



APMP-APLAC Joint Proficiency Testing Programme
(APLAC T102)
Pesticides in Fruit Juice



Instructions for Participants

1. Objectives

With the aim of enhancing the quality and traceability of measurements in various economies of the Asia-Pacific region through a better regional scientific infrastructure, the Asia-Pacific Metrology Programme (APMP) and the Asia Pacific Laboratory Accreditation Cooperation (APLAC) agreed to strengthen bilateral cooperation. At the APMP General Assembly and Related Meetings held in Taipei in November 2013, both APMP and APLAC agreed to establish the APMP-APLAC Joint Proficiency Testing Working Group (PTWG) as a formal infrastructure to provide more proficiency testing programmes with metrologically traceable reference values for performance evaluation purpose. To echo this new initiative, the Government Laboratory, Hong Kong (GLHK) proposed a new PT study for the determination of pesticides (organochlorine pesticides and carbamates) in fruit juice at the first preparatory meeting of the APMP-APLAC Joint PTWG. The purpose of this study is to demonstrate the capability of participating laboratories in measuring pesticides in a relatively simple food matrix (e.g. fruit juice). Endosulfan sulphate and carbofuran, which are commonly used organochlorine pesticides and carbamates for the growth of fruits and vegetables, are selected as the analytes in this PT study. The maximum residue levels (MRLs) required by the Codex Alimentarius Commission (CODEX) for endosulfan (sum of alpha-endosulfan, beta-endosulfan and endosulfan sulphate) are 0.02 to 5 mg/kg and those for carbofuran are 0.01 to 1 mg/kg in various primary food commodities of plant origin.

The proficiency testing programme is coordinated by GLHK. The objective of this study is to enable participating laboratories to demonstrate their capabilities in determining the mass fractions of two analytes (carbofuran and endosulfan sulphate) at $\mu\text{g/kg}$ levels in the proficiency test sample of tomato juice by various analytical techniques.

2. Analysis of the proficiency test sample

Participating laboratories will be provided with **ONE** sample unit containing about **100 mL** of tomato juice. The sample will be distributed by courier service. Upon receipt of the sample, please complete the Sample Receipt Form and return it to GLHK (E-mail: APLAC-T102@govtlab.gov.hk). Replacement of a new sample unit will be arranged if the proficiency test sample is identified to be not suitable for analysis.

Participants should treat the proficiency test sample in the same manner as the majority of routinely tested samples. They are expected to use the test method of their choice (accredited, validated, in-house, etc.), which should be consistent with their routine procedures.

The proficiency test sample should be stored and kept frozen prior to analysis, where the



APMP-APLAC Joint Proficiency Testing Programme
(APLAC T102)
Pesticides in Fruit Juice



recommended temperature should be $\leq -18^{\circ}\text{C}$.

The proficiency test sample should be thawed and mixed thoroughly before conducting the tests. The analysis should be conducted with a recommended sample size of at least 1 g. Participants are requested to determine the mass fractions of carbofuran and endosulfan sulphate (in $\mu\text{g/kg}$) in the proficiency test sample as received.

The organizer performed the homogeneity and stability tests using 1 g of sample. The expected mass fraction range for both carbofuran and endosulfan sulphate in the proficiency test sample is from 100 $\mu\text{g/kg}$ to 1000 $\mu\text{g/kg}$.

For safety considerations, the proficiency test sample should be handled with care. The sample is not for human consumption.

For this proficiency testing programme, return of the untested proficiency test sample is not necessary.

3. Reporting and submission of results

Participants should complete the Result Proforma. The manners of reporting test results are as follows:

- Units of measurement: Report the mass fractions of the analytes and associated uncertainties in $\mu\text{g/kg}$;
- Number of significant figures: Report the test results to 3 significant figures;
- Reporting basis: Report the test results on “as received” basis;
- For each analyte, the mean value of at least three independent measurements, the associated expanded uncertainty and the coverage factor (which gives a level of confidence of approximately 95 %) should be reported; and
- Participants should provide information on the methods of analysis.

Participants should aware that any submitted results are considered to be final and such results and units should be thoroughly checked before submission. Participants should submit the Result Proforma electronically to GLHK (E-mail: APLAC-T102@govtlab.gov.hk) on or before the deadline 6 March 2016. Results submitted after the deadline will not be accepted. Participants are reminded that the ability to report results in the specified unit and within the given time scale are part of the proficiency testing programme.

4. Performance evaluation

The performance of the participating laboratories is assessed using z-score which is calculated as:



APMP-APLAC Joint Proficiency Testing Programme
(APLAC T102)
Pesticides in Fruit Juice



$$Z = \frac{X_i - X_{pt}}{\sigma_{pt}}$$

where X_i : proficiency test result from participant i
 X_{pt} : the assigned value*
 σ_{pt} : the standard deviation for proficiency assessment. It is estimated from the Horwitz equation $[\sigma = 0.02c^{0.8495}]$, where c is the assigned value of the analyte expressed as a dimensionless mass ratio (e.g. 1 mg/kg = 1 ppm = 10^{-6}) [5]

* Note: The reference values determined by GLHK will be used as the assigned values. The reference values are based on the gravimetrically spiked values or the IDMS measurement results. This is in accordance with the ISO/IEC 17043 recommendations on the determination of assigned values for proficiency testing schemes [2].

z-score is commonly interpreted as:

(i)	$ z \leq 2.0$	Satisfactory
(ii)	$2.0 < z < 3.0$	Questionable
(iii)	$ z \geq 3.0$	Unsatisfactory

Participants having a $|z|$ score equal to or larger than 3.0 shall thoroughly investigate their results for the discrepancy and those having a z-score in the range $2.0 < |z| < 3.0$ are also encouraged to review their results.

For reference purpose, the performance of the participating laboratories will be assessed using zeta-score (ζ), which is calculated as follows [3]:

$$\zeta = \frac{X_i - X_{pt}}{\sqrt{u^2(X_i) + u^2(X_{pt})}}$$

where X_i : proficiency test result from participant i
 X_{pt} : the assigned value*
 $u^2(X_i)$: the participant's own estimate of the standard uncertainty of its result X_i .
 $u^2(X_{pt})$: the standard uncertainty of the assigned value X_{pt} .



APMP-APLAC Joint Proficiency Testing Programme
(APLAC T102)
Pesticides in Fruit Juice



ζ -scores are interpreted as in the same way as z-scores using the same critical values of 2.0 and 3.0. ζ -scores may be used in conjunction with z-scores, as an aid for improving the performance of laboratories as follows. If a laboratory obtains $|z|$ scores that exceed 3.0, they may find it of value to examine their test procedure step by step and derive an uncertainty budget for that procedure. The uncertainty budget will identify the steps in the procedure where the largest uncertainties arise, so that the laboratory can see where to expend effort to achieve an improvement. If their $|\zeta|$ scores also exceed the critical value of 3.0, it implies that their uncertainty budget does not include all significant sources of uncertainty [3]. Laboratories are encouraged to review their uncertainty budget.

An electronic copy of the final report on the performance of participating laboratories would be distributed to the participants by August 2016. The report will reveal only the code number assigned to the designated participating laboratory and the identity of participants in this proficiency testing programme will be kept confidential. A summary of the final report will be posted on the website of GLHK for public information.

4. Programme schedule

The time schedule for the various phases of the proficiency testing programme is as follows:

Event	Period
Call for Participation	Nov 2015
Deadline for Registration	15 Dec 2015
Distribution of Samples	Jan 2016
Deadline for Submission of Results	6 Mar 2016
Distribution of Interim Report	Jun 2016
Distribution of Final Report	Aug 2016

5. Confidentiality

The proficiency testing programme is conducted in the belief that participants will perform the analysis and report results with scientific rigour. Collusion and falsification of results are clearly against the spirit of the proficiency testing programme.

The concerned parties (APMP, APLAC and GLHK) strive to maintain strict confidentiality of the characteristic properties of the proficiency test sample distributed and the performance of all



APMP-APLAC Joint Proficiency Testing Programme
(APLAC T102)
Pesticides in Fruit Juice



participating laboratories. To preserve the confidentiality, participants receive reports giving all results for assessment but without identifying individual laboratories. The code number assigned to a participant in the proficiency testing programme will be provided only to the contact person/authorized person of the participating laboratory and/or the respective accreditation body.

In general, all information on participant performance shall not be disclosed to any third party unless prior agreement with the concerned participants has been obtained or applicable laws or regulations stipulate such disclosure. GLHK, the proficiency testing provider for this proficiency testing programme, shall also take into consideration local regulatory requirements for the disclosure of confidential information. GLHK may disclose any relevant information to Hong Kong Accreditation Service for accreditation purposes, with the consent/agreement obtained from participating laboratories through completion of the Registration Form / Sample Receipt Form / Result Proforma for this proficiency testing programme.

6. Contact

Participants may wish to contact the organizer for any enquires by e-mail to APLAC-T102@govtlab.gov.hk.

7. References

- [1] CODEX Alimentarius, Pesticide Residues in Food online database (36th Session, July 2013).
- [2] ISO/IEC 17043:2010 “Conformity assessment – General requirements for proficiency testing”, 2010, Geneva, Switzerland.
- [3] ISO 13528:2015 “Statistical methods for use in proficiency testing by interlaboratory comparison”, 2015, Geneva, Switzerland.
- [4] ISO/IEC Guide 98-3:2008 “Uncertainty of measurement -- Part 3: Guide to the expression of uncertainty in measurement (GUM:1995)”, 2008, Geneva, Switzerland.
- [5] Horwitz, W. Evaluation of analytical methods used for regulations of food and drugs, *Anal. Chem.* 1982, 54:67A-76A.