validation for the quantitative identity test for zeta-cypermethrin by Mrs Mary Ellen McNally (5143, 5144)

Mrs McNally presented the results of a study which described a chiral method which can distinguish zeta cypermethrin, in conjunction with CIPAC 332, from other cypermethrin blends.

The chiral method consisted of HPLC analysis based on a HiChrom® Chiral D-PGC (25 cm x 4.6 mm, d_f 5µm) column, elution with a flow rate of 1.0 ml/min of 1,2-dichloroethane/hexane 0.91% (v/v), UV detection at 280 nm, and quantification based on a methyl benzoate internal standard. Two laboratories participated in the study and specificity, linearity, precision and accuracy were determined. During the study no interferences at the retention times of the 1*R trans* alpha *S* and 1*S trans* alpha *R* isomers was encountered proving the specificity of the method. Precision and accuracy was proven with recoveries around 100% and RSDs <2% for both isomers. Statistical evaluation resulted in no Cochran or Grubbs stragglers or outliers and all results complied fully to the Horwitz criteria.
The organizers consider this method to be acceptable to move into a CIPAC trial.

No comments were received from the meeting.

5.3 Imidacloprid method extension to UL by Mr Kevin King (5161, 5162)
Mr King presented the results of a validation study in which the extension of the CIPAC method for imidacloprid TC (582/TC/M2) to an ultra-low volume liquid (UL) formulation type was investigated. The proposed method, based on reversed phase high performance liquid chromatography using UV detection at 260 nm and external standardization, was identical to the original method with exception of the chromatographic run time which was considered to be a minor modification. The run time was extended from 10 min. to 30 min. due to an additional peak at approx. 16 min. whereas imidacloprid elutes at approx. 2 min. An additional identity check can be performed with the aid of GC-MS on an Agilent HP-5ms (5%-phenyl)-methylpolysiloxane: 30m x 250µm x 0.25µm).
The validation study was performed by two participating laboratories (five replicates) and resulted in an overall RSD_R of 0.97% which is well within the Horwitz criteria (HorRat 0.29), and proven linearity.
The organizers propose to extend CIPAC 528/TC/M2/3- to UL formulations.

No comments were received from the meeting.

5.4 Prallethrin method extension to UL by Mr Kevin King (5163, 5164)
Mr King presented the results of a validation study in which the extension of the CIPAC method for total prallethrin LV (743/LV/M) to an ultra-low volume liquid (UL) formulation type was investigated. The proposed method, based on capillary gas chromatography using flame ionization detection and triphenyl phosphate (TPP) as internal standard, was identical to the original method with exception of the inlet and detector temperature which were changed 270ºC to 325ºC. This was considered to be a minor modification. During the study it became clear that a matrix effect caused suppression of the prallethrin signal with approx. 25%. Correct quantification was obtained by using standard addition methodology. An additional identity check can be performed with the aid of GC-MS on an Agilent HP-5ms (5%-phenyl)-methylpolysiloxane: 30m x 250µm x 0.25µm).
The validation study was performed by two participating laboratories (five replicates) and resulted in an overall RSD_R of 2.28% which is well within the Horwitz criteria (HorRat 0.54), and proven linearity.
The organizers propose to extend CIPAC 743/LV/M/- to UL formulations.

No comments were received from the meeting.

5.5 Discharge Rate of Trigger Sprayers including clogging by Mr Oliver Gutsche (5152)
Mr Gutsche presented on behalf of DAPF the results of a validation study for the discharge rate (DR) of trigger sprayers (unknown CIPAC classification). The purpose of the developed method was to evaluate whether trigger sprayers are fit for use.
Based on preliminary experiments a draft method was proposed. After preparation of the sprayer (thorough shaking followed by as many strokes as are needed until the product is expelled followed

by an additional five strokes) the bottle is weighed, perform ten full strokes and weigh the bottle again. Repeat this procedure two times resulting in four weightings per sprayer. Calculate the DR per ten full strokes and calculate the average DR based on the three individual DRs.
Eight participants received three trigger sprayers. All trigger sprayers were tested with the standard procedure whereas the third trigger sprayer was also tested at 60% and 20% of the total volume. Overall 3x8x5 = 120 results were obtained resulting in a mean RSD_R of 0.26% proving that the method was fit for purpose and a draft MT method was proposed.

5.6 Discharge Rate of Aerosol Dispensers including clogging by Mr Oliver Gutsche (5153)
Mr Gutsche presented on behalf of DAPF the results of a validation study for the discharge rate (DR) of aerosol dispensers (AE). The purpose of the developed method was to evaluate whether aerosol dispensers are fit for use. Based on preliminary experiments a draft method was proposed. . After preparation of the sprayer (shaking for 10 s, followed opening the valve for 5 s) the bottle is weighed, shaken for 10 s, sprayed for 10 s, and weighed again. Repeat this procedure until the bottle is empty. Calculate the DR per 10 s, the fill level and the residue. The FAO manual (8.11, note 9) describes that the temperature of the bottle should be controlled for good repeatability. However experiments with two different types of AE have proven that temperature equilibration is not required.
Six participants received two AEs. All participants performed the test according to the draft procedure. Overall 84 results were obtained for the AE based on a propane/butane propellant and 140 results were obtained for a compressed air bag based AE. Average deviations of the mean DR were equal or less than 10% proving that the method was fit for purpose and a draft MT was proposed.

- Mrs Nováková mentioned that her colleague remarked that the calculation is quite complicated and proposed an alternative calculation method for consideration.

5.7 Dinotefuran method extension to RB by Mr Onie Tsabari (5165)
Mr Tsabari presented the results of an additional study which resulted from remarks made at the 61st CIPAC annual meeting (Rome, 2017). In 2017 the CIPAC meeting concluded that a second dataset was missing and that this had to be added.
The analytical method consisted of extraction with water/methanol (solid material) or dilution with water (liquid formulations) followed by HPLC chromatography on a reversed phase C8 type column and UV-detection at 270 nm. The study (five replicates, one day) was performed in another laboratory when compared to the previous experiment and resulted in and RSD_r of 2.6%. No additional validation parameters were reported.

No comments were received from the meeting.

6. Revision/update of CIPAC guidelines

6.1 CIPAC guidelines for Multi Active Ingredient and Matrix Methods for pesticides (MAIMM) by Mr Olivier Pigeon (5145)
Mr Pigeon presented on behalf of ESPAC a proposal for CIPAC guidelines for the development and adoption of Multi Active Ingredient and Matrix Methods (MAIMM) for pesticides. Current CIPAC methods are designed for one active ingredient (AI) whereas PPPs with more than one AI are becoming more and more common. Separate extraction methods are often not required as many AIs show similar extraction efficiencies with comparable methanol or acetonitrile based extraction mixtures. Furthermore the obligation to analyse each component separately for official control is not very efficient with regard to capacity and costs. Additional advantages are that the same procedure reduces the quantity of disposables and chemicals; it will lead to a reduction of analysis time and reporting time and, as a result, reduces the amount of errors.
In the design of the MAIMM the scope should be well defined as formulation type or different

physical-chemical properties of the AI will influence the procedure to a large extent. Furthermore preference for GC-FID or HPLC-UV should be specified, and the MAIMM should be applicable for commonly used equipment and low toxicity solvents. The validation should follow the same procedure as single AI methods: first a small scale trial (minimum five participants) followed by a full scale trial.
MAIMM should be additionally referenced in FAO/WHO specifications for official control, however in case of enforcement action the single AI method remains the reference. The proposal was circulated among ESPAC and CIPAC members in January 2018, and comments of several countries were incorporated in a consolidated version. The method is proposed to progress by incorporating the remarks of the meeting, to circulate the renewed consolidated version among all CIPAC members and eventually adoption at the 2019 CIPAC meeting. Mr Pigeon proposed two collaborative trials:
- A full scale collaborative trial on alpha-cypermethrin and chlorfenapyr in 2 ACY TC, 2 CFP TC and 4 LNs to be organized by CRA-W for presentation at the 2019 CIPAC TC Meeting
- A small scale collaborative trial to be organized by ESPAC on a MAIMM on several AI and PPP formulations (method from PCL, Ireland) to be organized by ESPAC for presentation at the 2019 CIPAC TC Meeting.
The following comments were received from the meeting:

- Mr Bascou made the clarification that "multi-active" methods for WHO products are always for a known formulation and can be used with the specification. He also mentioned that Industry wouldn't like to see these methods to become compulsory methods. Mr Pigeon replied that single methods remain the reference methods, the aim of multi methods is to facilitate QC. The aim is not to remove single methods but to have additional methods.
- From the audience a remark came that multimethods are being used as day-to-day approach because of capacity and/or reporting time pressure from authorities.
- Mr Hänel remarked that the CIPAC systems remains as it is. Nevertheless, the MAIMM could be helpful for QC-laboratories.

6.2 Extension of the methods

No documents were presented to the secretariat.
Mr Bura urged the audience to come with criteria (or guidelines) for method extension as it is increasingly difficult to decide whether a CIPAC method can be extended or that a full collaborative study has to be performed. Mr Bura asked the participants to send him all the proposals and comments by the end of the year.

6.3 DAPA proposal concerning the conduction of collaborative trials (5166)

Mr Hänel presented the DAPA proposal for a CIPAC Guideline "How to conduct a CIPAC collaborative trial". The proposal regulates the tasks for the collaborative trial coordinator, CIPAC, and the participants and foresees the following duties for the coordinator:

- Contact the Secretary of CIPAC to clarify open issues
- Provide a draft info sheet including:
  - the contact person
  - a method description containing the essential method parameters including the required equipment
  - the time frame of the trial
  - the max. number of possible participants (if is required to be limited).
- In cases that special equipment is required, the conductor of the trial should consider to provide this equipment to the participants
- The declaration of the samples sent out is clearly and correct (the samples itself as well as the cover letter)
- At the end of the trial, the participants will be informed concerning the results and the code used for the laboratory. This should be done three to four weeks before the CIPAC meeting.

Duties of CIPAC are as follows:

- Double check with the conductor of the trial whether all essential information are available
- Making the info sheet available to the interest public (via CIPAC website and e-mail distribution list)
- The procedure of selection the participants should start four weeks after the CIPAC information sheet has been sent out and is finalised within five days
- Selection of participants in the case of full scale trials. This will be done by the following procedure:
  - Drawing of lots
  - In the first round one participant of each region will be drawn
  Proposal for the regions: America (North, Latin, South); Europe, Asia, Africa/Oceania
  - In the second round all notified possible participants are put in one pot and the remaining number of participants will be drawn
  - CIPAC informs the conductor of the trial, the participants as well as the labs that were not selected

Duties of the participants are as follows:

- Participation in a trial should be indicated to CIPAC (e.g. via cipac-trial@...) and in "cc" to the respective contact person/company given in the info sheet
- The participants must be able to perform the required analysis (e.g. availability of the equipment incl. the described column)
- The method description has to be followed. The aim of the trial is to validate the method!
- Recommendations to improve the method are welcomed of course, but these should be done separately from the method validation.
- Any deviation from the original method described has to be documented and justified. This is important for the coordinator of the trial to judge whether this is an acceptable deviation or the deviation is so essential that the respective results cannot be considered in the assessment of the results
- The application should include the explicit address where the samples have to be sent.

The following comments were received from the meeting:

- Mr di Loreto remarked that the industry will be happy with the clarified procedure. However the requirement of providing equipment is seen as a drawback. Mr Hänel replied that this relates only to e.g. specialised glassware and not to complicated equipment.
- Mrs Nováková expressed her concern that laboratories from regions in which many potential participants are present will get less and less possibilities to participate. She therefore proposed to exclude laboratories in the 2nd round of the draw if a participant from the same country is already selected in the first round. Furthermore she proposed to exclude laboratories which were selected for participation in the first trial of a certain year from participating in other trials of the same year.
- Mr Wiese remarked that diversity between laboratories is important in obtaining a correct view of the capabilities of a CIPAC method.
- Mr Garvey remarked that expelled laboratories should have a favourable position in the next trial.

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

7.1 Revision of MT methods

Mr Hänel remarked that the revision of the Handbooks G, H, J, and K is scheduled for the end of August 2018, but the publication will be indicated by the CIPAC distribution list.

7.1.1 Revision of MT 30.5 Karl Fischer Method by Mr Bruno Partian (5154)

Mr Patrian presented on behalf of DAPF a proposal for revision of MT 30.5, Karl Fischer method using pyridine-free reagents to MT 30.6, Water Determination by Karl Fischer. The revision was motivated by the addition of coulometric titration, modified sample weight, changed equipment description, and as a result an editorial overhaul. After a short description of the current method the principle and advantages of coulometric titration were highlighted. It was also proven that reduction of the sample weight resulted in identical quantitative results. Therefore DAPF recommends adopting this method as a provisional CIPAC MT method.

7.1.2 Revision of MT 172.1 Flowability of granular formulations (5155)

Mr Wiese proposed on behalf of DAPF the revision of MT172.1 in order to make it a stand-alone method, to update references, to harmonize the test sieve, to clarify the hardness of the rubber mat, and to define the reporting of results. As all revisions are regarded as minor changes or only clarifications there is no need for additional validation and it is proposed to accept the revised method as MT 172.2.

7.1.3 Revision of MT 184.1 Suspensibility (5156)

The presentation was done during the CIPAC symposium. Mr Kundel could not be present at the meeting. Any comments should be forwarded to Mr Hänel.

7.2 Comments to existing methods

Methomyl (AOAC) method 264

In method 264 the elution order of methomyl and benzamide (internal standard) was reported to be reversed. As this method is an AOAC method (presented in 1996 in Beijing) it is impossible to check the raw data to see whether it is experimental or a typing error. Additional information is highly appreciated.

MT 58.3 Sieve analysis

In the description of MT 58.3 it is not clear whether the mesh size of a certain sieve is 420 µm or 425 µm as both sizes are mentioned. Probably it is only a typing error. Mr Wiese remarked that this should be known by DAPF. Errata will be put on the website after clarification.

MT 193 Friability of tablets

According to Mr Pigeon MT193 is replaced as it was not applicable to all different types of tablets. Comments can be sent to Mr Wiese and Mr Watanabe, who planned to revise this method.

MT 178

No remarks were made.

8. Minutes of the 61st meeting (5136/P)

The minutes were circulated to the participants by e-mail and were available on the website. No comments were received, as a conclusion the minutes are accepted as a true record of the last year meeting.

- No remarks, comments, questions were received.

9. Secretary's report (5137/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.

- No remarks, comments, questions were received.

10. Discussion of individual compounds

221.202: Chlorpyrifos-ethyl

At the previous meeting, the method was accepted as provisional. No further comments were received.
The method can be promoted to a **full** CIPAC method.
The reversed phase HPLC method using internal standard (CIPAC/5080) for the determination of chlorpyrifos ethyl in long lasting insecticidal nets was accepted as a full CIPAC method.

989: d-tetramethrin
At the previous meeting, the method was accepted as provisional. No further comments were received.
The method can be promoted to a **full** CIPAC method.
The capillary GC method (CIPAC/5101) using internal standard for the determination of d-tetramethrin in TC formulations and the chiral phase HPLC method (CIPAC/5101) for the determination of the isomer ratio of d-tetramethrin in TC formulations were accepted as full CIPAC methods.

987: Flupyradifurone
At the previous meeting, the method was accepted as a provisional CIPAC method. No further comments were received.
The method can be promoted to a **full** CIPAC method.
The reversed phase HPLC method (CIPAC/5094) for the determination of flupyradifurone in TC, AL, EC, EW, FS, SL and WG formulations was accepted as a **full** CIPAC method with the need to insert a comment concerning the sample preparation for the WG formulation.

749: Dinotefuran
The extension of the scope (CIPAC/5097) of CIPAC method 749/TC/M/3 for the determination of the dinotefuran content in bait formulations (sugar solution), with the modification of the eluent profile and sample preparation, was accepted as a **provisional** CIPAC method.

582: Imidacloprid
The extension of the scope (CIPAC/5108) of CIPAC method 582/TC/M2/ for the determination of the imidacloprid content in UL formulations, with the modification of the run time, was accepted as a **provisional** CIPAC method.

804: d,d-*trans*-cyphenothrin (5.6 Extension of CIPAC/804/EW/(M) for metofluthrin/d,d-*trans*-cyphenothrin/PBO EW (5082, 5083))
The extension of the scope (CIPAC/5082) of CIPAC method 804/EC/(M)/ for the determination of the d,d-*trans*-cyphenothrin content in Metofluthrin/d,d-*trans*-Cyphenothrin/Piperonyl butoxide EW formulations was accepted as a **full** CIPAC method.

33 Piperonyl butoxide (5.7 Extension of CIPAC/33/TC/M for metofluthrin/d,d-trans-cyphenothrin/PBO EW (5084, 5085))
The extension of the scope (CIPAC/5084) of CIPAC method 33/EW/M/3 for the determination of the piperonyl butoxide content in Metofluthrin/d,d-*trans*-Cyphenothrin/Piperonyl butoxide EW formulations, with the use of triphenyl phosphate as internal standard, was accepted as a **full** CIPAC method.

Active substances discussed this year:

338 Acephate
It was postponed to the next year.

994 Broflanilide

The small scale trial presented was proposed for a **full scale collaborative study** with the conditions of the proposed method (as the participating labs used different conditions).

…. Etpyrafen
A small scale trial was presented and the method was proposed for a **full scale collaborative study.** It was proposed to check if UV is possible as ID test.

34 Mancozeb
Additional work is required and Mr Hänel and Mr Bura will contact Mr Linhu about the extent of the work. It was proposed to repeat the study with formulations of different compositions, for example those provided by Mrs Bos to the company using the proposal of sample preparation of Mr Ramesh. Especially the focus should be on:

- testing lower concentrations than the reference
- testing whether the environmental conditions of <17°C are required
- testing the analysis with maneb and to resolve the identification issue (can the method differentiate between maneb and mancozeb).

408. Propiconazole
A full scale trial was presented and the method can be promoted to a **provisional** CIPAC method, with the note that acetone can also be used instead of MIBK.

745 Prothioconazole
A full scale trial was presented and the method can be promoted to a **provisional** CIPAC method. However a comment on the applicability of filtration instead of centrifugation should be added.

737. Spirodiclofen
A small scale trial was presented and the method was proposed for a **full scale collaborative study**.

Permethric acid anhydride (5.1)
The method was noted and adopted.

zeta-cypermethrin (5.2)
Mr Bura will contact Mrs McNally as it is not clear whether FMC would like to propose the method as a quantitative method and go for a full scale trial or as a stereospecific identity test to be used with the existing CIPAC method 332. It was clarified that the intention of the method is to use it in conjunction with CIPAC method 332 to determine the *S*-isomer ratio of zeta-cypermethrin in zeta cypermethrin technical samples.

582 Imidacloprid (5.3)
The requested additional dataset was presented, therefore the method extension can be promoted to a **provisional** method.

743 Prallethrin)5.4)
The requested additional dataset was presented, therefore the method extension can be promoted to a **provisional** method.

Trigger sprayers (5.5)
Mr Hänel remarked that the trial was only validated by DAPF and therefore was not compliant to CIPAC guidelines. Mr Garvey replied that the remark of Mr Hänel was correct but that the method will only be applied within “DAPF-territory”. Mr Hänel will contact DAPF for clarification about their intentions.
Mr Hänel clarified with the head of DAPF that the intention of DAPF was not to get provisional

status. Consequently, the decision was that CIPAC full trials are recommended.

Aerosol dispensers (5.6)
The same as for trigger sprayers.

749 Dinotefuran (5.7)
The requested additional dataset was presented, therefore the method extension can be promoted to a **provisional** method. Mr Bascou remarked that the formulation type RB consists of a large variety of products which makes it difficult to assess whether the performed very basic validation is adequate for all products in RB formulations. As the validation was conducted for sugar solution, this will be mentioned in the description of validity of the method.

CIPAC guidelines for Multi Active Ingredient and Matrix Methods for pesticides (MAIMM) (5145) (6.1)
An animated discussion followed in which the pros and cons of the proposed MAIMM approach were strongly discussed. Mr Pigeon clarified that the intention was not to skip the validation by collaborative trials of the individual methods, but to help the QC in the laboratories. In addition to his remark after the presentation of Mr Pigeon Mr Hänel asked why CIPAC should be involved and Mr Bura added that many structural problems were associated with the use of multimethods. Mr Garvey responded that about 90% of the AIs could be covered by an MAIMM method and therefore an MAIMM method would be highly beneficial for official control laboratories. Mr Hänel remarked that CIPAC supports the idea of an MAIMM but that the discussion (and a possible decision) remains still open. CIPAC might create a new type of methods under CIPAC umbrella, especially for public health formulations, analysing for more a.s.(but these probably will not be called multi-methods). Mr Pigeon replied that ESPAC will continue with the work related to MAIMM. Mr Bascou underlined once again that the industry (CropLife) does not want the MAIMM to be mandatory. Mr Garvey proposed to present next year a proposal how a multi-method for CIPAC would look like.

Extension of the methods (6.2)
Mr Hänel asked the audience to come forward with ideas for updating the guidance document for method extensions, as it is more and more difficult for the secretariat to decide whether an extension of a method is applicable or that a full (lengthy and costly) validation procedure has to applied. Mr Bura will send a letter to CHIPAC, ESPAC, DAPA, DAPF, JAPAC asking for proposals, how they would like to have the method extension, proposals for reviewing the existing guideline. Ideas should be sent to the secretariat.

DAPA proposal concerning the conduction of collaborative trials (5166) (6.3)
Also the DAPA proposal concerning the conduction of collaborative trials resulted in an animated discussion. Mr Hänel did not see the reason why certain laboratories should be granted a favourable position in certain steps of the DAPA proposal as was proposed by Mrs Nováková in the meeting. Both Mr Hänel and Mrs Nováková could not reach an agreement on this subject. It was remarked that the raised situation was only reality when too many laboratories apply for participation in a collaborative trial, which is not always the case. However it was acknowledged that feedback of the organiser of the collaborative trial to the CIPAC secretariat was a major advantage compared to the current practice. The feedback should lead to a more transparent process for the selection of potential collaborative trial participants. It was decided that the DAPA proposal is accepted, excluding selection but including a feedback to the CIPAC secretariat related to the selection procedure. It will be put on the website as a pdf document, as recommendation to run a CIPAC trial. Mr Chen drew the attention that in China there are a great number of laboratories without qualification and it was proposed to consider the list of acceptable laboratories available at ICAMA when selecting participants from China.

It was also proposed to exclude from the next trial those laboratories which did not sent back the results. It was proposed to think about acceptability criteria for the explanations acceptable in such cases.

Revision of MT 30.5 Karl Fischer Method (5154) (7.1.1)
The method was accepted as **provisional** CIPAC MT method MT 30.6.

Revision of MT 172.1 Flowability of granular formulations (5155) (7.1.2)
The revisions are accepted however Mr Wiese is contacted about the ownership of the drawings in the method. The method was accepted as **provisional** CIPAC MT method MT 172.2.

Revision of MT 184.1 Suspensibility (5156) (7.1.3)
Mr Hänel remarked he would try to get additional clarification from Mr Kundel considering the changes made to the method. The method was accepted as **provisional** CIPAC MT method MT 184.1.

11. Matters related to FAO and WHO specifications
Mrs YongZhen Yang expressed her gratitude for the excellent collaboration between CIPAC and FAO/WHO.
Mr Pigeon (in his role as JMPS chairman) agreed completely.
Mr Pigeon also remarked that CIPAC needed to agree on the adoption of methods determining more a.i. at least for public health products. Companies have to know whether they are allowed to develop multi AI-methods in the process of applying for WHO specifications. Mr Hänel replied that companies are free to do so at any time and if a full data set is presented for a method containing two a.i. it will be accepted.

12. Any other business
No remarks, comments, questions were received.

13. Closure

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

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