Experience Sharing Seminar on Food Chemical Testing

Provision of Proficiency Testing Schemes with Metrologically Traceable Reference Values for Food Testing

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Proficiency Testing (PT)

- Definition:
 - evaluation of participant performance against pre-established criteria by means of interlaboratory comparisons (*ISO/IEC 17043:2023, Cl 3.7*)
- **Objectives**: assist participating laboratories to
 - demonstrate technical competence
 - identify problems and opportunities \rightarrow self-improvement
- ISO/IEC 17025 requirement
 - testing laboratory demonstrates measurement capabilities



Provision of PT Schemes by Government Laboratory (1)

- First PT scheme: 1987
- Now ~ 80 PT Schemes (Testing Areas: Commodity, Environmental, Toy Safety, Drug, Food Safety, Chinese Medicine, Forensic Science)
- Accredited Proficiency Testing Provider (PTP) since 2006



Provision of PT Schemes by Government Laboratory (2)

- Characteristics
 - Non-profit making
 - Aims support (1) testing and certification sector in Hong Kong and (2) international cooperation (Asia-Pacific region) on quality infrastructure (via APAC/APLAC/APMP)*
 - Main focuses on food and Chinese Medicine testing
 - Metrologically traceable reference value = PT assigned value for some PT schemes



*APMP: Asia Pacific Metrology Programme (亞太計量規劃組織) *APLAC: Asia Pacific Laboratory Accreditation Cooperation (亞太實驗室認可組織) *APAC: Asia Pacific Accreditation Cooperation (亞太認可組織)

Evaluation of PT Results

$$z_i = \frac{x_i - x_{pt}}{\sigma_{pt}}$$

where

- z_i is the z score;
- x_i is the participant's result
- x_{pt} is the assigned value;

 σ_{pt} is the standard deviation for proficiency assessment

The result is considered to be

- acceptable when $|z_i| \le 2.0$
- questionable (warning signal) when $2.0 < |z_i| < 3.0$
- unacceptable (action signal) when $|z_i| \ge 3.0$



ISO/IEC 17043:2023, B.4.1.3

PT Assigned Value (ISO 13528)

- 1. Consensus value from participant results
- 2. Using certified reference material (CRM) as PT sample
- 3. Consensus value from expert laboratories (reference laboratory, e.g. National Metrology Institute (NMI) / Designated Institute (DI))
- 4. By formulation
- 5. Results from one laboratory using a reference method (primary method, e.g. IDMS)



PT Assigned Value – Consensus Value from Participants

Advantages	Limitations	
No additional measurements to obtain the assigned value	Cannot reflect bias	
	May be insufficient agreement among the participants	
Useful for a standardized, operationally defined measurand (empirical measurement e.g. extractable cadmium)	Sufficient number of participants required for meaningful estimation of assigned value	
	Careful selection of statistical calculation method required when there are extreme results	



PT Assigned Value – Reference Value with Metrological Traceability

Advantages	Limitations
Not limited by the number of participants	Need commutability between the reference method
Can reflect bias	and all measurement methods used by participants
Location of assigned value not affected by participants' data	
More effective in evaluating the performance of participants	



PT Scheme with Metrologically Traceable Reference Value

- Enhance the quality of the PT scheme and enable meaningful performance evaluation
- Enable assessment of bias and metrological comparability of the participants' results



Metrological Traceability

- Essential for maintaining confidence in the measurement
- Property of a measurement result whereby the result can be related to a reference through a documented unbroken chain of calibrations, each contributing to the measurement uncertainty*
- Reference e.g. measurement unit International System of Units (SI)
- The expression "traceability to the SI" means 'metrological traceability to a measurement unit of the International System of Units'.*



*Source: Clauses 2.41 & 2.43, JCGM 200:2012, International vocabulary of metrology - Basic and general concepts and associated terms





Primary Reference Measurement Procedure

- Reference measurement procedure used to obtain a measurement result without relation to a measurement standard for a quantity of the same kind
 - Also known as "primary methods of measurements" or "primary methods"
- Essential first link in a chain of traceability
- Metrologically traceable measurement results with the highest level of accuracy
- Examples: Coulometry, gravimetry or isotope dilution mass spectrometry



Source: Clause 2.8, JCGM 200:2012 Eurachem, Terminology in Analytical Measurement, 2023 Metrologia, 38(4), 289-296

Reference Value by Formulation – Boric Acid in Food

- Gravimetric spiking of certified reference material (CRM) grade high purity boric acid
- Assigned value = gravimetric value of mass fraction of boric acid spiked (traceable to SI)
- Standard uncertainty of the assigned value associated with gravimetric measurements and the purity of materials used in formulation.
- Critical: homogeneity of the sample



Determination of Assigned Value by Primary Method - Propionic Acid in Flour Confectionery

 Consensus value obtained by robust statistics of Before participant results 2022 Reference method using isotope dilution mass spectrometry (IDMS) 2022 Converted to PT with reference value 2023 Metrological traceability of the assigned value established through the use of CRM calibrant and primary method – IDMS

Results of Participants on Propionic Acid in Flour Confectionery



Robust average – 715 mg/kg



Re-examination of the participants' results using reference value – 748 mg/kg

Assigned Value Linked to CCQM/RMO Comparison Reference Value





CCQM: Consultative Committee for Amount of Substance (物質量諮詢委員會) RMO: Regional Metrology Organisation (區域性計量組織) APLAC: Asia Pacific Laboratory Accreditation Cooperation (亞太實驗室認可組織)

APLAC T081 Organochlorine Pesticides in Tea (2013)



One of the factors attributed to the bias may be the extraction method.



Extraction efficiency of incurred sample of *beta*-endosulfan in tea varied with extraction conditions.



Problem discussed and investigated in CCQM-K95

Different extraction conditions:

- A: Wetted sample / ethyl acetate / Soxhlet extraction
- B: Wetted sample (for 2 days) / ethyl acetate / Soxhlet extraction
- C: Wetted sample (0.5 g) / ethyl acetate / Soxhlet extraction
- D: Wetted sample / acetone -hexane / Soxhlet extraction

- E: Wetted sample / ethyl acetate / shaking
- F: Dry sample / acetone-hexane /Soxhlet extraction
- G: Dry sample / ethyl acetate / Soxhlet extraction
- H: Dry sample / ethyl acetate / shaking

Note

For extraction condition **A** (Wetted sample / ethyl acetate / Soxhlet extraction), it denotes that 1 g of tea powder sample was wetted with water overnight and then extracted with ethyl acetate using Soxhlet extraction technique for 16 hours.



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Anal Bioanal Chem 407, 3009–3021 (2015)

APLAC T106 Organochlorine Pesticides in Ginseng Root (2019)

Perform	α-ΒΗC		Lindane	
Wetting before extraction	Number of Participants (Percentage)	z-score ≤ 2.0	Number of Participants (Percentage)	z-score ≤ 2.0
Yes	36 (82%)	69%	38 (83%)	71%
No	8 (18%)	63%	8 (17%)	63%

Another PT Linked to RMO supplementary comparison

Wetting of sample was emphasized in this PT

Improved performance of participants was observed

Wetting time	α-ΒΗC		Lindane	
	Number of Participants (Percentage)	z-score ≤ 2.0	Number of Participants (Percentage)	z-score ≤ 2.0
≤ 0.5 hour	25 (69%)	60%	26 (68%)	58%
> 0.5 hour	11 (31%)	91%	12 (32%)	100%



Assigned Value from Reference Value Supported by Calibration and Measurement Capability (CMC) Claims of PTP





APMP: Asia Pacific Metrology Programme (亞太計量規劃組織) APAC: Asia Pacific Accreditation Cooperation (亞太認可合作組織)



Both performance of participants of APAC T113 and GLHK PT 21-04 were satisfactory



Points to Note When Participating in PT Scheme with Metrologically Traceable Reference Value

- Encouraged to use
 - CRM
 - Internal standard (especially isotope labelled standard)
 - Confirmation method (e.g. using mass spectrometry)
- Investigate the bias in the method



Tell us what PT schemes you need...



GOVERNMENT LABORATORY

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Survey on the needs of the local testing community

Objective of the survey: This survey is conducted by the Analytical and Advisory Services Division (A&ASD) of the Government Laboratory (GL). Your feedback will be valuable for improving and planning the services of the Laboratory. Please take a few minutes to complete the following questionnaire. **Data Privacy Statement:** The information gathered from this survey will be used for the planning of future services. The information will be kept confidential and will only be released, if necessary, in aggregate form.



References

- 1. ISO 13528:2022, Statistical methods for use in proficiency testing by interlaboratory comparison
- 2. ISO/IEC 17043:2023, Conformity assessment General requirements for the competence of proficiency testing providers
- 3. JCGM 200:2012, International Vocabulary of Metrology Basic and General Concepts and Associated Terms
- 4. Eurachem, *Terminology in Analytical Measurement Introduction to VIM3, 2023*
- 5. Milton, M. J. T., & Quinn, T. J. (2001). *Primary methods for the measurement of amount of substance. Metrologia, 38(4), 289–296.*
- 6. Sin, D.Wm., Wong, YL., Cheng, E.Cc. *et al.* S1 certification of *alpha*-endosulfan, *beta*-endosulfan, and endosulfan sulfate in a candidate certified reference material (organochlorine pesticides in tea) by isotope dilution gas chromatography-mass spectrometry. *Anal Bioanal Chem* **407**, 3009–3021 (2015).



Thank You!

