Universität Stuttgart
Germany

EAC PT evaluation workshop

Arusha
23-24 February 2010

Report on the EAC
Proficiency Testing Evaluation Workshop
with Training Course on
Traceability, Reference Materials, Proficiency Testing and Measurement Uncertainty

Arusha, Tanzania, 23 – 24 February 2010

Prepared by Dr.-Ing. Michael Koch

Summary

The workshop covered the evaluation of the 4th Proficiency Testing rounds on the analysis of edible salt, wheat flour and edible vegetable oil, provided in 2009.

The results showed that the spread of the results from the different laboratories are broad, so that there is no consensus between the participants. Therefore results from reference measurements were used as assigned values for the PT.
The standard deviation in most cases is very high, so that improvement of the analyses is urgently needed. To facilitate this improvement the analytical methods were discussed in the working groups.
The training covered traceability of chemical measurements, the importance and use of certified reference materials, the background of proficiency testing and different ways to estimate measurement uncertainties.

Most of the participants are enthusiastic and very keen to improve their analyses. As the result of the evaluation questionnaire shows, the laboratories benefit very much from the PT scheme, the training and the exchange with colleagues form other labs.

Introduction

The workshop reported here followed the 4th PT rounds of the EAC PT schemes for edible salt, wheat flour and edible vegetable oil.
The PT rounds were organized with support from Physikalisch-Technische Bundesanstalt in Germany.
The workshop covered the report from the experiences of providers as well as participants and the evaluation of the results.
Besides this the opportunity of the workshop was used to provide a training course.

Participants and Organisation

The workshop was attended by 28 participants from the following countries:

- Burundi 1
- Kenya 12
- Tanzania 10
- Uganda 8

In addition the three PT providers, Mrs. Sara Prins (NMI South Africa), Mr. Tobias Diergardt (PTB Germany) and Dr. Michael Koch (consultant from University of Stuttgart) were present.
A complete list of participants is given in annex 1.

Tuesday, 23 February 2010

9:00 h Welcome – Kezia Mbwambo (TBS)
KM welcomed the participants to Arusha and made a short introduction to the workshop content.

9:05 h Introduction of participants

9:10 h Opening – Tobias Diergardt (PTB)

9:15 h Proficiency Testing – What you need to know – Kezia Mbwambo (TBS)
KM gave an overview on what is PT all about and explained the benefits and the background of the EAC PT schemes.
The complete presentation is included in annex 2.

9:45 h What is the truth? How to determine the assigned value – Michael Koch (Univ. Stuttgart)
MK explained the importance of correct assigned values in PT. He described the alternatives:

a) participants' mean and
b) reference measurements.

If there is no consensus between the participants alternative a) is not possible. Unfortunately this was the case for many parameters in the present PT round. Therefore reference measurements should have been made by laboratories selected by NMISA.
Unfortunately the selected laboratories turned out to be not sufficiently competent in this field of analysis. So the results were neither complete nor reliable. So it was decided to send the samples in addition to an experienced accredited food laboratory in Germany.
MK presented the PT data and explained the choice of assigned values for all parameters in all matrices.
The presentation is included in annex 3.
During the PT providers meeting preceding the workshop it turned not to be clear, if the results of the German reference laboratory for wheat flour were indeed reported on "dry basis". This was clarified via E-mail during the workshop. Since this really was not the case, the reference values had to be revised. This was presented by MK at a later stage, but is included here in annex 4 to avoid confusion.

10:30 h Coffee/tea break

11:00 h The Edible Vegetable Oil PT Provider's Experience – Phenny Kaviiri (UNBS)
PK described the preparation of the samples (sunflower oil, spiked with Cu and Ni). Homogeneity and stability were checked. 17 samples were sent out, 15 labs returned results.

Parameters to be analysed:

- Rel. density
- Refractive index
- Acid value
- Iodine value
- Peroxide value
- Copper
- Nickel
- Moisture and volatiles

PK presented the evaluation procedure and the results. The full presentation is given in annex 5.

11:35 h The Wheat Flour PT Provider's Experience – Felista Kerubo Nyakoe (KEBS)

FN also reported on the preparation of the samples. They were mixed using a drum hoop mixer. Packages for each participant contained approx. 100g. Homogeneity was checked. 23 samples were sent out and all participants returned results. Evaluation was made according to ISO 13528.
Parameters to be analysed:

- Moisture
- Total ash
- Crude fat
- Crude protein
- Acidity as lactic acid
- Acidity as sulphuric acid

FN presented the results and the challenges.
The full presentation is given in annex 6.

11:35 h The Edible Salt PT Provider's Experience – Kezia Mbwambo (TBS)

Two different samples were prepared and dispatched to the participants. Sample 1 was mainland salt and sample 2 was sea salt. KM explained the preparation of the samples (initial amounts of both salts were 20 kg, 40 samples each were made and sealed immediately).
Parameters to be analysed were:

- NaCl
- Mg
- Ca
- I
- Sulphate
- Moisture

26 samples were dispatched, 23 labs reported results.
The complete presentation is given in annex 7.

12:30 h Lunch break

14:00 h Which analytical method is the correct one? – Michael Koch (Univ. Stuttgart)

MK showed for all three matrices and all parameters the methods that were used or could be suitable. He stressed that the choice of suitable methods and harmonisation

of methods is crucial for improving the performance especially in the cases where the result of a measurement is strongly influenced from the choice of method.
This presentation (included in total in annex 8) formed the basis for the following working group discussion.

14:40 h Working Group Discussions
15:50 h Coffee/tea break
16:25 h Reports from the Working Group Discussions
Three working groups were formed (one for each matrix) and the guiding questions were discussed. There were 11 questions common to all working groups and matrix specific discussions about the methods that could be recommended.
The results of the working groups were to be presented to the plenary later. The following gives the summary of that answers:

Working Group Edible Salt

1. *Did you receive the samples in good time and good state?*
   Yes
2. *Was the time given for analysis enough?*
   Yes
3. *Was the sample quantity adequate?*
   Yes
4. *Was the information given sufficient?*
   No. The definition of the measurands were not really clear for
   - Chloride reported as NaCl
   - iodine determination (where iodate reported as iodine would have been the target analyte)
   - moisture (where the temperature should have been stated)
5. *Did you understand the PT report?*
   No, because of most of the labs didn't receive the report because of payment or miscommunication issues or received it very late
6. *Is there something more to be included?*
   Yes, mode of payment of PT participation. Sample to be sent out after payment
7. *Was the participation helpful?*
   Yes
8. *Any suggestions for the next round (e.g. parameters)?*
   New measurand: water-insoluble matter
9. *Is there a need for other PT rounds (other matrices)?*
   Fish, milk and milk products were suggested
10. *Any ideas how to solve the payment problem?*
    No
11. *Any ideas how to make the system sustainable without support from PTB?*
    - create awareness to decision makers to understand importance
    - increase fees
    - participants to explain importance of PT to decision makers

For the part specific for Edible Salt statements were made regarding the methods and questions asked (in italics)

- ***Moisture***
  - *Oven at*
    - *105°C*
    - *150°C*
    - *230°C*
    - *250°C*
  - *IR (which temperature?)*
  - *Standardisation of temperatures needed*
  - *Next PT round the requested temperature will be stated – which one?*

Answer: methods to be oven, temperature: 105°C, to constant mass

- ***Chloride as NaCl***
  - Obviously it was not absolutely clear, that determination of Cl- was requested
  - Mohr titration
  - Potentiometric titration
  - Possible problems:
    - Standardisation of $AgNO_3$
    - What else?

Answer:

- Proposed method: Mohr titration
  - standardisation with standard NaCl
  - endpoint detection easier with diluted solution

- ***Sulphate***
  - Gravimetric as $BaSO_4$
  - Turbidimetric (seems to have many problems)
  - Ion chromatography
  - Possible problems:
    - Sample not filtered prior to determination
    - Precipitation not complete ($\rightarrow$ low)
    - Filtration problems
    - Washing not complete ($\rightarrow$ high)

Answer:

- Proposed methods: IC and gravimetry
  - suggestion: filter sample before analysis

- ***Calcium***
  - Atomic absorption
  - Complexometric
  - ICP-OES
  - Ion chromatography

Answer:

- Proposed methods: AAS, ICP-OES and titrimetry with EDTA
- for AAS: flame to be uniform, use N_2O flame

- ***Magnesium***
  - Atomic absorption
  - Complexometric
  - ICP-OES
  - Ion chromatography

  Answer:
  - Proposed methods: AAS,ICP-OES and IC
  - for AAS: use Lanthanum fluoride to minimize interferences
- ***Iodine***
  - Confusion on what to be measured
  - Iodate
    - Titration with thiosulfate (acidification with H2SO4, addition of I^-, titration with $Na_2S_2O_3$)

      $IO_3^- \xrightarrow{H_2SO_4} I_2 \xrightarrow{I^-} I_3^- \xrightarrow[Na_2S_2O_3]{\text{Titration with}} I^-$
    - Iodate in iodated salt, reported as Iodine
  - Iodide:
    - Sandell-Kolthoff (photometric, reduction of Ce(IV) by As(III) catalyzed by I^-)

  Answer:
  - Target measurand: Determination of <u>iodate expressed as iodine</u>
    - standardisation of $Na_2S_2O_3$ is crucial
    - use fresh starch solution
    - modified evaluation formula to be given by PT provider

<u>Working Group Wheat Flour</u>

1. *Did you receive the samples in good time and good state?*
   Samples given was enough
   Sample received in good time and state.
2. *Was the time given for analysis enough?*
   Time given for was enough
3. *Was the sample quantity adequate?*
   Yes
4. *Was the information given sufficient?*
   Information given on the sample was sufficient though some participants were not aware since instructions were not read.
5. *Did you understand the PT report?*
   PT reports not received and therefore could not be understood without reading.
   PT provider says some reports have been sent for those who sent the payment proof. No much comment since the analysis has to be redone but PT provider took us through the general report which is in the same format as the SADC one.
6. *Is there something more to be included?*
   No statement
7. *Was the participation helpful?*
   Participation found so helpful.
8. *Any suggestions for the next round (e.g. parameters)?*
   More parameters like crude fiber, gluten content, calcium and phosphorus, starch, aflatoxins etc.

9. *Is there a need for other PT rounds (other matrices)?*
   Other PT rounds suggested are dairy products like powdered milk, imitation drinks (beverages), cosmetics (hydroquinone). Requests given to any lab that feels it has the ability to become a PT provider to make a proposal. We should not only rely on the bureau.
10. *Any ideas how to solve the payment problem?*
    Suggestions were that samples be dispatched after payment. PT providers to send an earlier invitation to participants, which will allow for quick payment.
11. *Any ideas how to make the system sustainable without support from PTB?*
    It was suggested that more sponsors should be invited e.g. industries, NGOs, chemical and equipment suppliers.

Specific part

- ***Moisture***
  - *ISO 712*
    - *oven at 131±1.5°C*
    - *reduced pressure (1.3 – 2.6 kPa) at 45°C-50°C with P2O5*
  - *Did you all use this temperature?*

  Answer: KEBS gives105°C, AOAC, ISO 712 gives 130°C and this has been recommended by all participants. One participant emphasized her use of a digital moisture meter, which she says is so effective

- ***Total ash***
  - *Ashing at 900°C or 550°C – who used what?*
  - *Decision on temperatures needed*
  - *Details on standards*
    - *ISO 2171:1980 □ 500-600 °C*
    - *AOAC 923.03?*
    - *ICC Method 104/1 (1990)?*
  - *Potential problems: Incomplete ashing*

  Answer: Constant monitoring of ash colour and achieving the constant mass were recommended. PT provider to compare the two temperatures of 550°C and 900°C and send the findings for the next analysis.

- ***Crude Fat***
  - *Acid digestion followed by Soxhlett extraction with petroleum ether, gravimetric determination*
  - *Anything else?*
  - *What could be potential problems?*

  Answer: Acid digestion followed by soxhlett extraction with petroleum ether, gravimetric method was recommended, but participants can also use their normal methods and compare the two results.

- ***Crude Protein***
    - *Kjeldahl nitrogen determination, factor 5.7 to convert to protein*
        - *ISO 1871*
        - *ISO 20483*
        - *ICC 105/l*
    - *Combustion method for nitrogen determination*
    - *Were other factors used?*
    - *Other potential problems:*
        - *Standardisation of acid*
        - *Cleaning of equipment*

  Answer: Kjeldahl nitrogen determination method was recommended with the factor of 5.7 in conversion to protein, ISO 1871, 20483. Acid used must be standardized. Cleaning is also very necessary to remove any residues.

- ***Acidity***
    - *There seems to be a big confusion*
    - *Who requires what for which purpose?*
        - *National regulation?*
        - *International regulations?*
        - *Codex Alimentarius requires Fat Acidity as Sulphuric Acid according to ISO 7305 or AOAC 939.05 (alcoholic extract)*
    - *Methods differ*
        - *in extracting agent*
        - *duration of extraction*
        - *temperature of extraction*

      and therefore deliver different results

  Answer: To be kept and a standard method be used e.g. ISO 7305.

NB. Participants recommended the use of Blanks for all parameters. Participants were also advised to check the validity of all reagents used in their organizations for reliable results.

<u>Working Group Edible Oil</u>

1. *Did you receive the samples in good time and good state?*
   Yes
2. *Was the time given for analysis enough?*
   Yes
3. *Was the sample quantity adequate?*
   Yes
4. *Was the information given sufficient?*
   Yes
5. *Did you understand the PT report?*
   Yes
6. *Is there something more to be included?*
   Details of the method to be included
7. *Was the participation helpful?*
   Yes
8. *Any suggestions for the next round (e.g. parameters)?*
   Parameters are ok

9. *Is there a need for other PT rounds (other matrices)?*
   Milk (fat content, protein, total solids), drinks(spirits for ethanol and acidity) were suggested
10. *Any ideas how to solve the payment problem?*
    Payment to be made in advance
11. *Any ideas how to make the system sustainable without support from PTB?*
    - Top management of all organisations to be involved
    - EAC to be asked for sponsorship
    - PT scheme to be marketed widely to get more participants

Specific part

- ***Refractive Index***
  - *Only possibility is using a refractometer*
  - *ISO 6320:2000 requires use of water bath and reference temperature of 20°C (for this kind of oil)*
  - *if the measurement temperature is within 20±3°C correct for the difference, otherwise discard the result.*
  - *Possible problems:*
    - *Temperature control might be an important factor*
    - *Air bubbles lead to nonsense values*
    - *The refractometer has to be checked regularly*

  Answer: all equipment to be calibrated

- ***Relative density***
  - Hydrometer
  - Pycnometer
  - Oscillating U-tube (density meter)
  - Possible problems:
    - Temperature
    - Filling of the pycnometer
    - Outside contamination of the pycnometer

  Answer:
  - U-tube method
  - Reference material to be used to check density meter

- ***Acid Value***
    - Definition: Number of milligrams of potassium hydroxide required to neutralize the free fatty acids present in 1 g of fat.
    - Unit: mg KOH/g
    - ISO 660
        - Hot ethanol method using indicator
            - Dissolve test portion in hot ethanol and titrate with aqueous solution of KOH, use phenolphthalein as indicator
        - Cold solvent method using indicator
            - Dissolve test portion in neutralized solvent mixture (diethyl ether / ethanol) and titrate with ethanolic KOH solution
        - Potentiometric method
            - Dissolve test portion in methyl isobutyl ketone, titrate and record neutralisation curve, determine inflection point graphically
    - Who uses which method?

  Answer:
    - No problem with the method
    - quality of reagent to be observed
    - standardisation of reagents
    - balances to be checked and calibrated

- ***Peroxide Value***
    - Definition: quantity of those substances in the sample, expressed in terms of active oxygen, that oxidize potassium iodide under the conditions specified (unit: meq O2/kg)
    - ISO 3960: The test sample is dissolved in isooctane and glacial acetic acid, and potassium iodide is added. The iodine liberated by the peroxides is determined iodometrically (visually) with a starch indicator and a sodium thiosulfate standard solution. The endpoint of the titration is determined iodometrically (visually).
    - Possible problems:
        - Standardisation of thiosulfate
        - Gross errors / calculation errors / unit problem

  Answer:
    - no problem
    - reagents to be checked

- ***Moisture and Volatiles***
    - ISO 662 Definition: loss in mass undergone by the product on heating at 103 °C ± 2 °C under the conditions specified in this International Standard
    - ISO 662 Method A
        - Heat a dish containing the test portion on the sand bath or electric hotplate, allowing the temperature to rise at a rate of about 10 °C/min up to 90 °C, and stirring constantly with the thermometer. Reduce the rate of heating, observing the rate at which bubbles rise from the bottom of the dish, and allow the temperature to rise to 103 °C ± 2 °C. Do not heat above 105 °C. Continue to stir, scraping the bottom of the dish until all evolution of bubbles has ceased. To ensure the removal of all moisture, repeat the heating to 103 °C ± 2 °C several times, cooling to 95 °C between the heating periods. Then allow the dish and thermometer to cool in the desiccator to room temperature and weigh to the nearest 0,001 g. Repeat this operation until the difference between the results of two successive weighings does not exceed 2 mg.
    - ISO 662 Method B
        - Keep a glass vessel containing the test portion for 1 h in the drying oven, set at 103 °C. Allow to cool to room temperature in the desiccator and then weigh to the nearest 0,001 g. Repeat the operations of heating, cooling and weighing, but use successive periods in the oven of 30 min each, until the loss in mass between two successive weighings does not exceed 2 mg or 4 mg, according to the mass of the test portion.
    - What was used by participants?
    - Possible problems:
        - Temperature
        - Not dried to constant mass

  Answer:
    - no problem with the method
    - temperature to be observed

- ***Iodine Value***
    - ISO 3961 definition: Mass of halogen, expressed as iodine, absorbed by the test portion following the specified procedure, divided by the mass of the test portion.
    - ISO 3961:
        - Dissolve in cyclohexane / glacial acetic acid;
        - add Wijs reagent (iodine monochloride);
        - leave in the dark for 1 h;
        - add KI and water;
        - titrate with sodium thiosulfate
    - Possible problems:
        - Quality of the reagents
        - Standardisation of thiosulfate
        - Starch indicator
        - Time not exactly kept

Answer:
- no problem

- ***Nickel and Copper***
  - ISO 8294
    - Graphite furnace atomic absorption using standards dissolved in oil
  - AOCS (American Oil Chemists‘ Society) 15-75 (03)
    - Extraction with MIBK (methyl isobutyl ketone), determination with AAS
  - ISO 5516
    - Ashing, dissolving in nitric acid, determination with AAS
  - Oxidative digestion (e.g. microwave) followed by determination using AAS, ICP-OES or ICP-MS

Answer:
- most of the labs not competent

17:15 h Wrap-up and end

Wednesday, 24 February 2010

Training on “Traceability – Reference Materials – Interlaboratory Tests” as well as on “Measurement Uncertainty Estimation”

M. Koch gave a full-day training on the mentioned topics including some exercises. The full presentations are included in annexes 9 and 10.

Evaluation questionnaire

M. Koch distributed an evaluation questionnaire (annex 11) for the workshop to be filled out by all participants.
The results of this questionnaire were as follows:

The venue of the workshop

Very good:	16
Good:	17
Fair:	0
Poor:	0
Very poor:	0

mean: 1.52 (1 for very good, 2 for good, 3 for fair, 4 for poor, 5 for very poor)

The content of the presentations

Very good:	27
Good:	6
Fair:	0
Poor:	0
Very poor:	0

mean: 1.18 (1 for very good, 2 for good, 3 for fair, 4 for poor, 5 for very poor)

The working group discussions:

Very good:	16
Good:	17
Fair:	0
Poor:	0
Very poor:	0

mean: 1.52 (1 for very good, 2 for good, 3 for fair, 4 for poor, 5 for very poor)

The evaluation of the PT

Very useful –	1	23
	2	8
	3	2
	4	0
Not useful –	5	0

mean: 1.36

Training:

Very useful –	1	26
	2	6
	3	0
	4	0
Not useful –	5	0

mean: 1.19

Expectations fulfilled:

Yes: 31
No: 2

Not fulfilled expectations:

- not 100%, because I would expect to have some more challenges on PT schemes
- Time was short to absorb all the presentations

The most important topics

(the number in brackets gives the number of participants that mentioned this topic):

- Uncertainty estimation (29)
- Traceability (25)
- CRM (15)
- Interlaboratory comparisons (14)
- Evaluation of PT (14)
- Method validation (8)
- Reference materials (7)
- Determination of the assigned value (6)
- Corrective actions (5)
- Interpretation of PT results (5)
- Quality of PT provider (4)
- PT sample preparation (3)
- Types of PT (2)
- PT provider requirements (2)
- Choice of analytical method (2)

- Methods to calculate consensus value (2)
- Laboratory bias (2)
- Importance of PT (2)
- Requirements needed to become a PT provider (2)
- Use of PT results for mu estimation (1)
- Use of CRM for mu estimation (1)
- EAC PT scheme background (1)
- The different analytical methods used in analysis (1)
- Importance of following test methods accurately (1)
- The introduction part by Mrs. Kezia (1)
- All presentations of Dr. Michael Koch (1)
- Identification of measurement problems (1)
- Standards and guidelines for PT (1)
- Bottlenecks in the exercise and the way forward (1)
- Homogeneity and stability of PT samples (1)
- Open discussions on how to improve the PT (1)
- Metrology (1)
- Statistics in general (1)
- Requirements and conditions for accreditation (1)
- Experience of the other bureau standards (1)
- To exchange experience (1)
- It is necessary to compare our results (1)
- Criteria upon which to base when choosing reference laboratories (1)
- Precision and trueness (1)

Benefits:

- Simplification of implementation of uncertainty and traceability
- Training is very useful and it adds value to the Quality Management skill
- Learned lot of new staff – networking – training on measurement uncertainty was very useful, but the time was very short. It should be repeated at another time, with more time devoted to it. The trainer did a wonderful job!
- I can easily validate my methods now. I need further explanation and training on method validation. Is it possible?
- Importance of participating in a PT
- How to calculate uncertainty of measurement and corrective action points to look for before validating method
- I appreciated the trouble and patience in making PT samples – Learned many factors that affects the accuracy of the results from the participants
- I learned a lot from the training part of the workshop which will be discussed and implemented in our laboratory. The group discussions were also an eye opener
- All the presentations of Dr. Michael Koch are very useful, only hunted by time – need more time for practical hands-on, more especially the uncertainty issue.
- To evaluate the capability of my laboratory, the staff and progress made since entering the 1st PT
- I will be in position to calculate uncertainty of measurements for the methods I participate in this PT – make use of range control charts
- The uses of CRMs – estimation of uncertainty

- I know about measurement uncertainty somehow – I gain the challenges when I will be in analysis of PT samples – I know the importance of participation in PT schemes
- Quite some important information on quality control, measurement and insight that I can carry back to my laboratory and make a difference as far as improving our services is concerned
- Importance of producing traceable measurements
- Feedback and technical advice from organizer – assistance in the identification of measurement problems
- Wide exposure to PT and its effectiveness – better understanding of uncertainty, limits and their implications
- How to estimate the uncertainty of measurement
- The most benefit is on the training on how to evaluate the PT and the estimation on uncertainty of measurement
- Made new contacts – got new ideas – new methods for insight into uncertainty of measurement
- Improves my understanding in PT and measurement uncertainty which I have never trained before
- more enlightened on calculation of uncertainty of measurement in different ways – I now understand the EAC PT better – Sharing of technical knowledge between participants
- Much help as far as accreditation is concerned (i.e. calculation of uncertainties)
- PT is a good check for validity of test – PT tests enable us to troubleshoot in case of derivation from the others – corrective action in case of outlier results
- Interpretation of PT results – the seriousness of a PT sample – statistical tool applied in PT – preparation of PT samples
- To improve the efficiency of the PT we have to work together
- We are intending to acquire accreditation. The workshop has enlightened us that to do before we send any request to the respective bodies
- More technical expertise which if implemented will improve on the operations of the ISO 17025:2005 in Chemiphar(U) Ltd
- More than one reference laboratory that are accredited for specific parameters to assign a true value.
- My laboratory is implementing the quality control system and later apply for accreditation. Therefore this were things that would help me be conversant with quality work

Comments:

- Uncertainty requires more time with examples at each step to simplify subject for participants
- Still needed more time to digest
- The workshop was good and meaningful though the time frame was too short to capture its full intended purpose
- Socially I have met new people from different countries and the list of my friends has increased, thanks to PTB
- The topics about measurement uncertainty and traceability need at least minimum two days. And more exercises were needed for better understanding. Thank you
- Calculation of bias, uncertainty etc. should have taken at least 2 days with more practical work
- The experience of other Bureaus of Standards
- All the topics covered apply to the laboratory – How to calculate uncertainty and its importance and the importance of CRMs and the use of validated methods

Report prepared by Dr.-Ing. Michael Koch
Stuttgart, 19.4.10