

# Report on the Workshop Proficiency Testing for Water Testing Laboratories

*Pretoria, South Africa, 1 – 2 November 2004*

Prepared by Dr.-Ing. Michael Koch

## **Summary**

Access to proper potable water is a human right. This is why the heads of governments agreed in 2002 in Johannesburg during the world summit for sustainable development on the goal to halve by 2015 the proportion of people without sustainable access to safe drinking water and basic sanitation. In the same direction targets the resolution of Evian where the 8 heads of states of the G8 countries adopted an action plan to improve proper water management in Africa. The improvement of water supply systems is crucial in the combat against worldwide poverty, to reduce the potential for conflicts and to strengthen the international security.

Concretely this means that sustainable concepts for the construction of satisfactory water supply systems for spread classes of society have to be developed in the concerned regions. In this process it is pivotal to investigate the pertinency of potential water resources in a very early stage of planning. For that purpose the execution of hydro geological investigations are of vital importance. Hydro geologists have to rely on water analysis, which are carried out in specialized water testing laboratories.

It is of advantage if these analysis can be carried out in local water testing laboratories. However, the experience gained during the implementation of projects in the water sector showed that the results of local water testing laboratories are sometimes unreliable with the consequence that in these cases unsuitable water resources are used within water supply systems. In these cases a negative impact on the health of the concerned population and high investments for a necessary after treatment of potable water can be the consequence.

Existing drinking water supply systems are also kept under surveillance by local laboratories. The special interest is here on the microbiological quality, where the water is analysed for pathogenic and potentially pathogenic germs. It is in the nature of these analyses, that they have to be especially reliable because peoples health depends on them.

But water analysis is a testing field, which has not only high influence on peoples health but on the total welfare of all people, because it also concerns the international trade, which suffers from incorrect analyses and the non-acceptance of results due to the absence of an accreditation of the laboratories.

The SADC MET pilot proficiency test has been carried out within the project "Support to SADC in implementing the SQAM-program", (**S**tandardisation, **Q**uality, **A**ccreditation, **M**etrology), which is implemented by the German Metrology Institute PTB on behalf the German Federal Ministry for Economic Cooperation and Development in cooperation with the SADC-secretariat and the SADC SQAM organisations SADC MET, SADC MEL, SADCA and SADC STAN. It was an important component for the improvement of these analyses and a help for the laboratories on their way to accreditation. The PT showed weaknesses at the laboratories with regard to precision (too high standard deviations between laboratories) and trueness (bias of the

mean for some parameters). A big part of the participants was not able to reach the necessary limit of determination for the analysis of iron at the lowest level. This shows that there is a necessity to further support the laboratories with ongoing proficiency testing but also with training. As can be seen from the evaluation questionnaire for this workshop, this was also recognised by the participants themselves.

The PT activity therefore should be flanked by supportive activities for water testing laboratories to implement quality management systems, to increase their technical competence and to integrate them in a accreditation system. It would be of advantage if for these supportive activities the knowledge of analytical chemists, familiar with quality management systems, and hydro geologists could be made available.

The workshop in Pretoria reported here was an important component on the way to improve the analytical quality in the water testing laboratories.

It was possible to show the participants where the weaknesses of the analyses are and what could be possible causes. The participants showed to be highly motivated to tackle these problems. The workshop not only allowed the advice and training of the participants, but formed also the basis for a network between the laboratories in the different countries. This network will enable a mutual support between the labs.

The participants are also highly motivated to go further on this way. They are willing, as far as possible, to bear the costs for these proficiency tests. The next PT is planned to be organised in march 2005. Financial support is necessary only to pay for the transportation costs to the national coordinator, which are very high because of the unfavourable geographical conditions.

The general conditions for this PT, which is extended compared with the pilot PT, were arranged during this workshop.

To optimize the mutual support it was decided to establish an "Association of Water Testing Labs in the SADC Countries". The participants of the pilot PT are supposed to be the preliminary steering committee and the SADCMET secretary is willing to hold also the secretariat of this new association.

The assurance of the quality of microbiological analyses is also very important for the laboratories. The results of these analyses have a direct influence on peoples health (drinking water is an important infection path for diseases). It is therefore considered to be very urgent to assure this analyses via proficiency testing, to uncover weaknesses und to offer assistance to the laboratories. For practical implementation it is recommended to train a potential PT provider in southern Africa in Germany first. After a preparation phase for the PT in Africa it would be helpful during the organisation and preparation of the samples to have support from an experienced German expert on site.

In summary it can be said that the implementation of a PT system for water testing laboratories in the SADC countries up to now was a big success. The laboratories are highly motivated, to do their best to push the process of quality enhancement.

The opportunity should be taken to support the laboratories on this way.

## **Zusammenfassung**

Der Zugang zu geeignetem Trinkwasser ist ein Menschenrecht. Deshalb haben sich die Regierungschef auf dem Weltgipfel für nachhaltige Entwicklung 2002 in Johannesburg auf das Ziel geeinigt, den Anteil der Bevölkerung ohne nachhaltigen Zugang zu sicherem Grundwasser und grundlegenden sanitären Einrichtungen bis zum Jahre 2015 zu halbieren. In dieselbe Richtung zielt die Resolution von Evian, in der die 8 Staatsoberhäupter der G8 Staaten einen Aktionsplan zur Verbesserung des Wassermanagements in Afrika verabschiedeten. Die Verbesserung der Wasserversorgungssysteme ist entscheidend im Kampf gegen die weltweite Armut. Sie reduziert das Konfliktpotential und stärkt damit die internationale Sicherheit.

Konkret bedeutet das, dass nachhaltige Konzepte für den Aufbau geeigneter Wasserversorgungssysteme für alle Gesellschaftsschichten in den betroffenen Regionen aufgebaut werden müssen. In diesem Prozess ist es unverzichtbar, die Eignung der Wasservorkommen in einem sehr frühen Stadium der Planung zu untersuchen. Dafür ist die Durchführung hydrogeologischer Untersuchungen von vitalem Interesse. Die Hydrogeologen müssen sich jedoch auf die Wasseranalysen verlassen können, die von den darauf spezialisierten Laboratorien durchgeführt werden.

Es ist von Vorteil, wenn diese Analysen in einem lokalen Wasserlabor durchgeführt werden können. Die Erfahrungen, die während der Durchführung dieser Projekte im Wassersektor gesammelt wurden, zeigen jedoch, dass die Ergebnisse der lokalen Wasserlaboratorien manchmal unzuverlässig sind. In solchen Fällen kann eine negative Auswirkung auf die Gesundheit der betroffenen Bevölkerung und hohe Investitionen für eine notwendige Nachbehandlung des Trinkwassers die Folge sein.

Auch bestehende Trinkwasserversorgungssysteme werden von den lokalen Laboratorien untersucht. Von besonderem Interesse ist dabei auch die mikrobiologische Qualität des Wassers, bei der das Wasser auf das Vorhandensein potentieller oder tatsächlicher Krankheitserreger geprüft wird. Es liegt in der Natur der Sache, dass auf die Ergebnisse dieser Untersuchungen aus Gründen des Gesundheitsschutzes für die Bevölkerung Verlass sein muss.

Die Wasseranalytik ist ein Prüfgebiet, dessen Ergebnisse großen Einfluss auf das Wohl der Bevölkerung haben. Dies beginnt bei den direkten Einwirkungen auf die Gesundheit (Trinkwasseruntersuchungen), erstreckt sich aber auch auf den Handel, der unter fehlerhaften Analysen und der Nichtakzeptanz von Analyseergebnissen aufgrund fehlender Akkreditierung der Laboratorien leidet.

Der SADC MET Pilotringversuch wurde durchgeführt im Rahmen des Projekts „Unterstützung der SADC bei der Einführung eines SQAM-Programms“ (**S**tandardisation, **Q**uality, **A**ccreditation, **M**etrology), das von der Physikalisch-technischen Bundesanstalt im Auftrag des Bundesministerium für wirtschaftliche Zusammenarbeit und Entwicklung in Zusammenarbeit mit dem SADC-Sekretariat und den SADC SQAM-Organisationen SADC MET, SADC MEL, SADCA und SADC STAN ausgeführt wird. Er war ein wichtiger Baustein zur Verbesserung dieser Analytik und eine Hilfe für die Laboratorien auf ihrem Weg zu einer Akkreditierung. Der Ringversuch zeigte Schwächen bei den Laboratorien sowohl hinsichtlich der Präzision (zu große Vergleichsstandardabweichungen) als auch hinsichtlich der Richtigkeit (systematische Abweichungen des Mittelwerts für einige Parameter). Im Falle der Eisenbestimmung konnte eine große Anzahl der Teilnehmer auch die erwartete Bestimmungsgrenze nicht erreichen. Dies zeigt, dass ein Bedarf besteht für eine weitere Unterstützung dieser

Laboratorien, durch die Fortsetzung des Ringversuchsprogramms, aber auch durch Fortbildung des Personals. Wie man aus den Ergebnissen des Fragebogens zu diesem Workshop ablesen kann, haben die Laboratorien dies auch selbst erkannt.

Die Ringversuchsaktivitäten sollten daher durch flankierende Maßnahmen unterstützt werden, die den Laboratorien helfen Qualitätsmanagementsysteme aufzubauen, ihre technische Kompetenz zu verbessern und sie in ein Akkreditierungssystem zu integrieren. Es wäre vorteilhaft, wenn für diese unterstützenden Maßnahmen die Fachkenntnisse von analytischen Chemikern, die mit Qualitätsmanagementsystemen vertraut sind, und von Hydrogeologen verfügbar gemacht werden könnten.

Der Workshop in Pretoria, über den hier berichtet wird, war ein wichtiger Baustein zur Verbesserung der Qualität der Wasserlaboratorien. Den Teilnehmern des Workshops konnte gezeigt werden, wo die Schwachstellen der Analytik liegen und welches die möglichen Ursachen sind. Die Teilnehmer zeigten sich hoch motiviert, diese Probleme anzugehen. Der Workshop ermöglichte nicht nur die Beratung und Schulung der Teilnehmer, sondern bildete vor allem die Basis für die Bildung eines Netzwerks zwischen den Laboratorien der unterschiedlichen Ländern, das es ihnen ermöglichen kann, sich gegenseitig zu unterstützen.

Die Teilnehmer sind hoch motiviert, auf dem eingeschlagenen Weg weiter zu gehen. Sie sind auch bereit, im Rahmen ihrer Möglichkeiten, die Kosten für diese Ringversuche selbst zu tragen. Ein nächster Ringversuch zur chemischen Analytik ist für März 2005 geplant. Eine finanzielle Unterstützung ist lediglich für die Begleichung der aus geographischen Gründen sehr hohen Transportkosten vom Ringversuchsveranstalter zum jeweiligen nationalen Koordinator notwendig. Die Rahmenbedingungen für diesen gegenüber dem Pilot-Ringversuch erweiterten Ringversuch wurden während des Workshops abgesprochen.

Um die gegenseitige Unterstützung zu optimieren, wurde beschlossen eine „Vereinigung der Wasserprüflaboratorien in den SADC-Ländern“ zu gründen. Die Teilnehmer des Pilot-Ringversuchs sollen dabei die vorläufige Lenkungsgruppe bilden und das SADC MET-Sekretariat ist bereit, auch für diese Vereinigung das Sekretariat zu übernehmen.

Ganz besonders wichtig für die Laboratorien ist die Sicherung der Qualität der mikrobiologischen Analysen. Die Ergebnisse dieser Untersuchungen haben einen noch direkteren Effekt auf die Gesundheit der Bevölkerung (Trinkwasser ist ein Übertragungsweg für Krankheiten). Es wird daher als sehr dringend angesehen, auch diese Analytik über Ringversuche abzusichern, Schwachstellen aufzuzeigen und Hilfen bei der Durchführung der Analysen anzubieten. Für die praktische Umsetzung wird empfohlen, den potentiellen Ringversuchsveranstalter im südlichen Afrika zunächst in Deutschland diesbezüglich zu schulen. Nach einer Vorbereitungsphase für den Ringversuch in Afrika wäre es hilfreich, bei der eigentlichen Durchführung des Ringversuchs Unterstützung durch eine deutsche Fachkraft vor Ort zu haben.

Zusammenfassend kann gesagt werden, dass die Implementierung eines Ringversuchssystems für Wasserlaboratorien in den SADC-Ländern bislang ein großer Erfolg war. Die Laboratorien sind hoch motiviert, alles Ihnen Mögliche dazu beizutragen, den Prozess der Qualitätsverbesserung voranzutreiben. Diese Chance sollte ergriffen werden, indem die Laboratorien hier unterstützt werden.

## **Introduction**

The workshop reported here was a follow-up of a previous workshop held in Windhuk, Namibia in February 2004 (see annex 1 and the report on the windhuk workshop, available from <http://www.sadcmnet.org>). As a result of this first workshop a pilot proficiency test for water testing laboratories was organised. The workshop in Pretoria was to evaluate and assess this first PT and to find ways forward to a regular PT system and other supportive measures.

## **Participants and Organisation**

The workshop was attended by 23 participants from the following countries:

- Angola 1
- Botswana 2
- Ethiopia 1
- Kenya 2
- Lesotho 1
- Malawi 2
- Mauritius 1
- Mozambique 2
- Namibia 2
- Seychelles 1
- South Africa 1
- Swaziland 1
- Tanzania 2
- Uganda 1
- Zambia 1
- Zimbabwe 2

The Workshop was organised by

Dr. Mukayi Musarurwa, CSIR, South Africa

Dr. Michael Koch, Universität Stuttgart, Germany

and led by

Dr. Michael Koch, Universität Stuttgart, Germany

Additional presentations were given by

Merle Smuts, Umgeni Waters, Pietermaritzburg, South Africa

A complete list of participants is given in Annex 2.

## **Workshop Programme**

### **Day 1 – The Pilot-PT**

#### **Morning-Session – 08:30 to 13:00 (with break from 10:00 to 10:30):**

- **M. Musarurwa:** Opening
- **M. Smuts:** Experiences of the PT provider – planning, sample preparation, sample distribution, problems
- **All Participants:** Experiences of participants – logistic problems, analytical problems
- **M. Smuts:** Preliminary evaluation and assessment

#### **Afternoon-Session – 14:00 to 17:30 (with break from 15:00 to 15:30):**

- **M. Koch:** Comparison of different evaluation and assessment methods
- **M. Koch:** Fitness for purpose – discussion about quality goals and consequences of bad results in routine analysis
- **M. Smuts and M. Koch:** Method comparison, possible error sources

**All: Decision about the most appropriate evaluation and assessment method**

## ***Day 2 – The way forward***

### **Morning-Session – 08:30 to 13:00 (with break from 10:00 to 10:30):**

- Discussion in working groups:  
Evaluation of the Pilot PT: benefits - weak points, what should be kept for future PTs? What should be changed? Is the PT a help on the way to accreditation? Are the costs appropriate?
- Summary for the Pilot PT
- Are there laboratories that didn't participate? Why not?
- Discussion in working groups:  
How can the participants help each other? Is a SADC Laboratory Association possible? First steps? What other measures can be taken to improve quality of measurements? Parameters for the next chemistry PT?
- Microbiological PT – possibilities and challenges? Which parameters are desirable – which are possible? Possibilities of know-how transfer from Germany to the SADC region.

### **Lab tours to NML and SABS – 14:30 to 16:30**

### **Evening braai (sponsored by NML) – 18:00 – 21:00**

## ***Monday, 01 November 2004***

### **Opening**

The Workshop was opened at 8:30 by Dr. Michael Koch.

### **M. Smuts: Experiences of the PT provider – planning, sample preparation, sample distribution, problems**

Merle Smuts reported about her experiences in the Pilot PT (Annex 3). The planning for the PT mainly was made during the workshop in Namibia. The realization was financially made possible with support from PTB, Germany. The selection of bottles was controlled by the availability in South Africa. After consultation with experts in Germany it was decided to distribute the original samples and not concentrates, although this raised the transportation costs.

Mrs. Smuts calculated the amounts for the spiking of the samples and the total volume required to supply all participants with samples. She prepared a result template to distribute together with the samples. DHL was chosen as courier to ensure the fastest possible delivery of the samples although this carrier was very expensive. For the preparation of samples laboratory grade water was spiked with chemicals as shown in the following table:

		<b>Cation samples (constituted to 25L)</b>		
<b>Determinand</b>	<b>Chemical</b>	<b>2004/06/1</b>	<b>2004/06/2</b>	<b>2004/06/3</b>
Calcium	CaCl <sub>2</sub> ·2H <sub>2</sub> O	2.3489 g	4.4224 g	7.0465 g
Magnesium	MgCl <sub>2</sub> ·6H <sub>2</sub> O	2.7041 g	4.3243 g	9.8145 g
Sodium	NaCl	0.6726 g	1.6555 g	3.2398 g
Potassium	KCl	0.1638 g	0.3658 g	0.4620 g
Iron	Fe Spectroscopic Grade Stock Solution (1000 mg/L)	2.50 mL	30.0 mL	100 mL
Manganese	Mn Spectroscopic Grade Stock Solution (1000 mg/L)	2.50 mL	10.0 mL	25.0 mL
Aluminium	Al Spectroscopic Grade Stock Solution (1000 mg/L)	2.50 mL	15.0 mL	25.0 mL
Preservative	HNO <sub>3</sub> (conc)	37.5 mL	37.5 mL	37.5 mL

		<b>Anion samples (constituted to 25L)</b>		
<b>Determinand</b>	<b>Chemical</b>	<b>2004/06/4</b>	<b>2004/06/5</b>	<b>2004/06/6</b>
Sulphate	K <sub>2</sub> SO <sub>4</sub>	0.7521 g	1.2808 g	2.2274 g
Chloride	KCl	1.5316 g	2.2499 g	3.4558 g
Fluoride	NaF	0.6517g in 500mL water (Stock) 5.00mL Stock used	2.0127g in 500mL water (Stock) 5.00mL Stock used	2.0127g in 500mL water (Stock) 20.0mL Stock used
Nitrate	KNO <sub>3</sub>	0.3831 g	0.6401 g	1.265 g

With this procedure a good estimate for the “true” value can be obtained from the weighing.

25 litre for each sample were prepared, thoroughly mixed, dispensed in bottles and labelled. Cations samples were stabilized using nitric acid, no preservation was made for anions.

For homogeneity check the first and the last dispensed sample was analysed at least 6 times each. For stability check these samples were analysed after 5 weeks again. No significant difference could be found using the F-Test.

Prior to shipping the customs documentation has to be completed.

Unexpectedly customs were no problem for this PT. All samples arrived at the laboratories within five days.

24 out of 27 participating laboratories reported results. One lab didn't report results because these chemical analyses were not routinely carried out, one lab had an instrumental breakdown and one lab didn't answer at all.

The results were sent back mainly by e-mail, some by fax.

A preliminary evaluation was done using simple robust methods. The median was used as assigned value and the normalized interquartile range (difference between 1st and 3rd quartile, normalised using a factor 0.7413) was used as standard deviation to calculate Z-scores.

The PT provider encountered no problems that hindered the progress, no problems occurred with the courier and fortunately no problems with customs. In some cases technical communication problems between PT provider and participants had to be overcome.

### **All Participants: Experiences of participants – logistic problems, analytical problems**

All participants in general were very happy with the PT. The samples arrived at the labs in almost all cases in good condition. Only one bottle was leaking and one package was opened.

The participants expressed their gratitude to have the possibility to participate in such a PT. Participation was seen as a good opportunity and motivation for the improvement of the analytical quality.

### **M. Smuts: Preliminary evaluation and assessment**

Merle Smuts explained (annex 4), how she made the preliminary evaluation using the median as assigned value and the normalized interquartile range to calculate Z-scores. She presented lists of all Z-scores for each parameter and each laboratory and the parameter assessment for each laboratory. For an assessment as "successful" two of the three Z-scores had to be in the range between -2 and 2.

She showed a graphical display of the percentage of successfully analysed parameters per laboratory. 58% of the laboratories (14 out of 24) analysed 80% or more of the parameters, in which they took part, successfully.

Mrs. Smuts distributed a preliminary evaluation report to each participant. An example can be found in annex 5

### **M. Koch: Comparison of different evaluation and assessment procedures**

Dr. Koch used 5 different methods for evaluation and assessment to prepare a comparison between these procedures (see annex 6):

- Method 1: Hampel-estimator/q-method for calculation of the statistical parameters mean and standard deviation and use of  $Z_U$ -scores, i.e. modified Z-scores, for the assessment. This method is described in DIN 38402-A45 and used for water PTs in Germany.
- Method 2: Median / normalized interquartile range and Z-scores. These robust methods were used by the provider of the pilot PT for preliminary assessment.
- Method 3: Algorithm A. This method, described and recommended in ISO/FDIS 13528, is also recommended in the draft for the new "International harmonized protocol for the proficiency testing of (chemical) analytical laboratories". It uses the Huber estimator for the calculation of the mean and a robust method derived from that for the estimation of standard deviation.



- Method 4: Conventional statistics (arithmetic mean and standard deviation) after outlier elimination via Grubbs test. Assessment with Z-score.
- Method 5: identical with method 1, but with limitation of the standard deviation based on experience from previous PTs in Germany and fitness for purpose criteria. The standard deviation first was calculated as in method 1, but if this value exceeds the limit, this limit is chosen for calculation of Z-scores instead of the standard deviation. The following limits were used
  - Sulphate: 8%
  - Chloride: 9%
  - Ca, Mg, Na, nitrate: 10%
  - K, Fe, fluoride: 12%
  - Mn: 15%
  - Al: 30%

In some cases it can be seen that the distribution of data is not normal but skewed. The 4 different statistical procedures showed that in most cases the **mean values lay close together**, but sometimes there were **big differences in the estimated standard deviation**, although all methods are widely accepted by the scientific community.

The standard deviations in many cases are too high, not fit for the purpose. So, if the calculated standard deviations are used for the assessment, this gives a **falsely good impression of the quality of the analyses**. In addition the comparison between spiked amounts and the mean of the participants results **for some parameters** showed a **strong bias of the analytical results**. In this case a reference value should be preferred as assigned value.

It could be seen from the calculated standard deviations that for the parameters iron the lowest level was below the limit of determination for most of the laboratories.

### **M. Koch: Fitness for purpose – discussion about quality goals and consequences of bad results in routine analysis**

Quality of analytical measurements is sufficient, if the accuracy of the results is fit for the purpose. In a strong sense these fit-for-purpose-criteria have to be set by the customer. For water analyses this is often very difficult, because either the customer is not able to define such criteria or there is no concrete customer, that could do this job. Dr. Koch gave hints from previous interlaboratory tests for proficiency testing as well as for method validation and from other sources like the European drinking water regulations (see annex 7). For each parameter of the pilot PT it was discussed with the participants, what the appropriate quality goal for the standard deviation could be, in order to define limits for the value which is used for the calculation of z-scores. In future proficiency testing rounds these limit will be applied. The participants agreed on the following limits:

- |                              |                             |
|------------------------------|-----------------------------|
| • Calcium: 10%               | • Aluminium: 30%            |
| • Magnesium: 10%             | • Sulphate: 10%             |
| • Sodium: 10%                | • Chloride: 10%             |
| • Potassium: 10%             | • Fluoride: > 0.5 mg/l: 12% |
| • Iron: > 1 mg/l: 12%        | • Fluoride: < 0.5 mg/l: 20% |
| < 1 mg/l: 20%                | • Nitrate: 15%              |
| • Manganese: > 0.5 mg/l: 12% |                             |
| < 0.5 mg/l: 20%              |                             |

## **M. Koch: Method comparison, possible error sources**

Dr. Koch presented a comparison between the different methods applied by the participants (annex 8). Sometimes it was difficult to identify from the specifications of the participants which method really was applied. In future PTs it is recommended to include a list of the mainly used methods. The participants can then mark the applied method with a cross.

### **Calcium:**

The data measured with AAS included a remarkable amount of values with values which are too low. The data measured by titration had a very broad statistical distribution.

### **Magnesium:**

The titrimetric data also showed a very large variability for this parameter, which is comprehensible, because the Mg concentration is calculated from the difference of the measured sum of Ca/Mg and the concentration of Ca.

### **Sodium/Potassium:**

For both parameters the values measured with ICP-OES showed a better interlaboratory precision.

### **Iron/Manganese:**

The spectrophotometric measurement gave a higher interlaboratory standard deviation for both elements.

### **Aluminium:**

The data set measured with AAS included a noticeable larger number of outliers. The mean of the values measured with spectrophotometric methods is biased to lower values.

### **Sulphate:**

The gravimetric data set showed more outliers than the other methods. The concentrations of sulphate might be too low for this method. The means for the turbidimetric and for the spectrophotometric methods are biased to higher values. This caused also the bias of the overall mean which was used as assigned value.

### **Chloride:**

Most of the data were measured with the argentometric method (Mohr). The mean of these data is biased to higher values which is also the cause for the bias of the overall mean. As a consequence some of the values measured with the ion chromatographic method are lower than the (biased) assigned value.

### **Fluoride:**

It is remarkable that the data set measured with the spectrophotometric method had more outliers with too high values.

### **Nitrate:**

The information about the spectrophotometric methods used by the participants were not very clear. So it is difficult to recognize trend for the different methods. It is highly recommended to limit the number of methods used in the future. The best way to do this is to develop a list of recommended methods in a working group of water testing laboratories in the SADC countries.

## **All: Decision about the most appropriate evaluation and assessment method**

The information presented were discussed in detail among all participants. It was then decided to have an assessment for this pilot PT in the way Umgeni Water made the preliminary evaluation, i.e. using the median as assigned value and calculating the standard deviation from the normalised interquartile range. Z-scores are calculated with these parameters, and  $|Z\text{-score}|=2$  is used as tolerance limit. In addition

Umgeni Water is asked to prepare an additional assessment just for information using the limits for the standard deviation decided earlier this day.

For future PTs the latter method should be applied for the official assessment. Dr. Koch recommended to keep the decision open to use other statistical methods, especially the so-called algorithm A, which is recommended in the ISO draft 13528 as well as in the new draft for the "International harmonized protocol for the proficiency testing of (chemical) analytical laboratories" published by ISO, IUPAC and AOAC. There was also an extensive discussion on the need to have further PTs as help to ensure good quality of analyses. The following consequences resulting from possibly bad results were discussed:

- Health hazards (drinking water analyses)
- Unnecessary treatment costs
- Pollution charges
- Environmental pollution penalties
- Legal requirements that might be failed
- Problems with accreditation, which could cause barriers to trade
- Export as well as import problems
- Loss of customers confidence
- Costs for repeated analyses
- Delay because of unnecessary repetition of analyses
- Wrong decision by the customer (e.g. during exploration)

## Summary of the decisions concerning the pilot PT

- The preliminary evaluation of the pilot PT is accepted to be the final evaluation and assessment
- Umgeni Water is asked to prepare an additional evaluation and assessment for information purposes only using the following limits of the standard deviation decided by the participants:
  - Ca: 10%
  - Mg: 10%
  - Na: 10%
  - K: 10%
  - Fe: > 1 mg/l: 12%  
< 1 mg/l: 20%
  - Mn: > 0.5 mg/l: 12%  
< 0.5 mg/l: 20%
  - Al: 30%
  - SO<sub>4</sub><sup>2-</sup>: 10%
  - Cl<sup>-</sup>: 10%
  - F<sup>-</sup>: > 0.5 mg/l: 12%  
< 0.5 mg/l: 20%
  - NO<sub>3</sub><sup>-</sup>: 15%
- All participants expressed their sincere gratitude to Umgeni Water for providing the pilot PT and to PTB and SADC MET for enabling this highly valuable PT

## **Tuesday, 02 November 2004**

The main subject of the second was the discussion on the way forward with proficiency tests for water analyses in the SADC countries.

### **Working group discussion: Evaluation of the pilot PT**

Three working groups were formed to discuss the following questions on the evaluation of the pilot PT:

- Benefits - weak points ?
- What should be kept for future PTs - what should be changed ?
- Is the PT a help on the way to accreditation?
- Which costs are affordable and appropriate?

The working groups came to the following conclusion:

#### **Benefits - weak points ?**

##### Group I

- Benefits:
  - helped in identification of weak and strong points in our laboratories
  - opportunity for comparison with other laboratories
  - opportunity of networking with other labs/countries
- Weaknesses:
  - some labs were not specific on methods (e.g. spectrophotometric)
  - the costs and if we will be able to pay them

##### Group II

- Benefits:
  - analyst/customer confidence
  - accreditation possibilities
  - learning experience from labs (e.g. methodology)
  - weak points in the lab highlighted
  - self assessment tool
  - QC tool
- Weaknesses:
  - Differing capacity of labs
  - Type of sample: should be health significant, concentration levels of PT should match reality of potable water

##### Group III

- Benefits:
  - positive improvement towards accreditation; PT participation is a major requirement for accreditation to ISO/IEC 17025
  - increases staff confidence and morale
  - QA tool for credible and reliable results
  - Pilot PT was free and easy for the labs to participate
  - Helped to evaluate different test methods and to evaluate reliability of different instrumental techniques
  - Better than other PTS which do not give participants information on methods/techniques used
  - Fully participatory PTS where all participants were involved in the planning from the onset. Hence ownership of scheme by participants. We are SADC MET PTS!
  - Managed to identify weak areas in the labs and also got hints on troubleshooting

- Weaknesses:
  - Communication problems with e-mail. Some participants did not receive detailed results prior to the workshop.
  - PTS provider not accredited as such to ISO Guide 43
  - Too much time allowed for tests. 1 month would be ok. Hence less rounds per annum (4 rounds would be ideal)

### **What should be kept for future PTs - what should be changed ?**

Group I:

- In terms of parameters: all parameters to be included and concentration of  $\text{SO}_4^{2-}$  and Fe to be increased. Add COD, phosphate, pH/alkalinity
- Courier: alternative skynet (point-to-point delivery), TNT, Fedex
- The costs are not affordable. Suggestion: PTB continues sponsoring until we stabilize
- The statistical assessment method 2 should be maintained
- PT rounds twice a year

Group II:

- Retain current parameters
- Make sure that Nitrate is reported and not N

Group III:

- parameters should be the same and PT provider should remain the same
- more information on support rates should be provided to participants when making travel arrangements
- microbiology should be included
- increase number of participants per country

### **Is the PT a help on the way to accreditation?**

All groups: definitely yes

### **Which costs are affordable and appropriate?**

Group II: if you pay for something, you appreciate it more

Group III:

- uniform costs for all countries
- request PTB to support 2<sup>nd</sup> round of PTS for sustainability
- US-\$ 50 per annum for all participants should be levied. Shortfalls could be subsidised by PTB for the subsequent rounds

A summary was made on the statements by Dr. Koch (annex 9) and agreed by all participants.

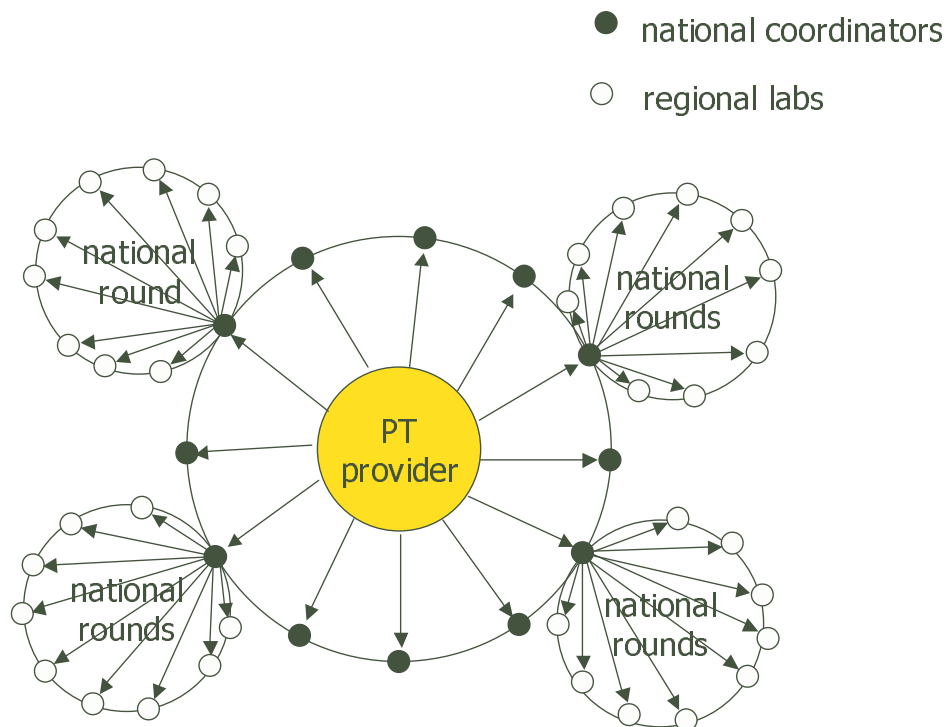
### **Discussion about future structure of PTs**

After an intense discussion the group agreed on the following statements regarding the next PT rounds:

- It would be beneficial, if more labs would participate
- It is reasonable that the participants pay for the PT samples itself, i.e. the costs for preparation etc., as well as the evaluation costs
- The biggest part of the costs were transportation costs, due to the difficult situations in southern Africa.
- To keep the transportation costs as low as possible the following structure is proposed:

- A national coordinator for each country will be nominated; it's obvious to ask one of the participants in the first round to do this job
- The national coordinator looks for as many potential participants as possible in his country
- Samples are prepared for each participants, but are sent to the national coordinator only. He is responsible for the transport to the participants.
- PTB is asked to sponsor the transportation from PT provider to the national coordinator. All other costs are on the participants.
- Results and the assessment will be communicated between all participants and the PT provider directly.

The following diagram shows this structure:



### Working group discussions: The way forward

The three working groups discussed the following questions:

- How can the participants help each other?
- Is a SADC Laboratory Association possible? - First steps?
- What other measures can be taken to improve quality of measurements?
- Parameters for the next chemistry PT?

The working groups came to the following conclusion:

### How can the participants help each other?

Group I:

- Information exchange on test methods and sharing experiences in operational issues
- Participants can act as hubs in regional networking to facilitate contact with suppliers in their respective countries on behalf of other labs.
- SADC MET PTS could be included on SADC MET webpage

- Participants could form clusters / small groups to check on communication and ensure cluster group members are up to date in respect of communication with the PTS provider

Group II:

- PT provider to have a website / database for informations
- Each lab to point out their strength through the capability of SADC MET
- Information sharing
- Capacity building and cost sharing

Group III:

- Laboratory networking through exchange of information e.g. methods of analysis, laboratory consumables and equipment
- Training – capacity building, attachment to laboratories with existing equipment

### **Is a SADC Laboratory Association possible? - First steps?**

Group I:

- It is possible
- SADC MET could spearhead the formation of the association
  - Initial meeting with country representatives
  - This (SADC MET PTS) group could be the steering committee as it is highly motivated and enthusiastic
  - Drafting constitution
  - Inaugural meeting

Group II:

- Yes – to address the above – but not now
- First steps:
  - To draw up a constitution
  - Write a proposal for funding
  - PT group should the members

Group III:

- Yes, it is possible
- This (PT group) to be an interim group for the association
- SADC MET to be the interim chairman and secretariat

### **What other measures can be taken to improve quality of measurements?**

Group I:

- PTB could provide CRMs to PTS members
- Training on
  - Implementation of ISO/IEC 17025
  - Validation of test methods
  - Uncertainty of measurement
  - Specific analytical areas such as toxicology
- Centre of excellence for calibration of laboratory glassware and other chemistry laboratory specific traceability requirements

Group II:

- Training of laboratory personnel
  - Quality management system
  - Route to accreditation
  - QC tools
  - Method validation

- Uncertainty of measurement
- Practical attachments of participants to other labs – like it is done in metrology labs

#### Group III:

- More training by SADCMET
  - Calibration of equipment
  - Quality control in analysis
  - Statistics
  - Uncertainty of measurement
- Procurement – supplier evaluation, where members help each other with information about suppliers
- Small cluster groups for exchange of information

### Parameters for the next chemistry PT?

#### Group I:

- Same as per pilot scheme until results are satisfactory for all participants in all parameters

#### Group II:

- Include the previous and add the following: Cu, Zn, Pb, Cr, Conductivity, pH, TOC, Ni, As
- All the elements to be together in one sample

#### Group III:

- All parameter from this PT including COD, Alkalinity, pH, phosphate. Add some more cations (Pb, As, Zn) in another PT

### All: Discussion on the way forward

#### Laboratory Association

All participants are very interested to have a laboratory association for mutual help between the laboratories in the different countries. The SADCMET secretary was asked to act as a secretary also for this association and he agreed. It was decided to start first only with water testing laboratories and to include other testing fields later. The SADC Water Testing Laboratory Association will have the possibility to use the SADCMET webpage as a platform for its work. The aim is to have in future national laboratory associations which are linked together in the SADC Lab Association. Each member of the new association is requested to check the possibility to install a national laboratory association in his/her country.

#### Chemistry PT

After some discussion there was a decision to propose to have the next PT in march 2005 in the structure shown above, provided that there is funding for the transportation, with the following parameters (new parameters in bold characters):

- |             |  |
|-------------|--|
| • Ca        | • <b>Cr</b>                            |
| • Mg        | • <b>Zn</b>                            |
| • Na        | • <b>Ni</b>                            |
| • K         | • <b>As (if possible)</b>              |
| • Fe        | • $\text{SO}_4^{2-}$                   |
| • Mn        | • $\text{Cl}^-$                        |
| • Al        | • $\text{F}^-$                         |
| • <b>Pb</b> | • $\text{NO}_3^-$                      |
| • <b>Cu</b> | • <b><math>\text{PO}_4^{3-}</math></b> |



Umgeni Water is requested to organise the future PTs. The statistical evaluation method used in the pilot PT will be applied also for the next PT, but with limitations for the standard deviation for calculation of Z-Scores, as shown above.

Dr. Koch pointed out that it could be wise to change the statistical evaluation method to the algorithm A, if in future this method is generally recommended by ISO.

### **M. Koch: Microbiological PT – possibilities and challenges? Which parameters are desirable – which are possible? Possibilities of know-how transfer from Germany to the SADC region**

Dr. Koch presented information about microbiological PTs for drinking water in Germany (annex 10).

The discussion after the presentation showed, that all laboratories are interested to have also a PT for microbiological parameters.

The following parameters were mentioned:

- coliformic bacteria
- E. coli
- salmonella
- total counts
- vibrio
- clostridium

The organization of a microbiological PT requires special skills for the provider. Umgeni Water is willing to act as a provider also for these PTs. In order to achieve this, it is proposed to accept the offer of the Public Health Authority of Lower Saxony (NLGA) to help to train the future PT provider in this sector. The best way would be to have a visit of the potential provider in Germany (if possible during a PT preparation). The second step could be to make all necessary preparation for a PT in the SADC countries (with advice from NLGA). In the third step an experienced person from NLGA could help during the preparation of the first microbiological PT.

For this first trial to install a PT system for microbiology funding is indispensable.

## Summary for the proposed way forward

### **Next chemistry PT**

- Parameters: Ca, Mg, Na, K, Fe, Mn, Al, Pb, Cu, Cr, Zn, Ni, As (if possible),  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$
- Same PT provider
- Same evaluation method but with the following limitations for the standard deviation for calculation of Z-scores:
  - Ca: 10%
  - Mg: 10%
  - Na: 10%
  - K: 10%
  - Fe: > 1 mg/l: 12%  
< 1 mg/l: 20%
  - Mn: > 0.5 mg/l: 12%  
< 0.5 mg/l: 20%
  - Al: 30%
  - $\text{SO}_4^{2-}$ : 10%
  - $\text{Cl}^-$ : 10%
  - $\text{F}^-$ : > 0.5 mg/l: 12%  
< 0.5 mg/l: 20%
  - $\text{NO}_3^-$ : 15%
  - Limits for the other parameters are still to be decided
- Distribution of samples in march 2005
- Distribution from PT provider only to national coordinators; PTB will be asked to cover the costs for this transport
- All other costs for the PT provider should be covered by participation fees
- National coordinators are asked to look for as other participants in their respective country
- Communication of results and evaluation should be directly between each participant and the PT provider

### **Microbiological PT**

All laboratories are highly interested to have also a microbiological PT.

PTB is asked for funding for:

- Training of the potential PT provider in Germany
- Preparation of a microbiological PT in the SADC countries
- Assistance during the first PT round by an experienced person from Germany
- Costs for the transport and evaluation of the first round

### **SADC Laboratory Association for Water Testing Labs**

It was decided to establish this association. The group of PT participants in the pilot PT will act as a preliminary steering committee for this association. The SADC MET secretariat agreed to preliminary hold also the secretariat of this association. All members try to install also national associations or act a contact point for their national colleagues.

## Evaluation questionnaire

All participants were requested to fill out an evaluation questionnaire (annex 11).  
Evaluation see below.

## Closure of lecture part

Dr. Musarurwa and Dr. Koch closed the workshop and thanked Mrs Merle Smuts for her excellent job in the preparation of the pilot PT and all participants for their enthusiastic cooperation.

## Lab visit and evening braai

The participants had the opportunity to visit three different laboratories in the CSIR in the afternoon.

In the evening all participants were invited by the national metrology lab of South Africa. At this opportunity certificates of attendance signed by Dr. Koch and Dr. Musarurwa were distributed to all participants by the head of the national metrology laboratory.

## *Evaluation of the questionnaire*

The judgement of the participants regarding

- **The venue of the workshop:**
  - Very good 3
  - Good 13
  - Fair 6
  - No answer 1Mean: 2.14 (1 for very good, 2 for good and 3 for fair)
- **The content of the presentations:**
  - Very good 11
  - Good 12Mean: 1.52 (1 for very good, 2 for good and 3 for fair)
- **The handout and documents:**
  - Very good 5
  - Good 13
  - Fair 5Mean: 2.00 (1 for very good, 2 for good and 3 for fair)
- **The working group discussions:**
  - Very good 12
  - Good 11Mean: 1.48 (1 for very good, 2 for good and 3 for fair)

## Were all aspects of the pilot PT covered?

Yes: 22  
No: 0  
No answer: 1

## The most important topics (in brackets the number of participants mentioning this point):

Comparison of evaluation and assessment methods: (20)

Method comparison: (14)

Setting limits for the standard deviations for assessment / quality goals: (13)

Experiences of the PT provider: (9)

Working group discussions: (8)  
Microbiology PT: (8)  
Preliminary evaluation of the PT: (7)  
Error sources / troubleshooting: (6)  
Experiences of the participants: (5)  
Benefits of PT / what does PT mean: (5)  
SADC Lab Association: (5)  
Next chemistry PT: (5)  
Consequences of bad results: (5)  
Measures for improvement of quality: (1)  
Strength and weaknesses of statistical methods: (1)  
Recovery and bias information: (1)  
Summary for the Pilot PT: (1)  
Confidence in results after evaluation procedure: (1)  
PT costs: (1)  
Analytical problems: (1)  
Toxic analyses: (1)

### **Did the workshop fulfil your expectations?**

Yes: 22

No: 1

Why not: "It hasn't point out how an outlier lab can take some corrective action / it hasn't forward anything"

### **What benefits did you draw from the workshop?**

- Exchange of information and probable corrective action for next PT round
- Sharing of experiences with participants. Learned about the five different assessment methods.
- Greater appreciation of statistical techniques. Had insight into possible causes for deviations from expected results.
- Continued networking, future progress of PTS, commitment and motivation of all participants
- Problems faced by various laboratories and how similar they were. Networking and experience sharing among the participants
- As I was attending for the 1<sup>st</sup> time, I was able to meet all the other PTS members and share my experiences with them and learn more on the methods of evaluation and assessment of the results
- I have learned new methods of analysis and the ways of improving the previous ones.
- Sharing experiences with peer groups
- Information on different methods and outline of my weakness / lab weakness
- The interaction between peers which has set a base for future communication
- I can improve some methodology that I use, for example calculate the bias
- Quality control by the assessment methods
- I learned how to improve my laboratory organization in terms of procedure and analytical method choice, because this influences a lot my results.
- Opportunity for quality improvement in the laboratory and exchange of information and networking. Better enlightened on statistical evaluation of results.
- The experiencing mistakes while analysis

- Coordinated networking
- Learning from others experience, networking
- Sharing information and improve laboratory analyses
- Information ?? is always invaluable, PTS is a requirement for accreditation, peers from other countries for networking
- Evaluation of PT results
- I had the possibility to understand the various methods that may be used for PT assessment and understand the measures that need to be taken for improvement
- The importance of PT
- To take corrective actions on my lab's defects on water analyses

**Any other comments:**

- Keep it up. We hope our labs will greatly improve
- Would like training on setting up of quality management system to ensure output of results with min 99 % confidence limit
- This was an all embracing evaluation workshop, where current as well as future needs were identified and addressed. The initiative to start a regional laboratory association is most welcome. Well done to the organisers and facilitators!
- It is very important that this programme continues by continual improvement in operations of our laboratories and at the same time validation of methods and checking of efficiency of our equipment. Workshop and participation in the PT was an eye opener of the condition of our laboratory and the corrective measures to be taken
- Training of the laboratory personnel on improvement of quality measurements and assistance in getting accredited are crucial for the PTS members
- Water PTS is a true development for accreditation and lab quality improvement therefore should be encouraged
- The program should be a bit relaxed to allow time for site seeing
- Accommodation was very good; food and the conference room ok; but the service is not very good.  
Some of us are not statisticians, do not practise. The little we knew about statistics and this means that we are not implementing full data analysis and do not even have quality checks in place
- I have problems in my lab with SO<sub>4</sub> and Al. I can see that this not my problem only and I can learn some methods to improve my work
- A second PT round and review workshop is suggested
- Capacity building / strengthening in QMS, AQA/OC, traceability and method verification
- Interesting information
- I hope that we shall be able to participate in future PT schemes and that a training programme will be organized for uncertainty of measurements, method validation, repeatability, reproducibility etc.
- I think that the PT samples should reflect the real samples with regard to their physico-chemical properties (interferences) and concentrations
- I think there is a lot to be learned by most SADC labs. They are ignorant as far as QC, CRMs and method validation is concerned. That's why the PT results are so poor.

- Water shouldn't be the only agenda. Other areas of testing should be included.

### **Summary of the evaluation**

From the questionnaires the conclusion can be drawn, that almost all of the participants were very happy with the workshop. The expectations of the participants have been fulfilled and most of them were quite enthusiastic. Almost all topics were mentioned in the list of most important topics, showing that there was constant interest throughout the whole workshop.

Stuttgart, 25 November 2004

Dr.-Ing Michael Koch