CIPAC

COLLABORATIVE INTERNATIONAL PESTICIDES ANALYTICAL COUNCIL LIMITED

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

Minutes of the 55th Annual meeting

The 55th meeting was held on Wednesday 15th June, and on Thursday 16th June 2011 at the Beijing Landmark Towers Hotel, Beijing.

Those attending
- Items 1 to 6 on 15th and 16th June: members, correspondents, observers and expert witnesses.
- Items 7 to 14 on Thursday 16th June: members, correspondents and observers (representatives of industry and commercial laboratories, by special invitation)

1. Welcome and introductory remarks by the chairman
The Chairman, Mr Ralf Hänel, opened the 55th CIPAC meeting, and welcomed all the participants. He noted that in terms of attendance this was one of the largest TC meetings in recent years.

2. Apologies
Apologies were received from:
Mr Warren Bontoyan, Mr Hans-Paul Bosshardt, Mr Walter Dobrat, Mr Roberto Dommarco, Mr Alain Dubois, Mr Jindřich Foltýn, Mrs Ada Hourdakis, Mrs Anna Kashouli-Kouppari, Mr Albertus Martjin, Mrs Fatima O'Neil Pedrosa, Mr Francisco Sánchez-Rasero, Mr Eric Sandmann and Mrs Julianna Schlosserova.

3. Adoption of the agenda
The agenda was adopted with the following amendments:
Two new items were added:
5.9 Summary presentation on the status of LN methods and the way forward by Mr Martin Rodler
5.10 Relevant impurity dihydrosafrole (DHS) in piperonyl butoxide technical by Mrs Maria Cristina Zanotti
Agenda point **5.8** was moved to after point **4.2.**
Agenda point **5.10** was moved to after point **4.6.**

4. Reports of expert witnesses

4.1 Cyazofamid by Mr Jim Garvey (4773, 4774)
Mr Jim Garvey presented the results of a **small scale** collaborative study, on the determination of cyazofamid in technical product (TC) and suspension concentrate (SC) using HPLC-UV detection at 280 nm and external standard calibration. The trial was organised by ESPAC in conjunction with ISK Belgium. 5 laboratories participated in the study. 2 samples of TC and 3 samples of SC were provided.
3 participating laboratories commented that the run time of 60 minutes was too long. Laboratory

3 commented that in all chromatograms there was an interference at the beginning of cyazofamid peak.
The statistical evaluation was carried out according to the CIPAC guidelines.
For TC 1, TC 2 and SC 2 Lab 4 was a Cochran's outlier. For SC1 and SC3 Lab 1 was a Cochran's outlier. No data were excluded from the initial evaluation.
TC 1, TC 2, SC 1 and SC 2 meet the Horowitz criteria when all the data are included. SC 3 did not meet the Horowitz criteria when all the data is included. When the results from Lab 1 (Cochran's outlier) were omitted and the statistical evaluation was repeated the Horwitz criteria were met in all cases.
ESPAC consider that the proposed method is appropriate for the determination of cyazofamid in TC and SC and that a full scale trial can be conducted.

The following comments were received from the meeting:

- Why is the acetic acid necessary in the mobile phase? Mr Garvey replied he believed it was there to adjust the pH.
- Methanol and acetonitrile are both used in the mobile phase. It would be preferable to use a mobile phase with only one organic solvent.
- Lab 3 reported interferences at the beginning of the peak. Was this noted by any other labs? What column did Lab 3 use and was it equivalent? Mr Garvey replied that no other labs reported this interference and that the interference was very small.
- Reducing the column length could shorten the run rime
- It would be preferred to have a fixed operating temperature for the HPLC analysis as ambient temperature can vary from country to country

4.2 Deltamethrin by Mr Gerhard Krautstrunk (4797, 4798)
Mr Gerhard Krautstrunk presented the results of a validation study for the **extension** of the scope of CIPAC method 333/LN/(M)/3 (CIPAC/4673) for the determination of deltamethrin in LifeNet®[deltamethrin long-lasting (incorporated into polypropylene) insecticidal net (LN)]. The existing CIPAC method 333/LN/(M) is suitable and validated for the determination of the total content of deltamethrin incorporated into polyethylene LN.
Samples are extracted by heating under reflux for 30 minutes with xylene in the presence of dibutyl phthalate as internal standard (to dissolve the net), an aliquot is evaporated and reconstituted in mobile phase. Deltamethrin is determined by normal phase HPLC-UV with detection at 230 nm.
The validation was conducted using 1 LN of nominal concentration 0.85% w/w and a blank LN made of the same material.
Linearity, specificity and non-analyte interference were demonstrated to be acceptable. Repeat-ability was acceptable with RSD meeting the Horwitz criteria. For accuracy the mean recovery was 103%, RSD < 2% for the 3 levels tested (*ca* 5 g/kg, 8 g/kg and 11 g/kg). Storage stability tests showed that standard and sample extracts were stable for 16 – 17 days.
Mr Krautstrunk concluded that the validation data were acceptable therefore the method can be considered fully applicable for LifeNet® LN.

No comments were received from the meeting.

5.8 Stereospecific identity test for triadimenol by Mr Gerhard Karutstrunk (4795, 4796)
Mr Gerhard Krautstrunk presented the results of a **peer validation** study for CIPAC method 398/TC/M3 for the determination of the diastereomer ratio for triadimenol.
The triadimenol FAO specification defines a certain ratio for the two diastereomers. A method extension for the identification and determination of 'total' triadimenol content (which also implied the determination of the diastereomer ratio was possible) in SC, FS, and EW formula-

tions has been adopted as a CIPAC method (first presented in 2009). The method for the determination of the diastereomer ratio therefore needed to be peer validated.
The method used was the same as that described in CIPAC 398/TC/M3 i.e. Capillary GC with FID detection and cold on-column injection with di-(2-ethylhexyl) phthalate as internal standard.
2 laboratories participated in the study. 2 samples of TC with different isomer ratios were provided.
Laboratory 1 used spilt injection rather than cold on-column injection and did not use the internal standard. Lab 1 discovered that using split injection meant the concentrations measured were not high enough to give good response (peak size) therefore they recommend the dilution step in method is omitted. Lab 1 also proposed that the detector temperature should be increased so that it is higher than the maximum temperature of the column used (to avoid condensation effects).
Laboratory 2 lowered the oven starting temperature to 60 °C as they were using cold on column injection and the samples are prepared in acetone.
The chromatograms from both laboratories show almost complete baseline separation. The results from both laboratories are in good agreement, with results for both TCs meeting the modified Horwitz criteria
Mr Krautstrunk proposed that with the modifications and comments from the laboratories included the method should be suitable, and recommend it to be adopted as the final CIPAC method.

The following comments were received from the meeting:

- Is triadimenol with a certified isomer ratio available for use as a reference material for control labs? Mr Krautstrunk replied that he did not know for certain but would make further enquiries.
- Is there a criterion that could be applied to demonstrate the minimum acceptable resolution for good integration of the peaks? It would be useful to calculate the minimum resolution and provide this in the method for guidance.

4.3 Flazasulfuron by Mr Jim Garvey (4791, 4792)
Mr Jim Garvey presented the results of a **small scale** collaborative trial on the determination of flazasulfuron in technical product (TC) and water dispersible granule (WG) formulations using HPLC-UV with detection at 230 nm and external standard calibration. The trial was organised by ESPAC in conjunction with ISK Belgium. A small scale trial was presented to CIPAC in 2010 for the same method but using an internal standard, which gave unacceptable results. ESPAC re-evaluated the data without the internal standard and the data were acceptable, however in after discussions with company, it was proposed by the company to conduct another small scale trial.
5 laboratories participated in the study. 2 samples of TC and 3 samples of WG were provided.
3 participating laboratories commented that there were difficulties in separating the a.i. and formulants in the WG samples, with Laboratory 5 commenting that using detection at 260 nm instead of 230 nm limited the influence of interferences. Laboratory 4 commented that the Day 1 results for both TCs were slightly lower than on Day 2.
The statistical evaluation was carried out according to the CIPAC guidelines.
For TC 2 Lab 3 was a Cochran's straggler. For WG 1, WG 2 and WG 3 Lab 3 was a Cochran's outlier. For WG1 Lab 5 was a Grubb's straggler and for WG 3 and Lab 5 was a Grubb's outlier.
No data were excluded from the initial evaluation.
TC 1 and TC 2 meet the Horwitz criteria when all the data are included. All 3 WG samples fail the Horwitz criteria when all the data are included. When the results from Lab 3 (Cochran's outlier) were omitted and the statistical evaluation was repeated the Horwitz criteria were met in all cases.
ESPAC considers that the proposed method was considered appropriate for the determination of flazasulfuron in TC and WG and that a full scale trial can be conducted.

The following comments were received from the meeting:

- It would be preferred to have a fixed operating temperature for the HPLC analysis as ambient temperature can vary from country to country.
- What was the preferred wavelength to use 230 nm or 260 nm? Mr Garvey replied that only one laboratory had an issue with interference at 230 nm. This was resolved by using 260 nm, but no other labs had this problem therefore 230 nm was the preferred wavelength.
- The issues with the results for the WG could be due to the extraction procedure as fluzasulfuron is not particularly stable to hydrolysis in acidic conditions. It might be better to use a different extraction solution at a higher pH to achieve a better recovery of flazasulfuron from the WG.

4.4 Flumioxazin by Ms Makiko Mukumoto (4763, 4764)

Ms Makiko Mukumoto presented the results of a **full scale** collaborative trial on the determination of flumioxazin in technical product (TC) and wettable powder (WP) formulations using reverse phase HPLC-UV with detection at 288 nm and external standard calibration. The trial was organised in conjunction with JAPAC.

15 laboratories participated in the study. 3 samples of TC and 2 samples of WP were provided.

All laboratories used HPLC column of identical polarity although several participating laboratories used different length columns and adjusted the flow rate accordingly. These changes were considered not to impact on the results.

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

For TC 1, TC and TC 3 Lab 14 was a Cochran's outlier. For WP 2 Lab 14 was a Cochran's outlier. No data were excluded from the initial evaluation.

TC 1, TC 2, TC 3 and WP 2 meet the Horwitz criteria when all the data are included. For WP1 the Horwitz criteria were not met when all the data are included.

Further investigation by Sumitomo indicated that the WP 1 sample provided for testing was not homogenous (i.e. was not a "good product"). It was porposed therefor that the results for WP1 were omitted completely form the collaborative trial. This is in line with CIPAC guidelines which state "The number of samples may be reduced to a minimum of 3 when only one concentration of one type of formulation is available"

JAPAC considers that the proposed method is appropriate for the determination of flumioxazin in TC and WP formulations and recommends the method is adopted as provisional.

The following comments were received from the meeting:

- Should an additional remark be included in the sample preparation for the WP that the homogeneity of the sample is very important? And that additional grinding is needed? Ms Mukumoto clarified that it was the homogeneity of the sample provided to the laboratories that was the issue and not the sample preparation in the method.
- Some laboratories found that the injection volume used was too high.

4.5 Fosthiazate by Mr Jim Garvey (4761, 4762)

Mr Jim Garvey presented the results of a **small scale** collaborative study, on the determination of fosthiazate in technical product (TC) and granules (GR) using HPLC-UV detection at 220 nm with dimethyl phthalate as an internal standard. The trial was organised by ESPAC in conjunction with ISK Belgium. A small scale trial was presented to CIPAC in 2010 for the same method but using an internal standard, which gave unacceptable results. ESPAC re-evaluated the data without the internal standard and it became apparent that the internal standard was in fact necessary. After discussions with the company, it was proposed by the company to conduct another small scale trial.

5 laboratories participated in the study. 2 samples of TC and 3 samples of GR were provided.

2 participating laboratories commented that the standard/sample weights used were low.

The statistical evaluation was carried out according to the CIPAC guidelines.
For TC 1 and TC 2 Lab 2 was a Cochran's straggler. For GR 3 Lab 2 was a Cochran's straggler.
No data were excluded from the initial evaluation.
TC 1 and TC 2 meet the Horwitz criteria when all the data are included. GR 1, GR 2 and GR 3 did not meet the Horwitz criteria when all the data are included. When the results from Lab 2 (Cochran's straggler) were omitted and the statistical evaluation was repeated the Horwitz criteria were still not met. A possible explanation for this is that the sample size is not large enough to get a representative sample for extraction of GR formulations. ESPAC therefore recommends that a larger sample (at least 5g) is extracted and an aliquot is then taken for analysis.
ESPAC consider that with some modifications the proposed method is appropriate for the determination of fosthiazate in TC and GR and that a full scale trial can be conducted.

The following comments were received from the meeting:

- Could you clarify if the mobile phase was just acetonitrile or acetonitrile/water with a gradient programme? Mr Garvey clarified that the mobile phase was a gradient programme beginning with 100% acetonitrile/water (2:1) and ending with 100% acetonitrile.
- Was the HPLC grade water used for the mobile phase?
- The extraction procedure for the GR extraction was already improved from previous small scale trial. Could it be that acetonitrile is not a suitable extraction solvent?
- A 1 µl injection for the method is very small. A higher volume would be preferable. Mr Garvey clarified that the method did actually use 10 µl but this was incorrectly stated to be 1 µl in the presentation to the meeting.

4.6 Piperonyl butoxide by Mrs Maria Cristina Zanotti (4765, 4766)
Mrs Maria Cristina Zanotti presented the results of a **full scale** collaborative trial on the determination of piperonyl butoxide in technical product (TC) using GC-FID with dibutyl phthalate as internal standard.
29 laboratories participated in the study. 3 samples of TC were provided.
Of the 29 laboratories that were sent samples 5 did not send results in time, and 3 sets of results were unusable, leaving 21 sets of data that could be used.
Several laboratories used different columns to the specified method. 6 laboratories preferred to prepare an internal standard stock solution and add it into the analysis solutions instead of weighing out the ISTD each time.
For TC 1, TC 2 and TC 3 2 laboratories were identifeid as Grubb's outliers. These laboratories were also identified as outliers by the "Anderson-Darling normality test".
No data were excluded from the initial evaluation.
All 3 TC samples meet the Horwitz criteria when all the data are included.
Mrs Zanotti proposed that the method was considered appropriate for the determination of PBO in TC and recommends the method is adopted as provisional.

The following comments were received from the meeting:

- The use of a stock solution of Istd rather than adding a known weight each time would be preferable. Both approaches are possible.
- The amount of reference standard material used for the calibration curve is high. It should be possible to use a single point calibration as an alternative.

5.10 Relevant impurity dihydrosafrole (DHS) in piperonyl butoxide technical by Mrs Maria Cristina Zanotti (4812, 4813)
Mrs Maria Cristina Zanotti presented the results of a **peer validation** on the determination of the relevant impurity dihydrosafrole in piperonyl butoxide technical product (TC) using GC-FID

with dibutyl phthalate as internal standard. The instrumental method is the same as that for the determination of PBO in TC, but with a different sample preparation technique.
5 laboratories participated. 1 laboratory used external standard calibration
Method validation by Endura before trial:
Calibration: at 4 levels, R2 > 0.999
Accuracy: As recovery by standard addition at concentrations of 100% and 120% of specification level. Recovery range = 104% -107%
Repeatability: 5 replicates. CV% = 1.9%.
LOQ: 30 mg /kg

Results of peer validation:
Calibration: at 4 levels, R 2> 0.999
Accuracy: Recovery range = 104% -109%
LOQ: 20 mg/kg - 30 mg/kg

Horwitz criteria were met.
Mrs Zanotti proposed that the method was considered appropriate for the determination of dihydrosafrole in PBO technical and that is should be adopted as the final CIPAC method.

No comments were received from the meeting.

4.7 Pirimiphos-methyl by Mr Andrew McIntyre (4778, 4779, 4780)
Mr Andrew McIntyre presented the results of both a **small scale** and a **full scale** collaborative trial for the determination of pirimiphos-methyl in technical product (TC) emulsifiable concentrate (EC) and capsule suspension (CS) formulations using GC-FID with 4,4-dimethoxybenzophenone as internal standard.
As background information Mr McIntyre explained that a new slow release CS formulation had been developed that required a CIPAC method extension and therefore CIPAC requested that the current CIPAC method for pirimiphos-methyl in TC & EC (239.a/TC/M/-, published in Handbook 1C using packed column GC) be updated.
An initial small scale trial was organised in conjunction with DAPA:
5 laboratories participated. 1 sample of TC, 1 sample of EC and 1 sample of CS were provided.
The statistical evaluation was carried out according to the CIPAC guidelines.
For the CS formulation Lab 5 was a Cochran's outlier. These data were therefore excluded from the evaluation.
The Horwitz criteria were met for all samples. Acceptable results for CS were only possible after elimination of the outlier. Sample homogenization is a critical part for the analysis of CS formulations therefore the sample preparation part of the method was re-phrased to emphasis this.

The full scale study was then initiated.
26 laboratories initially expressed interest in participating in the study. 17 laboratories participated (import/export issues with the samples). 2 samples of TC, 1 sample of EC and 2 samples of CS were provided.
Data from Lab 9 were excluded completely: a very high variation in area counts from one injection to the next (potential instrument malfunction) was noticed.
The statistical evaluation was carried out according to the CIPAC guidelines.
For TC 2 Lab 14 was a Grubb's straggler. For CS 1 Lab 13 was identified as a potential Cochran's straggler. For CS 2 Lab 16 was a Grubb's outlier. For EC 1 Lab 4 was a Cochran's outlier. No data were excluded from the initial evaluation.
TC 1, TC 2, and EC 1 meet the Horwitz criteria when all the data are included. For CS 2 the Horwitz criteria were not met when all the data are included. For CS 1 the RSDR was 2.43

against Horwitz criteria of 2.42. When all outliers and stragglers are removed the Horwitz criteria is met in all cases.
Mr McIntyre explained that homogenisation of the CS samples was critical to the success of the method and proposed the following changes to the sample reparation in the method:
'Thoroughly homogenize the formulation, as received in the original sales pack, by inverting/shaking the bottle for 2 minutes or by using a mechanical stirrer. Do not decant a smaller sample or remove the test sample without thorough homogenization.'
Mr McIntyre considers that the proposed method is appropriate for the determination of pirimiphos-methyl in TC, EC and CS formulations and recommends the method is adopted as provisional.

The following comments were received from the meeting:

- The split ratio is very high and this could be difficult for labs to achieve depending upon their instrumentation
- The issues with sample homogenisation for CS indicate that further instructions for homogenising the product should also be added to the product label. Mr McIntyre stated that this has been noted by the company.

4.8 Solution stability of STs by Mr Bruno Patrian (4771, 4772)
Mr Bruno Patrian presented the results of a **collaborative trial /method development for a new MT method** for the determination of the solution stability of water soluble tablets (ST). The trial was organised by DAPF.
Mr Patrian explained that the Manual on development of FAO and WHO specifications for Pesticides indicates that CIPAC method MT 179 should be used to determine solution stability for ST products. However MT 179 was originally developed for water soluble granules (SG) and may not be applicable to ST formulation due to the concentrations tested in the current method.
The outline of the method is as follows:
A water soluble tablet, or a fragment of a water soluble tablet, is dissolved in Standard water D at maximum use rate and stirred for a specified time. The solution is allowed to stand undisturbed for 2 hours and then poured onto a 75 µm sieve. Any residue is collected, dried, weighed and recorded
13 laboratories participated in the study. 3 samples of ST were provided.
2 of the samples required testing of a fragment of the tablet. It was also noted that a 2nd drying step was required for the residue on the sieve.
Lab 12 used the wrong size sieve mesh and so was excluded completely from the results. Lab 4 used CIPAC water D for rinsing the sieve rather than deionised water and had difficult in removing the residue from the sieves. The data from Lab 4 were excluded completely from the statistical evaluation.
The statistical evaluation was carried using Total Gage R&R apporach.
The data were acceptable when Labs 4 and 12 were removed, however they indicate that variability within tablets may be an issue when fragments are taken for analysis. It may be necessary therefore to conduct 3 or 4 determinations for each tablet to reduce these errors.
DAPF considers that the proposed method is appropriate for the determination solution stability in ST products and recommends the method is adopted as provisional.

The following comments were received from the meeting:

- Were all the tests conducted at ambient temperature or at a fixed temperature? This may account for some variation in the results seen. Mr Patrian stated that the method specifies a set temperature.
- Was the sampling of fragments difficult? Mr Patrian said it was not difficult but that it was important not to mill the tablets. They should be cut with a knife into fragments.

- Title of the method is solution stability - how is the stability of the solution determined by measuring the sieve residue? Mr Patrian said that this had been discussed within the DAPF. They believed that as the tablet is left to stand for 2 hours this demonstrates the stability of the solution.
- If the active substance is soluble in water then it should be soluble after 1 hour, 2 hour 24 hours – the method is determining dissolution characteristics rather than stability of solution.
- Another possibility is to change the name of the method to, for example solubility characteristics.

4.9 Total hardness of water by Ms Erika Seidel (4769, 4770)

Ms Erika Seidel presented the results of a **full scale** collaborative trial for the determination of total hardness of water using a revised method MT 73.1. The trial was organised by DAPF.

Ms Seidel explained that as part of the CIPAC MT review, DAPF was tasked with updating method MT 73 to give and easy to use method using commercially available reagents worldwide.

The outline of the method is as follows:

The total hardness of water is determined by titration of alkaline earth ions in water with chelating agent using colorimetric end point determination. Commercially available reagents are used.

15 laboratories participated. Each laboratory tested CIPAC water D and their own local tap water, to ensure that the method was suitable for waters of differ hardness.

The commercially available reagents mentioned in the method could be purchased worldwide. There are two concentrations of chelating agent available commercially and note is needed in the method to this effect

Colorimetric green end point detection as described in the procedure was successfully used by all 15 laboratories.

Total hardness of tested local tap water was in the range of 33 ppm (very soft) to 402 ppm (hard).

Total hardness of tested CIPAC water D used in local laboratories was in the range of 325 ppm to 353 ppm.

DAPF considers that the proposed method is appropriate for the determination of water hardness and recommends the method is adopted. The original method MT 73 could also remain.

The following comments were received from the meeting:

- There is an electronic device than can be used to indicate the end point. Did any labs use these devices? Ms Seidel replied that as far as she was aware only the colour change end point was used in the trial. Comments received from the laboratories were that the end point was easy to identify.

5. Reports of expert witnesses on other matters

5.1 Relevant impurities in the pirimiphos-methyl CS formulation by Mr Andrew McIntyre (4781, 4782)

Mr Andrew McIntyre presented the results of a **peer validation** for the determination of relevant impurities in pirimiphos-methyl in capsule suspension (CS) formulations by GC.

There are 5 relevant impurities in pirimiphos-methyl

- *O*,*O*-dimethyl phosphorochloridothioate (DMPCT, CAS No. 2524-03-0)
- *O*,*O*,*O*-trimethyl phosphorothioate (MeOOOPS, CAS No. 152-18-1)
- *O*,*O*,*S*-trimethyl phosphorothioate (MeOOSPO, CAS No. 152-20-5)
- *O*,*O*,*S*-trimethyl phosphorodithioate (MeOOSPS, CAS No. 2953-29-9)
- *O*-2-diethylamino-6-methylpyrimidin-4-yl-*O*,*S*-dimethyl phosphorothioate (iso-pirimiphos-methyl, CAS No. 76471-79-9).

Two methods had to be used as the iso-pirimiphos-methyl standard proved not to be stable and therefore could not be used within the initially proposed GC-MS standard addition method.

a) iso-pirimiphos-methyl
For iso-pirimiphos-methyl a GC-FID method was used with 4,4-dimethoxybenzophenone as internal standard. Quantification was against pirimiphos-methyl as the iso-pirimiphos-methyl standard proved to be unstable.
4 laboratories participated in the study. 1 samples of CS was provided.
Calibration: at 3 levels, $R^2 > 0.999$
Accuracy: As a blank CS formulation was hard to manufacture recovery was determined by standard addition using CS300 at 2 concentrations (100% and 150% of the prescribed sample amount). Recovery range = 98% - 102%
Repeatability: 5 replicates. RSD_R = 3.39% (within Horwitz criteria)

Mr McIntyre considers that the proposed method is appropriate for the determination of *iso*-pirimiphos-methyl in CS formulations and recommends the method is adopted as provisional.

b) DMPCT, MeOOOPS, MeOOSPO, MeOOSPS
For the other impurities a GC-MS method was used with 4,4-dimethoxybenzophenone as internal standard.
4 laboratories participated in the study. 1 sample of CS was provided. One lab was only able to perform 2 out of 5 replicates due to instrument failure.

DMPCT
Calibration: at 5 levels, $R^2 > 0.975$
Accuracy: As a blank CS formulation was hard to manufacture recovery was determined by standard addition using CS300 at 1 concentration. Recovery range = 91-94%
Repeatability: 5 replicates. RSD_R = 4.75% (outside Horowitz criteria)

MEOOOPS
Calibration: $R^2 > 0.980$
Accuracy: Recovery range = 97% - 103%
Repeatability: RSD_R= 2.69 (within Horwitz criteria)

MEOOPS.
Calibration: $R^2 > 0.981$
Accuracy: Recovery range = 97% - 102%
Repeatability: RSD_R = 9.5 (outside Horwitz criteria)

MEOOSPS.
Calibration: $R^2 > 0.981$
Accuracy: Recovery range = 96% - 102%
Repeatability: RSD_R = 7.58 (outside Horwitz criteria)

Mr McIntyre indicated that due to the difficulties with the analysis of CS products a RSD_R of < 10 would give a good indication of a suitable method. He therefore considers that the proposed method is appropriate and recommends the method is adopted as provisional.

The following comments were received from the meeting:

- Given that *iso*-pirimiphos-methyl is not stable, did you spike the *iso*-pirimiphos-methyl or pirimirphos-methyl? Mr McIntyre states that they used the linearity data to determine recovery as it was difficult to prepare a blank CS formulation. Couldn't guarantee that a

poor recovery was due to poor recovery or standard degradation.

- For the GC-MS method the ramp rate for the GC temperature programme is quite steep. This gives a short run time but possibly at the loss of sensitivity. Were enough data points collected to allow construction of a good peak shape? It would be useful to have some optimisation parameters included in the methodology to ensure that sufficient data points are collected. Mr McIntyre agreed this could be added.
- One laboratory noted variability in the peak area of the Istd. It might be better to use another internal std that elutes earlier and is optimised for the impurities rather than for the a.i.
- What causes the instability of the *iso*-pirimiphos-methyl? Mr McIntyre stated it was mainly due to temperature.
- *Trans*-methylation of OPs can occur at higher temperatures– this may account for the differences in stability of the standards.
- Was an HPLC method considered rather than GC? Mr McIntyre stated that HPLC would have been difficult due to the nature of the relevant impurities.
- In the WHO specification the method for the TC and EC uses NMR which is unusual. Would it be possible to extend the GC methods developed here to also cover the EC & TC? Mr McIntyre stated there may be possibility to do this but it would need to be discussed further within his company.

5.2 Free AI content of the pirimiphos-methyl CS formulation by Mr Andrew McIntyre (4785, 4786)

Mr Andrew McIntyre presented the results of a **small scale** collaborative study for the determination of the free AI content of pirimiphos-methyl in capsule suspension (CS) formulations by GC. The study was conducted in conjunction with DAPA.

Mr McIntyre indicated that it is difficult to extract the free a.i. without rupturing the capsule during extraction.

The sample containing pirimiphos-methyl is suspended in water, free pirimiphos-methyl is extracted with hexane containing dicyclohexyl phthalate as an internal standard, and the pirimiphos-methyl content determined by GC-FID

4 laboratories participated in the study. 3 CS were provided; 2 x "good" products 1 x "poor" product

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

For CS 2 Lab 2 was a Grubbs outlier. For CS 3 ("poor" product) Lab 2 was a Cochran's straggler. No data were excluded from the evaluation.

Higher standard deviation than expected when compared to Horwitz was noted.

Mr McIntyre offered the following possible explanations:

- "Free"-AI is not a well defined concept.
- AI can be on the surface of capsules, contained in micelles or in the emulsion creating variability during extraction
- Samples cannot be homogenised using techniques such as sonication and high shear mixing in case capsule walls are ruptured or extraction from capsules is promoted.
- Measurement can vary due to the dynamic equilibrium between the inside and the outside of the capsules. Increased levels seen due to some extraction from within the capsules especially with poor quality samples.

Mr McIntyre proposed that the method is suitable to distinguish between good and poor products and that method is adopted as provisional.

The following comments were received from the meeting:

- Does the time for the rolling phase need to be specified? Mr McIntyre stated that is was specified (5 -10 minutes). There is also a standing period required to allow the material to settle. The timings are critical to standardising the method.

- Does the free ai content differ from the amount within the capsule? Mr McIntyre replied that it did.
- It is noted that hexane is used and that this is not a nice solvent to use. It is also used in the method to determine free a.i. content of *lambda*-cyhalothrin but there should be safety precautions included in the method. Mr McIntyre stated that they had used the lambda-cyhalothrin free a.i. method as a starting point for the development of this method which was why hexane had been used. He thought that some preliminary work had been done to look at heptane as an alternative; however this had not been completed in time for the meeting. He agreed that some precautionary phrases should be added to the method.

5.3 Release rate characteristics of the pirimiphos-methyl CS formulation by Mr Andrew McIntyre (4783, 4784)

Mr Andrew McIntyre presented the results of a **small scale** collaborative study for the determination of the release rate characteristics of pirimiphos-methyl capsule suspension (CS) formulations by GC. The study was conducted in conjunction with DAPA.

Mr Andrew McIntyre stated the aim was to try to mimic the WHOPES efficacy tests using analytical chemistry, i.e. to have a method to determine if the product is fit for use. It is difficult to take samples to determine the release rate at different time points without rupturing the capsule during extraction.

The CS formulation is suspended in water; pirimiphos-methyl is released and extracted with a mixture of hexane / ethanol (90+10) containing dicyclohexyl phthalate as internal standard while placed on a horizontal roller. At 3 different time points a subsample from the hexane layer is taken, and the pirimiphos-methyl content determined by GC-FID.

4 laboratories participated in the study. 3 CS were provided; 2 x "good" products 1 x "poor" product. 2 laboratories used as different roller speed to that stated in the method.

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

Numerous outliers and strugglers were identified:

2 Cochran outliers have been detected:-

- CS300-2, 15 min release time (Lab 1)
- CS300-3, 60 min release time (Lab 3)

7 Grubbs outliers have been detected:-

- sample 1, 60 min release time (Lab 1)
- sample 1, 180 min release time (Lab 2)
- sample 2, 15 min release time (Lab 2)
- sample 2, 180 min release time (Lab 2)
- sample 3, 15 min release time (Lab 1)
- sample 3, 60 min release time (Lab 1)
- sample 3, 180 min release time (Lab 1)

1 Cochran straggler has been detected:-

- CS300-2, 60 min release time (Lab 1)

1 Grubbs straggler has been detected:-

- sample 2, 60 min release time (Lab 1)

No data were excluded from the evaluation.

Higher standard deviations than expected when compared to Horwitz were noted. However the results clearly showed that the "poor" product releases the a.i. in about 15 minutes compared to a longer release time for the "good" products.

Mr McIntyre offered the following possible explanations:

- Analytical uncertainty can be introduced by:-
  - composition of the extraction solvent (proportion of ethanol)
  - the extraction process itself which is trying to mimic a biological system

    - sonication and high shear mixing has to be avoided in case the capsules are ruptured. Leads to homogenisation issues
    - variation in temperature. Diffusion from capsules followed by liquid/liquid extraction
- Effective roller speed appears to have no significant impact (from 22 rpm – 50 rpm) although an increased release rate at 60 minutes was seen for a slower speed. This is not conclusive as there are other variables that can contribute to the variation.
- Method is atypical and therefore cannot be measured using the Horwitz criterion. Total analyte content not being measured.
- Although it is extremely difficult to mimic a biological release profile the simple solvent extraction process can be used to illustrate the restriction provided by the capsule walls and is fit for its purpose as an indicative method to determine good and poor batches

Mr McIntyre proposed that the method is suitable to distinguish between good and poor products and that method is adopted as provisional.
The following comments were received from the meeting:

- Did you consider the stability of pirimiphos-methyl in the extracts as it is assumed that analysis for all time points will be done at the end of the study? Mr McIntyre stated that the total a.i. content was also determined at the beginning of the tests to give the "100% a.i. content" for each sample. From the poor quality product where almost instant release occurred the a.i. content released was almost 100% after the first time point and remained at 100% from the later time points.
- Have you considered using SPE to determine the free & release rate? Mr McIntyre stated that this had not been considered but he was unsure if it would work as you would still need to have some sort of liquid to get the release from the capsules to happen.
- Release rate can be affected by temperature. It was noted that most of the labs in the collaborative trial were Northern European countries. Given the proposed uses for this product will be in hotter countries is there anything else that can be done to minimize this? Mr McIntyre stated that they had tested the extraction procedures under freezer conditions and this showed that the release rate decreases at lower temperatures.
- Is there a period of standing to allow the two solvent phases to separate? Mr McIntyre stated that there have to be controlled time periods to ensure the method is standardised.

5.4 Pre-testing of the CIPAC washing/rinsing movement on Olyset by Mr Markus Müller and Mr Olivier Pigeon (4789)

Mr Olivier Pigeon presented the meeting with the results of **development** work on optimisation of the shaking movement used in the CIPAC LN washing method.
The key aim of the LN washing method is that it is comparable with the WHOPES test data. Previous work on the LN washing method has resulted in a standardised detergent that is of different viscosity and slightly different detergency from the Savon de Marseille used in the WHOPES testing. Therefore the washing/rinsing movement needs to be optimised to obtain comparability.
3 washing/rinsing movements were compared using one net type:
Water bath shaker; 155 beats/minute; amplitude 5 mm; 30 ± 2 °C for 10 minutes. (WHOPES)
Horizontal roller; 60 rpm or 210 rpm; 30 ± °C for 10 minutes.
Hand shaking; invert 1 L bottle 10 times or 30 times; keep static at 30 ± 2 °C for 10 minutes

Horizontal rolling and hand shaking gave comparable results for the wash retention index with the WHOPES evaluation.
For horizontal rolling, there is a correlation between the speed of rotation and the power of washing. The higher rotating speed is required to give the same result to the reference result.
For hand shaking, there is a correlation between the number shakes and the power of washing.

The result for inverting 10 times is closer to the reference value that that for inverting 30 times. Mr Pigeon concluded by stating that further work was needed to generate additional data by using other LN products (including coated LN) to make a comprehensive evaluation of the final movement method.

The following comments were received from the meeting:

- Was there any reason for choosing a detergent concentration of 5 g/L. Data seen so far indicate that 4 g/L is the optimum concentration to use. Mr Pigeon stated that there was no significant difference seen between the concentration & retention index when either 4 g/L or 5 g/L were used. Therefore 5 g/L was chosen as it was an easier amount to weigh out.

5.5 Testing of the CIPAC washing agent concentration on Olyset, PermaNet 2.0, NetProtect and DuraNet by Ms Yumiko Kozuki (4788)

Ms Kozuki presented the meeting with the results of **development** work on optimisation of the washing agent concentration used in the CIPAC LN washing method. The work was a collaboration between Sumitomo, Japan; Agroscope, Wädenswil, Switzerland and CRA-W, Gembloux, Belgium.
4 different LN products were tested comprising incorporated and coated products.
The following soap / detergents were compared:

Marseille soap at 2 g/L
CIPAC washing agent at 2 g/L
CIPAC washing agent at 4 g/L
CIPAC washing agent at 8 g/L

Samples of 3 pieces of 25 cm x 25 cm were taken from each net after wash cycles 0, 1, 2, 3, 4 and 5. Each piece was analysed separately using the relevant CIPAC methods. The mean and RSD of the 3 pieces and retention (wash resistance) index were calculated for each wash cycle.
For incorporated LNs there was no significant difference between the 4 detergents tested
For coated LNs the retention index decreases when the CIPAC washing agent concentration increases
4 g/L CIPAC washing agent gave results that were most comparable to 2 g/L Marseille soap
Ms Kozuki proposed to specify 5 g/L in the CIPAC method

No comments were received from the meeting

5.9 Summary presentation on the status of LN methods and the way forward by Mr Martin Rodler

Mr Rodler presented a summary on the **history and current status** of the development of the method to determine the wash resistance of LN
Aspects / Parameters where consensus has been reached:

- A method that allows determination of the wash resistance of LN in a normal analytical / quality control laboratory;
- Use of instruments, equipment and chemicals that are easily and globally available
- Easy, safe, unambiguous, robust and reproducible experimental procedure
- Transparent calculation of wash resistance: Use of the free migration equation agreed.
- Washing agent that has a well defined and constant chemical composition: CIPAC Washing agent developed
  Concentration of washing agent to use: Presented at the meeting 2011
- Movement during washing (and rinsing): Presented at the meeting 2011
- Replenishing step: If these conditions lead to excessive „sweating“ of the AI from the inside the fibres to the surface or degradation, a reasoned case can be made to reduce the temperature (not the time).

In conclusion, we have reached consensus with regards to all experimental parameters!
Proposed Way Forward:

- Perform tests using this proposed method with a coated LN to compare with the WHOPES method.
- Perform a small scale collaborative trial applying this proposed method, using coated as well as incorporated LNs with different AIs and polymers.
- Aim to present the results at the CIPAC meeting in 2012. If the results of this small scale study are acceptable, the method may get adopted as a provisional CIPAC method.

No comments were received from the meeting

5.6 Extension of the CIPAC method MT 180 to DC and OD formulations by Mr Ralf Hänel (4794)

Mr Ralf Hänel presented on behalf of DAPF a **proposal for the extension** of CIPAC method MT 180 to include DC and OD formulations.
MT180, dispersion stability of suspo-emulsions currently only includes SE in the scope with a footnote to indicate that this method may be used as screening method for other water dispersible formulations. The original collaborative study CIPAC/3979, presented at the 41st meeting, 1997 in Roskilde included SC, WG, WP, EW and EC formulations as it seemed to be necessary to have the gap filled between MT 173 (low concentrations) and MT 36 (high concentrations). At that meeting it was decided that the method for the determination of the dispersion stability of suspo-emulsions (SE), CIPAC/3978, should be adopted as provisional CIPAC method with the footnote for other water dispersible formulations. The method was accepted as a full method at the 42nd meeting, 1998 in York.
CIPAC MT 180 was developed to characterise spray mixtures which are formed when suspo-emulsions are diluted with water in terms of dispersion stability. In particular, the parameters creaming and sedimentation in the spray mix are determined.
DAPF consider that taking the physical and chemical properties of such heterogeneous systems into account, it can be concluded that other formulation types forming a dispersion in form of solid particles and fine globules in the continuous water phase of the spray dilution, can be characterised using the same method. Therefore there would be no reason to conduct a small scale trial to confirm this.
Therefore DAPF propose the scope of method MT180 is extended from SE only to include DC and OD products.

No comments were received from the meeting.

5.7 Extension of the CIPAC method MT 46.3 for the accelerated storage stability of LN by Mr Olivier Pigeon (4793)

Mr Pigeon presented a **proposal for the extension** of CIPAC method MT 46.3 to include sampling for LN products to cover determination of active ingredient content and retention index (wash resistance index).

The proposal is to fold the required number of pieces net once, roll them, and place in a 1 L glass bottle, tightly seal the bottle, and keep in an oven at the specified temperature and for the defined period of time.

The following comments were received from the meeting:

- The proposal could also be cross referenced with the washing methods and a.s content methods.

6. Replacement of obsolete methods

6.1 Update on Review of MT methods by Mr Ralf Hänel (4790)

Mr Hänel informed the meeting that the review of MT methods is finalised and the results of the MT review in an excel file are on the website. He indicates however that it is still possible for people to provide comments. The results of the MT review will be transferred into a new "MT handbook". Timeline for this is not yet known.

No comments were received from the meeting:

6.2 Comments on existing methods

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

CIPAC 441/TC/M/3 - Metsulfuron-methyl

It appears that there are two versions of the method published and there is a difference between the versions in hardback and the CD-ROM with regard to the preparation of the mobile phase. Mr Cosgrove from DuPont agreed to check with his company representatives and will respond in writing to CIPAC in due course.

CIPAC 384/TC/(M)/4: Fosetyl-aluminium by titration

The following comments had been received about the method:

> "In the methodology, as described, the fosetyl-Al is dissolved in about 50 ml water and 200 ml 0.1 mol/l sodium hydroxide. After that the volume is brought to 500 ml with 1 mol/l NaOH and this procedure results in a hydroxide concentration of about 0.45 mol/l. To 10 ml of that homogenized solution 40 ml of NaOH 0.1 mol/l is added and refluxed for 1 hour. The available NaOH concentration is less than 0.18 mol/l. Instead of 10 ml 2 mol/l sulfuric acid, as written in the CIPAC procedure, less than 5 ml was necessary to neutralize the solution after hydrolysis.
> When the analysis was performed in the way it is described in the Handbook G only about 70% of the triethyl phosphonate appeared to be hydrolysed into phosphite.
>
> Alternatively, when we used in a more logical approach by dissolution and dilution in 0.1 mol/l NaOH and adding 40 ml of 1 mol/l NaOH for the hydrolysis step, the hydroxide concentration was about 0.8 mol/l; the resulting hydrolysis was for almost 99% complete. By using 1 mol/l all over the procedure an accuracy of 99.9% was found.
>
> So the concentration of sodium hydroxide at 1 mol/l in the hydrolysis step gives the best result.
>
> However this specific result should be corrected for the present inorganic phosphite as described in CIPAC 384/TC/(M)/4 .
>
> For Method 384/TC/(M)/4 in the text of the procedure no buffer pH 7.3 is added. Our experience is that if no buffer is added, it leads to too low results for inorganic phosphites and consequently too high fosetyl–Al results. Addition of an amount of buffer is essential, as neutralised sodium hydroxide with sulfuric acid has no buffer capacity at all. The reaction of iodine with phosphite to form phosphate also generates 2 protons and the pH will drop fast and consequently no further oxidation with iodine will occur. Therefore it should be emphasised that an amount of buffer should be added, because otherwise too high results for fosetyl-Al will occur."

Mr Bura requested any comments from the meeting on this issue to be sent in writing.

MT 162: Determination of ETU
A comment has been received that with the current method it is not possible to analyse the correct amount of ETU in a product as the extraction process also causes the formation of ETU. Thus the method can only be regarded as an indication rather than a true concentration.

The following comments were received from the meeting:

- This will not occur if the samples are analysed immediately therefore there should be a footnote addition to the method that analysis should be conducted immediately.
- Could CIPAC move to other types of method for ETU and regard this method as "obsolete". Is IR equipment commonly available?
- IR is not qualitative analysis so there will still need to be confirmation that the compound measured is indeed ETU.

Mr Bura requested any further comments from the meeting on this issue to be sent in writing.

MT193: Friability of tablets
A comment was sent regarding the misleading name and formula calculation for this method.

It was noted that this issue had already been identified (MT 193 was discussed at the 54th meeting, 2010 in Slovenia) and that a revised version of MT193 had since been added to the CIPAC website.

Chairman's remark

The Chairman made the following remarks to the meeting:
We have recently had some collaborative trials where a large number of laboratories have participated. To avoid disappointment if more labs offer to participate than the company can provide samples for, the CIPAC information sheet will indicate if there are any limits on the number of samples available.

There appear to have been some problems recently with the supply of samples to laboratories. This is a problem with importing the samples possible due to classification & labelling issues and import taxes. It is not clear why this issue has arisen now but please could companies be aware of this and inform the respective labs that this is the reason why they cannot participate. Unfortunately CIPAC does not have much influence in this area.

Mr Hänel offered his thanks to all those who had contributed to the work of CIPAC over the previous year, in particular to industry colleagues who prepared the trials and all those who participated in the trials. He also thanked FAO, WHO and industry for continuing to use the CIPAC platform to test their methods.

Mr Hänel declared the open meeting closed.

7. Minutes of the 54th meeting (4578P)
The minutes were circulated to members by e-mail. No corrections were received therefore the Minutes of the 54th meeting were unanimously accepted as correct.

8. Secretary's report (4759/P)
Mr László Bura presented the Secretary's report for the period from the 54th CIPAC meeting held in Ljubljana, Slovenia, 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

738: Clothianidin (FS, WS extension)

The method extension was presented at the 53rd meeting, 2009 in El Salvador. It could not be accepted as a method extension for technical reasons as the method itself was also presented at the same meeting. At the 54th meeting, 2010 in Slovenia, the method was accepted as provisional method.
Mr Martjin raised the issue in writing before the meeting that for suspensibility (where the a.i. content should be determined) the sample preparation is different to what was proposed for the method and method extensions.
The meeting considered that this was not a major issue.
The method extension can be promoted to **full CIPAC method**.

333: Deltamethrin (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.
It was also considered that in practice this may not be a method extension– rather a new method but the situation was not clear. The Chairman and Secretary will compare in detail both methods and circulate to members for further discussion. It should also be considered whether to send this to full members only or correspondents also.
The method **remains provisional**.

739: Dimoxystrobin

At the 54th meeting, 2010 in Slovenia the method was adopted as provisional. However there was discussion over whether the number of laboratories removed from the statistical analysis was acceptable. There were many labs removed. But the labs were removed because they were statistically identified as outliers. The analyst considered that it was not a problem of the method rather a problem of the results i.e. as the results were very close any small variation would indicate an outlier.
According to CIPAC guidance 2 out of 9 labs can be removed. In this instance 4 out of 38 were removed therefore this is in line with guidelines
The method can be promoted to **full CIPAC method**.

521: Fluazinam

At the 54th meeting, 2010 in Slovenia the method was adopted as provisional. 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 company have contacted the Secretary to ask if there was anything else they could do to or was there any more information they could provide to CIPAC to ensure the method was promoted to full. The meeting considered that there is not any more real information CIPAC asks for. 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.
The method **remains provisional**.

331: Permethrin (EC, extension)
At the 54th meeting, 2010 in Slovenia the method was adopted as provisional. No further comments were received
The method can be promoted to **full CIPAC method**.

33: PBO (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.
It was also considered that in practice this may not be a method extension – rather a new method but the situation was not clear. The Chairman and Secretary will compare in detail a comparison of both methods and circulate to members for further discussion. It should also be considered whether to send this to full members only or correspondents also.
The method **remains provisional**.

636: Spinosad (EC extension)
The EC is for public health use. At the 54th meeting, 2010 in Slovenia the method was adopted as provisional with a requirement to include a footnote that mineral oil is not causing clogging of the column. This has been addressed. No further comments were received.
The method can be promoted to **full CIPAC method**.

653: Cyazofamid (4773, 4774)
The meeting considered that provided the comments received were taken on board CIPAC could recommend moving to a full scale trial.
A full scale trial is recommended.

333: Deltamethrin (4797, 4798)
The extraction process is different to that already published for PermaNet® LN but the instrumental measurement is the same. A second CIPAC method (333 - total content in incorporated PE LN formulations) uses the same extraction process as used for LifeNet® LN
Some amendments may be needed to the current method to make it clear that the method is suitable for polyethylene & propylene nets of the incorporated types.
The method can be accepted as **provisional**.

398:Stereospecific identity test for triadimenol (4795, 4796)
Currently the method is already a full method. The Meeting agreed that it is accepted as an amendment to the full method and it should be amended in Handbook N before publication. The method as it stands will need to be revised to be put into CIPAC method format.
The method is accepted as an **amendment** to the current full method

595: Flazasulfuron (4791, 4792)
The meeting considered that provided the comments received were taken on board CIPAC could recommend moving to a full scale trial.
However it was important than more development work on the extraction and sampling of the WG was conducted to optimise the procedures before conducting the full scale trial.
A full scale trial is recommended.

578: Flumioxazin (4763, 4764)
The meeting considered if the trial was acceptable given the number of samples analysed. It was agreed that the samples met CIPAC guidance criteria.
The method can be adopted as **provisional**.

585: Fosthiazate (4761, 4762)
Despite a repeated small-scale trial there still appears to be a problem with the analysis of the GR. The meeting considered that a larger sample size for the GR would help with the sample preparation. If the GR issue is resolved it may not be necessary to use an internal standard, but a full scale trial using an internal standard means that there is an option to consider the results and statistical analysis with and without the internal standard.
The meeting considered that is was difficult to make a sound recommendation at this time as there are still several unknowns; the method does not appear to be optimised or robust.
A full scale trial **CANNOT** be recommend

33: Piperonyl butoxide (4765, 4766)
The method should include a note that the internal standard can be added either as a known volume of solution or by weight. In addition it should be amended to note that a single point calibration can be used. Subject to these amendments the method can be accepted as **provisional**.

33: Relevant impurity dihydrosafrole (DHS) in piperonyl butoxide technical
There were no comments.
The method can be **adopted**.

239: Pirimiphos-methyl (4778, 4779, 4780)
The sample preparation step of the method needs to be amended as proposed to take into account issues with the homogeneity of CS products. Subject to these amendments the method can be accepted as **provisional**.

Solution stability of STs (4771, 4772)
The gravimetric method proposed is not sufficient on its own. If there is a high residue on the sieve then an analytical method to determine the a.i. content should be used.
The meeting questioned the relevance of the test i.e. what is this for? Surely the test is the same as MT 179 for granules & powders as by the definition of STs the a.i. should be soluble in water? The tablets may contain water-insoluble co-formulants and if these drop out of solution over time then this could lead to nozzle blockage.
The meeting agree that the scope and title of the method needs to be clarified Subject to these amendments the method can be adopted as **provisional**.

MT 73.1 Total hardness of water (4769, 4770)
There were no comments.
The method can be accepted as **provisional**.

239: Relevant impurities in the pirimiphos-methyl CS formulation (4781, 4782)
There were no comments for the method for *iso*-pirmiphos-methyl.
For the other method a note needs to be included about system optimisation to ensure sufficient data points are collected by the MS detector. Subject to these amendments the methods can be **adopted**.

239: Free AI content of the pirimiphos-methyl CS formulation (4785, 4786)
239: Release rate characteristics of the pirimiphos-methyl CS formulation (4783, 4784)
The meeting considered that these will be compound specific MT methods. However it was questioned whether 4 participating laboratories were sufficient to collaboratively test the methods. For the other CS methods considered by CIPAC previously (lambda-cyhalothrin and parathion –methyl) full scale collaborative trials were conducted. Other points raised were:
One of the products analysed was a “bad product” and the method showed it can distinguish between good and bad products.

The labs used were only company labs. Would be important to know how this works in a QC government lab.
Why is this different from any other CIPAC method? What is to stop someone coming for a small scale trial for a "standard a.i" determination and asking for provisional status?
Are the current CIPAC guidelines specific enough about what data are needed in these situations?
The meeting considered 3 options:

1) Accept as a Provisional MT method.
2) Go to full scale.
3) Accept this as provisional BUT clarify the future guidelines and use this as a test case to set the precedent for a reduced number of labs for this type of formulation only. Would also need to set requirements for the types of sample analysed (i.e a good or bad samples).

The meeting agreed with option 3. Sonia Tessier, Markus Müller and Tony Tyler agreed to draft some guidance for discussion at next year's meeting.

The method can be accepted as **provisional**.

Post meeting note: It was not decided whether the method can be accepted as separate MT method or as method extension of MT 189 and MT 190, respectively, with the necessary amendment in the scope of the method and the renumbering as follows: MT 189.1 lambda-cyhalothrin and MT 189.2 pirimiphos-methyl.

Pre-testing of the CIPAC washing/rinsing movement on Olyset (4789)
Testing of CIPAC washing agent concentration on 4 LNs (4788)
Summary presentation on the status of LN methods and the way forward
The meeting considered that they would need to see the results of the full scale trials scheduled to be presented in 2012 before reaching a conclusion.

MT180: Extension of the CIPAC method MT 180 to DC and OD formulations (4794)
There were no comments.
The method can be accepted as **provisional**.

MT 46: Extension of CIPAC MT 46.3 for the accelerated storage stability of LN (4793)
The meeting considered whether a small study was required to confirm that the proposal is workable, in particular the effects having 4 or 5 pieces of net stored in the bottle together.
The meeting agreed that it should be suggested that a small scale trial is considered in conjunction with the other ongoing LN work.
The method can be adopted as **tentative** with some further work on validating the method required.

10. Matters related to FAO and WHO specifications

None

11 Any other business

It was remarked that it is very difficult for meeting to follow all the information and discuss fully the methods on the basis of the presentations alone. In previous years copies of the reports were either circulated to members before the meeting electronically or were made available at the meeting in hard copy. Over the last few years only a very small number of reports were received in advance.

This will be communicated to industry. They will also be reminded that they need to prepare report and method documents and not just provide CIAPC with a copy of the PowerPoint presentation given at the TC.
It was questioned whether in the future the presentations of the TC would be added onto the CIPAC website? The Chairman remarked that this was not planned at this time.

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