

# **Study protocol for proficiency testing**

## **Pesticides in fruit 2018/19**

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## Foreword

The National Metrology Institute of South Africa (NMISA) was established under the Measurement Units and Measurement Standards Act No 18 of 2006. The NMISA is committed to supporting laboratories through the provision of proficiency testing schemes (PTs) that afford participating laboratories the opportunity to regularly demonstrate their continued analytical measurement competence.

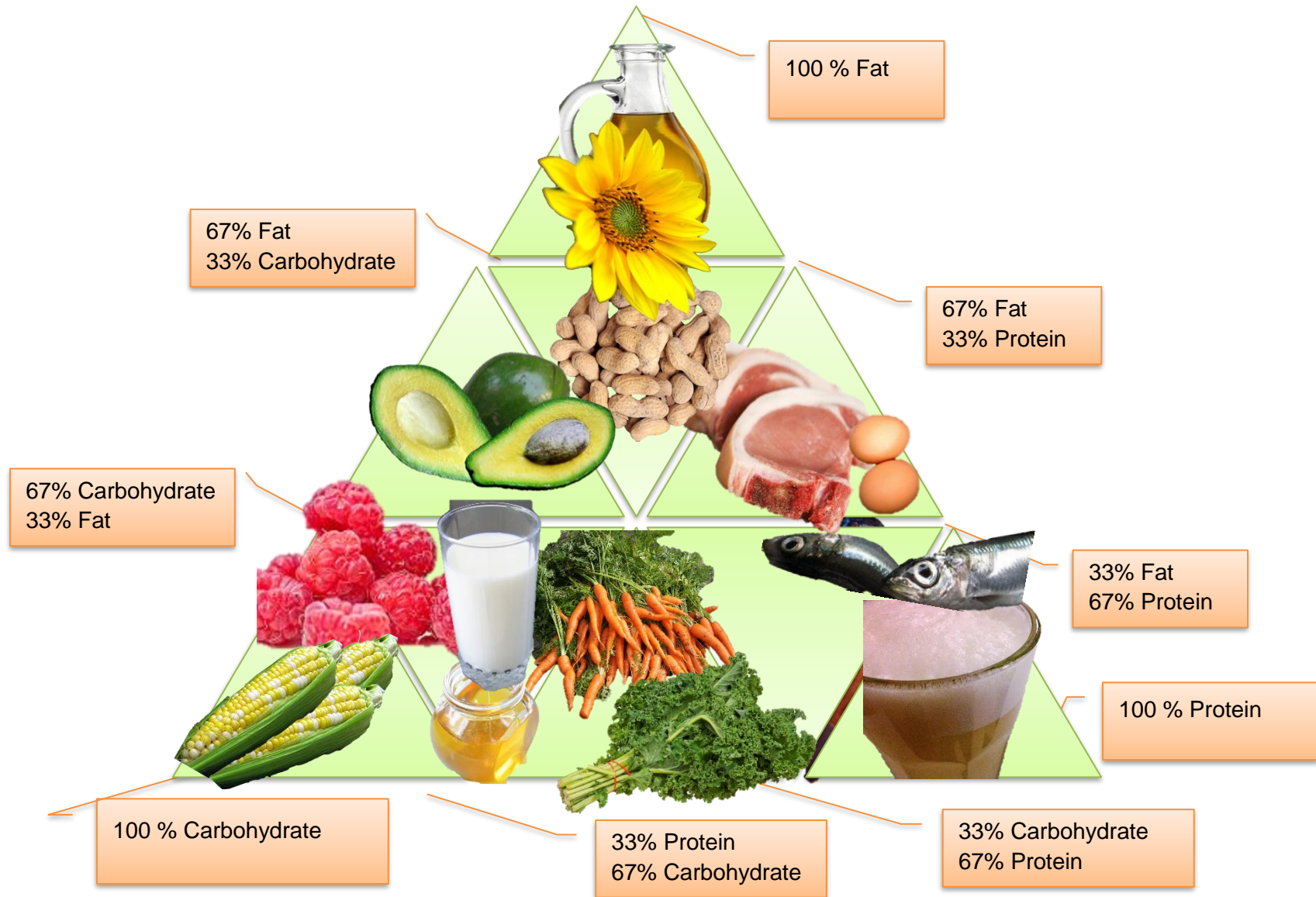
PTs currently offered by the NMISA Organic Analysis Section include:

- Organochlorine pesticides in water
- Aqueous ethanol (alcohol content in beverages and forensic blood alcohol analysis)
- Aqueous sodium fluoride (blood sample preservatives)
- *Ad-hoc* traceable gravimetrically prepared spike solutions for benchmarking when no PTs are commercially available.

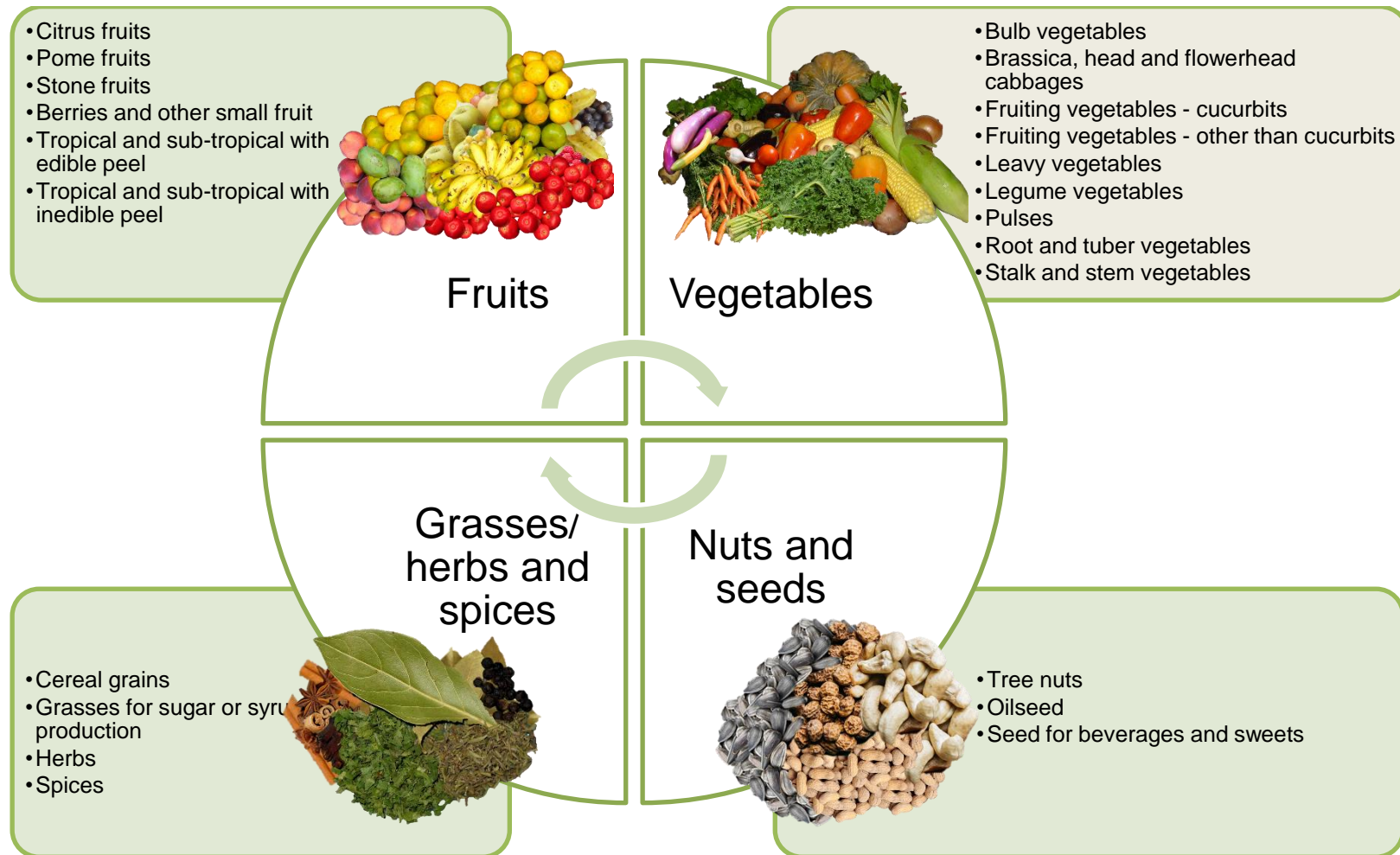
The NMISA provides a confidential service to participants that allows a laboratory to assess the accuracy of their test results using their routine laboratory methodologies, thereby testing the effectiveness of their methods and quality assurance programs. The provided PT report is generated to assist laboratories in identifying areas of improvement within their current quality system. A workshop will be held annually to discuss technical difficulties and assist with resolving general analytical problems identified.

The current study protocol has been designed to support routine analytical laboratories testing pesticide residues in agricultural commodities. The PT will be used to assess the various matrices represented in the AOAC food composition triangle (**Figure 1**) over the course of five years. For the 2018/19 financial year PTs will focus on pesticides in fruit, a high carbohydrate, low protein and fat matrix. These are Class A commodities, primarily of plant origin (**Figure 2**). The matrices selected for this year are lemons and apricots.

Specific attention has been paid to tailoring the scheme to current export limits as well as maximum residue levels for the South African market. The target pesticide and commodities were selected to match the growth season within South Africa. Pesticides selected for analysis in this PT represents various chemical classes associated with the specific commodity selected. Thereby accommodating the routine analysis performed by the majority of laboratories at the time the proficiency test material is circulated.



**Figure 1:** The AOAC food composition triangle (modified from Phillips *et al.*, 2013)



**Figure 2:** A summary of class A commodities, primarily of plant origin (modified from Codex *Alimentarius*, 2016)

# Proficiency testing program

## Scheme provider

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## Participation fees and charges

The cost of participation in one round of the PT scheme is R 6000.00 (0% VAT, please note that we are not a VAT registered company). This fee includes two test samples and a blank sample of 50 g. Two participants may submit a result per laboratory using the sample provided. For more than two participants per laboratory an additional fee will be levied and additional material supplied. A discount will be offered for laboratories participating in all three of the PT rounds, please refer to **Table 1**. After conclusion of the PT round, a report will be issued. Please find registration form attached as an addendum to this document, for participation an official quotation will be provided. Transport costs are not included in these fees please refer to the section "Test sample transport" below.

**Table 1:** Summary of participation fees

Participation	Participation fees
Single round	R 6 000.00
All three rounds	R 15 000.00

## Reports provided to participants

A report will be issued to each participant detailing their performance in the PT. The report will contain the following information: description of the material used and how it was prepared; verification of target values, a summary of participating laboratories analytical techniques and data evaluation. The PT value will be determined using participant consensus or using the gravimetrically spiked values depending on the number of participant results received. A full PT report will be issued to each participating laboratory within one month of the submission deadline.

## Statistical analysis

The participant data will be processed according to ISO 13528:2005 (Statistical methods for use in proficiency testing by interlaboratory comparisons). A z-score will be used to determine the individual laboratories performance based on the following equation:

$$z = \frac{x_{laboratory} - x_{PT\ value}}{\sigma}$$

Where:

$x_{laboratory}$	= the result reported by the participant
$x_{PT\ value}$	= the PT value (NMISA reference value or participant consensus value)
$\sigma$	= the standard deviation for the PT

The target standard deviation used to calculate the z-score will be based on the Horwitz performance model, where the maximum measurement result variation expected between laboratories is 22%.

## Scheme details

The agricultural commodities and pesticide residues selected for this proficiency testing scheme have been selected based on routinely tested seasonal commodities and their regulated pesticide residue limits respectively. Concentration levels range from below the regulated export limits to above the maximum residue limit for South Africa.

## Test samples

The test samples will consist of a homogenised raw fruit sludge that has been spiked with a known concentration of **selected pesticides** from the pesticide list described in **Table 2**. For each round a participant will be provided with 50 g of test sample. A portion of the un-spiked commodity that may contain pesticide residues not spiked in the round will also be provided to be used as a blank control.

**Table 2:** List of possible matrix specific pesticides included within the 2018/19 proficiency testing scheme

Pesticide	Pesticide	Pesticide
2.4 D	Ethylene bisdithiocarbamates	Oxydementon-Methyl
Abamectin	Fenamiphos	Oxytetracycline
Acetamiprid	Fenazaquin	Parathion
Acrinathrin	Fenbuconazole	Phenthoate
Aldicarb	Fenbutatin oxide	Phosalone
Amitraz	Fenpropathrin	Phosphorus acid
Azinphos-methyl	Fenthion	Piperonyl Butoxide
Azoxystrobin	Fipronil	Pirirmicarb
Benomyl	Fluazifop-P-Butyl	Prochloraz
Cypermethrin	Flucorochloridone	Procymidone
Bitertanol	Formetanate	Profenofos
Bromucinazole	Fosetyl-A1	Propargite

<b>Pesticide</b>	<b>Pesticide</b>	<b>Pesticide</b>
Bromopropylate	Fosthiazate	Propineb
Buprofezine	Gamma-BHC	Propyzamide
Cadusafos	Gauzatine	Prothiofos
Captan/Captab	Gibberellic acid	Pyraclostrobin
Carbaryl	Haloxypop	Pyrethrins
Chinomethionat	Imazalil	Pyriproxyfen
Chlorphenapyr	Imidacloprid	Spinosad
Chlorpyrifos	Iprodione	Spirodiclofen
Chlorpyrifos	Isazophos	Tebuconazole
Copper Oxychloride	Kresoxim-Methyl	Teflubenzuron
Cyhalothrin	Mancozeb	Temephos
Cyhexatin	Maneb	Terbufos
Dementon-S-Methyl	Malathion	Tetradifon
Diazinon	Metalaxyl- M	Thiabendazole
Dichlofluanid	Methamidophos	Thiometon
Dicofol	Methidathion	Thiophanate-methyl
Difenoconazole	Methiocarb	Thiram
Dimethoate	Methomyl	Triazophos
Dimethyl-didecyl	Methyl- Parathion	Trichlopyr
Diothiocarbamates	Metiram	Trichlorfon
Dithianon	Mevinphos	Trifloxystrobin
Endosulfan	Omethoate	Triflumuron
Ethoprophos	Oryzalin	Zineb

## **Test sample transport**

Samples will be packaged and transported in a manner to minimise deterioration of the sample in transit. Transport costs are calculated depending on the location of the participating laboratory and are therefore not included in the PT cost price. Upon registration, a quotation will be issued including transport costs. Local laboratories may collect the sample from the NMISA premises.

For international laboratories, please note that any import or quarantine permits remains the responsibility of the participating laboratory, and must be submitted to the NMISA prior to the shipment date. Participants are accountable for all customs and import duties.

All PT material shall be delivered and collected at the Applicant's own risk. The NMISA will not take responsibility for samples damaged during transport, although all due care will be exercised during packing to prevent this from occurring.

## **Methods of analysis**

Participants are requested to use the methods/ procedures used during routine sample analysis.

## **Information required for reporting**

An electronic result submission form will be sent to participants when samples are delivered/ collected. For each participant two results per pesticide per sample may be submitted.



The following information will be requested from participating laboratories:

- Method validation information
- Quality control measures implemented
- Method of extraction used
- Sample size analysed
- Instrumentation specification
- Analytical method information
- Recoveries for method and if a correction for recoveries is applied
- The method limit of detection and limit of quantification

## Scheme dates

**Table 3:** Pesticide in fruit PT scheme important dates

Matrix	Sample distribution	Results submitted by	Report issued by
Oranges	02 July 2018	30 July 2018	30 August 2018
Apples	08 October 2018	08 November 2018	08 December 2018
Apricots	10 December 2018	14 January 2019	15 February 2019

## References

- F. Cordeiro. Statistical methods for use in proficiency testing (2009). Institute for Reference Materials and Measurements. JRC –EC
- M.M. Phillips, K.E. Sharpless and S.A. Wise. Standard reference materials for food analysis (2013). *Analytical and Bioanalytical Chemistry*, 405: 4325 – 4335
- Codex Alimentarius International Food Standards: Codex pesticides residues in food online database (July 2016).

## PESTICIDES IN FRUIT PROFICIENCY TESTING SCHEME

### REGISTRATION FORM

PLEASE COMPLETE AND RETURN BY E-MAIL TO [lquinn@nmisa.org](mailto:lquinn@nmisa.org)

Deadline for registration is 31 May 2018

Name of laboratory			
Department			
Contact	Name		
	E-mail		
	Telephone		
	Address		
	Town/ City		
	Postal code		
	Country		
Delivery	Self-collect	<input type="checkbox"/>	Delivery <input type="checkbox"/>
My laboratory is interested in participating in the following tests:			
Oranges	<input type="checkbox"/>	Apples	<input type="checkbox"/>
		Apricots	<input type="checkbox"/>

I, \_\_\_\_\_ hereby confirm that a NMISA customer registration form has been completed and submitted to NMISA for official quotation and invoicing purposes. It is understood that registration for the proficiency testing scheme will only be confirmed upon receipt of a purchase order. Customs clearance and duties for International participants is for customer account.

\_\_\_\_\_  
Signature  
**Conditions of service**

\_\_\_\_\_  
Date

The NMISA is empowered by the Measurement Unit and Measurement Standards Act, Act No. 18 of 2006.

1. Services are carried out at the discretion of the NMISA, which reserves the right to decline any application for performance of services when deemed to be outside the scope of services of the NMISA.
2. Through acceptance of the original quotation, the Applicant agrees to the quoted fee and the conditions stated herein.
3. Payment is strictly 30 days from the date of invoice; or as mutually agreed in writing between the Applicant and the NMISA before the service commenced. The NMISA retains the right to ask for a deposit for international services.
4. Regarding certificates and reports:
  - a. A certificate or report, as appropriate, will be furnished to the Applicant on completion of the service;
  - b. Reports or certificates may be freely published by the Applicant provided that such publication is verbatim and in full;
  - c. The NMISA reserves the right after the termination of a period of one year or any period agreed upon, to publish or report in whole or in part together with any comments or additional matter which is considered desirable but will not in general expect to exercise that right except as regards service results deemed to be of general interest;
  - d. All participants details will remain fully confidential
  - e. Additional certified copies of certificates or reports, or re-issued certificates or reports will be subject to an additional fee, as determined on a case by case basis.
5. The NMISA cannot guarantee to complete the work within the estimated time but will consult the Applicant if it becomes apparent that estimate will be exceeded.
6. The Applicant hereby consents that the legal liability of the NMISA with regard to any damage whatsoever or a mistake made by the NMISA in services performed for the Applicant will be limited to the original quoted fee.

The values assigned to materials by NMISA are correct at the time of issue. Subsequently the accuracy will depend on such factors as the care exercised in handling and use of the material, the storage and transport of the material as well as the frequency of its use.