### **13th Proficiency testing scheme for chemical analysis of** Water in Africa

Frieda Nambahu NamWater Applied Scientific Services Windhoek Namibia



**Namibia Water Corporation Ltd** 

## NAMWATER

- The bulk water supplier for Namibia
- ✓Established in 1997 from MAWF
- 100% GRN owned
- /+/- 80 million m3 potable water per annum
- 28 000 customers
- Asset base N\$4 billion
- 670 employees
- Supplies all towns except 5
- Operating on cost recovery basis since establishment





## OUTLINE

- Background of the SADCMET PT scheme
- Participation
- **Growth of the SADCMET PT Scheme**
- Overview of a PT round
- ✓ Details of the PT process
- ✓Evaluation & Assessment
- Performance scoring
- Changes and Progress of Parameters
- Summary of the Parameters
- **Overall Success**
- Challenges 2017
- Conclusion M Conradie





## **BACKGROUND OF THE SADMET PT SCHEME**

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	2004	The first workshop was held in February in Windhoek, Namibia, with participants from 16 countries where the need for a PT scheme was identified. Training on basic issues of quality in analytical laboratories was also addressed at this workshop.
C	2004	1 <sup>st</sup> PT round; Evaluation workshop in Pretoria, South Africa
	2005	2 <sup>nd</sup> PT round; Evaluation workshop in Dar es Salaam, Tanzania Training session on measurement uncertainty
	2006	3rd PT round; Evaluation workshop in Gaborone, Botswana Training session on method validation and control charts
	2007	4th PT round; Evaluation workshop in Dar es Salaam, Tanzania Training session on validation and measurement uncertainty
NAM Namibia Wate		October: Poster presentation at the Eurachem workshop in Proficiency testing in analytical chemistry, microbiology and medicine in Rome, Italy

### **BACKGROUND OF THE SADCMET PT SCHEME cont..**

5 <sup>th</sup> PT round; Evaluation workshop in Kampala, Uganda Training session on the Management requirements of the ISO17025			
6 <sup>th</sup> PT round; Evaluation workshop in Mahé, Seychelles			
Test & Measurement conference: Presentation of Chemical analyses of water in Africa, South Africa			
7 <sup>th</sup> PT round; Evaluation workshop in Windhoek, Namibia Training session on estimation of measurement uncertainty using validation and quality control			
October: Poster presentation at the Eurachem Workshop in Proficiency testing in analytical chemistry, microbiology and laboratory medicine in Istanbul, Turkey			





## **BACKGROUND OF THE SADCMET PT SCHEME cont..**

2011	8 <sup>th</sup> PT round; Evaluation workshop in Port Louise, Mauritius Training session on ensuring the quality of analytical results – Trueness and Precision
2013	10 <sup>th</sup> PT round; Evaluation workshop in Nairobi, Kenya Training session on control charts
2014	11 <sup>th</sup> PT round; Evaluation workshop in Lusaka, Zambia Training session on measurement uncertainty
	October: Poster presentation at the Eurachem workshop in Proficiency testing in analytical chemistry, microbiology and laboratory medicine in Berlin, Germany
2015	12 <sup>th</sup> PT round; Evaluation workshop in Gaborone, Botswana Training session on Inter-laboratory tests, basic statistics and control charts





## % PARTICIPATION PER COUNTRY



Let's go forward



### **# LABORATORIES PER COUNTRY**

	2006	2007	2008	2009	2010	2011	2013	2014	2015	2016
Angola	0	0	1	0	0	0	0	0	0	0
Botswana	2	4	2	3	3	3	3	3	3	3
Burundi					1	1	1	2	2	2
Congo					4	5	3	8	7	5
Eritrea	0	0	1	0	0	0	0	0	0	1
Ethiopia	1	0	0	0	0	1	1	2	1	2
Ghana						1	0	0	0	0
Kenya	5	3	3	7	9	7	12	13	8	10
Lesotho	1	1	1	1	1	1	1	1	1	1
Madagascar	2	2	3	3	2	2	2	3	3	3
Malawi	2	3	1	1	2	2	1	1	1	2
Mauritius	4	3	5	6	6	5	4	5	5	4
Mosambique	2	0	0	0	0	0	0	0	0	0
Namibia	3	3	3	3	3	3	3	3	3	4
Rwanda					1	1	1	1	0	0
Seychelles	2	1	1	1	1	1	1	3	3	3
South Africa	0	1	1	1	1	1	1	1	1	1
Swaziland	0	1	2	3	0	0	0	0	1	1
Tanzania	6	12	11	12	13	10	12	15	18	14
Uganda	5	5	5	5	4	5	4	2	3	5
Zambia	2	3	1	3	3	1	1	2	2	2
Zimbabwe	2	5	5	5	4	4	6	7	5	5
Expert labs										3
TOTAL	39	47	46	54	58	54	57	72	67	71





### **GROWTH OF THE SADCMET PT SCHEME**







## **OVERVIEW OF A PT ROUND**







## **OVERVIEW OF A PT ROUND cont..**







# **DETAILS OF THE PT PROCESS**

### **Preparation phase**

Sample bottles:

- Wash all 480 bottles twice with deionized water
- Bottles & caps were put in the oven @ 60 °C overnight
- Check dryness
- Cap bottles to prevent them from dust
- Prepare the exact amount of labels for the number of bottles (480 for 80 laboratories)
   Stick labels on the bottles
- Complete for all the sample bottles and store the bottles in numbered crates

#### **Balances:**

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- Calibration of the balances is done by an external body (Namibian Standards Institution)
- Calibration certificates are obtained for the 3 balances
- Verification with certified internal mass pieces



### **Purity:**

The certificates of all the salts and wires are obtained
 The purity for all substances and wires is used to calculate the reference values

### **Glassware:**

Label the glassware appropriately

Arrange the glassware accordingly to create a systematic flow







### **Sample preparation phase**

Weighing of the stock solution

- Weigh the different target masses for the 3 levels of each parameter in a beaker by difference on balance
- Start with the wires since the wires needs to digest for the substance to dissolve completely
- **Continue with the salts**

### **Preparation of stock solutions**

Weigh empty flask, transfer the substance into the volumetric flask

- Fill up the flask and weigh the final mass
- Dilutions, especially for the heavy metals, Weigh 100g of stock solution in a beaker by difference weighing

Follow the same procedure for all the 20 parameters(3 levels)





## **DETAILS OF THE PT PROCESS**

#### Washing of sample bottles







#### Weighing of the stock solutions







## **DETAILS OF THE PT PROCESS**



#### **Digestion of the wires**



#### Weighing of the stock solutions







### **Preparation of bulk samples**

Initial weighing of the empty containers
Fill the containers with deionized
Calculate target weight from density
Rinse stock solutions into the 100L container
Fill to target weight
Stir combined solution for 20 minutes







**Anions :** SO<sub>4</sub>, Cl, NO<sub>3</sub>, F, PO<sub>4</sub>, TDS, Conductivity



Cations : Na, K, Ca, Mg, Fe, Mn, Cd, Cu, Pb, Zn, Al, As, Cr, Co, Ni 4 5 6







### Sample dispensing

- After 20 minutes of stirring, 1 L is flushed out
- The conductivity of the sample is checked before dispensing into the sample bottles and after every 20 samples
- **Tank is washed properly (4-5times) with deionized water between the batches**
- Before starting with the next batch, check the conductivity of the wash water until it reads the same as the deionized water
- Pack the samples in the appropriate crates and pack the crates into the walk in fridge
   Samples kept at 4°C in the Fridge

### **Preparation of the documentation**

- Prepare hard copy of results sheets and the method information
- Prepare all the labels and documentation for transportation for all the countries and participants





## **DETAILS OF THE PT PROCESS**



#### **Preparation of bulk samples**





#### **Dispensing of samples**





### **Packaging of the samples**

Request quotes from the courier
Pack the samples ( one at a time) into the boxes
Add documentation and addresses of all the participants
Confirm the cost with the PTB to proceed







Pick up of the parcels

Parcels were pick up on the 07 July 2016 at NamWater

- Delays:
- Some parcels were left behind by the courier and were picked up later







### **DETAILS OF THE PT PROCESS**

Left NamWater on 07 July 2016









### **Testing phase**

**Calculation of reference values** 

Identity all sources of uncertainty in the analytical measurements and list them with the use of a fish bone diagram
mrssque ( calibration 1 ) mrssque ( calibration 2 ) Fsources of buoyancy

### The identified sources were:

- Purities of the substances used
- Uncertainty of the three balances used
- Uncertainty of molecular mass were neglected
- Density of final samples
- Buoyancy

$$c_{lot} = \frac{m_{K_2 S O_4} \cdot F_{S O_4 / K_2 S O_4} \cdot P \cdot m_{ss} \cdot \rho_{lot}}{m_{ss_t} \cdot m_{lot} \cdot K}$$





### Density

 Samples and a bottle with pure water were kept in the balance room

- Temperature of the water and the samples were measured with a calibrated thermometer
- A 100mL pycnometer was used to determine the density of the 6 Samples
- The pycnometer was filled with water and weighed10 times

 Between each measurement the pycnometer was opened and filled repeatedly to determine the uncertainty of the filling process

The pycnometer was filled and weighed with the 6 samples 3 times repeatedly

The densities and uncertainty of the measurements were calculated

### Pycnometer







### **Measurement uncertainty of reference values**

- The combined standard uncertainties (mg/l), the combined relative uncertainty(%), the combined expanded uncertainties (mg/l) and the combined relative standard uncertainty (%) were calculated and reported
- The size of the different contributions was compared using a histogram showing all the standard uncertainties
- The reference values were calculated with the combined expanded standard uncertainty taken into consideration for all the parameters for the different levels





The biggest uncertainty components from histograms that was identified were:



 Fe, Mn (Level 1 & 3), Al, Cu, Zn, Ni, As, Cd, Co

Purity of salts

 SO, Cl, F, NO<sub>3</sub>, PO<sub>4</sub>, Ca, Mg, Na, K, Mn (Level 2), Pb, Cr ,





## **EVALUATION & ASSESSMENT**

- Reference values are calculated from the synthetic, gravimetrical samples with an uncertainty budget
- Calculation of standard deviation is done by using the Algorithm A method from ISO 13528 provided it is lower than the calculated value
- Where the calculated value is higher, the fitness-for-purpose value is used
- The fitness-for-purpose [limit] value was agreed on between participants
   The process that applied for the elimination of gross outliers is:
  - All values < ref.-value/8 and all values > ref.-value \* 8 were excluded before applying statistical procedures

#### The report contains:

- a graphical display of lab results vs the assigned value to assist with corrective actions
- A method specific evaluation to assist the laboratories in methods choices
- Assistance is provided for laboratories that need corrective actions





### **PERFORMANCE SCORING**

- The assessment of performance is based on Z-scores
- ✓ Use of Z-scores are a common practice in the assessment of laboratory results
- ✓ Z-scores reflects the actual accuracy achieved the difference between the participant's result and the reference value
- A score of zero implies a perfect result
- Z-scores are rounded to one digit after decimal point as requested by ISO17043 and ISO13528
- ✓ Usually laboratories produce scores between -2 and 2
- The sign(i.e., + or -) of the score indicates a negative or positive error respectively.

  - \* 2.0 < | z-score | < 3.0 questionable</p>





### **CHANGES AND PROGRESS OF PARAMETERS**

PARAMETER	Std Limit (%)
Sulphate	10
Chloride	10
Fluoride	10
Nitrate	10
Phosphate	10
TDS	10
Conductivity	10
Calcium	10
Magnesium	10
Sodium	10
Potassium	10

PARAMETERS	Std Limit (%)
Iron	20
Manganese	20
Aluminium	20
Lead	20
Copper	20
Zinc	20
Chromium	20
Nickel	20
Cadmium	20
Arsenic	20
Cobalt	20





### **RANGES FOR PARAMETERS**



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	PARAMETER	RANGES	PARAMETER	RANGES
10000	Sulphate in mg/l	9.50 - 80.00	Iron in mg/l	0.09 - 4.61
	Chloride in mg/l	10.00-73.40	Manganese in mg/l	0.03 - 5.10
-	Fluoride in mg/l	0.20 - 2.54	Aluminium in mg/l	0.05 – 4.41
G	Nitrate in mg/l	9.10 - 88.00	Lead in mg/l	0.05 – 3.33
	Phosphate in mg/l	3.20 -30.50	Copper in mg/l	0.05 – 4.05
	TDS in mg/l	0-1000 mg/l	Zinc in mg/l	0.45 – 5.89
	Conductivity in mg/l	0-400 mS/m	Chromium in mg/l	0.05 – 2.90
	Calcium in mg/l	8.40 - 90.0	Nickel in mg/l	0.06 – 3.55
	Magnesium in mg/l	7.45 – 55.3	Cadmium in mg/l	0.02 - 1.10
	Sodium in mg/l	8.50 - 90.0	Arsenic in mg/l	0.04 - 1.20
	Potassium in mg/l	5.00 - 50.0	Cobalt in mg/l	0.05 – 2.68
NAMW	ATER			



### **SULPHATE**



#### **Summary Sulphate**

- Average recovery was higher than in the previous round with 95.9 %
- STD are still > 10 %, especially for low conc.
- 47 data points outside the limits
- 28.6 % of methods still classified as "other"





### **SULPHATE**



25.8% of the data is outliers (32.1% in 2015)

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### CHLORIDE



#### **Summary Chloride**

- Average recovery was higher than in the previous round with 103.3 %
- STD are still > 10 %, especially for low conc. (13.79%)
- 31 data points outside the limits
- 16.2 % of methods still classified as "other"





### **CHLORIDE**





15.7% of the data is outliers (36.9% in 2015)



## FLUORIDE



#### **Summary Fluoride**

- Average recovery was 90.4 %
- STD are still > 10 %, especially for low conc. (20.7%)
- 30 data points outside the limits
- ✓ 23.8 % of methods still classified as "other"




# FLUORIDE





23.1 % of the data is outliers (44.4% in 2015)





#### **Summary Nitrate**

- Average recovery was 82.5 %
- STD are still > 10%, especially for low conc. (Sample 1 - 26.8%; Sample 2 24.0%, Sample 3 - 27.2%)
- ✓ 69 data points outside the limits
- 41.6% methods still classified as "other"









Wrong units again as  $NO_3^--N$  instead of  $NO_3^-$ 







Wrong units again as NO<sub>3</sub><sup>-</sup>-N instead of NO<sub>3</sub><sup>-</sup>







Wrong units again as NO<sub>3</sub><sup>-</sup>-N instead of NO<sub>3</sub><sup>-</sup>







39.9 % of the data is outliers (46.5% in 2015)





#### **Summary Phosphate**

- Average recovery was 95.9 %
- STD are still > 10%, especially for low conc. (Sample 1 – 31.72%; Sample 2 28.81%, Sample 3 – 23.44%)
- ✓ 69 data points outside the limits
- 32.9 % of methods still classified as "other"









most probably reported in PO<sub>4</sub><sup>3-</sup>-P instead of PO<sub>4</sub><sup>3-</sup>







most probably reported in PO<sub>4</sub><sup>3-</sup>-P instead of PO<sub>4</sub><sup>3-</sup>





most probably reported in PO<sub>4</sub><sup>3-</sup>-P instead of PO<sub>4</sub><sup>3-</sup>

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36.8% of the data is outliers (34.6% in 2015)



# **TOTAL DISSOLVED SOLIDS (TDS)**



#### **Summary TDS**

- Average recovery was 96.3 %
- STD are between 12.0-21.2 % for low conc. (21.2%)
- 44 data points outside the limits
- 29.3 % of methods still classified as "other"





## TDS



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# CONDUCTIVITY



#### **Summary Conductivity**

- Average recovery was 100.4 %
- STD are all < 10 %, Sample 1 6.7%; Sample 2 – 8.2 %, Sample 3 – 6.9%)
- ✓ 52 data points outside the limits
- ✓ 29.2% of methods still classified as "other"





# CONDUCTIVITY



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27.5 % of the data is outliers (34.5 % in 2015)



# CALCIUM



#### **Summary Calcium**

- Average recovery was 98.2 %
- STD > 10 % for all three levels ( lowest level 23.63 % )
- ✓ 52 data points outside the limits
- v 28.1% of methods still classified as "other"





### CALSIUM



# MAGNESIUM



#### **Summary Magnesium**

- Average recovery was 97.3 %
- STD below 20 % for Sample 5 and 6
  Sample 4 (lowest level 27.42 %)
- ✓ 52 data points outside the limits
- 28.1% of methods still classified as "other"





## MAGNESIUM





29.1 % of the data is outliers (46.2 % in 2015)



## **SODIUM**



#### **Summary Sodium**

- Average recovery was 104.2 %
- STD above 10 % for all three samples ( lowest level – 26.25 % )
- 45 data points outside the limits
- 40.7% of methods still classified as "other"





## SODIUM



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32.1 % of the data is outliers (22.5 % in 2015)



# POTASSIUM



#### **Summary Potassium**

- Average recovery was 106.7 %
- STD below > 10 % for all three levels
- ✓ 53 data points outside the limits
- 42.2 % of methods still classified as "other"





# POTASSIUM





36.1 % of the data is outliers (31.4 % in 2015)



## IRON



#### **Summary Iron**

- Average recovery was 92.0 %
- STD below 20 % for Sample 5 and 6
  Sample 4 (lowest level 42.66 %)
- 41 data points outside the limits
- 44.0% of methods still classified as "other"











23.4 % of the data is outliers (23.0 % in 2015)



# MANGANESE



#### **Summary Manganese**

- Average recovery was 93.3 %
- STD below 20 % for Sample 5 and 6
  Sample 4 (lowest level 20.17 %)
- 39 data points outside the limits
- 50.9% of methods still classified as "other"





### MANGANESE





22.8 % of the data is outliers (30.2 % in 2015)



# **ALUMINIUM**



#### **Summary Aluminium**

- Average recovery was 90.2 %
- STD above 20%, 62.2 for lowest level; sample 4 ( 21.6%) Sample 6 (27.2 % )
- $\checkmark$  32 data points outside the limits
- 42.2% of methods still classified as "other"





## **ALUMINIUM**





28.8 % of the data is outliers (20.6 % in 2015)



### LEAD



#### **Summary Lead**

- Average recovery was 99.1 %
- STD below 20 % for Sample 5 and 6
  Sample 4 ( lowest level 50.76 % )
- $\checkmark$  27 data points outside the limits
- 44.5% of methods still classified as "other"











22.3 % of the data is outliers (22.7 % in 2015)



### **COPPER**



#### **Summary Iron**

- Average recovery was 96.0 %
- STD below 20 % for all three samples ( lowest level – 11.32 % )
- ✓ 21 data points outside the limits
- 45.1% of methods still classified as "other"





### **COPPER**





13.7 % of the data is outliers (20.5 % in 2015)



### ZINC



#### **Summary Zinc**

- Average recovery was 91.6 %
- STD below 20 % for all three samples ( lowest level – 15.1 % )
- 22 data points outside the limits
- 42.2% of methods still classified as "other"











16.3 % of the data is outliers (19.5 % in 2015)



# **CHROMIUM**



#### **Summary Chromium**

- Average recovery was 95.6 %
- STD below 20 % for all three samples
- ( lowest level 16.5 % )
- ✓ 29 data points outside the limits
- 40.0% of methods still classified as "other"




# **CHROMIUM**



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23.6 % of the data is outliers (36.3 % in 2015)



## NICKEL



#### **Summary Nickel**

- Average recovery was 95.6 %
- STD below 20 % for all three samples
  ( lowest level 16.6 % )
- $\checkmark$  25 data points outside the limits
- 40.0% of methods still classified as "other"





#### NICKEL





18.5 % of the data is outliers (16.7 % in 2015)



### ARSENIC













26.0 % of the data is outliers (22.0 % in 2015)



# CADMIUM



#### **Summary Cadmium**

- Average recovery was 90.5 %
- STD below 20 % for all three samples ( lowest level – 19.6 % )
- ✓ 30 data points outside the limits
- 35.5% of methods still classified as "other"





## CADMIUM





24.2 % of the data is outliers (32.5 % in 2015)



## **COBALT**



#### **Summary Cobalt**

- Average recovery was 96.5 %
- STD below 20 % for all three samples ( lowest level – 12.29 % )
- 22 data points outside the limits
- 13.3% of methods still classified as "other"





# COBALT





19.8 % of the data is outliers (13.3 % in 2015)



# **# PARAMETERS ANALYSED**



# % OVERALL SUCCESS OF ANIONS







# % OVERALL SUCCESS OF CATIONS

Let's go forward



## % OVERALL PERFORMANCE



Let's go forward

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# **CHALLENGES 2017**

#### Adhere to the stated deadlines

- Clear and fully completed registration forms will be a requirement for participation.
- Absence of registration forms complicates communication
- Results submission done after the due date delay the reports
- We need to improve— still high standard deviations
- Vuse of non-standard methods are high
- The same mistakes are being done Reporting of results in wrong units
- Corrective actions are still not implemented
- ✓Laboratories are still not sending their proof of payments
- Problems with the website (back to manually submitting results)
- ✓Laboratories that registered and requested samples should aim to analyse them as well





# CONCLUSION

Overall the results of this PT round show a good performance for many labs - Too many outliers for most of the parameters

- **SDS** are still high for some parameter and levels.
- There are still many labs that are not putting enough emphasis on corrective actions after unsatisfactory results - PT participation does not add any value if corrective actions are not done
- Root cause analyses are not done
- ✓ Method selection is still a big problem Laboratories should identify the gaps that prevent them from applying a proper method
  - A list of recommended methods were compiled and it is sent to all participants but they do not use it
  - \* "ICP" reported as a method is not an international method ISO 11885:1996-ICP-AES is !

The same mistakes are being done - Reporting of results in wrong units (N and not NO3 and as P and not PO4

The evaluation and assessment procedure is fit for the purpose





# CONCLUSION

#### Software & report developments

- New software was develop by Dr M Koch to address the changes from ISO/IEC 17043 and ISO 13528.
- Name and address of the PT provider and name of the round can be inserted
- Usage of median is not possible anymore
- Graphical display of kernel densities included. You may find more information about kernel density diagrams <u>http://www.rsc.org/images/data-distributions-kernel-density-technicalbrief-4\_tcm18-214836.pdf</u>
- z-scores are rounded to one digit after decimal point as requested by ISO/IEC 17043 and ISO 13528
- assessment changed to satisfactory, questionable, non satisfactory as requested by ISO/IEC 17043 and ISO 13528





# CONCLUSION

- PT plays a vital role in laboratory management for ongoing maintenance of confidence and improvement, irrespective of whether or not the laboratory needs to participate for accreditation.
- The SADCMET Water PT schemes offers an additional educational role for participants to help the participants to improve – do not to miss this opportunity!
- The SADCMET Water PT is a good possibility for the participants to compare with peers and with stated fitness-for-purpose criteria
- Frieda Nambahu did a very good job





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- Local coordinators
- Participants
- **√TFDA**





















# **THANK YOU**



