Study protocol for proficiency testing

Pesticides in fruit 2017/ 2018

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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, operated according to ISO 17043 requirements, include:

- Organochlorine pesticides in water
- Organophosphate 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 2017/2018 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 each represent one of the major subsections in this class: orange, a citrus; apple, a pome fruit; peaches a stone fruit and table grapes a representative of berries and other small fruits (**Figure 2)**.

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.

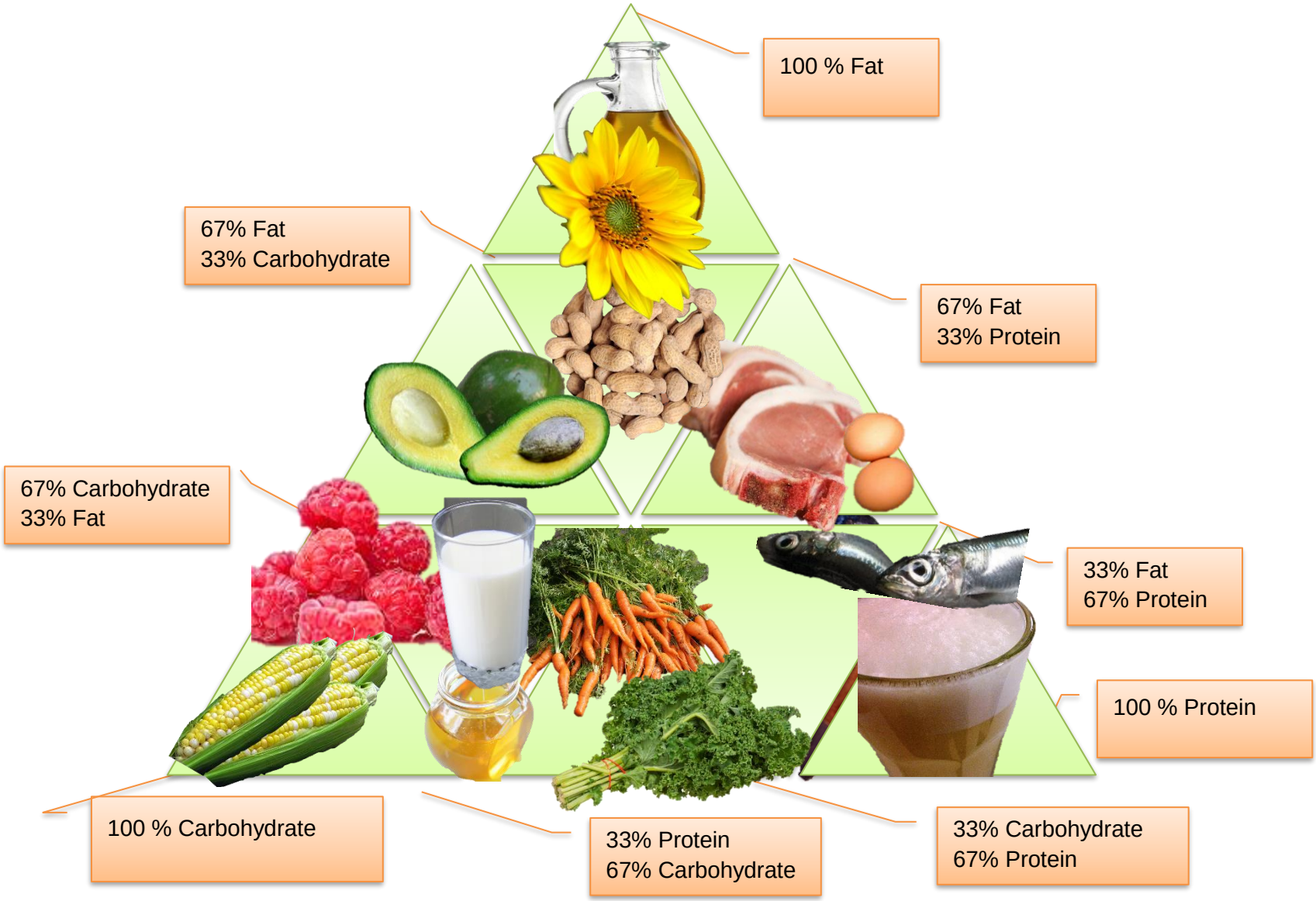

Figure 1: The AOAC food composition triangle (modified from Phillips *et al.,* 2013)

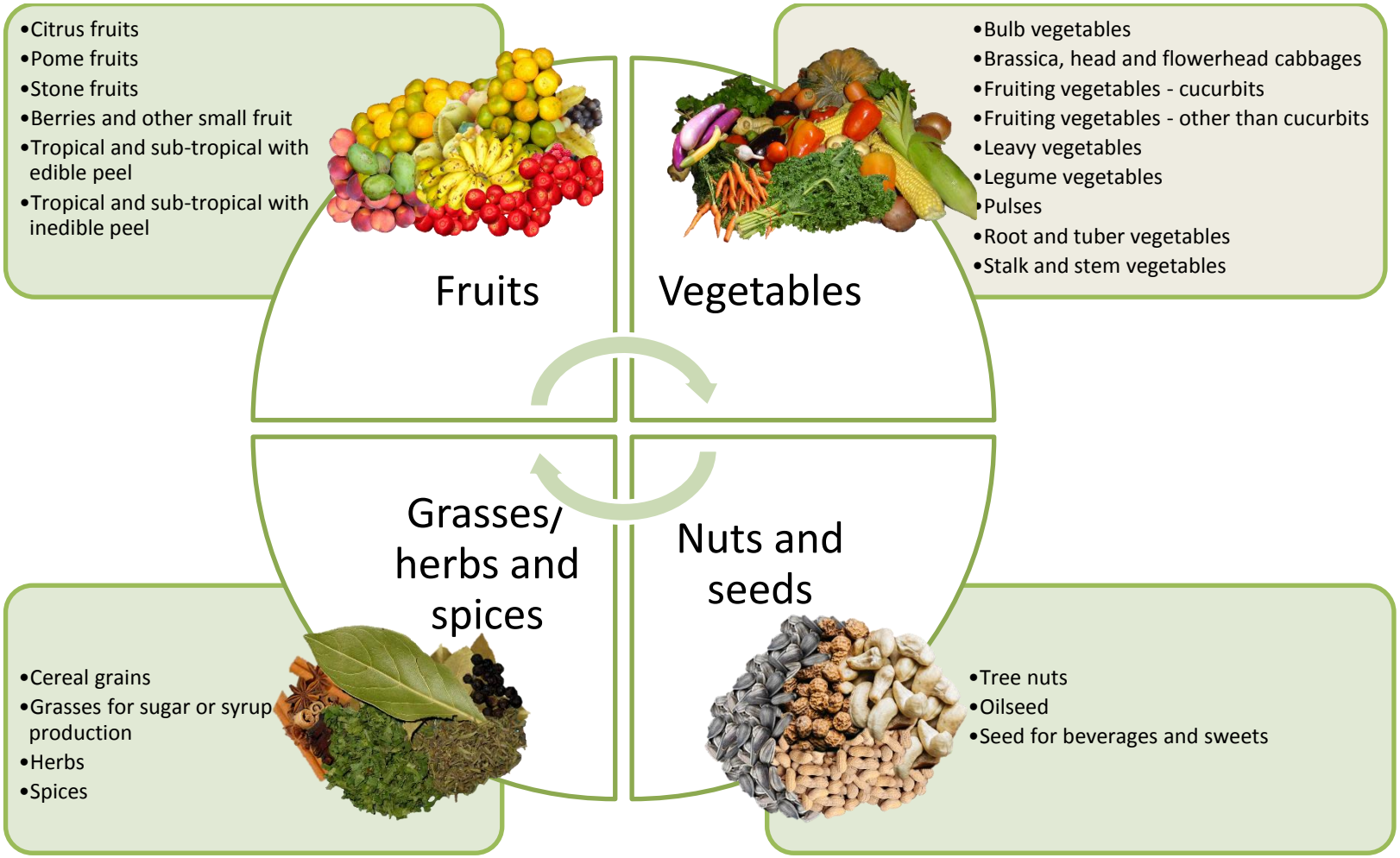

Figure 2: A summary of class A commodities, primarily of plant origin (modified from Codex *Alimentarius*, 2016)

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 each. 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 four of the PT rounds, please refer to **Table 1**. After conclusion of the PT round, a report will be issued. Upon registration for participation an official quotation will be provided. Please find registration form attached as an addendum to this document. 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 per round**
Single round	R 6 000.00
Two to three rounds	R 5 500.00
All four rounds	R 5 100.00 (R 20 400.00 in total)

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 for two of the studies (oranges and peaches) will be determined

using participant consensus. For the remaining two studies (apples and table grapes) a reference value will be issued by NMISA. This value will be calculated using gravimetrically spiked values. A report detailing a participant's z-score will be issued within one week and 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)
σ = 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 will also be provided to be used as a blank control.

Table 2: List of possible matrix specific pesticides included within the 2017/2018 proficiency testing scheme

Pesticide	**Pesticide**	**Pesticide**
4,4-DDT and related compounds	Diphenylamine	Phosmet
Azoxystrobin	Endosulfan and related compounds	Prochloraz
Bifenthrin	Esfenvalarate	Procymidone
Boscalid	Fenarimol	Profenofos
Bromophos Methyl	Fenbutatin-Oxide	Propiconazole
Bromopropylate	Fenthion	Proquinazid
Bupirimate	Fludioxonil	Prothiophos
Buprofezin	Fluopicolide	Spirodiclofen

Pesticide	Pesticide	Pesticide
Chlorothalonil	Folpet	tau-Fluvalinate
Chlorphenapyr	Hexaconazole	Terbufos
Chlorpyrifos	Iprodione	Tetradifon
Cyfluthrin (sum of isomers)	Kresoxim-methyl	Thiabendazole
Cymoxanil	Mercaptothion (Malathion)	Thiamethoxam
Cypermethrin	Methidathion	Triadimenol
Cyprodinil	Myclobutanil	Triazophos
Deltamethrin	Parathion	Trifloxystrobin
Demeton-S-methyl Sulphone	Parathion Methyl	Vinclozolin
Dichlofluanid		

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 directly 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 participant'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	03 July 2017	31 July 2017	11 August 2017
Apples	25 September 2017	23 October 2017	06 November 2017
Peaches	20 November 2017	11 December 2017	08 January 2018
Grapes	26 January 2018	19 March 2018	30 March 2018

Please note:

- Through acceptance of the original quotation, the Applicant agrees to the quoted fee and the conditions stated herein.
- 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. NMISA retains the right to ask for a deposit for international services.
- NMISA cannot guarantee to complete the work within the estimated time but will consult the Applicant if it becomes apparent that the estimate will be exceeded.
- The Applicant hereby consents that the legal liability of NMISA with regard to any damage whatsoever or a mistake made by NMISA in services performed for the Applicant will be limited to the original quoted fee.

Regarding certificates and reports:

- A report, will be furnished to the Applicant on completion of the service;
- Reports or certificates may be freely published by the Applicant provided that such publication is verbatim and in full;
- 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;
- All participants details will remain fully confidential
- Additional copies of reports may be subject to an additional fee, as determined on a case by case basis.
- 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.

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

Deadline for registration is 31 May 2017

Name of laboratory							
Department							
Contact		Name					
		E-mail					
		Telephone					
		Address					
		Town/ City					
		Postal code					
		Country					
Delivery		Self-collect			Delivery		
My laboratory is interested in participating in the following tests:							
Oranges		Apples		Peaches		Table grapes	

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 Date