14th Proficiency testing scheme for chemical analysis of Water in Africa

Justina Endjala / Merylinda Conradie 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
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- Overview of a PT round
- > Details of the PT process
- > Evaluation & Assessment
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- Summary of the Parameters
- > Overall Success
- Challenges 2018
- Conclusion





Backgound & history of the scheme

	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.					
	2004	1 st PT round; Evaluation workshop in Pretoria, South Africa					
	2005	2 nd 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					
3		October: Poster presentation at the Eurachem workshop in Proficiency testing in analytical chemistry, microbiology and medicine in Rome, Italy					
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Backgound & history of the scheme

	-				
	2008	5th PT round; Evaluation workshop in Kampala, Uganda Training session on the Management requirements of the ISO17025			
	2009	6th PT round; Evaluation workshop in Mahé, Seychelles Test & Measurement conference: Presentation of Chemical analyses of water in Africa, South Africa			
	2010	7th 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			
1	2011	8th PT round; Evaluation workshop in Port Louise, Mauritius Training session on ensuring the quality of analytical results – Trueness and Precision			





Backgound & history of the scheme

2013	10th PT round; Evaluation workshop in Nairobi, Kenya Training session on control charts
2014	11th 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	12th PT round; Evaluation workshop in Gaborone, Botswana. Training session on Inter-laboratory tests, basic statistics and control charts
2016	13th PT round; Evaluation workshop in Dar Es Salaam, Tanzania. Training session the update on the revision of ISO/IEC 17025ion on Inter-laboratory tests, Root cause analysis and Estimation of Uncertainties

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% Participation per country



of laboratories per country

	2006	2007	2008	2009	2010	2011	2013	2014	2015	2016	2017
Angola	0	0	1	0	0	0	0	0	0	0	0
Botswana	2	4	2	3	3	3	3	3	3	3	3
Burundi					1	1	1	2	2	2	2
Congo					4	5	3	8	7	5	8
Eritrea	0	0	1	0	0	0	0	0	0	1	0
Ethiopia	1	0	0	0	0	1	1	2	1	2	2
Ghana						1	0	0	0	0	0
Kenya	5	3	3	7	9	7	12	13	8	10	12
Lesotho	1	1	1	1	1	1	1	1	1	1	0
Madagascar	2	2	3	3	2	2	2	3	3	3	3
Malawi	2	3	1	1	2	2	1	1	1	2	2
Mauritius	4	3	5	6	6	5	4	5	5	4	5
Mosambique	2	0	0	0	0	0	0	0	0	0	0
Namibia	3	3	3	3	3	3	3	3	3	4	3
Rwanda					1	1	1	1	0	0	0
Seychelles	2	1	1	1	1	1	1	3	3	3	3
South Africa	0	1	1	1	1	1	1	1	1	1	2
Swaziland	0	1	2	3	0	0	0	0	1	1	1
Tanzania	6	12	11	12	13	10	12	15	18	14	22
Uganda	5	5	5	5	4	5	4	2	3	5	6
Zambia	2	3	1	3	3	1	1	2	2	2	3
Zimbabwe	2	5	5	5	4	4	6	7	5	5	5
Expert labs										3	3
TOTAL	39	47	46	54	58	54	57	72	67	71	85





Growth of the SADC PT scheme







Details of the PT processes Overview of a round

- The annual notification is send out by the end of February with the schedule of activities for the year.
- Phase 1 Registration usually close by the end of April
 - Identification & calculation of target values
 - Ordering of Chemicals & Consumables
- Phase 2 Download certificates of analyses (COA)
 - Preparation of the stock solutions and bulk samples
- Phase 3 Packing and distribution of the parcels





Details of the PT processes Overview of a round







Details of the PT processes Sample bottle preparation



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- > Wash 540 bottles twice with deionized water
- » Bottles & caps were put in the oven @ 60 °C overnight
- > Check dryness
- Prepare the exact amount of labels for the number of bottles (540 for 90 laboratories)
- Stick labels on the bottles

Store the bottles until needed





Details of the PT processes Labelling of the bottles







Details of the PT processes Preparation of the balances

- We make use of gravimetric weighings throughout the process
- Calibration of the balances is very important
- This is done by an external body (Namibian Standards Institution)
- Calibration certificates are obtained for all three balances
- Daily verification with certified internal mass pieces
- > Certificates are documented:
 - Certificate of analyses (COA) for reagents used
 - Calibration certificate for thermometer
 - Calibration certificate for pycnometer
 - Calibration certificates for balances





Details of the PT processes Preparation before weighing

Purity:

- The COA (Certificate of Analysis) of all the salts and wires are obtained
- The purity for all substances and wires is used to calculate the reference values

Glassware:

- > Only clean and properly labelled glassware is used
- Arrange the glassware accordingly to create a systematic flow





Details of the PT processes Weighing of substances







Details of the PT processes Preparation of stock solutions



Weigh empty flask, transfer of substance into flask, fill, weigh full flask, balance 2

Dilution (where necessary) – Weigh 100g of diluted stock solution in beaker, difference weighing, balance 2

Repeat for all 20 parameters – 3 levels





Details of the PT processes Digestion of the wires







Details of the PT processes 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





Details of the PT processes Preparation of bulk samples



Anions : SO₄, Cl, NO₃, F, PO₄, TDS, Conductivity



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







Details of the PT processes Sample dispensing



1 L is flushed out from the tank sample is dispensed into the sample bottles.Sample bottles (90) were filled after each batch

Put in crates in fridge at 4 ° C

Tank washed properly (4-5 x) in between . Check the conductivity of the wash water until = deionized water and also after every 20th sample

Start to prepare for the next batch







Details of the PT processes Storing of the samples







Details of the PT processes Preparation of documentation



- Prepare hard copies of all the documentation
- Prepare all the labels and documentation for courier for the transportation for all the countries and participants







Details of the PT processes 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 costs with the PTB before proceeding







Details of the PT processes Packaging of the samples







Details of the PT processes Sample pick up and dispatch





Parcels were picked up on the 01 September 2017 at NamWater





Details of the PT processes Calculation of the reference values

- All sources of uncertainty in the analytical measurements were identified with the use of a fishbone diagram.
- > The identified sources were:
- > Purities of the chemicals
- > Uncertainty of the three balances used:
- Sartorius Balance ED124S
- Sartorius Balance ED42025-CW
- Sartorius Balance FBG64EDE-H
- > Uncertainties of molecular mass were neglected
- Densities of final samples
- Buoyancy





Details of the PT processes Fish Bone diagram



Details of the PT processes Determination of the uncertainty of the 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 weighed 10 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







Details of the PT processes 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 all the parameters for the different levels











Details of the PT processes Evaluation & assesment

- 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 x 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





Details of the PT processes Performance scoring

- > The assessment of performance is based on Z-scores
- > 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 q-
- o | z-score | ≥ 3.0

- q- questionable
- n-non satisfactory



Details of the PT scheme Limits for the standard deviation

PARAMETER	Std Limit (%)	PARAMETERS	Std Limit (%)		
Sulphate 10		Iron	20		
Chloride	10	Manganese	20		
Fluoride	10	Aluminium	20		
Nitrate	10	Lead	20		
Phosphate	10	Copper	20		
TDS	10	Zinc	20		
Conductivity	10	Chromium	20		
Calcium	10	Nickel	20		
Magnesium	10	Cadmium	20		
Sodium	10	Arsenic	20		
Potassium	10	Cobalt	20		





Details of the PT scheme Ranges of the round 1-14



PARAMETER	RANGES	PARAMETER	RANGES
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	Aluminum in mg/l	0.05 – 4.41
Nitrate in mg/l	9.10 - 88.00	Lead in mg/l	0.05 – 3.33
Phosphate in mg/l	3.20 -50.00	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





Sulphate mean vs. ref.-value



Sulphate Calculated standard deviation and limit



Sulphate Percentage non-satisfactory results





25.8% in 2016 to 32.7% in 2017



Method used







Summary Sulphate

- > Average recovery was higher than in the previous round with 98.0 %
- > STD are still > 10 %, with the lowest level at 30.94 %
- > 64 data points outside the limits
- > 28.4 % of methods classified as "other
- Many results too low from participants using the Hach method 8051 – 12 labs obtained correct results from the same method
- Not a big change compared to 2016





Chloride mean vs. ref.-value







Chloride Calculated standard deviation and limit







Chloride Percentage non-satisfactory results





15.7 % to 32.2 % in 2017



Method used







Summary Chloride

- > Average recovery was 106.4 %
- STD are still > 10 %, especially for low conc. (33.8 %)
- > 76 data points outside the limits
- > 24.5 % of methods still classified as "other"





Fluoride mean vs. ref.-value







Fluoride Calculated standard deviation and limit







Fluoride Percentage non-satisfactory results





23.1% to 69.6% in 2017



Method used







Summary Fluoride

- Many results too high results for lowest level mainly for the colorimetric results
- STD very high, > 268.9% ! for the low level
- Increase in the percentage of non-satisfactory results – 23.1% in 2016 to 69.6% in 2017
- > 76.8 % of the results are too high for the Hach method 8029 –correct results are possible !
- > It was also the same situation for 2017





Nitrate mean vs. ref.-value







Nitrate Calculated standard deviation and limit







Nitrate Percentage non-satisfactory results





39.9% to 51.3% in 2017



Nitrate 1





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



Nitrate 2





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



Nitrate 3





Wrong units again as NO₃⁻-N instead of NO₃⁻



Method used







Summary Nitrate

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- Still problems with reporting of NO₃ in the wrong units
- Labs either do not read / do not understand / are not able to calculate or convert to the correct unit
- STDs very high mostly because of wrong units
- Percentage of non-satisfactory results again very high (units!) – from 39.9% to 51.3% in 2017

> 48.7% of the labs are using "other" methods



Phosphate mean vs. ref.-value







Phosphate Calculated standard deviation and limit







Phosphate Percentage non-satisfactory results





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Phosphate 1



most probably reported in PO₄³⁻-P instead of PO₄³⁻





Phosphate 2







Phosphate 3





most probably reported in PO₄³⁻-P instead of PO₄³⁻



Method used







Summary Phosphate

- > Laboratories reported in the wrong units again
- Standard deviations are too high
- Percentage of non-satisfactory results increased from 36.8 % to 40.7 in 2017





TDS mean vs. ref.-value







TDS Calculated standard deviation and limit







TDS Percentage non-satisfactory results





25.3% to 40.8% in 2017



Method used







Summary **TDS**

- > Average recovery was 90.5 %
- > STD's still too high
- Percentage of non-satisfactory results improved from 25.3% to 40.8% in 2017
- > 35,2% "other" methods





Conductivity mean vs. ref.-value






Conductivity Calculated standard deviation and limit







Conductivity Percentage non-satisfactory results





27.5% to 31.3% in 2017



Method used







Summary Conductivity

- Laboratory still do not report method information - "other"
- > Average recovery of 90.5 %
- > STD are below the 10% limit
- Percentage of non-satisfactory results slightly higher but still high - 27.5% to 31.3% in 2017





Calcium mean vs. ref.-value







Calcium Calculated standard deviation and limit







Calcium Percentage non-satisfactory results





29.1 % to9 33.8 % in 2017



Method used







Summary Calcium

Perfect average recovery of 100 %
STD for the lowest level is 50.8%
Percentage of non-satisfactory results from 29.1 % to 33.8 % in 2017- no improvement





Magnesium mean vs. ref.-value







Magnesium Calculated standard deviation and limit







Magnesium Percentage non-satisfactory results





29.9% to 47,3% in 2017



Method used







Summary Magnesium

- > 17,4 % of "other" methods
- STD higher too high 71.6 % for the lowest level
- Titrimetric results a high portion of too high results for this method
- No improvement in comparison with last year





Sodium mean vs. ref.-value







Sodium Calculated standard deviation and limit







Sodium Percentage non-satisfactory results





32.1% to 29.0% in 2017



Method used







Summary Sodium







Potassium mean vs. ref.-value







Potassium Calculated standard deviation and limit







Potassium Percentage non-satisfactory results





36.1% to 36.2% in 2017



Method used







Summary **Potassium**

- > Average recovery is 101 % k
- > STDs still outside the limits
- Percentage of non-satisfactory results still high





Iron mean vs. ref.-value







Iron Calculated standard deviation and limit







Iron Percentage non-satisfactory results





23.4% to 30.8% in 2017



Method used







Summary Iron

- > Average recovery is 98%
- Significant improvement in 2017 for the lowest (68% to 28%) Now we are back to a SD of 94.23
- > Problems with the lowest level high blank
- Number of non-satisfactory results increased from 23.4% to 30.8% in 2017





Manganese mean vs. ref.-value



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Manganese Calculated standard deviation and limit







Manganese Percentage non-satisfactory results



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22.8% to 32.8% in 2017

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Method used







Summary Manganese

- STDs for second highest level and highest level are below 20 %
- > Lowest level STD of 101.5%
- Percentage of non-satisfactory results 22.8% to 32.8% in 2017





Aluminium mean vs. ref.-value

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Aluminium Calculated standard deviation and limit






Aluminium Percentage non-satisfactory results





28.8% to 24.8% in 2017



Method used







Summary Aluminium

- > 41.9 % "other methods"
- > SDs above the limit for all three levels
- Percentage outliers reduced from 28.8% to 24.8% in 2017
- > Problems with the AAS method







mean vs. ref.-value







Lead Calculated standard deviation and limit







Lead

Percentage non-satisfactory results





22.3% to 26.4% in 2017



Method used







Summary Lead

- > Average recover is 103.2%
- > Obviously problems with the lowest level high blank?, high STD (97.9 % !)
- STDs for the other levels are 21.42% and 14.36%
- > Variety of all the other methods causes a problems
- > 28% of "other" methods





Copper mean vs. ref.-value







Copper Calculated standard deviation and limit







Copper Percentage non-satisfactory results





13.7% to 14.0% in 2017



Method used







Summary Copper

- > Perfect recovery of 100.3%
- Standard deviations below 20% for all three levels
- Non satisfactory results remained similar than in 2016 - 13.7% to 14.0% in 2017
- > 31.8% of "other" methods





Zinc mean vs. ref.-value







Zinc Calculated standard deviation and limit







Zinc Percentage non-satisfactory results





16.3% to 15.6% in 2017



Method used







Summary **Zinc**



- > Perfect recovery of 101.69%
- Standard deviations below 20% for all three levels
- > 22.2 % of "other" methods
- Slight improvement for the percentage of non-satisfactory results - 16.3% to 15.6% in 2017





Chromium mean vs. ref.-value







Chromium Calculated standard deviation and limit







Chromium Percentage non-satisfactory results





23.6% to 31.4% in 2017



Method used







Summary Chromium

- > Average recovery is 95.6% not bad
- Blank problems with the lowest level SD of 49.1%
- > 21.9% "other" methods
- Percentage non-satisfactory results slightly improved - 23.6% to 31.4% in 2017





Nickel mean vs. ref.-value







Nickel Calculated standard deviation and limit







Nickel Percentage non-satisfactory results





23.6% to 31.4% in 2017



Method used







Summary Nickel

- > High STD for the lowest level Blank problems with the lowest level – SD of 37.6%
- > The other two were both below 20%
- Percentage non-satisfactory results increased from 23.6% to 31.4% in 2017
- > Average recovery is 99.1%
- > 33.6% "other" methods





Arsenic mean vs. ref.-value







Arsenic Calculated standard deviation and limit







Arsenic Percentage non-satisfactory results





26.0% to 19.0% in 2017



Method used







Summary Arsenic

- > Average recovery is 100.1%
- > Low number of values
- > Problems with ICP and AAS method
- > High STD for the lowest level Blank problems with the lowest level – SD of 25.98%
- > The other two were both below 20%
- Percentage non-satisfactory results increased from 26.0% to 19.0% in 2017





Cadmium mean vs. ref.-value







Cadmium Calculated standard deviation and limit







Cadmium Percentage non-satisfactory results







24.2% to 23.2% in 2017
Method used







Summary Cadmium

- STDs varies were below 20% for all three levels
- > % Percentage non-satisfactory results similar than in 2016
- No serious problems





Cobalt mean vs. ref.-value







Cobalt Calculated standard deviation and limit







Cobalt Percentage non-satisfactory results





19.8 % to 13.5% in 2017



Method used







Summary Cobalt



- > Average recovery is 95.8%
- > STDs all below 20%
- > 35.1% use "other" methods
- > No serious problems





Parameters analysed



■ Tot acept ■ Tot un-acept





% Overall success of anions

Overall success of Anions %





Lab code



% Overall success of cations







% Overall performance



Challenges 2018

- Participants do not honour the stated deadlines
- Rregistration forms are sometimes still not clear email addresses are important participation.
- No registration forms no samples
- No proof of payment no samples
- No results no evaluation reports
- Standard deviations are too high
- > Correct procedures for implementation of methods
- Wrong unit reporting remains a challenge
- Corrective actions are still not implemented





Conclusion

- Laboratories will have to pay for distribution and participation if you do not analyse the samples – waste of money
- Overall the results of this PT round indicated a worse performance than 2016
- 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 evaluation and assessment procedure is fit for the purpose



Conclusion

- Software addresses 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 and to compare with peers and
- Jessica Klazen did a very good job





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Questions



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