CIPAC

COLLABORATIVE INTERNATIONAL PESTICIDES ANALYTICAL COUNCIL LIMITED

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

Minutes of the 56th Annual meeting

The 56th meeting was held on Wednesday 13th June, and on Thursday 14th June 2012 in Dublin Castle, Dublin.

Those attending
- Items 1 to 6 on 13th and 14th June: members, correspondents, observers and expert witnesses.
- Items 7 to 14 on Thursday 14th June: members, correspondents and observers (representatives of industry and commercial laboratories, by special invitation only)

1. Welcome and introductory remarks by the chairman
The Chairman, Mr Ralf Hänel, opened the 56th CIPAC meeting, and welcomed all the participants. He commented that the number of trials that were to be presented this year were very encouraging and expressed his thanks to industry for providing their documentation well in advance before the meeting.

2. Apologies
Apologies were received from:
Mr Hans-Paul Bosshardt, Mr Walter Dobrat, Mr Roberto Dommarco, Mrs Ana Gregorčič, Mrs Fátima O'Neil Pedrosa, Mr Francisco Sánchez-Rasero, Mrs Julianna Schlosserova, Mr Tony Tyler and Mrs Ji Ying

3. Adoption of the agenda
The agenda was adopted with no amendments.

4. Reports of expert witnesses

4.1 Amisulbrom by Mr Keiji Yokouchi (4839, 4840)
Mr Yokouchi presented the results of a **small scale** collaborative study on the determination of amisulbrom in technical product (TC), water dispersible granules (WG) and suspension concentrate (SC) formulations using HPLC-UV, detection at 254nm and external standard calibration. The trial was organised by JAPAC. Two samples of TC, one sample of WG and two samples of SC were provided. Three laboratories participated.
One laboratory commented that further ultrasonication was needed for WG and that both the analytical standard and the TC were affected by static during weighing.
The statistical evaluation was carried out according to the CIPAC guidelines. No stragglers or outliers were identified during the statistical analysis of the data.
The "pure" between lab standard variation was not calculated for two formulations.
JAPAC consider that the proposed method is appropriate for the determination of amisulbrom in TC, WG and SC and that a full scale trial can be conducted.

No comments were received from the meeting.

4.2 Chlorfenapyr by Mr Jürgen Fries (4825, 4826)

Mr Fries presented the results of a **full scale** collaborative study on the determination of chlorfenapyr in technical product (TC) and suspension concentrate (SC) formulations using HPLC-UV, detection at 300nm and external standard calibration. Two samples of TC and two samples of SC were provided. 22 laboratories offered to participate and results and data were received from 20.

Several remarks were received from the participating laboratories; in the main these were related to the use of different but comparable HPLC columns.

The statistical evaluation was carried out according to the CIPAC guidelines.

For TC 1 Lab 5 was a Dixon outlier and Lab 17 was a Cochran's outlier

For TC 2 Lab 17 was identified as a Dixon straggler

For SC 1 Lab 12 was identified as a Cochran's outlier and Lab 17 as a Dixon straggler

For SC 2 Lab 5 was identified as an outlier and a straggler, and Labs 11 and 17 as Dixon outliers

No data were excluded from the initial evaluation. Will all the data included SC2 fails the Horwitz criteria. When the results from Lab 17 were omitted and the statistical evaluation was repeated the Horwitz criteria were met in all cases.

Mr Fries concluded that the proposed method is appropriate for the determination of chlorfenapyr in TC and SC and proposed that the method by adopted by CIPAC as a provisional method.

Separation occurs during isocratic stage of HPLC run. Gradient is for cleaning up column & interference. Can also run as solely isocratic but would give longer run time.

The following comments were received from the meeting:

- Elution time = 2.6 minutes at "ambient temperature". What did ambient temperature mean? If the ambient temperature is >25°C then is it likely that there may be co-elution with any co-extractives? If it is necessary to maintain a fixed temperature of e.g. 20°C then this should be highlighted in the method. Mr Fries replied that the ambient temperature was considered to be 23-25°C and would propose to replace the term ambient temperature in the method with 25°C.
- Preparation of the calibration solutions for the TC and the formulations is not the same – it would be useful to have them the same for both sample types.
- One laboratory did some work and noted that detection at 260nm was more specific than the wavelength of 300 nm proposed. Mr Fries clarified that 300 nm was used as this enables the detection of other pesticides present in their formulations. He agreed that 260 nm would be acceptable for preparations that just contained clorfenapyr, however it is usually manufactured as a mixture with other pesticides.
- Please provide interpretation of the IR spectra as given in the method document.
- Lab 17 had no comments or remarks so they must have conducted the method exactly as written. It is strange therefore that this lab is an outlier throughout. Did you investigate this further? Mr Fries replied that he had e-mailed the lab in question but did not receive an answer before the meeting.

4.3 Cyazofamid by Mr Frédéric Joris (4833, 4834)

Mr Joris presented the results of a **full scale** collaborative study on the determination of cyazofamid in technical product (TC) and suspension concentrate (SC) formulations using HPLC-UV, detection at 280 nm and external standard calibration. Two samples of TC and three samples of SC were provided. 15 laboratories participated however only results for 14 labs were presented for the TC due to problems with sample shipment to 1 lab.

The temperature of the HPLC analysis had been adapted to 40°C following the small scale trial in order to reduce the run time from 60 minutes to 45 minutes; however 3 labs commented that the run time was still too long.

3 labs commented that a longer sonication time was needed to dissolve some samples fully.

No data were excluded from the initial evaluation. Will all the data included all samples meet

the Horwitz criteria. Some outliers were identified for the SC samples however the Horwitz criteria were met with all data included.
Mr Joris concluded that the proposed method is appropriate for the determination of cyazofamid in TC and SC and proposed that the method be adopted by CIPAC as a provisional method.

The following comments were received from the meeting:

- The run time of the HPLC analysis is long. It is not so common to have such long runs these days. Looking at the chromatograms it seems that there is nothing eluting after 30mins so perhaps it not necessary to have a run for 45 min? Mr Joris replied that this was true but the company believes that the long runtime was needed as some impurities in the TC can be eluted at about 40 min.
- It may still be possible to change the HPLC conditions to shorten the run time.
- It was noted that the identity of the labs was given in the report. Please kindly note that this is not standard practice.

4.4 Deltamethrin by Ms Liya Zhou (4837, 4838)
Ms Zhou presented the results of a validation study for the **extension** of the CIPAC method 333/LN/1 for determination of deltamethrin in long lasting (coated onto filament) insecticide nets. The existing CIPAC method 333/LN/1 is suitable and validated for the determination of deltamethrin in LN ("Permanet"). Samples are extracted in a mixture of iso-octane and 1,4-dioxane. The deltamethrin content is determined by normal phase HPLC-UV using dipropyl phthalate as internal standard and detection at 236 nm.
Ms Zhou stated that some minor changes were made to the current method such as a change in the ratio of extraction solvents/mobile phase and a change to the injection volume.
Validation data in accordance the CIPAC guideline for a method extension were presented. The method meets these criteria.
Ms Zhou concluded that the proposed method is appropriate for the determination of deltamethrin in "Fonyi LN" and proposed that the method extension be adopted by CIPAC.

The following comments were received from the meeting:

- The extraction solvent ratio has been changed from the original method from 80:20 to 95:5. Can you explain why? Ms Zhou replied that preliminary testing had shown there were some minor interfering peaks using the ratio 80:20 and that these were removed when ratio was changed to 95:5.
- A CIPAC method was developed in 1985 for deltamethrin using an eluent ratio 95:5, but in 2005 a newer method developed where the eluent ratio was changed to 96:4 and the HPLC column changed. Was there a reason to use the solvent as described in the older method for this particular LN type? The Chairman noted that there would be further discussion of the deltamethrin methods under agenda item 6.1 as there are now many methods and extensions which are all very similar. It would be ideal to have all the methods consolidated but this will be discussed under agenda item 6.1.

4.5 Flazasulfuron by Mr Frédéric Joris (4831, 4832)
Mr Joris presented the results of a **full scale** collaborative study on the determination of flazasulfuron in technical product (TC) and water dispersible granule (WG) formulations using HPLC-UV, detection at 260nm and external single point standard calibration. Two samples of TC and three samples of WG were provided. 16 laboratories participated however only results for 15 labs were presented for the TC due to problems with sample shipment to 1 lab.
Several changes were made to the method based on the result of the small scale trial:

- A grinding step was included for preparation of the WG samples
- All samples need to be analysed within 8 hours of preparation. This is because flazasulfuron is not particularly stable in acetonitrile solutions.

- The internal standard was removed.
- The temperature of the HPLC analysis was changed to 40°C
- Injection volume
- The detection wavelength was changed from 230 nm to 260 nm to get better resolution from interferences.

One lab commented that it was not necessary to grind WG samples – instead they added water.
Another lab commented that the sonication time for WG was not sufficient.
No data were excluded from the initial evaluation. With all the data included all samples meet the Horwitz criteria. One laboratory was identified as an outlier for most samples however the Horwitz criteria were met with all data included.
Mr Joris concluded that the proposed method is appropriate for the determination of flazasulfuron in TC and WG and proposed that the method be adopted by CIPAC as a provisional method.

The following comments were received from the meeting:

- Regarding the statistical evaluation while removing outliers it is interesting that the evaluation of the data without the outliers should also be presented in more detail. If the criteria are met without outliers being removed then the method should be published with all the data included. Mr Joris agreed that the most important results are those with all the data included. The Horwitz criteria are met with all data points included.
- Flazasulfuron is soluble at a concentration of 2g/l in water at pH 7. Based on this and the concentrations of the products flazasulfuron would be soluble/a suspension in water rather than dispersible so is it really a WG? Mr Joris replied that this would need to be discussed internally in his company.
- Is there a method for measuring suspensibility for the WG? Mr Joris replied he would need to check to see if there is data available after the meeting.

4.6 Fosthiazate by Mr Frédéric Joris (4829, 4830)
Mr Joris presented the results of a **full scale** collaborative study on the determination of fosthiazate in technical product (TC) and granule (GR) formulations using HPLC-UV, detection at 220 nm and internal standard calibration. Three samples of TC and two samples of GR were provided. 15 laboratories participated however only results for 14 labs were presented for the TC due to problems with sample shipment to 1 lab.
Several changes were made to the method based on the result of the small scale trial:

- A larger sample size was used to ensure a representative sample for analysis.
- The shaking and sonication extraction procedure is needed twice for the GR.
- Increase in injection volume

Two laboratories commented that they had used a lower sample weight for the GR than recommended.
Two laboratories used different extraction solvents to those outlined in the method (acetonitrile/water and methanol instead of the stated acetone).
No data were excluded from the initial evaluation, including the laboratories that had significantly deviated from the method (extraction solvent). With all the data included all TC samples meet the Horwitz criteria, however the criteria for the 2 GR samples were not met.
For GR 2 Lab 12 was identified as a Cochran's outlier and as a Grubb's straggler
When the outliers were omitted and the statistical evaluation was repeated the Horwitz criteria were still not met for the GR samples.
When the results from Labs 6 & 12 (those that used different solvent) and the outliers were removed the Horwitz criteria were still not met for the GR samples.
When the results from Labs 6 & 14 (those that did not use the recommended sample weight) and the outliers were removed the Horwitz criteria were met for the GR samples.

Mr Joris concluded that this indicated that the minimum sample weight of 1g is crucial for the good performance of the method. He concluded that the proposed method is appropriate for the determination of fosthiazate in TC and GR and proposed that the method be adopted by CIPAC as a provisional method.

The following comments were received from the meeting:

- Please include more detail in the method for the sample preparation and the extraction of the GR so that it's clear why this is needed.
- Is the internal standard really needed? Mr Joris replied that during the small scale test it was investigated whether or not an internal standard was needed. It was shown that the internal standard was needed from the small scale trials.
- Have you had time to evaluate the results without internal standard to see if the results show that it is not necessary? Mr Joris replied that unfortunately they had not but could do this if needed.
- GR will not dissolve completely so the internal standard could be needed to correct for any un-dissolved material.
- Why is acetone used for the extraction when the small scale study did not use acetone? Mr Joris replied that use of acetone is important. The small scale trial used acetonitrile and results were very variable.
- On lab commented that they tried several different solvents for the GR and found that acetone was the best solvent. They also noted that EPSAC had identified that acetone extraction was necessary.
- Why was Lab 6 excluded when it was not identified as an outlier by the statistical analysis? Mr Joris replied that Lab 6 was excluded as they used a different extraction procedure, but agreed that there was no statistical reason to exclude.
- If sample size is the critical criteria and not the extraction solvent then the results from Lab 6 should be included. Mr Joris replied that they had also calculated the Horwitz criteria with just Lab 14 removed and in this case Horwitz is met. But for consistency they removed both labs where different extraction solvents were used.

4.7 Permethrin/PBO by Ms Makiko Mukumoto (4841, 4842, 4843)

Ms Mukumoto presented the results of a validation study for the **extension** of the scope of CIPAC method 331/LN/M/3 for determination of permethrin and CIPAC method 33/LN/(M)/3 for the determination of PBO in LN. There are two existing CIPAC methods; one for permethrin and one for PBO. The study was organised with JAPAC.

It was necessary to change the internal standard used in method 331/LN/M/3 (permethrin) as it elutes close to PBO that is also present in their LN

Validation data in accordance with the CIPAC guideline for a method extension were presented for both methods. The method extensions meet these criteria in both instances.

Ms Mukumoto concluded that the methods are appropriate and proposed that the method extensions be adopted by CIPAC.

The following comments were received from the meeting:

- When you changed internal standard did you look at dicyclohexyl phthalate to see if there are any interfering compounds in the internal standard. Ms Mukumoto replied that they had checked and no interference was found.
- Why was a higher detector temperature used than stated in the original method? Ms Mukumoto replied that although 265°C was recommended by the CIPAC method, in order to remove any interference at end of run the column is heated more rapidly to its maximum so the detector temp was increased.
- In the chromatograms for the method extension for permethrin you can also separate PBO. Have you tried to quantify PBO by using the 1st method and if yes could you

compare those with the data for the PBO extension? Would it be possible to quantify PBO using the permethrin method extension instead of the PBO one? Ms Mukumoto replied that it would be possible but they considered it better to respect the existing CIPAC method.

4.8 Pyraxostrobin by Mr Yu Liang (4851, 4852)

Mr Liang presented the results of a **small scale** collaborative study on the determination of pyraxastrobin in technical product (TC) and suspension concentrate (SC) formulations using HPLC-UV, detection at 280 nm and external standard calibration. One sample of TC and two samples of SC were provided. 5 laboratories participated.
One lab commented that more time was needed to dissolve the SC using sonication.
The statistical evaluation was carried out according to the CIPAC guidelines. No stragglers or outliers were identified. All samples meet the Horwitz criteria.
Mr Liang proposed that a full scale study should be conducted.

The following comments were received from the meeting:

- The HPLC conditions state room temperature. It would be helpful to define a standard temperature for the method.
- It would be helpful to indicate the time of sonication. The problems with dissolution may be due to differences in the ultrasonic baths - it might be that different labs have baths that sonicate at different frequencies.
- For preparation of the SC it might help to add maybe 1-2ml of water to improve extraction.
- For both the sample and calibration solution an additional dilution step is included – why is this needed as the chromatograms show the response is not too high? Mr Liang replied that the column is very sensitive for this analysis so they wished to protect the column by diluting the standards and samples. It was suggested that using 20mg of standard and no dilution would be an alternative to dilution before analysis.
- Would it be possible to give a range/limit for column pressures to avoid any variation in retention time? Mr Liang replied that they will include a temperature for the column to avoid variations.
- The ISO common name refers to *E*-isomer only. We need to consider if there would be any resolution of the *E*- and *Z*- isomers. Do you have any info on the amount of *Z*-isomer in the TC and if the *Z*-isomer would be separated under the analytical conditions used? Mr Liang replied that he would check this and provide a response after the meeting.

4.9 Spinosad by Mr David Heim (4847, 4848)

Mr Heim presented the results of a validation study for the **extension** of the scope of CIPAC method 636/GR/(M)/- for determination of spinosad in GR. The study was organised with ESPAC. The existing CIPAC method 636 is suitable and validated for the determination of spinosad in TC, SC, GR and DT; however the existing GR method does not cover a new higher concentration granule that is now available. 5 laboratories participated. Each laboratory was provided with 5 different batches of the formation and 1 blank formulation.
One laboratory commented that sample vessels larger than 100ml were needed in order to ensure efficient shaking for extraction.
Validation data in accordance the CIPAC guideline for a method extension were presented. No stragglers or outliers were identified, however the Horwitz criteria were met for only two of the 5 SC samples.
Mr Heim reminded the meeting that for the full scale collaborative trial conducted on the other GR sample in 2007 the Horwitz criteria were met for only 1 of 3 batches. RSD values found in this study are comparable with those found in the original 2007 study.
Mr Heim proposed that the method is extended.

No comments were received from the meeting:

4.10 Thiamethoxam by Mr Andrew McIntyre (4845, 4846)

Mr McIntyre presented the results of a **full scale** collaborative study on the determination of thiamethoxam in technical product (TC), water dispersible granule (WG), suspension concentrate (SC) and suspension concentrate for seed treatment (FS) formulations using reverse phase HPLC-UV, detection at 230 nm and external standard calibration. Two samples of TC, one sample of WG, one sample of SC and one sample of FS were provided. 26 laboratories requested participation, of which 20 were sent samples. Results received from 18 laboratories were received within the timeline of the trial.

One laboratory commented that they had issues using the short HPLC column recommended.

No data were excluded from the initial evaluation.

For TC 1 Lab 3 was identified as a Cochran's outlier. For WG Lab 3 was identified as a Grubbs straggler.

With all the data included all samples met the Horwitz criteria therefore no further refinment was necessary.

Mr McIntyre noted that the RSD_R for the SC and FS were higher than for the solid samples, although within the acceptable Horwitz values and thought this may be due to the less homogeneous nature of the formulation types. He therefore proposed to include a remark regarding sample homogenisation before sample weighing to the method.

Mr McIntyre concluded that the proposed method is appropriate for the determination of thiamethoxam in TC, WG, SC and FS and proposed that the method be adopted by CIPAC as a provisional method.

No comments were received from the meeting.

5. Reports of expert witnesses on other matters

5.1 Determination of quaternary ammonium compounds in disinfectant formulations by potentiometric titration with an ionic surfactant electrode by Mr Adrian Burns (4849, 4850)

Mr Burns announced the initiation of a collaborative trial on the determination of quaternary ammonium compounds in disinfectant formulations.

A method was already available that used biphasic titremetric determination with a visual determination of end point however there were several disadvantages with the existing method:

- Used carcinogenic solvents
- End point difficult to determine particularly for products containing dyes, foaming products etc.
- Low concentration products needed large sample sizes – not ideal for titration.

The new method uses an ion surfactant electrode to determine the end point potentiometrically. The electrode is commercially available.

A small scale work has already been conducted and products tested already include thick & thin liquids, foaming products. Aerosol products were also tested but it was noted that the presence of alcohols may eventually irreversibly damage the electrode.

Mr Burns concluded that a collaborative trials would soon be underway and requested interested partied to contact him if they wished to participate. The trials will not include aerosol samples (for shipping reasons.)

The following comments were received from the meeting:

- CIPAC members have already indicated they are interested in participation in this trial. This will be a good chance to show collaboration between CIPAC and AOAC

5.2 Wash resistance index of LNs by Mr Olivier Pigeon (4827, 4828)

Dr Pigeon presented the results of a **small scale** collaborative study for a CIPAC MT method to determine the wash resistance index of LN formulation. Four samples of LN were provided; 2 of the coated type and 2 of the incorporated type. The samples covered a mixture of multi- and mono-filament yarns. 5 laboratories participated.

All laboratories commented that minor changes were needed to the methods used to determine the a.i. content after the washing tests were completed.

One lab commented that the hand shaking should be replaced by a machine to avoid human error and save time.

One lab commented that the time needed to reach equilibrium at 40°C between washes can be very different from product to product and suggested that that different temperatures, as well as different times between washes can be proposed for different products, depending on the nature of the technology.

One lab commented that they used a different way to fold the net pieces before placing in the sample bottles.

The data from each lab were reviewed and the mean and RSD of the active ingredient content, a.i. wash resistance and average a.i. wash resistance were calculated.

The inter-laboratory relative standard deviation (RSD_R) of the average wash resistance index after 4 washes (as recommended in the CIPAC method) ranged from 0.7%-3.8% for the four LNs and shows the acceptable reproducibility of the washing method. The inter-laboratory relative standard deviation (RSD_R) of the average wash resistance index after 3 and 5 washes was very close to the value obtained after 4 washes.

The method is straightforward and easy to carry out. If the washing and rinsing operations are well planned and organized, the method permit to perform the washing and rinsing of 36 net pieces (12 samples in triplicate) in a half day with 2 technicians.

Dr Pigeon proposed that the method is acceptable proposed some minor changes to the method:

- The use of a thermostat oven at 30°C ± 2°C as an option for laboratories not having access to a vibration free water bath.
- In the heating step : "fold the sample carefully once or twice in each direction" instead of "fold the sample carefully once in each direction".
- In the assay for determination of the total active ingredient content, adding of a footnote specifying that "Unwashed samples and wash samples must be analysed simultaneously to reduce the analytical error"
- Clarification of the footnote regarding the heating step at 40°C ± 2°C for 22 ± 2 hours before the next washing: "Lower <u>or higher</u> heating temperatures <u>as well as an extended storage time</u> may be necessary and justifiable for certain net / active ingredient combinations.
- Clarification of the footnote regarding the inversion of the bottle.
  Add : "<u>An appropriate machine can be used to invert the bottle</u> ."

Dr Pigeon concluded that the proposed method be adopted by CIPAC as a provisional method.

The following comments were received from the meeting:

- The goal of the wash method should be to be comparable with old WHO method. Have you compared the results from this trial with those from the old WHO method? Dr Pigeon replied that he had not done a comparison study, but when the results from this method are compared with the results generated in previous tests and the results used to set specification the data are quite consistent. Nevertheless the next step in developing the method will be to ask all manufactures to generate data using this new method and to confirm that the retention index in the current interim WHO specifications is still met or to provide a retention index based on the new method.

- It was mentioned that Ms Kozuki already generated data and showed during the previous meeting that the soap used is the best replacement of the Savon du Marseille.
- You did not include any combination nets in the collaborative study. In case of combination nets how many samples would you take? Dr Pigeon replied that for combination nets each part of the net would need to be tested and there is a footnote in the method to address this. There is no reason why the method cannot be used for other types of nets, too.

5.3 CIPAC MT 47.3 persistent foam by Mr Jürgen Zindel (4835, 4836)

Mr Zindel on behalf of DAPF presented a proposal to update CIPAC method MT 47 Persistent foaming with the aims of

- Providing a method applicable to all formulation types (MT 47.2 is only for SC)
- Standardising the glassware used
- Standardising the CIPAC water used
- Including a temperature at which to conduct the test.
- Clarifying which time points are critical.

The proposals included a recommended temperature of 25 ±5°C and recording the volume of foam after 1 and 12 minutes only.

Mr Zindel presented data from a DAPF collaborative trial that compared results generated using CIPAC MT 47.2 with those generated using the updated method for SC, SL ,EW and SG formulations.

- The results of new "MT 47.3" are comparable to MT 47.2
- Standard deviation of both methods is similar.
- No tendencies if extreme volumes are used.
- The New MT 47.3 is applicable to all tested formulation types.

Mr Zindel concluded that the proposed method is appropriate and DAPF proposed that the method MT47.3 be adopted by CIPAC as a provisional method.

The following comments were received from the meeting:

- Is it your proposal that MT 47.3 will supersede MT 47.2? Mr Zindel confirmed this was the proposal.
- Temperature of the measurement is important. We would suggest that perhaps 30°C is better than 25°C as this would be in line with other standard CIPAC methods. Mr Zindel replied that the suggested temperature was 25 ±5°C and this would also cover 30°C
- You have proposed a BS EN ISO number for the cylinder. It's not that easy to determine from the catalogue if the cylinder has markings up to 25ml. Mr Zindel replied that the standard number given was the same as that used in CIPAC MT 184. He also noted that the 25ml mark is not critical to persistent foam.
- We have seen differences in persistent foaming when testing the highest and lowest in-use concentrations? Surely we should include both the lowest and highest concentrations in the test for FAO? Mr Zindel replied that as the FAO only recommend the highest concentration is tested that is what the method also stated. It was noted in the meeting that other laboratories have not had the same experience
- ASTM have indicated that they have some preliminary testing that indicates that measuring foam at the shorter time points are critical. Mr Zindel replied that he believed the ASTM method is different as it addresses de-foaming and anti-foaming agents rather than the amount of foam produced
- The method states it is applicable to "all formulations that can be diluted with water" however you have only tested some formulations types. Mr Zindel replied that the DAPF small trial only covered a few formulations but given that test has been used for years we believed that this was sufficient information to extend the scope to all formulation types.

6. Replacement of obsolete methods

6.1 Comments on existing methods

Mr Bura presented the following comments received since the last meeting:

CIPAC 333/ - deltamethrin (4853)

At the 55th meeting held in Beijing, China in 2011 it was agreed that a comparison of the existing deltamethrin methods should be made. Mr Bura presented a comparison table to the meeting and noted that there are now 6 methods for deltamethrin in various forms using two different types of columns and 2 different wavelengths. He notes that CIPAC may need to consider whether or not to combine some of these methods or consider some way to simplify the situation.

The following comments were received from the meeting:

- Method 333/TC/M in Handbook D was developed in 1985 using a silica column. The method was revised as 333/TC/M2 in Handbook L using a cyano stationary phase.
- The column used in the method in Handbook D is still available but only a list of retention times is given and there is no representative chromatogram in the method
- The method in Handbook D is the only method capable of analysing the enantiomers therefore it cannot be considered as obsolete unless there is a chiral method developed.
- There are currently two methods for coated LNs; one in Handbook M and one on the CIPAC website. The majority of labs involved in this analysis are using the version on the website as this uses a calibration curve rather than single point calibration and the internal standard is useful in analysis of nets due to sampling procedures needed. However the method on the web uses a silica column and not a CN column.

The Chairman requested that any thoughts and suggestions to resolve this issue should be sent to either the Chairman or the Secretary of CIPAC.

CIPAC 33/ - PBO (4857)

At the 54th meeting held in Ljubljana, Slovenia in 2010 and also at the 55th meeting held in Beijing, China in 2011 comments were received that the extension of the PBO AOAC method to LN formulations is not a true extension. CIPAC were tasked to compare results. Mr Bura presented a comparison to the meeting.

It became apparent that the only difference is in the extraction solvent used. As CIPAC have previously accepted extension of methods where the extraction procedure is different for LNs (e.g. deltamethrin) this similar approach should also be acceptable to the meeting.

No comments were received from the meeting

ETU

Comments were received that changes are need to the description of method MT162 for determination of ETU in dithiocarbamates as it appears the method is overestimating the amount of ETU present.

Ceregaxi b.v. have indicated that they would like to conduct a new collaborative trial for ETU determination to resolve the issues. Therefore it was agreed that CIPAC will not consider the issue further and await the results from the collaborative trials.

Chairman's remarks

The Chairman, Mr Hänel thanked the participants of the open meeting for their support and discussions. He also thanked the Industry for their continued support in conducting the trials and thanked all who participate in the trials.

He noted that as always if participants had any proposals to improve the CIPAC process e.g. if further guidance is needed then CIPAC would be pleased to receive them.

Finally Mr Hänel expressed his thanks to John Dawson, retiring chair of the SEG for all his help and support through CropLife.

Mr Hänel declared the open meeting closed.

7. Minutes of the 55th meeting (4822/P)
The minutes were circulated to members by e-mail. One comment was received regarding the incorrect name of the presenter of agenda item 5. The corrected version will be placed on the website. No other corrections were received.

8. Secretary's report (4823/P)
Mr László Bura presented the Secretary's report for the period from the 55th CIPAC meeting held in Beijing, China, covering the attendance, number of trials conducted, the decisions taken concerning the methods and the election of correspondents and members of CIPAC.

9. Discussion of individual compounds

454: alpha-cypermethrin (wash method)
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)

333: Deltamethrin (LN extension, wash method)
At the 55th meeting, 2011 in China the method was adopted as provisional. The meeting agreed that the method should remain **provisional** because of the ongoing general work on LN washing method(s)

578: Flumioxazin
A small-scale trial was considered at the 54th meeting in Slovenia, 2010 and full scale collaborative trial was considered at the 55th meeting in China, 2011. The method was adopted as provisional at the 55th meeting in China. No further comments were received
The method can be promoted to **full CIPAC method**.

767: 1-MCP
At the 54th meeting, 2010 in Slovenia it was agreed that the method should remain provisional as further feedback was required from laboratories using the method. The method is difficult and uses specific equipment - therefore there needs to be more experience gained. The method is not routinely used and for that reason until more experience is gained it should remain provisional. It will remain on the agenda to see if any more information is received.
No new information has been received there the meeting agreed the situation remains as stands.
The method **remains provisional**.

331: Permethrin (wash method)
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)

33: PBO (TC, LN extension)
At the 54th meeting, 2010 in Slovenia it was agreed that the method should remain provisional as there were many differences from the originally proposed method. The meeting considered that if the method were to remain provisional we should provide the company with information (requirements) they need to fulfil in order to promote the method to full.
At the 55th meeting, 2011 in China it was agreed that the method should remain provisional.

No further comments were received
The method can be promoted to **full CIPAC method**.

239: Pirimiphos-methyl
At the 55th meeting, 2011 in China the method was adopted as provisional.
No further comments were received
The method can be promoted to **full CIPAC method**.

Solution stability of STs
At the 55th meeting, 2011 in China the method was adopted as provisional, subject to amendments to clarify the scope and title of the method.
DAPF have provided further information explaining the scope of the method and proposed a new title of "solution properties of STs" instead of "solution stability".
The meeting agreed that this partially addressed the concerns and proposed that in order to address the concerns fully, one sentence from the scope should be moved to the outline of the method.
The method can be promoted to **full CIPAC method**.

Extension of CIPAC MT 46.3 for the accelerated storage stability of LN
At the 55th meeting, 2011 in China the method was adopted as tentative with some further work on validating the method required.
No validation data has been received as the focus for the "LN group" has been on finalising and collaboratively testing the washing method for LNs.
The method remains **tentative.**

MT 73.1 Total hardness of water
At the 55th meeting, 2011 in China the method was adopted as provisional. No further comments were received
The method can be promoted to **full CIPAC method**.

MT180: Extension of the CIPAC method MT 180 to DC and OD formulations (4794)
At the 55th meeting, 2011 in China the method was adopted as provisional. No further comments were received.
The method can be promoted to **full CIPAC method**.

MT189 lambda-Cyhalothrin, free, determination in CS formulations
MT 190 lambda-Cyhalothrin, determination of release properties CS formulations
Extensions for pirimiphos–methyl
At the 55th meeting, 2011 in China as well as discussion of a method for the determination of pirimiphos methyl in TC, CS and EC (see 239: pirimiphos-methyl above) the meeting considered data on the determination of the release rate and content of free pirimiphos-methyl in CS formulations.
The Chairman proposed that as an alternative to adopting the methods in their own right they should be considered as method **extensions** to CIPAC methods MT 189 and MT 190. i.e. the methods become MT methods for the release rate and free a.i content, and are then extended for each active substance as required.
The scope of these MTs would need some amendments. The Chairman proposed that there is a general scope for each method followed by e.g. MT 189.1 lambda-cyhalothrin and MT 189.2 pirimiphos. The same would apply for MT 190. The meeting agreed with this approach.
Mr Hänel and Mrs Tessier agreed to propose a draft for comment.

Amisulbrom (4839, 4840)
There were no comments.
A full scale trial is recommended.

570: Chlorfenapyr (4825, 4826)
The meeting discussed the comments received.
It was discussed whether to edit the method to cover the alternative wavelengths and to note to the reasons for using 300 nm. It was agreed that the method should remain as it was currently written. It was agreed the method should be edited to reflect a fixed temperature of 25°C for the HPLC conditions.
The method can be adopted as **provisional**.

653: Cyazofamid (4833, 4834)
The meeting discussed the comments received.
The meeting considered the issue of the long run time. The analysis used an isocratic run so it was suggested that a flush gradient could be added towards the end of the run to speed up the run time. This may be more time consuming as you would have to re-equilibrate the system after gradient but the company should consider this option.
The meeting agreed that CIPAC could not cut the length of the run time if, as was suggested, some impurities could elute later in the run. It was also agreed that the length of the run is not a good enough reason to reject the acceptability of a method. The meeting agreed that the company should be asked to add a footnote suggesting it may be a possible to include a flush gradient in the run.
The method can be adopted as **provisional** with a proposal to the company to include a footnote about a column flush gradient programme.

333: Deltamethrin (4837, 4838)
The meeting discussed the issue of the different solvent ratio. It was agreed that it would be logical to use the HPLC mobile phase as the extraction solvent, however this should be considered in the context of the other deltamethrin methods.
The meeting discussed if this method extension was necessary as the LN product is similar to other LNs for which there are already method extensions in place. This may add more confusion. It was noted that the company had followed the CIPAC guideline and submitted an extension although it was not clear why they have submitted the extension.
The study can be considered as a confirmation that the existing LN method is applicable to the Fonyi Long-Lasting Insecticidal Mosquito Nets, too.
The meeting agreed **to take note of the method**, and discuss further with the company.

595: Flazasulfuron (4831, 4832)
The meeting raised concerns about the need to analyse samples within a certain time after extraction as this may indicate instability of active substance. It was noted that the samples that were sonicated for extraction gave consistently lower results but were within the acceptable range.
The meeting agrees that there were some reservations with the method but the statistical results indicate that the method is working acceptably.
The method can be adopted as **provisional**.

585: Fosthiazate (4829, 4830)
The meeting considered that this method had already been through 2 small scale trials with ESPAC and that two critical issues were identified with the method – one was the sample size and the other was the extraction solvent. ESPAC specifically recommended that acetonitrile was not suitable. Of these two issues it appears that the sample size was most critical as shown by the

results of the studies. It was however not made clear in the information provided with the method that that these were critical steps. The method as written is not clearly defined as the critical issues are not defined. This should be clearly written in the methods.
It was noted that there is a good chemical reason to remove Lab 6 (used different solvent). But it doesn't matter as when lab 6 is included the criteria are met. It was the results from the other Lab that also changed the sample size which are not acceptable. Lab 6 commented that they had used acetonitrile/water to extract and also not used an internal standard and their results were excellent.
Considering the structure and the ISO common name fosthiazate has 2 diastereoisomers. The meeting noted that sample chromatograms of the TC show that the peak is quite broad and this may be due to partial resolution of the diastereoisomers. It may be that depending on the HPLC conditions some HPLC systems may resolve the isomers. The meeting agreed that a footnote is needed to warn future users of the method that diastereoisomers are present, the HPLC conditions may resolve them and to advise what to do if this happens.
The meeting considered whether an internal standard was needed. It was noted that the company had indicated that they are willing to re-calculate the data set without the internal standard to see what impact the internal standard has on the method. The meeting agreed that they could not conclude until this information was available. The small scale trial clearly indicates that the internal standard was needed. It may be that one lab can get robust results without the internal standard, but in order for the method to be reproducible and robust the internal standard is needed.
The method can be adopted as **provisional,** subject to a clearer description of the method, the additional notes needed in the method, and to the provision of the statistical analysis with and without the internal standard.

Permethrin/PBO (4841, 4842, 4843)
The meeting considered that it would be logical to combine the methods and only have one method for both but the company took the easier path of extending 2 existing methods as then a full scale trial is not needed.
The PBO method is not really a method extension it is just proof that the current method is applicable to their product, therefore there is no need for CIPAC to adopt this.
The permethrin method can be adopted as **provisional.**

Pyraxostrobin (4851, 4852)
The meeting commented that a specific column was not clearly recommended in the method and that this would need clarifying. The meeting also noted that only 1 TC was analysed in the small scale trial. The company should be made aware that they will need to analyse 2 TCs, with a minimum of 5 samples overall in the full scale study.
The meeting recommended go to **a full scale trial.**

636: Spinosad (4847, 4848)
There were no comments.
The meeting recommended that the method extension can be adopted as **provisional.**

637: Thiamethoxam (4845, 4846)
There were no comments.
The meeting recommended that the method extension can be adopted as **provisional.**

Determination of quaternary ammonium compounds in disinfectant formulations by potentiometric titration with an ionic surfactant electrode (4849, 4850)
This agenda item was from information only and to request participants for the collaborative trial therefore no recommendations are required.

Wash resistance index of LNs (4827, 4828)
The meeting discussed the necessity of the footnote for reaching equilibrium between washes as there was concern that this would leave the door open for endless future extensions of the method. The meeting agreed that the temperature/time for equilibration between washed should be covered by the WHO specification.
The meeting discussed whether the method should be accepted as provisional based on only 5 labs? It was argued that this method is considered a phys/chem. method and that some phys/chem. methods are not amenable to direct validation therefore a smaller number of labs were used. It was also argued that several examples exist from previous phys/chem. methods where only a small number of laboratories were included. The meeting considered whether from a procedural point of view this method should follow a similar process as for 1-MCP i.e. should the method remain provisional until sufficient additional validation data are available?
If the method is declared provisional then the companies with existing WHO specifications will have to provide data on their nets to WHO to ensure that the current specifications are still valid. Therefore once all this data is received CIPAC could look at it in more detail to provide additional information.
The meeting recommended that the method can be adopted as **provisional**. However it will remain provisional until further validation is provided to give a sufficiently large data set.

CIPAC MT 47.3 persistent foam (4835, 4836)
The meeting considered the comments received in the open meeting. It was agreed that CIPAC will officially contact ASTM and get confirmation about the data from the shorted time points before deciding if the earlier measure points can be removed from the method.
The meeting recommended that the method can be adopted as **provisional**.

Existing methods for CIPAC 333/ - deltamethrin (4853)
The meeting considered the comments received in the open meeting. It was noted that Bayer CropScience had indicated they will develop a chiral method for deltamethrin through DAPA. It was also noted that the relevant companies are already getting together to discuss a way forward.

10. Matters related to FAO and WHO specifications
Dr Müller presented to the meeting the comments made by the SEG on proposed revisions to the FAO/WHO manual. This was for information only.

11 Any other business
None

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

Sonia Tessier	László Bura
Assist. Secretary	Secretary