



APFAN PT-2 Workshop

Food Analysis Workshop: Proficiency Testing and Reference Materials Development



Australian Government
Department of Industry,
Innovation and Science

National
Measurement
Institute

Highlights of ISO 17043

Paul Armishaw

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Proficiency Testing

Proficiency testing is:

“evaluation of participant performance against pre-established criteria by means of interlaboratory comparisons.”

ISO 17043

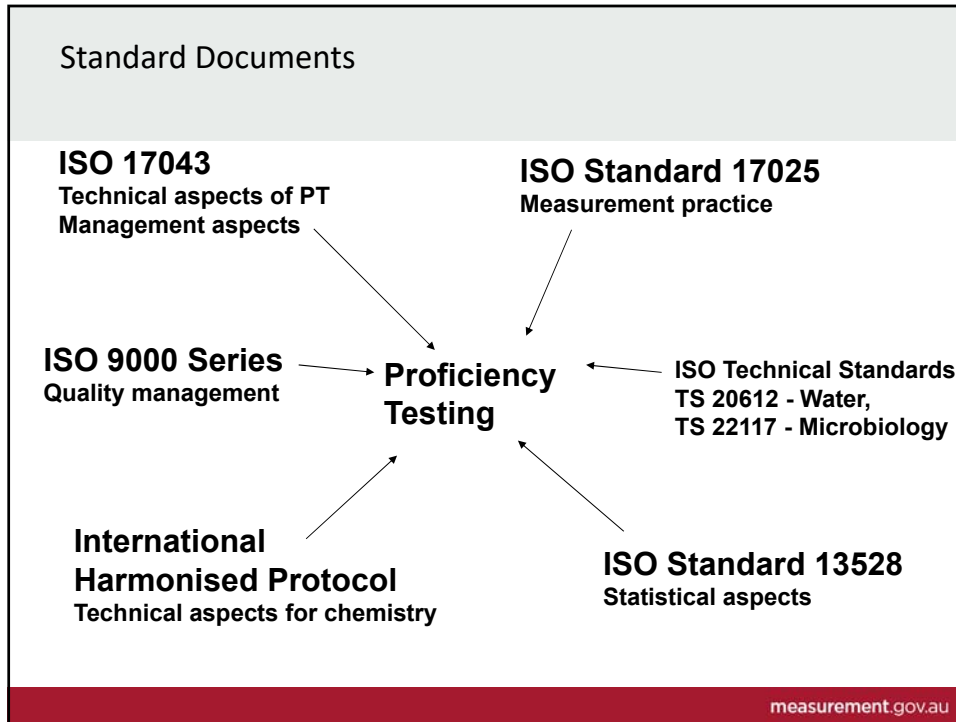
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19th - 21st June 2019, Bangkok, THAILAND



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NATA Accredited Proficiency Testing Scheme Provider

National Association of Testing Authorities, Australia
(ABN 58 324 379 748)


has accredited

National Measurement Institute
Chemical Proficiency Testing Laboratory


following demonstration of its technical competence to operate in accordance with

ISO/IEC 17043

This facility is accredited for the proficiency testing schemes shown on the *Scope of Accreditation* issued by NATA


Eric P W Lo
Acting Chief Executive

Date of accreditation: 17 November 2000
Accreditation number: 14476



NATA is Australia's government-endorsed laboratory accreditation, and a leader in cooperation internationally.

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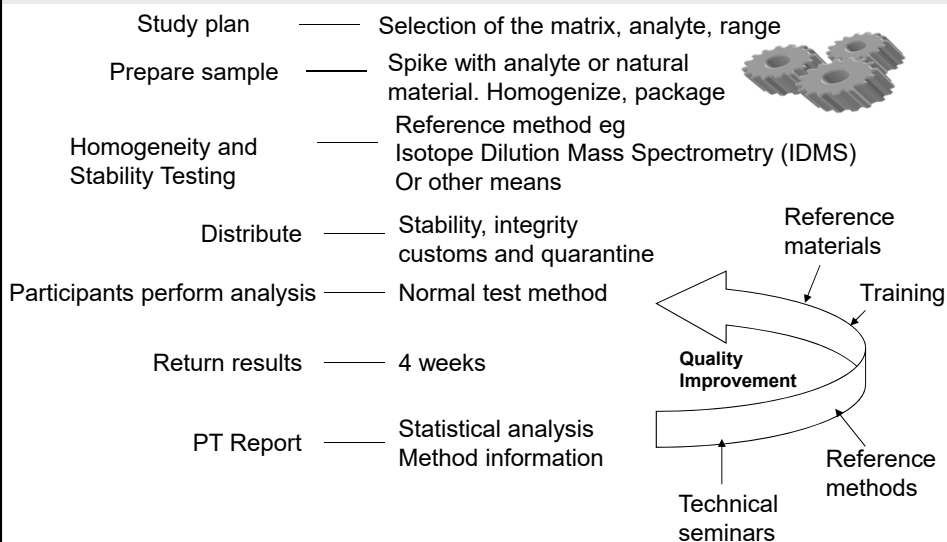
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Management Aspects

- Harmonised with the previous version of ISO9000.
- Similar to previous ISO17025, ISO Guide34
- Describes a complete management system
 - document control, contracts, corrective action, management review etc
- Subcontracting of services
 - cannot subcontract:
 - planning, performance evaluation, authorising the final reports
 - advise participants
 - assure competence of subcontractors
- Complaints and appeals
 - must have a procedure for appeal of PT assessment

Mechanics of a PT Round



PT Sample Preparation

- PT samples
 - should closely resemble routine samples
 - must be homogeneous and well characterised

Practical PT sample
sufficiently homogeneous
concentration known with
acceptable uncertainty



Why homogeneity is important

- Samples are prepared in bulk, placed into aliquots and distributed to participants
- Only true solutions are homogeneous at the molecular level
 - any multi-phase material will be inhomogeneous to some degree
- In-homogeneity of the test materials will cause variation in the results reported by participants
 - may invalidate the study
- Risk management approach
 - cost of using an unsuitable test material
 - cost of homogeneity testing



Sufficient homogeneity

- The differences between units of test material must be negligible compared to the differences in the measurements conducted by the laboratories.
- The variability of participants' results is expected to be the target standard deviation (σ)
- An allowable degree of variability of the samples (s_{total}) can be set based on (σ)
- The real differences between units of test material (s_{sam}) can be estimated by making duplicate measurement on a selection of units.

Why Stability Testing ?

- To ensure that the z-score is a reflection of variation introduced by the participants' measurements.
 - the variation introduced by instability of a *sufficient stable sample* is negligible through the conduct of the PT study.



When a PT Sample is “sufficient stable”?

• **ISO/IEC 17043 :**

“will not undergo any significant change throughout the conduct of the proficiency testing, including storage and transport conditions”.

• **ISO 13528 :**

“sample is adequate stable – if its instability does not change z-score by more than 0.3”.

• **International Harmonised Protocol (2006):**

“a change in analyte concentration of $0.1\sigma_p$ can be tolerated if z-score does not change more than 0.1”.



The NMIA Approach to Routine Stability Testing in PT Studies

STABILITY INFORMATION

1. From stability study – validate the procedure
2. From relevant literature
3. From experience or judgement



Cost effective

Demonstrate the stability of proficiency testing material through the conduct of the study

Stability Information- From Stability Study

General procedure – follow ISO 13528 recommendation:

- **Method:**
 - The same laboratory/method as for homogeneity check is used.
 - Use highly reproducible methods.
 - When routine methods are used then:
 - Use matrix match control samples.
 - Analyse samples in duplicate
- **The stability study design:**
 - It should be based on the investigated factors:
 - time (over the entire period of the PT study)
 - storage condition (simulate conditions encounter by the sample during the transport and storage).
 - storage container (glass, HDPE, PP).
- **Statistical tests**
 - Linear regression or
 - Two sample t-test are used.

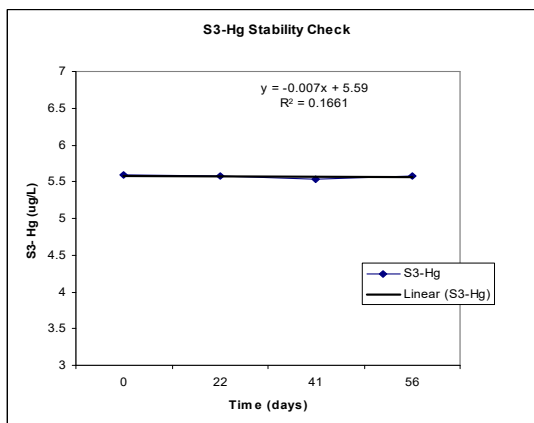


Stability Information- From Stability Study

Does Hg Concentration changed in time?

Results:

Days elapsed from the first measurement	Hg $\mu\text{g/L}$
0 days	5.59
22 days	5.58
41 days	5.54
56 days	5.58



Conclusion: There are no significant changes in Hg concentration with the elapsed time ($a=-0.007$).

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Stability Information- From Literature

- published reports
- published stability studies in journals
- example:



Stability Data for Analytes used in September 2009 Pesticides in Fruit & Vegetables Proficiency Study (AQA 09-14)

ANALYTE	STABILITY INFORMATION	SOURCE OF DATA
Abamectin	Stable in hops when stored in freezer for periods of 150 to 190 days. Susceptible to photodegradation. Americans established a half-life of 18 days on pears. Good agricultural practice in the Netherlands factors in photodegradation as an effective means of reducing contamination of glasshouse tomatoes.	JMPR 1997 - Report of the 1997 Joint FAO/WHO Meeting of Experts

Assigned Value

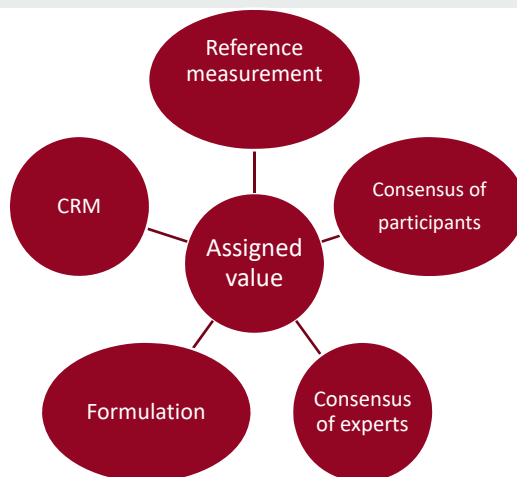
- ISO Definition
 - ‘value attributed to a particular property of a proficiency test item’.

or

 - the correct result.

- The determination of the assigned value shall be the responsibility of the study coordinator.

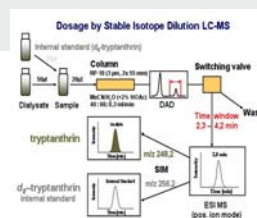
Establishing the assigned value



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Reference measurement

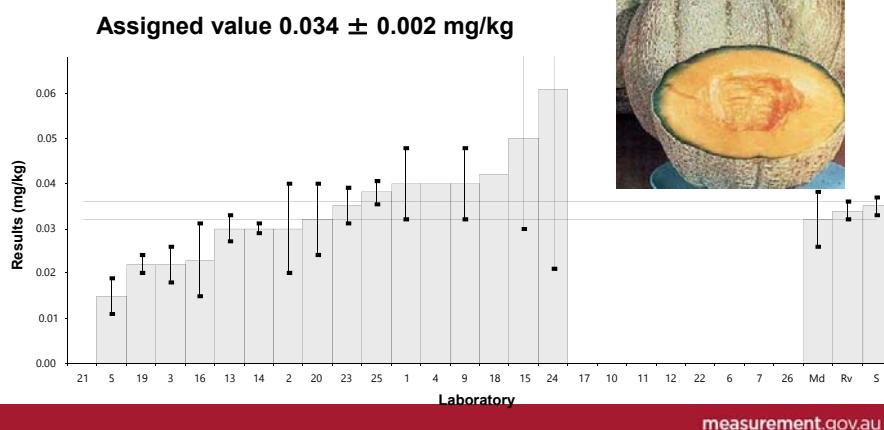
- **Assigned value is a reference value from:**
 - a suitably qualified laboratory -such as an NMI
 - a suitable method
 - traceability of the result to SI
 - sufficiently small uncertainty
 - well validated
- **Traceability**
 - assigned value set using reference measurements is traceable to SI through standards (e.g. standards certified by NIST for ICP-MS calibration by d-IDMS via high standard e.g. standards certified by NIST for ICP-MS calibration by d-IDMS)
- **Advantages**
 - the material is tailored to the scheme requirements
- **Disadvantages**
 - can be expensive.



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Example chlorpyrifos in rockmelon

- Assigned value result of reference measurements using isotope dilution mass spectrometry (IDMS).
- Traceability: The measurements of the reference value are traceable to the SI.



Formulation

- **Formulation**
 - The addition of a known amount of analyte to base material containing none or a small but very well characterised amount.
- **Assigned value**
 - by calculation gravimetric and volumetric
- **Traceability**
 - via calibration standards
- **Advantages**
 - uncertainties of the assigned value are usually very small
 - very good for amount added to individual test objects (e.g.filters)
- **Disadvantages**
 - analyte might be already in the base material
 - might be difficult to obtain sufficient homogeneity
 - the analyte may be more loosely bonded than the native one



Consensus of participants
Most widely used method

- Robust Average – Huber robust mean or “algorithm A”
 - algorithm in ISO 13528
 - makes more use of the data than the median does
 - uncertainty is smaller than for median
 - robust against outlying results

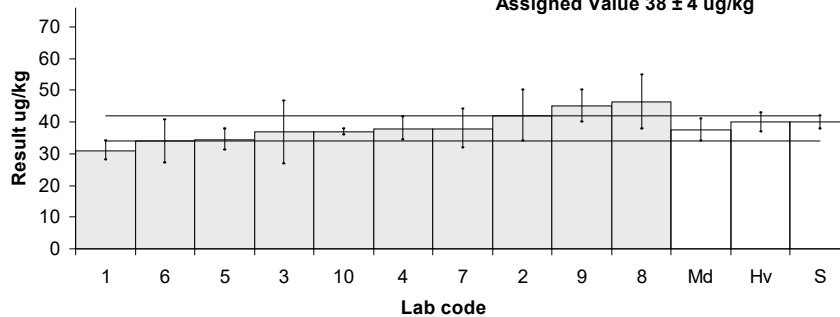
Assigned Value Cadmium in Wine

- Robust average (ISO 13528)



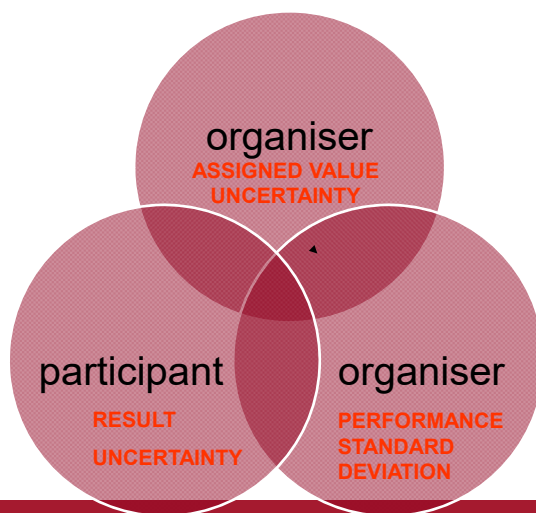
Result S2 Cd

Assigned Value 38 ± 4 ug/kg



Scoring

- Converting participants results into a form that adds information about performance;
- Judging the laboratory pre-determined performance criteria.



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z-Score

How much the reported results differs from the assigned value?

$$z = \frac{(\chi - X)}{\sigma_p}$$

χ = participant's result

σ_p = performance standard deviation

X = assigned value

z = z-score

- $|z| < 2$ Satisfactory
- $2 < |z| < 3$ Questionable
- $|z| > 3$ Unsatisfactory

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E_n – Score

Accounts for uncertainties

$$E_n = \frac{(\chi - X)}{\sqrt{U_\chi^2 + U_X^2}}$$

E_n = E_n -score

χ = individual laboratory result

U_χ = expanded uncertainty of the individual laboratory result

X = assigned value

U_X = expanded uncertainty of the assigned value.

- $|E_n| < 1$ Satisfactory
- $|E_n| > 1$ Unsatisfactory

Conclusion

- The ISO17043 standard provides comprehensive guidance for good practice in PT
 - management
 - technical
- It is supported by other standards and guidance documents
 - ISO13528: Statistical methods
 - IUPAC harmonised protocol: chemistry PT
 - ISO17025: measurement practice
 - ISO Technical standards: water, microbiology
- Accreditation provide PT customers with assurance of the competence of their PT provider.



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National Measurement Institute
105 Delhi Road
North Ryde

Phone: + 61 2 9449 0111

Email: proficiency@measurement.gov.au

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