Minutes from EURL workshop Holte 20-22 September 2016

Tuesday, 20 September 2016

- **Welcome** by **Mette Erecius Poulsen.**
  Mette welcomed the participants and talked a bit about Denmark and happy Danish and Technical University of Denmark. She talked about relocation of food institute to the university campus and reorganization in the institute.

  The agenda was presented

  All participants presented themselves and said number of years working with pesticides. Some of participants are new in pesticides field and some are experienced (from 1 to over 30 years).

- **EUPT-CF10 results** by **Mette Erecius Poulsen.**
  Mette presented how many NRLs participated in EUPT-CF10 and the plan and time schedule of the PT.

  178 labs from 41 countries and 12 labs from outside EU participated in EUPT-CF10.

  For the first time organochlorines were included as the voluntary list to the pesticides list.

  For the first time this year there was no false negative.
  A Quite many high Z-score was reported for Carbandazim due to un-proper standard solution. Stock solution should not be so strong.
  Many high Z-score were also reported for Cypermetin. Low Z-scores was achieved by the labs who didn't add water during the extraction.

  Z score for all the compounds were bellow Alg A RSD EU

  For all the pesticides, there were over 95% of acceptable results.

  75 labs were in category A (47%).

  Next year oat flour will be used as material for PT.

- **News and updates** by **Susan Strange Herrmann**

  Susan presented about expert meeting on MACP 2015.

  She presented about processing factor for cereals. A table of processing factor reported for barley, maize, oat, brown rice, polished rice, rye, wheat. Buckwheat was removed because it is not consumed by all EU member states. There is need for general discussion and decision is needed about the processing factor of cereals.

She talked about changes in general protocols. Some new compounds are introduced for 2017. Reasons for selection of the new compounds were explained.

Obligation of the NRLs: all NRLs should participate in EUPTs.

Network map in EURL portal was presented. NRLs should check if their information provided in the map is correct otherwise they have to update their information.

If there is underperforming, a 2-step protocol by DG-SANTE is applied.

- **Pesticides in fish feed** by **Parvaneh Hajeb**
  Parvaneh presented about their current project on method validation for pesticides residues in fish feed which the EURL-CF task for 2016-2017.
  She discussed the challenges for clean-up of fish feed with high fat content. There were a discussion abbot EMR clean-up with the participants.

  She also presented the statistics of fish production in EU member states and requested to the NRLs to participate in the upcoming survey on fish feed. Participants were requested to send 2 samples of fish feed from their country to EURL-CF to be analysed using the validated multi method.

- **10-year anniversary of EURL-CF** by **Mette Erecius Poulsen**
  Mette presented the history of EURL-CF from 1 July 2006 to 1 July 2016.
  She talked about the history of PTs and mentioned that the number of participants in PTs was growing during years.

  A web tool to submit PTs results were developed this year.

  With PT5-rice, the certificate was issued.

  With PT9-maize, for first time there was no incurred residue because maize is covered with leaves. Therefore they have to spike all the pesticides.

  It was mentioned that it is important to store the PT grain especially the flour in the freezer because the chemistry of cereals changes and it effects the detection of pesticides residues.

  She explained the spiking procedure for PT. And she also talked about instruments history at EURL-CF and that the centre will receive new instruments soon.

- **QuEChERS automated extraction in feed** by **Anne Ochem**

  Anne presented a video of automated extraction method they use for pesticides residues analysis in feed since March 2016. The QuEChERS extraction take 7 hours using this instrument and the capacity is max. 40 samples.

  The automated extraction instrument is made by Tekma, USA and it cost 100,000 euro.

  They compared manual C18, automated C18, and automated EMR clean up, and the result showed that automated extraction was more effective and removed fat efficiently.

- **Status of Albanian NRL by Ederina Ninga**
  Ederina presented about their organization and the analysis carries out there. They don't analysis feed samples so often, unless there is some issues with health problem of animals and they suspect pesticides for instance some fishes die in the farm.

- **Evaluation of Rapid Methods for Pesticides Analysis** by **Michael Hetmanski**
  Michael presented that they selected SweEt method for their routine analysis as it is easier and more reliable and rapid. However, this method is not applicable to high fat content samples such as oat.

- **Validation of standards and control at NVWA** by **Jos Scholten**
  Jos presented that at NVWA (Food and Consumer Product Safety Authority), they prepare stock standard solutions in toluene, and working standard solutions in methanol for LC and isooctane for GC analysis.

  The stock solutions (1 mg/ml) prepared with their method stay stable for more than 10 years at -18 C. The working solutions are stable for 2 years at -18 C. Calibration standards are stable for one year in freezer and 3 months in the refrigerator.

- **Validation of pesticides in wheat using LC-MS/MS TQ** by **Jos Scholten**
  He presented about validation of pesticides in wheat using GC-MS/MS and LC MS/MS-TQ.

  It was mentioned that they only do clean up in QueCheRS for GC-MS/MS and nout for LC-MS/MS analysis.

  They validated 272 compounds for LC and 309 for GC analysis at 5, 10, 50 ng/g. LOQ of 5 ppb were reported for both LC and GC. They didn't face any problem with LC analysis but they had some difficulties with GC analysis and some compounds were not detected.

  There were no issues of matrix effect with LC but with GC, a high matrix effect was observed.

Average recovery and RSD were very good in negative mode both in LC and GC. LOQ was 10 ppb in LC negative mode.

They obtained good results and z-scores for EUPT10 using this method.

- **NRL study, effect of milling procedure on pesticide residue result**s by **Parvaneh Hajeb**
  Parvaneh presented the result of survey on cereal milling by NRLs. 23 NRLs participated in the survey and milled oat and rye samples which they received from EURL-CF.

  Four different types of mill instruments with different brands and efficiencies were used by NRLs.

  The survey result showed that milling affects the particle size distribution of the cereal flours and also the pesticides residues recoveries in the cereals.

- **Clean up of oat extract** by **Susan S Herrmann**
  Susan explained that oat is a problematic cereal for pesticides residues analysis due to the high fat content.

  She explained how matrix can affect the analysis by broadening the peak and shifting the retention time which make quantification difficult. Matrix can also protect the compound so it can have positive effect as well. Matric effect is more common in GC analysis than LC.

  Her study showed that PSA was very efficient of removing matrix of oat as compare to EMR and Z-sep clean-up. It was mentioned that more PSA is needed for clean-up of oat as compared to wheat.

  There were some questions by participants about EMR clean-up which Susan explained that EMR is a pre-packed clean-up material and its ingredients is not revelled yet.

Wednesday, 21 September 2016

- **Swedish multiresidue method SweEt goes into Orbitrap** by **Susanne Ekroth**
  Susanne started with history of Sweden and Uppsala.

  She explained about SweEt method and mentioned that they are trying to apply the method developed for cereal to vegetables and fruits.

  She also explained about LC orbitrap which they are currently using in their lab and mentioned that they are very pleased with this instrument.

- **Discussion on TOF and Orbitrap mass analysers** by **Susanne Ekroth, Mette Erecius Poulsen and Jørn Smedsgaard**
  After description abouth orbitrap by Susanne, Jørn explained the difference between TOF and Orbitrap and advantage and disadvantages of each technique. He mentioned that accuracy is more important than resolution.

  Mette talked about her experience with GC orbitrap in Manchester and screening of barley, oat, rye, rice and wheat. She mentioned that resolution in TOF is much lower as compared to orbitrap. She was impressed that they just injected 1 µl of sample extract to GC orbitrap.

  Ralf argued that they used orbitrap for baby food and they are not so impressed with orbitrap results as compared to GC QTOF.

  Orbitrap is used by NRL in Iceland, France and Germany.

- **Shoot-and-Dilute GC-MS/MS: Matrix Effects Evaluation and Calibration Approaches** by **Becky Wittrig**

  Becky presented about reducing matrix effect. She explained about sample preparation and how to reduce the analytes by split injection.

  It was mentioned that the reactivity of pesticides compounds is very important in using split injection; for instance Captan and DDT are very reactive. Active pesticides like omethoate stick to the inlet system.

  It was mentioned that split injection give better detection as compare to splitless. RSD and response are better using split injection.

  Using analytes protectants can help better detection of many compounds like DDT, DDD, DDE.

Split injection at low temp (150 C) can give better separation of chlorinated pesticides.

A special type of liner is needed for split injection.

- **Work program 2016-2017** by **Mette Erecius Poulsen**
  Mette presented EURL-CF work program 2016-2017.
  She mentioned that for the first time we have 2-years program. 4 main tasks has been mentioned for 2016-2017.

- **Evaluation and closing of workshop** by **Mette Erecius Poulsen**
  Mette announced the closing of the workshop and asked the participants to fill in the evaluation form.

- **Training - Interpretation of validation data** by **Susan S Herrmann**
  Susan presented about interpretation of validation data according to SANTe documents.

  Then, participants were grouped into 7 groups of 4 persons. Each group were given 4 different exercises and they had 30 min time to work on the tasks and present and discuss their answers.

  A validation data set (recovery and RSD at 3 levels) given to each group and they discussed which level should be chose as LOQ for each compounds.

  There was discussion on how people practice this issue in their lab and even though there are rules that should be followed (SANTE documents), there is still sometimes based on personal opinion how to select LOQs.

- **Training - Summing up of LOQs in case of complex residue definition - in practice** by **Ralf Lippold**
  Ralf presented what is complex residue definition. Then, he gave one exercise for the group work to be done in 20 min.

Thursday, 22 September 2016

- **Training - Preparation and control of standards** by **Mette Erecius Poulsen**
  Mette presented about preparation of standard solution as instructed by SANTE document. Thereafter, she gave 4 different exercises to each group to practice. A set of data of stock solution analysed on the GC instrument was given and the participants asked to comment on the sequence, calculate the averages, the RSDs and the differences between the old and the new stock solutions according to

SANTE document. The groups were also asked to evaluate if the new weighing is acceptable for all the compounds and discuss what to do if one or more of the weighing is not acceptable.

Groups discussed with their answers to each exercise. A group argued that 3 replications is not enough, and based on SANTE document at least 5 replication is needed. Another group discussed that if recovery is below 60%, a new standard solution should be prepared, but before preparing new standard, we have to analyse using instrument again.

- **Training - Measurement uncertainty and bias** by **Ralf Lippold**
  Ralf presented about measurement uncertainty according to SANTE document and explained how to calculate uncertainty. He gave an exercise for group work which they have to calculate the uncertainty of the given data.

- **Evaluation**
  Mette closed the training sessions and asked the participants to fill in the evaluation form and give their comment about the training and suggestions for future trainings.

  Certificate of participation in workshop and training was given to every one after collection of evaluation forms.