Co-ordination of an organochlorine pesticides in drinking water proficiency testing scheme in South(ern) Africa

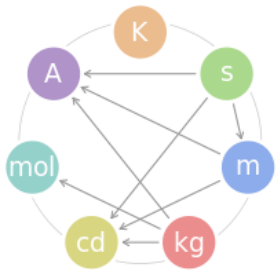
D Prevoo-Franzsen

8th Eurachem PT workshop, Berlin, Germany

09 Oct 2014

Your measure of excellence

NMISA



Our mandate:

- To maintain the **SI units**
- To **ensure global measurement equivalence.**
- Reference measurements, CRMs

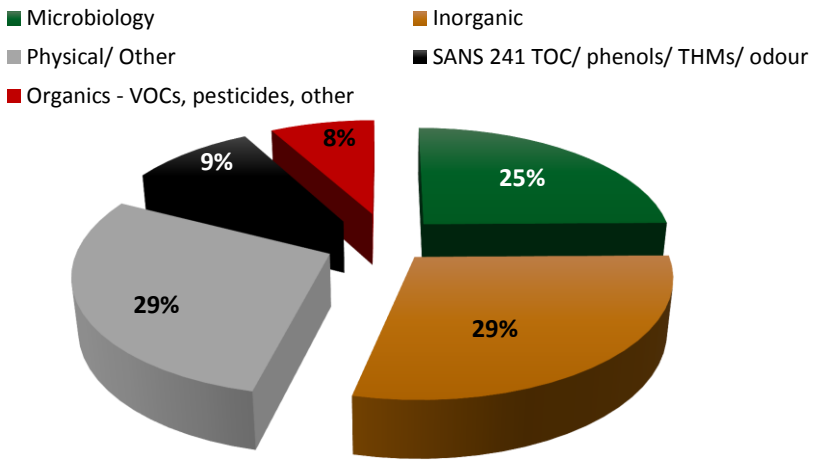
Proficiency testing schemes

- Currently 4 accredited PT providers in South Africa
  - 3 - Medical/Clinical diagnostics
  - 1 - Water Chemistry

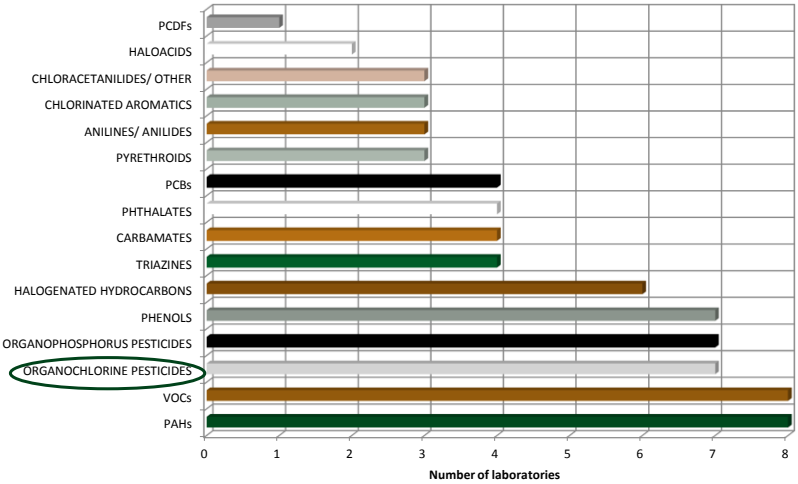
Typical accreditation schedules for PT providers

Materials Supplied	Title of Scheme	Test Performed	
Water	Heavy Metals (Group 1)	Aluminium	Manganese
		Barium	Molybdenum
		Beryllium	Nickel
		Boron	Silicon
		Cadmium	Strontium
		Chromium	Vanadium
		Cobalt	Zinc
		Copper	Mercury
		Iron	Arsenic
		Lead	Selenium
	Nutrient and Oxygen demand (Group 2)	Kjeldahl Nitrogen	Oxygen Absorbed
		Nitrate	Chemical Oxygen demand
		Ammonia	Total Organic Carbon
		Total Phosphate	Dissolved Organic Carbon
		Orthophosphate	
	Major Constituents (Group 3)	pH	Potassium
		Conductivity	Chloride
		Dissolved solids	Flouride
		Calcium	Sulfate
		Magnesium	Alkalinity
		Sodium	Turbidity
		Nitrate	

Water quality testing – ISO 17025 SANAS accredited facilities



Water testing survey – organics



Analyte	Concentration range (ng/ℓ)		NMISA-PT-ORG10 TRIAL: May 2012	NMISA-PT-ORG12 R1: Feb 2013	NMISA-PT-ORG12 R2: Aug 2013	NMISA-PT-ORG15 R1: Feb 2014
Aldrin	10	50	43.8		42.2	
cis-chlordane	10	50		35.3		
trans-chlordane	10	50				39.0
p,p'-DDT	20	120	66.5		107.7	
o,p-DDT	20	120			104.9	
p,p'-DDE	20	120	69.5			97.5
p,p'-DDD	20	120		60.3		
Dieldrin	10	50				39.7
Endosulfan I	100	300		242.7		
Endosulfan II	100	300			135	
Endosulfan sulphate	100	300				242.2
Endrin	20	120		108.3		
Heptachlor	10	50		35.8		
Heptachlor epoxide	10	50				
Alpha HCH	20	120			87.0	
Beta HCH	20	120				
Delta HCH	20	120				98.8
Gamma HCH (Lindane)	20	120	132.1			

Sample description

500 ml or 1000 ml water sample

- ✕ Accommodation
- ✕ Bulk preparation
- ✕ Homogeneity
- ✕ Stability

€ 140

2 ml solvent sample

- ✓ Accommodation
- ✓ Bulk preparation
- ✓ Homogeneity
- ✓ Stability

€ 310

Sample description

2 x 1000 mL diluted water sample previously spiked with OCPs

Results due within **3 weeks**

Sample preparation - assigned value

5.2 Formulation

Purity and density-corrected gravimetric preparation value of the solutions;

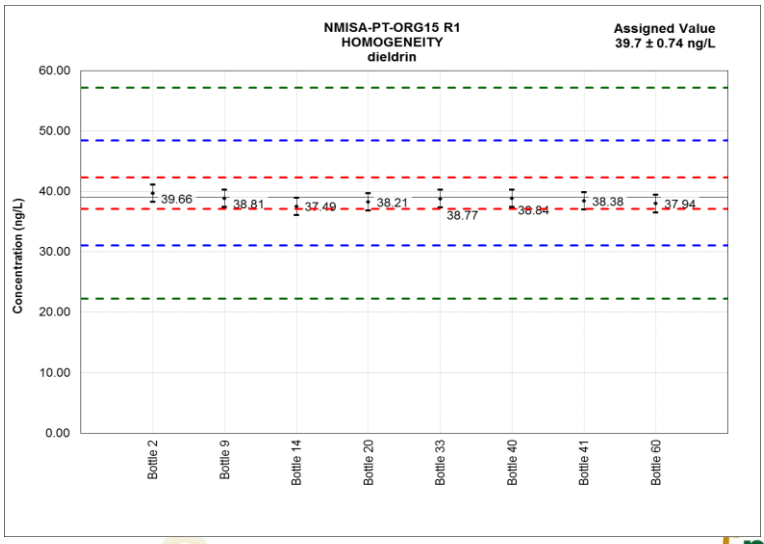
The uncertainty associated with the PTS assigned values was determined using the following uncertainty contributors described in equation 1:

$$u_{AV} = \sqrt[2]{u_{purity}^2 + u_{mass}^2 + u_{bottling}^2 + u_{homog}^2} \quad [1]$$

Homogeneity and stability assessment

- Extraction
  - 1 L extracted
  - Horizon SPE DEX C18 Disks
- Pre-concentration
  - Water removed (DryDisk)
  - Solvent dried down (N_2, 35°C)
  - Reconstituted in 100 µL
- Analysis
  - GC-TOFMS
- Quantification
  - Double isotope dilution mass spectrometry

Homogeneity

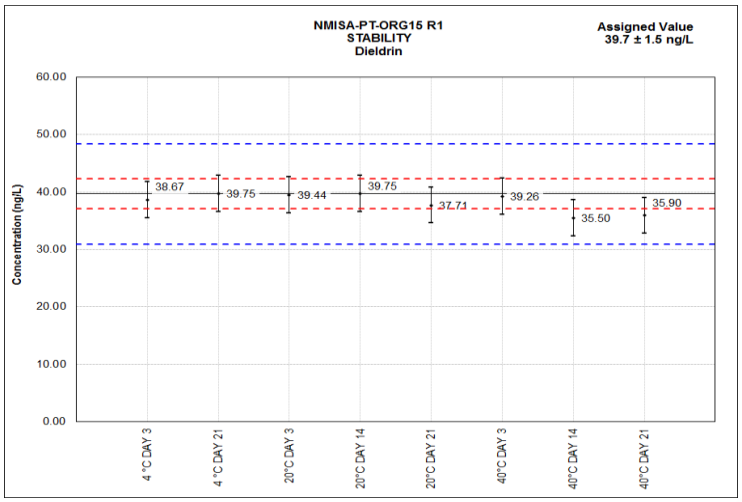


RV + 1x σ_p

0.3 x σ_p

RV + 2 x σ_p

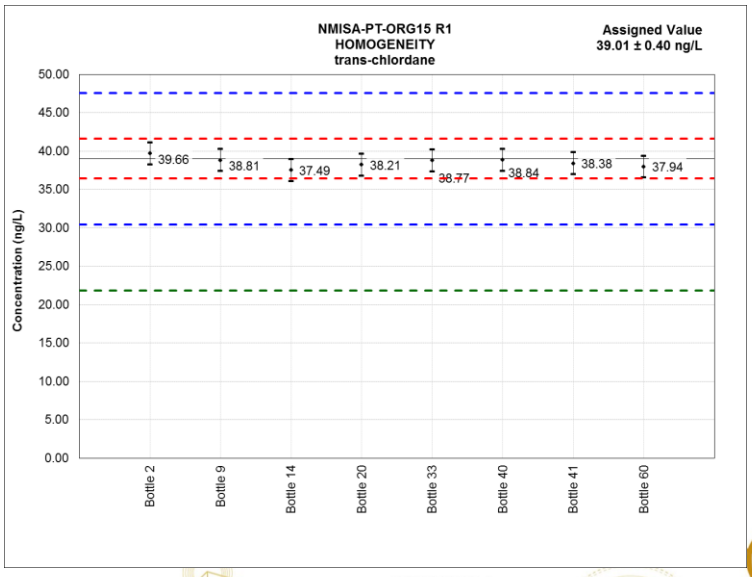
Stability testing



RV + 1x σ_p

0.3 x σ_p

Homogeneity

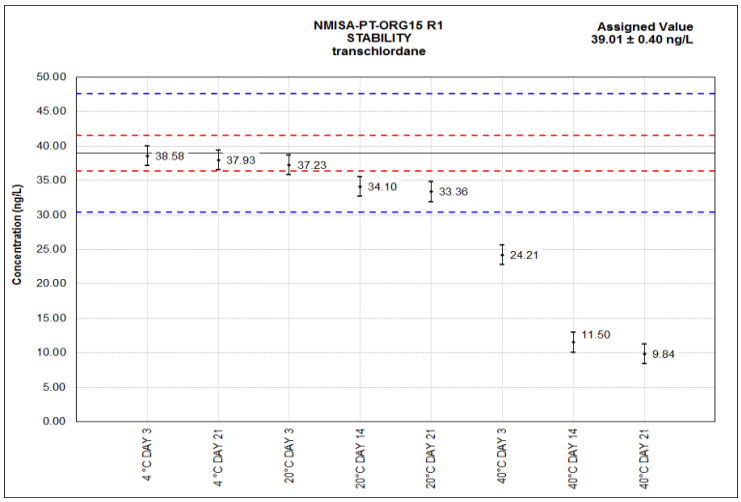


RV + 1x σ_p

0.3 x σ_p

RV + 2 x σ_p

Stability testing



RV + 1x σ_p

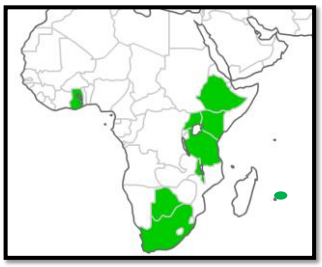
0.3 x σ_p

Reporting results

- Measurement results (ng/L) incl. uncertainty of measurement
- Technical information
  - Extraction
  - Instrumental Analysis
  - Quantification
    - Recoveries
    - Purity
    - Traceability of calibration standards
    - Measurement equation
    - Uncertainty budget
- Other observations

nmisa
National Metrology Institute of South Africa

Standard deviation of proficiency assessment



- 7 local laboratories
- 7 countries (2 laboratories in Kenya)

6.2 Prescribed value

6.3 By perception

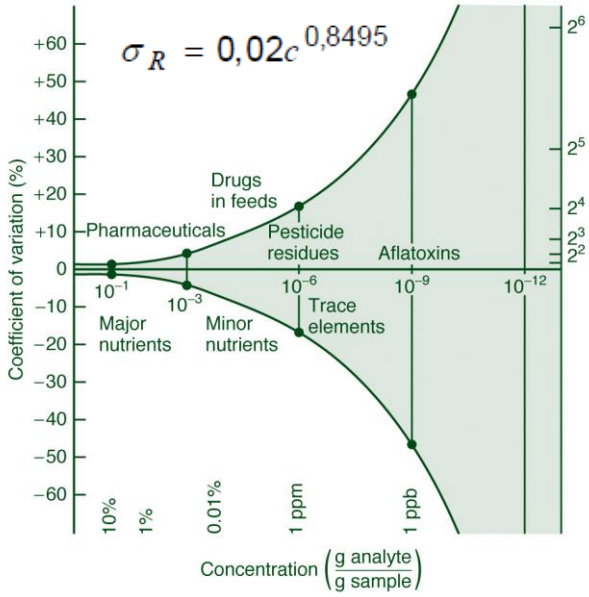
6.4 **From a general model** HORWITZ

6.5 From the results of a precision experiment

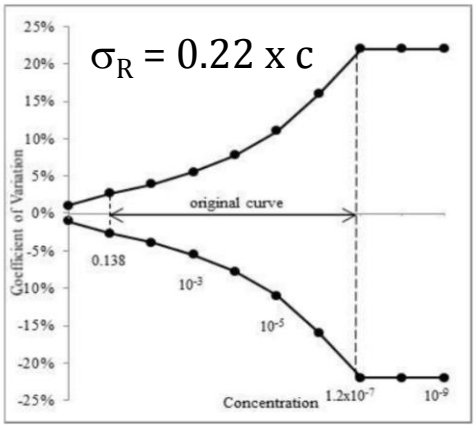
6.6 From data obtained in a round of a proficiency testing scheme

nmisa
National Metrology Institute of South Africa

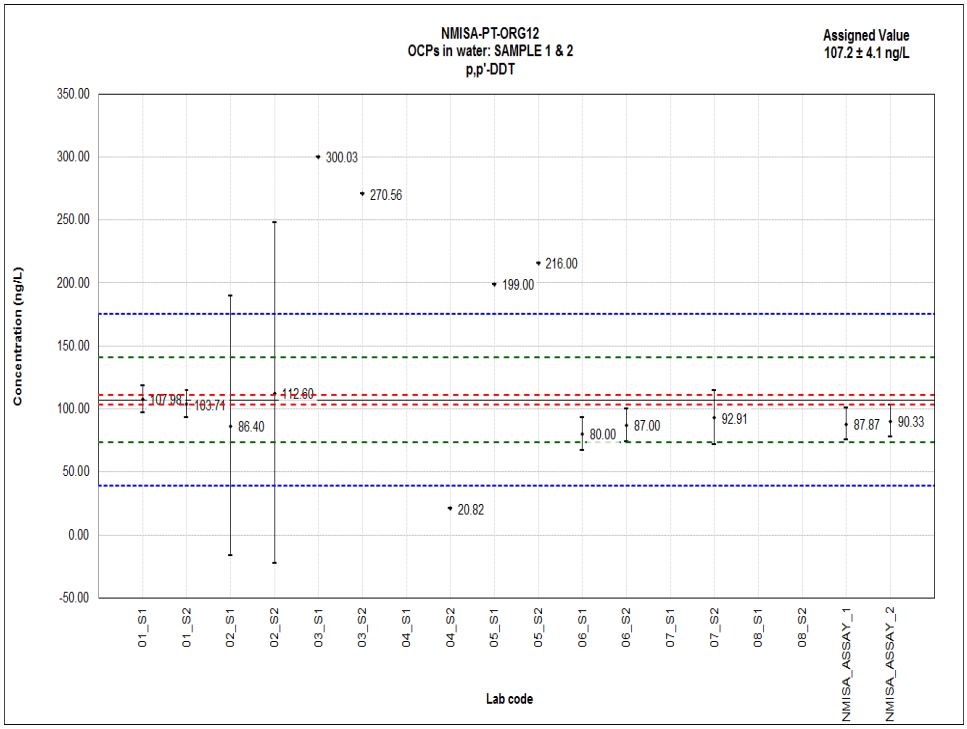
Horwitz model

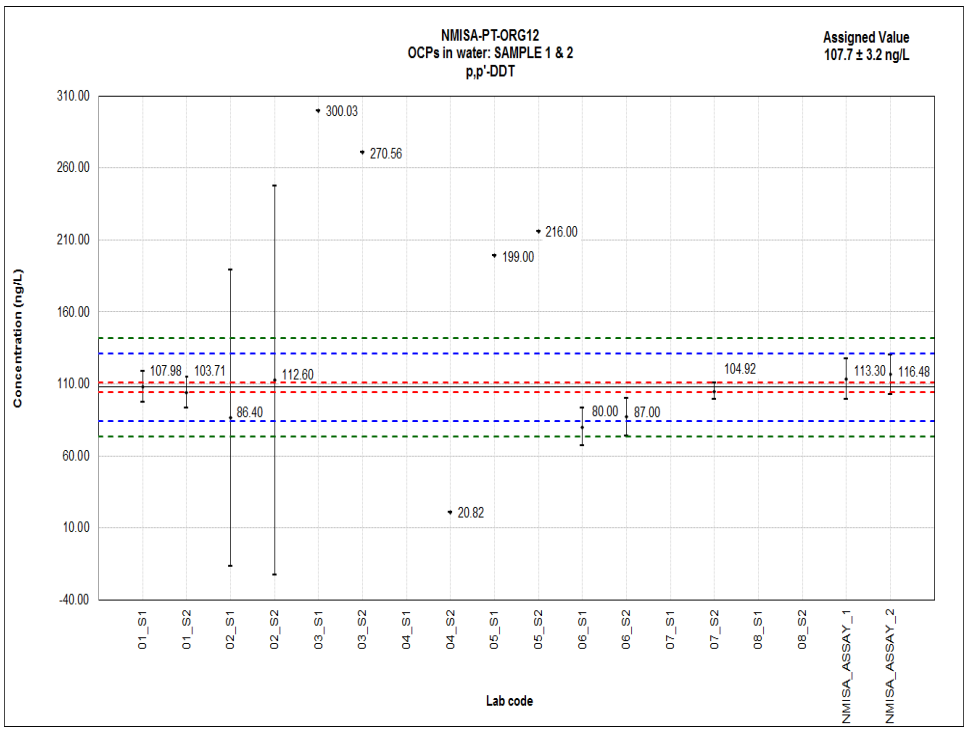


Adjusted Horwitz model

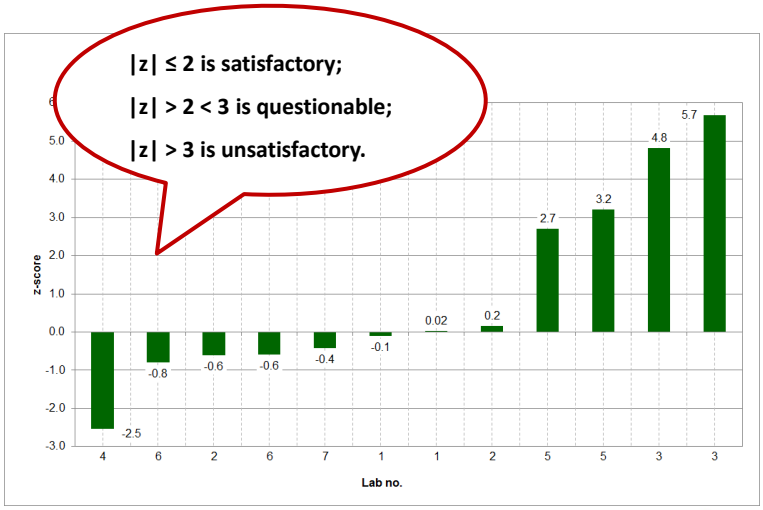


Images sourced from: "Horwitz equation as quality benchmark in ISO/IEC 17025 testing laboratory" (14)


NMISA-PT-ORG12
OCPs in water: SAMPLE 1 & 2
p,p'-DDT
Assigned Value
107.2 ± 4.1 ng/L
Concentration (ng/L)
350.00
300.00
250.00
200.00
150.00
100.00
50.00
0.00
-50.00
300.03
270.56
216.00
199.00
107.98
103.71
112.60
86.40
80.00
87.00
92.91
87.87
90.33
20.82
01_S1
01_S2
02_S1
02_S2
03_S1
03_S2
04_S1
04_S2
05_S1
05_S2
06_S1
06_S2
07_S1
07_S2
08_S1
08_S2
NMISA_ASSAY_1
NMISA_ASSAY_2
Lab code


NMISA-PT-ORG12
OCPs in water: SAMPLE 1 & 2
p,p'-DDT
Assigned Value
107.7 ± 3.2 ng/L
Concentration (ng/L)
310.00
260.00
210.00
160.00
110.00
60.00
10.00
-40.00
300.03
270.56
216.00
199.00
107.98
103.71
112.60
86.40
80.00
87.00
104.92
113.30
116.48
20.82
01_S1
01_S2
02_S1
02_S2
03_S1
03_S2
04_S1
04_S2
05_S1
05_S2
06_S1
06_S2
07_S1
07_S2
08_S1
08_S2
NMISA_ASSAY_1
NMISA_ASSAY_2
Lab code

Reporting - Performance statistics



Reporting – E_n number

$|E_n| \leq 1$ is satisfactory;

$|E_n| > 1$ is unsatisfactory.

Lab Code	SAMPLE 1&2				
	Analyte	Concentration (ng/L)	Coverage Factor (k)	Expanded Uncertainty (ng/L)	En
1	p,p'-DDT	107.98	1.96	10.74	0.1
	p,p'-DDT	103.71	1.96	10.74	-0.3
2	p,p' DDT	86.4	2	103	-0.2
	p,p' DDT	112.6	2	135	0.04
6	p,p'-DDT	87	2	13	-1.5
	p,p'-DDT	80	2	13	-2.0
7	p'p-DDT	92.91	1.96	21.53	-0.7
(AV)	p,p'-DDT	107.2	2	4.1	RV

Reporting

Lab Code	Sample volume (mL)	Sample preparation	Analysis	Calibration	Analytical standards	Recovery% and correction applied
1	1000	Samples were extracted using automated SPE with a C18 disk. Prior to extraction samples were spiked with labelled isotopes. A labelled isotope was added for each analyte that could be present at the median of the expected concentration range. After extracts were filtered using a hydrophobic membrane filter to remove trace amounts of water, evaporated to dryness at 35℃ under a gentle stream of nitroge n. The extracts were then reconstituted in 50 µl of iso-octane and proceeded to instrumental analysis.	LECO Pegasus III GC-TOFMS	A seven point matrix-matched calibration was used	Carbon labelled internal standards were used and the standards were added prior to extraction	Due to the use of labelled isotopes no recovery corrections were applied to these results
			Rxi-XLB (30 meter; 0.25 mmID, 0.25 µm df)	IDMS	All standards purchased from ISO34 Accredited supplier	
			Three triplicate 1 µl splitless injection was used with an inlet temperature of 225℃. Oven ramp: 120//10//230/2//10//320/1. The transfer line and source temperature was 250℃, the mass spectra was collected at a rate of 6 spectra per second.		Restek Lot AO82301 Exp Jun 2015;Restek Lot AO89924 Exp Nov 2016;Restek Lot AO92438 Exp Dec 2016;Restek Lot AO89487 Exp Nov 2016	
2	250	Measure 250 ml of the water using measuring cylinder in a separating funel. Add 5 g of anhydrous sodium sulphate and extract it with 50ml of dichloromethane. Dry the DCM layer with anhydrous sodium sulphate. Rota evaporate at 45℃. Solvent exchange with; acetonitrile for LC/MS/MS (azinphors methyl) or isooctane for GC/MS (chlorpyriphors). Transfer 2ml in GC or LC/MS/MS vial for analysis. Inject 2µl for GC and 5µL for LC/MS/MS analysis.	GC- MS (GC- 7890ALS, MS-5975), LC/MS/MS (6430)	external calibration used	Dr Erhenstopher Germany, purity 99±0.5%	N/A
			GC/MS (DB5MS- 30 mx0.1 µmx.0.25 µl), LC/MS/MS (Zorbax Eclipse plus C18 rapid resolution HD, 2.1x50 mmx1.8 µm	5 calibration points used for all the above analytes (0.01-1mg/l)		
			GC MS- 60℃ to 165℃ hold 1 min, 165℃ to 280℃ hold for 5 minutes. LC MS/MS- mobile phase composition acetonitrile: water (5mM formic acid): time 0 gradient 100% water time 15 minutes 100% acetonitrile flow rate 0.5			

Reporting

Lab Code	Estimation of uncertainty
1	For each analyte, the purity of the standard used for quantification, the recovery and reproducibility of the measurement and the error on the calibration curve were considered in the uncertainty
2	Reference Technical Report No. 1/2007 March 2007 on Measurement uncertainty revisited: Alternative approaches to uncertainty evaluation pg 54 estimation of uncertainty based on relative standard deviation of recoveries
3	UoM reported with major contributors from precision and recovery.
4	UoM was done according to the GUM method to obtain UoM.
5	Estimated UoM provided - no details
6	UoM estimated, uncertainty contributors incl. standards purity, absorbance, recovery, volume and mass.
7	None determined
8	For each analyte, the purity of the standard used for quantification, the recovery and reproducibility of the measurement and the error on the calibration curve were considered in the uncertainty
NMISA	UoM estimated using bracketing IDMS equation.

Reporting

	classical approach	limited sample vol. extracted	large vol. inj.	reduced recon. vol.	pre-concentr. & thermal desorption
lowest expected OCP conc. (ng/ℓ)	10	10	10	10	10
sample volume used (ℓ)	1	0.2	1	1	0.02
*expected OCP mass in extract (ng)	10	2	10	10	0.2
after drying down, reconstit. vol (mℓ)	1	1	1	0.1	n/a
conc. in GC vial (ng/µℓ)	0.01	0.002	0.01	0.1	n/a
splitless GC inj vol (µℓ)	1	1	5	1	#
mass on GC column (pg)	10	2	50	100	200
		"ND"			

*** assuming 100% recovery**

 # assuming 100% recovery and desorption

Summary - participant challenges

- Appropriate use of traceable calibration standards
- external/ internal standards
- appropriate use of uncertainty
- Cost (courier fees)
- analysis delays (sample stability)/limited time frame
- appropriate sample preparation/ pre-concentration

Summary - co-ordinator challenges

- Courier/customs challenges
- Sample stability
- Financial Feasibility
  - Labour intensive
  - CRMs
  - Limited number of participants

Workshop/meetings planned

- Re-evaluate participant needs
- Technical training
- Consider courier options

Acknowledgements

- NMISA proficiency testing schemes are funded by the **South African department of trade and industry**
- Additional support from the International Technical Cooperation (ITC) of the Physikalisch-Technische Bundesanstalt **(PTB)**, the national metrology institute of Germany
- **laboratories** that participated in the various rounds of the PTS
- **Co-authors**

  Dr M Fernandes-Whaley; Dr L Quinn and Dr N Nhlapo

nmisa
National Metrology Institute of South Africa