CIPAC

COLLABORATIVE INTERNATIONAL PESTICIDES ANALYTICAL COUNCIL LIMITED

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

Minutes of the 53rd Annual meeting

The 53rd meeting was held on Wednesday 10th June, and on Thursday 11th June 2009 at the Hotel Decameron Salinitas, Sonsonate, El Salvador

1. Welcome and introductory remarks by the chairman

The Chairman, Mr Ralf Hänel, opened the 53rd CIPAC meeting, and welcomed all the participants.

2. Apologies

Apologies were received from:
Mr Warren Bontoyan, Mr Walter Dobrat, Mr Roberto Dommarco, Mr Alain Dubois, Mr Jindřich Foltýn, Ms Teodora Iuraşcu, Mr Albertus Martijn, Ms Ji Ying

3. Adoption of the agenda

The agenda was adopted with the following amendments:
Agenda point 4.1 was moved to after point 4.6, and new items were added:
5.7 Influence of the temperature on the determination of persistent foam by Mr Héctor di Loreto,
5.8 Clothianidin in FS and WS formulations by Mr Martin Feyerabend

4. Reports of expert witnesses

4.1 Clothianidin by Mr Yasushi Asada (4658, 4659)

Mr Yasushi Asada presented the results of a full-scale collaborative study on the determination of clothianidin in technical product (TC), water dispersible granule (WG), suspension concentrate (SC), granule (GR), and water soluble granule (SG), using RP HPLC analysis with UV detection at 269 nm and external standardization. The results of all 19 participating laboratories have been taken into account for the statistical evaluation. For all samples, the values of RSD_R (reproducibility relative standard deviation) were smaller than those calculated by Horwitz's equation. The proposed method is considered appropriate for the determination of clothianidin in the TC, WG, SC, GR, and SG. JAPAC proposes that the method be accepted as a provisional CIPAC method. In the method it is specified "Zorbax Eclipse XDB-C18 (5 µm), or equivalent", clarification was requested on the columns considered equivalent. Mr Asada's answer was that according to the column manufacturer this is a common C18 column. It was also suggested and accepted that the injection volume should be changed to 5 µl and to modify the sample preparation for the SC and SG formulations by adding water before acetonitrile is added.

4.2 Deltamethrin by Mr Matthieu Zellweger (4673, 4674)

Mr Matthieu Zellweger presented the results of the extension of the scope of method CIPAC 333/LN proposed to coated nets to the determination of deltamethrin content in incorporated type polyethylene LNs of PN 3.0 net roof, using NP HPLC with dibutyl phthalate as internal standard and UV detection at 254 nm. The sample is extracted by refluxing with xylene. The extracted solution is evaporated and reconstituted in mobile phase. It was proposed that the extension of the scope of the existing CIPAC method 333/LN to be accepted. It was suggested to include a footnote

to inform the user that attention should be paid to the peak form and an example chromatogram should be included.
The stability of the active ingredient during the reflux step was questioned. The stability was not checked, but can be investigated on request. The influence of temperature in hot climate countries was also questioned. The method was tested in Vietnam, as a consequence this influence (30 °C – 35 °C) was tested. The use of xylene in chromatography was also questioned, and the change of the internal standard was also noted. It was clarified that xylene is used only for the extraction, then removed and the eluent is used as solvent for the chromatography.
Mr Pigeon explained that epimerisation does not occur during extraction with xylene. It was asked if any work to correlate analytical work with biological efficacy had been carried out? The answer was that no special work was carried out but the surface concentration might have an influence on efficacy.

4.3 Dimoxystrobin by Mr Reiner Kober (4671, 4672)

Mr Reiner Kober presented the results of a DAPA small-scale collaborative study on the determination of dimoxystrobin in TC, SE, and SC formulations using GC-FID analysis with a DB-1 capillary column, H_2 as carrier gas and internal standardization. The results of 6 laboratories that participated in the collaborative study have been taken into account for the statistical evaluation. One laboratory could not perform the trial because of problems with the equipment. All RSD values were low in the TC and all formulations. It was proposed to include a suspensibility test in the full trial, to use He instead of H_2 to avoid the hydrogenation of the internal standard or to change the I_{std} and use H_2. For the SE formulation the applicability of the method was questioned if the second a.s. is changed in the formulation. It was clarified that SC1 and SC2 are well defined formulations, but one cannot anticipate what other formulations will contain. Before sending out the information sheets for the full scale trial, these issues will be clarified with the company.

4.4 Fluazinam by Mrs Sarah Stiénon (László Bura) (4685, 4686)

Mr László Bura (in the place of Mrs Sarah Stiénon who could not participate to the meeting for justified reasons) presented the results of a full-scale collaborative study on the determination of fluazinam and related impurity 5 [5-chloro-*N*-(3-chloro-5-trifluoromethyl-2-pyridyl)-*α,α,α*-trifluoro-4,6-dinitro-*o*-toluidine] in the TC and SC formulations using RP HPLC with UV detection at 240 nm and external standard calibration. The results of all 8 participating laboratories have been taken into account for the statistical evaluation.
After careful examination of all provided laboratory data and removal of the outliers, retention of the remaining laboratory data is statistically valid for the determination of fluazinam or impurity 5 in TC and SC formulation. One of the laboratories determined the content of fluazinam and impurity 5 in on TC and one SC formulation instead of 2 respectively 3.
As a consequence, the minimum number of data sets necessary for a valid trial did not meet the requirements of the CIPAC guidelines for the determination of the active ingredient. The data for the determination of impurity 5 were acceptable. Observations were made that the methods are very time consuming.

4.5 lambda Cyhalothrin by Mr Martin Rodler (4664, 4665)

Mr Martin Rodler presented the results of the extension of the scope of method 463 to the determination of the content of lambda-cyhalothrin in LN formulations.
The active ingredient is extracted from the net section and dissolved in acetone containing dicyclohexyl phthalate internal standard. The specificity of the method has been demonstrated. It was noted that some evidence of epimerization was found (in alkaline medium) and it was questioned whether there is the possibility of hydrolysis. It was explained that the acidic conditions are used to prevent the epimerization, and hydrolysis was never experienced. The epimerization

takes place most probably during the manufacture and in the injector. If not a properly treated liner is used, significant epimerization may occur.

4.6 Metalaxyl-M by Mr Jim Garvey (4677, 4678)

Mr Jim Garvey presented the results of a small-scale collaborative study with 6 laboratories on the determination of metalaxyl and metalaxyl-M in TC, WP, WG and FS formulations, using GC-FID and chiral HPLC.

To determine the metalaxyl-M content, two methods are required. The total metalaxyl content (*R* + *S* enantiomers) is determined by achiral GC using a fused silica wide bore column with a DB5 stationary phase. An identity test is then used to determine the enantiomeric purity using HPLC using a chiral column. For technical materials, WP and WG formulations, a Chiralcel OJ column is used. This column is used in normal phase and is susceptible to damage by water, and thus a ChiraGrom2 column is used for FS formulations. This column can be used with RP HPLC.

Seven laboratories received samples for this collaborative trial and 6 of these laboratories submitted results. After the identification and removal of some outliers in the initial evaluation, the calculated RSD_R met the Horwitz criteria in all cases.

Three methods were supplied to the laboratories and although the achiral part was not significantly different for these methods, the chiral part involved the use of two different chiral columns. In this study four of the laboratories used the ChiraGrom2 column for all identity tests and a fifth laboratory identified an equivalent Chiralcel OD-H column and used this for all three identity tests. On the basis of these results ESPAC considers that this method is suitable to go forward to a full-scale collaborative trial with some minor changes to the methodology. ESPAC feels that the three methods provided can be condensed into a single method to cover the technical materials and the formulations tested in this collaborative study.

4.7 1-Methylcyclopropene by Mr Dennis Verona (4669, 4670)

Mr Dennis Verona presented the results of a full-scale collaborative study on the determination of 1-methylcyclopropene in the VP (vapour releasing product) using capillary GC-FID and a CP-PoraBOND Q column. The results of all 13 participating laboratories have been taken into account for the statistical evaluation.

The RSD_R value exceeded the Horwitz $RSD_{R(Hor)}$. However, given the unusual nature of the VP formulation, and the procedural difficulties encountered applying test methodology to a gaseous a.i. (encapsulated reactive gas), it may be that the Horwitz value is not realistic in this case. It was proposed to accept the method as a provisional CIPAC method for the determination of 1-methylcyclopropene in SmartFresh™ 3.3% Technology. Explanation was requested concerning the selection of the column. It was explained that this column was the only one which could meet all the requirements needed for this special analysis. The opinion of the participants to the trial was that the method is applicable in the laboratories without complications.

4.8 Piperonyl butoxide by Mr Matthieu Zellweger (4675, 4676)

Mr Matthieu Zellweger presented the results of the extension of the scope of method CIPAC 32+33+345/TK/M to the determination of piperonyl butoxide content in polyethylene LNs.

The piperonyl butoxide content is determined by capillary gas chromatography using flame ionization detection and internal standard. Xylene is used under reflux to dissolve the PE.

Specificity was proved, and the validation parameters i.e., linearity, accuracy and precision all met corresponding criteria of CIPAC guidelines for method validation.

4.9 Triadimefon by Mr Martin Feyerabend (4689, 4690)

Mr Martin Feyerabend presented the results of the extension of the scope of method 352/TC to the determination of triadimefon in EC, WG and GR formulations. Concentration range is acceptable, the method was specific for all the formulation types, and no change in sample preparation was necessary. Relative standard deviation was lower than the Horwitz, so reapeatability levels below

Horwitz. Recommend as provisional method for determination of triadimefon in EC, WG and GR formulations.

4.10 Triadimenol by Mr Martin Feyerabend (4687, 4688)

Mr Martin Feyerabend presented the results of the extension of the scope of method 398/TC to the determination of triadimenol in SC, FS and EW formulations.
Concentration range was inside the acceptable range. The method was found to be specific for all formulation types. Replacement of toluene by acetone for sample preparation was necessary. Good recovery with no critical interferences was achieved. It was recommend as provisional method for determination of triadimenol in SC, FS, and EW formulations. It was asked whether toluene should be changed to acetone in the original method, too? The answer was that it might be possible, but it should be checked for selectivity.

5. Other matters

5.1 Peer validation of determination of 1-CMP and 3-CMP in 1-MCP by Mr Dennis Verona (4667, 4668)

Mr Dennis Verona presented the results of the peer validation for the determination of 1-methylcyclopropene impurities in SmartFresh™ 3.3% Technology by capillary gas chromatography. Three lots of SmartFresh™ 3.3% Technology with a range of 1-CMP and 3-CMP concentrations were sub sampled and distributed to four independent laboratories. The laboratories prepared each sample in duplicate and chromatographed each preparation twice under the conditions of the method. Mean and %RSD were calculated for each sample from the analytical results. The reproducibility was evaluated from the interlab %RSD. The %RSD calculated over the four laboratories is <20% for both 1-CMP and 3-CMP in all three samples and on that basis the reproducibility was considered acceptable.
In conclusion, the proposed capillary GC method is considered appropriate for the determination of 1-chloro-2-methylpropene and 3-chloro-2-methylpropene in the formulation SmartFresh™ 3.3% Technology.

5.2 Peer validation of determination of TMPP in fenitrothion technical and formulations by Mr Yasushi Asada (4660, 4661)

Mr Yasushi Asada presented the results of the peer validation for the determination of the tetramethyl pyrophosphorothioate (TMPP) content in fenitrothion TC, WP, EC, and UL formulations, using capillary GC–FID and internal standardisation (*n*-butyl benzoate). The peer validation was conducted with four independent laboratories through the network of JAPAC.
For all samples, the analytical method was peer-validated in terms of specificity, linearity, repeatability and LOQ. The RSDs of repeatability for the TC and all formulations were found to be less than 20% for all laboratories that participated in this peer validation. The proposed method was successfully peer-validated and was considered appropriate for the determination of TMPP in fenitrothion TC, WP, EC and UL formulations.

5.3 Determination of retention/release index (wash resistance) of LNs by Mr Markus D. Müller (4680, 4681)

Mr Markus D. Müller presented a progress report on the draft CIPAC wash method for LN mosquito nets. The aim is to determine the retention or release index of LNs as a slow release formulations. It was proposed to replace the WHO wash method with soap 0.2% (pH 10-11). For the indirect validation of the wash method a small-scale study is proposed on 2 net types: coated and incorporated type. It was explained why ‘IEC detergent A’ was proposed as detergent. Suitable pieces of the net are subjected to successive wash-rinsing-drying cycles and the total active ingredient content determined in washed samples representing different wash points. The retention or release index is determined by the decrease of the total content of the insecticide after selected wash points using the appropriate analytical method. The aims of the small-scale study are to

answer questions such as wash steps 2 and 3 are representative or not, triplicate samples are adequate, what is the reproducibility of the wash steps, what are the acceptance criteria for analysis, is the detergent solution stable, what is the best practice for data evaluation? The proposed timelines for the trial were presented.
The number of optimal washing steps was discussed and agreed that for the method development up to 10 washes will be used, to be able to select the proper number. It was questioned why the bleacher is left out and was explained that because of stability issues. Nets will be rinsed 2 times to remove the adhering detergent. It was also explained that this wash method should mimic the WHO wash method as much as possible, but also to use internationally accepted (and available) standardized soap. This is the reason why the last year' proposal of using Savon du Marseille was changed, the replacing standardized soap will harmonize the wash method. It was also proposed to add some physical stress, exposing to light and temperature. Synthetic polymers don't really get wet, so after line drying, nets are folded and dried at 40 ^{o}C for 22 hours. The pyrethroid migrates to the surface, and concentration is re-established. It is important to have a defined temperature and time, so that concentration is re-established.

5.4 Validation of a new method for determination of deltamethrin and PBO in incorporated type polyethylene LNs by Mr Olivier Pigeon (4682, 4683)

Mr Olivier Pigeon presented the results of the validation of a GC-FID method for the determination of deltamethrin and PBO in incorporated type LNs, applicable also for deltamethrin determination in coated type nets. He recommended the method for a small scale or a full scale collaborative trial. An explanation was requested for the higher ratio of the *R* isomer at the roof in comparison to the side net. Mr Zellweger explained that the *R* isomer content is process related. Mr Zaim questioned whether the sampling scheme, which is for mosquito nets, can also be applied to Permanet 3, where the sides and the roof are of different fabric? The answer was that as the content expressed in g/kg is the same, this should not be a problem. The number of samples to be taken from the roof should be however further investigated.

5.5 CIPAC Guideline for analytical methods for the determination of relevant impurities by Mr Ralf Hänel (4684)

Mr Ralf Hänel presented the updated draft Guideline for analytical methods for the determination of relevant impurities, which contained the modifications after the comments received. It was proposed to change plant protection products to pesticides in the footnote to make it more general. It was decided to delete the LOQ definition of S/N ratio of 5 and that the LOQ of the analytical method is needed and not that of the determination step. Clarification was asked on what "independent" lab means? The time frame for adoption of methods was also subject of discussions. Mr Zaim said that both JMPS and CIPAC meet annually, the methods should be submitted to both, but taking into account the technical resources available there is no need to have two separate systems for adoption.

5.6 Publication of CIPAC Methods - view of a user by Mr Jürgen Zindel (4666)

Mr Jürgen Zindel presented the way how a user is searching for a CIPAC method, underlined the problems and made proposals for simplification. Mr Hänel answered that these comments are much appreciated by CIPAC and the proposal will be considered during the CIPAC closed meeting. Mr Müller appreciated this feedback which helps the editors to correct the mistakes for the next version of the CD-ROM. He also underlined the real improvement realised comparing to what was available several years ago.

5.7 Influence of the temperature on the determination of persistent foam by Mr Héctor Di Loreto (4691)

Mr Héctor Di Loreto presented the results of an experimental work aimed to answer the question: is the temperature an important parameter to set during the persistent foam determination? The

experiments were performed at 2 temperatures and 2 standard waters on 3 types of formulations. He concluded that temperature has some influence on the foam persistence which is unpredictable and depends on the type of formulation and standard water. A method was validated using temperatures of 30 ^{o}C.

5.8 HPLC analyses of Clothianidin in FS and WS formulations by Martin Feyerabend (4692)

Mr Martin Feyerabend presented the results of the extension of the scope of a method collaboratively tested to the determination of clothianidin in FS and WS formulations. The only change proposed was in the sample preparation, addition of 5 ml water prior to addition of acetonitrile. The inject volume was also reduced.

6. Replacement of obsolete methods

6.1 Update on Review of MT methods by Mr Ralf Hänel (4623)

The start of reviewing of the MT methods was delayed, report will be presented at the next year's meeting.

7. Minutes of the 52nd meeting (4652/P)

With the corrections received in writing, the Minutes of the 52nd meeting were unanimously accepted as correct.

8. Secretary's report (4654/P)

Mr László Bura presented the Secretary's report for the period from the 52nd CIPAC meeting held in Braunschweig, Germany, covering the attendance, number of trials conducted, the decisions taken concerning the methods and the election of correspondents and members of CIPAC, as it was detailed in the report circulated by e-mail before the meeting.

9. Discussion of individual compounds

Alpha-cypermethrin

The soap washing method for the determination of remaining active ingredient concentration remains a **tentative** MT method because of the ongoing general work on LN washing method(s)

Boscalid

The reversed phase HPLC method (CIPAC/4611) for the determination of boscalid in TC, WG, SC and SE formulations was accepted as a **full** CIPAC method

Cyprodinil

The reversed phase HPLC method (CIPAC/4625) for the determination of cyprodinil in TC, EC and WG formulations was accepted as a **full** CIPAC method. (clarification for the use of TFA and the introduction of a note concerning the use of the Teflon filter)

Deltamethrin

The extension of the scope of CIPAC method 333 (CIPAC/4497) for the determination of the total content of deltamethrin in LN formulations was accepted as a **full** CIPAC method.
The method for the determination of wash retention of LN formulations remains a **provisional** washing MT method because of the ongoing general work on LN washing method(s).

Fenitrothion

The normal phase HPLC method (CIPAC/4602) for the determination of fenitrothion in TC, WP, EC and UL formulations was accepted as a full CIPAC method. (the results of laboratory 5 was removed from the statistical evaluation)

Fipronil
The method extension to the reversed phase HPLC method (581/TC, CIPAC Handbook J) for the determination of fipronil in FS, SC, WG, GR and FG formulations (CIPAC/4630) was accepted as a **full** CIPAC method (a note concerning the addition of water to avoid insufficient dissolution to be added)

Haloxyfop-P-methyl
The chiral normal phase HPLC method (CIPAC/4618) for the determination of haloxyfop-P-methyl in TC and EC formulations was accepted as a **full** CIPAC method, subject to the official confirmation of the manufacturer that the column can be used at higher pressures. (the maximum recommended pressure of the column should be modified).

Indoxacarb
The chiral normal phase HPLC method (CIPAC/4613) for the determination of indoxacarb in TC, TK, OD, WG and EC formulations was accepted as a **full** CIPAC method. (With note explaining why the SC formulation should be renamed as OD, *n*-hexane was substituted with *n*-heptane).

Mefenpyr-diethyl
The reversed phase HPLC method (CIPAC/4627/A) for the determination of mefenpyr-diethyl in TC, and the normal phase HPLC method (CIPAC/4627/B) for the determination of mefenpyr-diethyl in WG, OD, EW and EC formulations was accepted as a **full** CIPAC method. (The calculation in the method description should be corrected).

Permethrin
The "washing method" (CIPAC/4503) remains as a **tentative** MT method because of the ongoing general work on LN washing method(s).

Prochloraz
The method for the determination of prochloraz in prochloraz-Zn-complex was accepted as a **full** CIPAC method

MT194: Adhesion to Treated Seed
The MT method for the determination of adhesion of seed treatment formulations to treated seeds (CIPAC/4580) was accepted as a **full** CIPAC MT method and is replacing MT 83 and MT 147

Clothianidin
The reversed phase HPLC method (CIPAC/4658) for the determination of clothianidin in TC, WG, SC, GR and SG formulations was accepted as a **provisional** CIPAC method, subject to changing the injection volume to 5 µl, to modify the sample preparation in the case of SC and SG formulations by adding water and introducing a footnote to the column drawing attention to the shape of the peak.

Deltamethrin
The extension of the scope of CIPAC method 333 (CIPAC/4673) for the determination of the total content of deltamethrin in incorporated PE LN formulations was accepted as a **provisional** CIPAC method

Dimoxystrobin
It was recommended to use He instead of H_2 and to go to a full collaborative trial.

Fluazinam
The reversed phase HPLC method (CIPAC/4686) for the determination of fluazinam in TC and SC formulations was accepted as a **tentative** CIPAC method, based on a previous decision on a similar case (acetamiprid in Brno) where the criterion of having minimum 8 valid set of results was not met.
The reversed phase HPLC method (CIPAC/4686) for the determination of the relevant impurity 5 in fluazinam TC and SC formulations was noticed and adopted

Lambda cyhalothrin
The extension of the scope of CIPAC method 463 (CIPAC/4664) for the determination of the content of lambda cyhalothrin in LN formulations was accepted as a **provisional** CIPAC method

Metalaxyl-M
It was proposed to go for a full scale collaborative trial.

1-Methylcyclopropene
The capillary GC method (CIPAC/4669) for the determination of 1-methylcyclopropene in the SmartFresh 3.3% vapour-releasing product was accepted as a **provisional** CIPAC method

Piperonyl butoxide
The method extension to the capillary GC method (AOAC-CIPAC 32+33+345/TK(M)) (CIPAC/4675) for the determination of piperonyl butoxide in incorporated PE LN formulations was accepted as a **provisional** CIPAC method

Triadimefon
The extension of the scope of CIPAC method 352 (CIPAC/4689) for the determination of the content of triadimefon in EC, WG and GR formulations was accepted as a **provisional** CIPAC method.

Triadimenol
The extension of the scope of CIPAC method 398 (CIPAC/4687) for the determination of the content of triadimenol in SC, FS and EW formulations was accepted as a **provisional** CIPAC method.

1-CMP and 3-CMP in 1-MCP
The capillary GC method for the determination of the relevant impurities 1-CMP and 3-CMP in 1-MCP formulation (CIPAC/4667) was noticed and adopted.

TMPP in fenitrothion technical and formulations
The capillary GC method for the determination of the relevant impurity TMPP in fenithrothion TC, WP, EC and UL formulations (CIPAC/4660) was noticed and adopted

Deltamethrin and PBO in incorporated type polyethylene LNs
It was proposed to go for a small scale trial.

Clothianidin
A method extension to a method just presented which got the provisional status at the meeting cannot be accepted. It needs to be discussed at the next meeting.

10. CIPAC Guideline for analytical methods for the determination of relevant impurities
The comment concerning the footnote (to use the word “pesticides”) was accepted. The comments

concerning the LOQ were accepted, the S/N ratio of 5 will be deleted. References will be inserted at the end of the document. Amendments will be made a.s.a.p. and shown to industry, and try to put on CIPAC website by end of June 09.

11. Matters related to FAO and WHO specifications
This item was discussed in the Joint CIPAC-FAO-WHO Open meeting
Mr Zaim announced that Dr Markus D. Müller is now the new chairman of JMPS.

12. Allocation of CIPAC numbers
This item was discussed in the Joint CIPAC-FAO-WHO Open meeting

13. Date and place of next meeting
The venue of the next meeting in 2010 will be in Ljubljana, Slovenia. The proposed dates for the JMPS Meetings are from 2nd June, Wednesday, ending on Saturday 5thJune, the CIPAC/FAO/WHO Open Meeting on Monday 7th June, CIPAC Symposium on 8th and the CIPAC technical meetings on 9th and 10th June 2010.

14. Any other business
None

15. Closure
The Chairman thanked the organising team and the participants for their contribution to the success of the meeting and closed the meeting.

Eric Sandmann	László Bura
Assist. Secretary	Secretary