# 9th Proficiency testing scheme for chemical analysis of Water in Africa

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AQS Baden-Württemberg iswa

PTB

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# NamWater

- Officially registered as a company on 9 December 1997
- The bulk water supplier for industries, municipalities and ministries
- Strive to supply a reliable source of quality water at the lowest possible rates
- Operates on a cost recovery basis
- Namibian Government is the sole shareholder

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# Overview

- Participation per country
- Project activities
- Growth of the SACMET PT scheme
- % Presentation per country
- Steps of a PT round
- Details of the PT processes
- Evaluation & assessment
- Measurement uncertainty
- Closure

# Project Activities

| | |
|---|---|
| **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** | 1st PT round; Evaluation workshop (Pretoria) |
| **2005** | 2nd PT round; Evaluation workshop with training on measurement uncertainty (Dar es Salaam) |
| **2006** | 3rd PT Round; Evaluation workshop with training on validation and control charts (Gaborone) |
| **2007** | 4th PT round; Evaluation workshop (Dar es Salaam) with training on validation and measurement uncertainty |
| **2008** | 5th PT round; Evaluation workshop (Kampala) with training on management requirements.<br><br>October: Poster presentation at the Eurachem Workshop in Proficiency testing in analytical chemistry, microbiology and laboratory medicine in Rome |

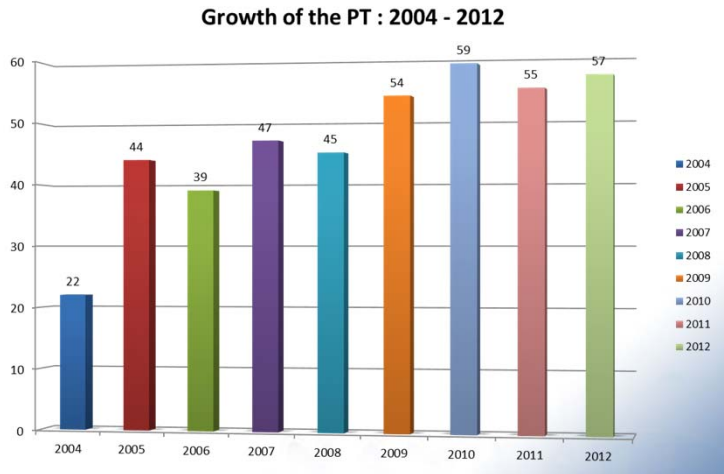
# Project Activities II

| | |
|---|---|
| **2009** | Test & Measurement conference : Presentation of Chemical analyses of water in Africa, South Africa<br><br>6th round; Evaluation workshop (Seychelles) |
| **2010** | 7th round:Evaluation workshop (Windhoek) with training on estimation of measurement uncertainty using validation and quality control. |
| **2011** | 8th round:Evaluation workshop (Mauritius) with training on Ensuring the Quality of Analytical Results – Trueness and Precision<br><br>October: Poster presentation at the Eurachem Workshop in Proficiency testing in analytical chemistry, microbiology and laboratory medicine in Istanbul |

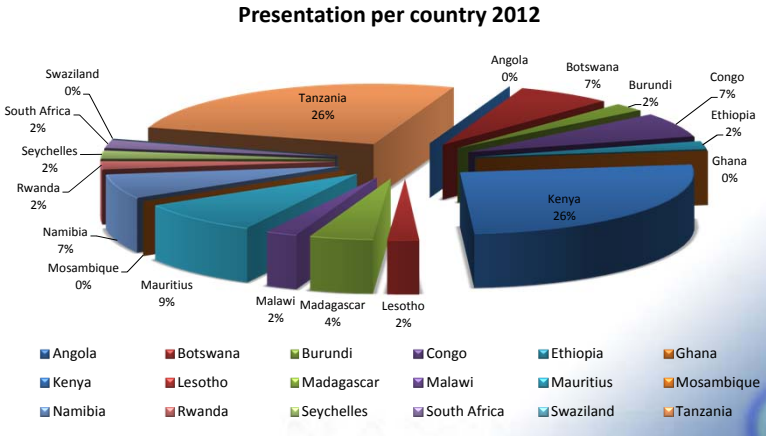
# Participation per country

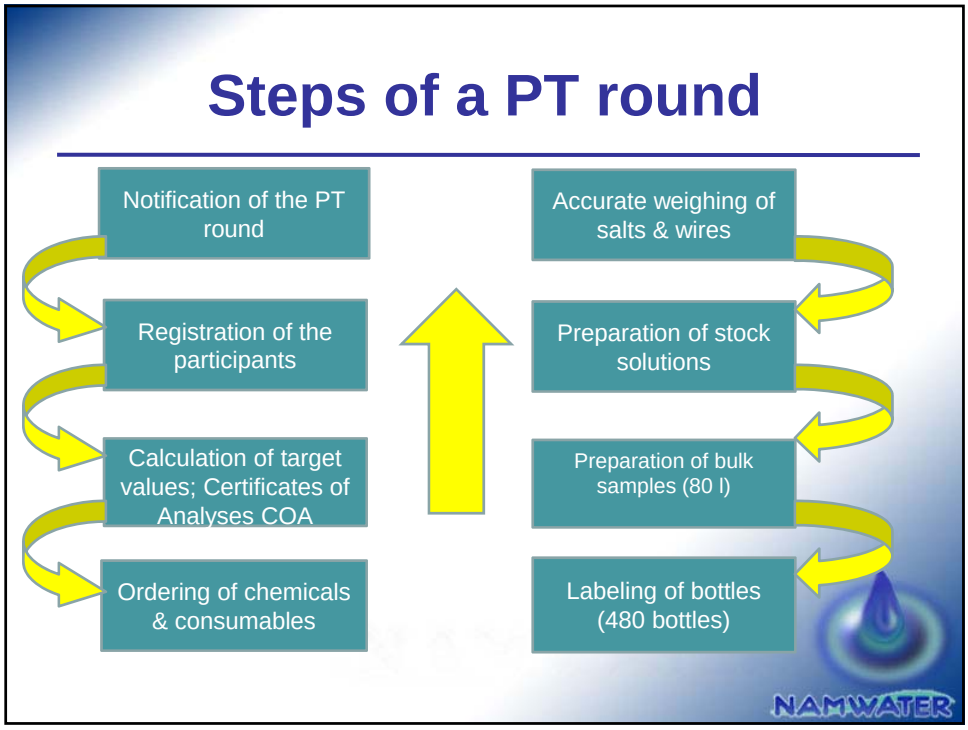
| | 2006 | 2007 | 2008 | 2009 | 2010 | 2011 | 2012 |
|---|---|---|---|---|---|---|---|
| Angola | 0 | 0 | 1 | 0 | 0 | 0 | 0 |
| Botswana | 2 | 4 | 2 | 3 | 3 | 3 | 3 |
| Burundi | | | | | 1 | 1 | 1 |
| Congo | | | | | 4 | 5 | 3 |
| Ethiopia | 1 | 0 | 0 | 0 | 0 | 1 | 1 |
| Ghana | | | | | | 1 | 0 |
| Kenya | 5 | 3 | 3 | 7 | 9 | 7 | 12 |
| Lesotho | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| Madagascar | 2 | 2 | 3 | 3 | 2 | 2 | 2 |
| Malawi | 2 | 3 | 1 | 1 | 2 | 2 | 1 |
| Mauritius | 4 | 3 | 5 | 6 | 6 | 5 | 4 |
| Mosambique | 2 | 0 | 0 | 0 | 0 | 0 | 0 |
| Namibia | 3 | 3 | 3 | 3 | 3 | 3 | 3 |
| Rwanda | | | | | 1 | 1 | 1 |
| Seychelles | 2 | 1 | 1 | 1 | 1 | 1 | 1 |
| South Africa | 0 | 1 | 1 | 1 | 1 | 1 | 1 |
| Swaziland | 0 | 1 | 2 | 3 | 0 | 0 | 0 |
| Tanzania | 6 | 12 | 11 | 12 | 13 | 10 | 12 |
| Uganda | 5 | 5 | 5 | 5 | 4 | 5 | 4 |
| Zambia | 2 | 3 | 1 | 3 | 3 | 1 | 1 |
| Zimbabwe | 2 | 5 | 5 | 5 | 4 | 4 | 6 |
| TOTAL | 39 | 47 | 45 | 54 | 58 | 54 | 57 |

# Growth of PT SADCMET Scheme




# % Representation / Country




Steps of a PT round
Notification of the PT round
Registration of the participants
Calculation of target values; Certificates of Analyses COA
Ordering of chemicals & consumables
Accurate weighing of salts & wires
Preparation of stock solutions
Preparation of bulk samples (80 l)
Labeling of bottles (480 bottles)
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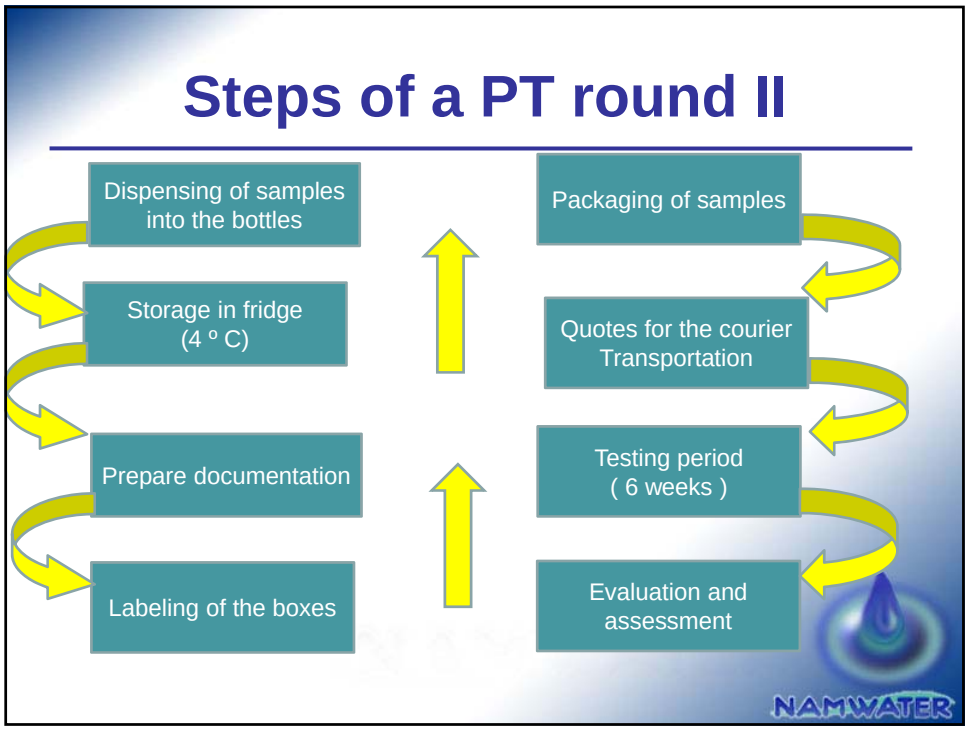
Steps of a PT round II
Dispensing of samples into the bottles
Storage in fridge (4 ° C)
Prepare documentation
Labeling of the boxes
Packaging of samples
Quotes for the courier Transportation
Testing period ( 6 weeks )
Evaluation and assessment
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# Sample bottle preparation

- Wash all 480 bottles twice with deionised water
- Bottles & caps were put in the oven @ 60 °C overnight
- Check dryness
- Cap bottles to prevent them from dust
- Label and store them until needed

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# Labeling of bottles

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# Weighing of substances

Start of by weighing the different target masses for the 3 levels of each parameter in a beaker, difference, balance 1

Start of with the wires , digest wires until completely dissolved, continue with salts

Continue to prepare the stock solution

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# Digestion of the wires

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# 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

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# Preparation of bulk samples

Weigh empty 100 l container and stirrer, balance 3
Weigh empty 25 l container , balance 3

Partly filled container with water
Fill with deionised water only

Rinse solution solutions in 100 l container to nearly complete

Calculate target weight from density 0,998 g/ml

Fill to target weight I, balance 3
Fill to target weight I, balance 3

Stir for combined solution for 20 minutes

Fill samples bottles

Determine the density of samples

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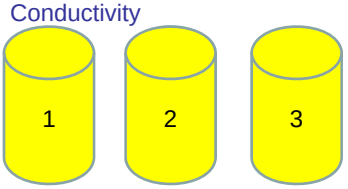
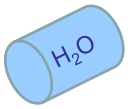
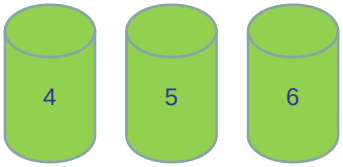
# Preparation of bulk samples

**Anions :** $SO_4$, Cl, $NO_3$, F, $PO_4$, TDS, Conductivity




**Cations** : Na, K, Ca, Mg, Fe, Mn, Cd,Cu,Pb,Zn, Al, As, Cr, Co

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# Sample dispensing

Samples bottles (80 ) were filled after each batch

↓

Put in crates in fridge at 4 º C

↓

Tank washed properly (3 x ) in between the batches

↓

Start to prepare for the next batch

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## Storing of the samples

## Fridge

- Space limited in the fridge
- Stack the samples in crates
- Samples were stored at 4 ° C until all six batches were prepared

## Preparation of the documentation

- Hard copies of the forms for the results and the method information were included in each box
- Labels of all the participants were prepared

## Packaging of the samples

## Packaging of the samples

## Labeling & sorting

# Sample pick-up and dispatch

# Transport of parcels DHL , 29 June 2012

## Calculation of reference values

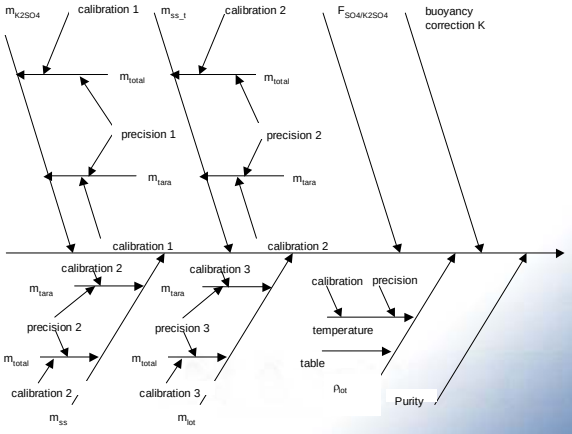
- Identify all sources of uncertainty in the analytical measurements and list them with the use of a fishbone diagram.
- The identified sources were:
  - Purities the chemicals
  - Uncertainty of the three balances used:
    - Sartorius Balance ED124S
    - Sartorius Balance ED42025-CW
    - Sartorius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

## Measurement uncertainty of reference values

- The combined standard uncertainties (mg/l), the combined relative standard 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.

# Identification of uncertainties using fishbone diagram

$$c_{lot} = \frac{m_{K_2SO_4} \cdot F_{SO_4/K_2SO_4} \cdot P \cdot m_{ss} \cdot \rho_{lot}}{m_{ss\_t} \cdot m_{lot} \cdot K}$$

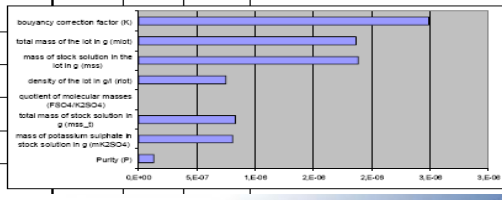





# Calculation of measurement uncertainty

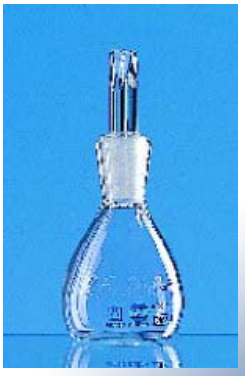
$$c_{lot} = \frac{m_{K_2SO_4} \cdot F_{SO_4/K_2SO_4} \cdot P \cdot m_{ss} \cdot \rho_{lot}}{m_{ss\_t} \cdot m_{lot} \cdot K}$$

| parameter | estimated value | specification | probability distribution | divisor | standard uncertainty ($u_i$) | sensitivity coefficient ($c_i$) | sensitivity coefficient ($c_i$) |
|---|---|---|---|---|---|---|---|
| Purity (P) | 0,99999 | 0,00001 | Rechteck | $\sqrt{3}$ | 5,7735E-06 | $\frac{m_{K_2SO_4} \cdot F_{SO_4/K_2SO_4} \cdot m_{ss} \cdot \rho_{lot}}{m_{ss\_t} \cdot m_{lot} \cdot K}$ | 0,022641974 |
| mass of potassium sulphate in stock solution in g ($m_{K2SO4}$) | 5,1308 | | | | 0,000163291 | $\frac{F_{SO_4/K_2SO_4} \cdot P \cdot m_{ss} \cdot \rho_{lot}}{m_{ss\_t} \cdot m_{lot} \cdot K}$ | 0,004412908 |
| total mass of stock solution in g ($m_{ss\_t}$) | 501,44 | | | | 0,016412909 | $-\frac{m_{K_2SO_4} \cdot F_{SO_4/K_2SO_4} \cdot P \cdot m_{ss} \cdot \rho_{lot}}{m_{ss\_t}^2 \cdot m_{lot} \cdot K}$ | -4,51535E-05 |
| quotient of molecular masses ($F_{SO4/K2SO4}$) | 0,55126425 | | | | 0 | $\frac{m_{K_2SO_4} \cdot P \cdot m_{ss} \cdot \rho_{lot}}{m_{ss\_t} \cdot m_{lot} \cdot K}$ | 0,041072403 |
| density of the lot in g/l ($\rho_{lot}$) | 997,5835337 | | | | 0,032977359 | $\frac{m_{K_2SO_4} \cdot F_{SO_4/K_2SO_4} \cdot P \cdot m_{ss}}{m_{ss\_t} \cdot m_{lot} \cdot K}$ | 2,26966E-05 |
| mass of stock solution in the lot in g ($m_{ss}$) | 201 | | | | 0,016735821 | $\frac{m_{K_2SO_4} \cdot F_{SO_4/K_2SO_4} \cdot P \cdot \rho_{lot}}{m_{ss\_t} \cdot m_{lot} \cdot K}$ | 0,000112646 |
| total mass of the lot in g ($m_{lot}$) | 49901 | | | | 4,111707712 | $-\frac{m_{K_2SO_4} \cdot F_{SO_4/K_2SO_4} \cdot P \cdot m_{ss} \cdot \rho_{lot}}{m_{ss\_t} \cdot m_{lot}^2 \cdot K}$ | -4,53733E-07 |
| bouyancy correction factor (K) | 1,001031487 | | | | 0,00011 | $-\frac{m_{K_2SO_4} \cdot F_{SO_4/K_2SO_4} \cdot P \cdot m_{ss} \cdot \rho_{lot}}{m_{ss\_t} \cdot m_{lot} \cdot K^2}$ | -0,022618417 |
| result (g/l) | 0,022641747 | | | | | | $u_c$ |
| **result in mg/l** | **22,64174733** | | | | | | |
| **standard uncertainty in mg/l** | **0,063891594** | | | | | | |
| **rel Unsicherheit** | **0,02%** | | | | | | |
| **erw. Unsicherheit** | **0,007783987** | | | | | | |
| **erw. rel. Unsicherheit** | **0,03%** | | | | | | |



# Density

- Samples and a bottle with pure water were put in the weighing room.
- Temperature of the water and the samples were measured using a calibrated thermometer.
- A 100 ml empty pycnometer was weighed 10 times.
- Pycnometer was filled with water and weighed again 10 times.
- Between each measurement the pycnometer was opened and filled again - uncertainty of the filling process.
- The pycnometer was filled and weighed with the samples (3 x )
- The densities and uncertainty of the measurements were calculated.



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# Biggest uncertainty components from histograms

**Mass of the stock solution**

- F, Fe, Mn, Al,
- Pb, Cu, Zn, Cr,
- Ni, As, Cd,Co

**Purity**

- $K_2SO_4$,KCl,$KNO_3$,
- $KH_2PO_4$,CaCl,
- $Mg(NO_3)_2.6H_2O$,NaCl,
- Cr

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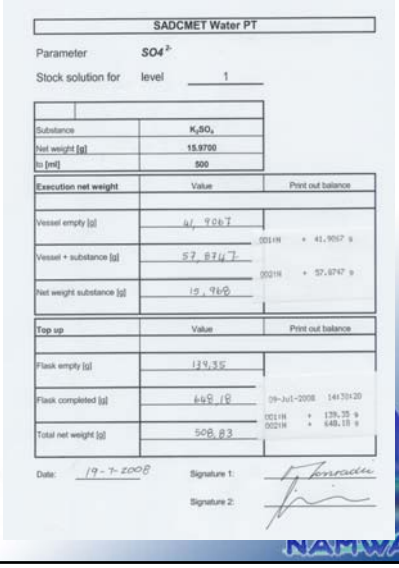
# Documentation

Certificates are documented:

- Certificate of analyses (COA) for reagents used
- Calibration certificate for thermometer
- Calibration certificate for pycnometer
- Calibration certificates for balances

# Documentation of weighing

- Proof of printings were pasted against all weighings
- Cut and pasted next to the written weighing for proof of the traceability
- Calculations are checked signed
- Confirmed by 2nd person



SADCMET Water PT

Parameter $SO4^{2-}$

Stock solution for level 1

| Substance | $K_2SO_4$ |
|---|---|
| Net weight [g] | 15.9700 |
| to [ml] | 500 |

| Execution net weight | Value | Print out balance |
|---|---|---|
| Vessel empty [g] | 41.9067 | 0011N + 41.9067 g |
| Vessel + substance [g] | 57.8747 | 0021N + 57.8747 g |
| Net weight substance [g] | 15.968 | |

| Top up | Value | Print out balance |
|---|---|---|
| Flask empty [g] | 139.35 | |
| Flask completed [g] | 648.18 | 09-Jul-2008 14:30:20 0011N + 139.35 g 0021N + 648.18 g |
| Total net weight [g] | 508.83 | |

Date: 19-7-2008 Signature 1: Signature 2:

## Problems during 2012

- Angola: Paid but did not submit results
- Kenya: Delay with customs
- Kenya: One lab requested 2 parcels and an additional parcel was sent without any delays.
- Again problems with files > 5MB is blocked by NamWater IS and cannot be received
- Shortage of staff in and scheduling of a PT round between normal laboratory activities is a challenge.

## Problems

- Registration forms not received in time or some not at all
- Laboratory information and contacts are not available
- Registration forms often not all clear
- Return date for the results : 10th of August 2012
- Last results were received in October only
  - caused a delay with evaluation report
- The evaluation report not distributed according to schedule

# Closure