PT/EQA STANDARDS AND GUIDELINES: QUALITY AND RELIABILITY OF TEST ITEMS

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ISPRA activities

- production and characterization of matrix reference materials
- methods development and harmonization
- organization of Proficiency testing
- organization of collaborative studies for method validation

Test material/test item

- IUPAC "The International Harmonized Protocol for the proficiency testing of (chemical) Analytical Laboratories" - 1993 does not define specifically the Test materials, but reports RM and CRM definitions as given by ISO REMCO
- IUPAC "The International Harmonized Protocol for the proficiency testing of (chemical) Analytical Laboratories" – 2006 cross-refers to ISO standard definitions. It is given a definition for **Distribution unit** ***"a packaged portion of the test material that is sent to participant laboratories"***

Test Item

- ***"material or artefact presented to the participating laboratory for the purpose of proficiency testing"***

ISO Guide 43-1:1997

- ***"a sample, product, artefact, piece of equipment or measurement standard sent to one or more participants in a proficiency testing scheme"***

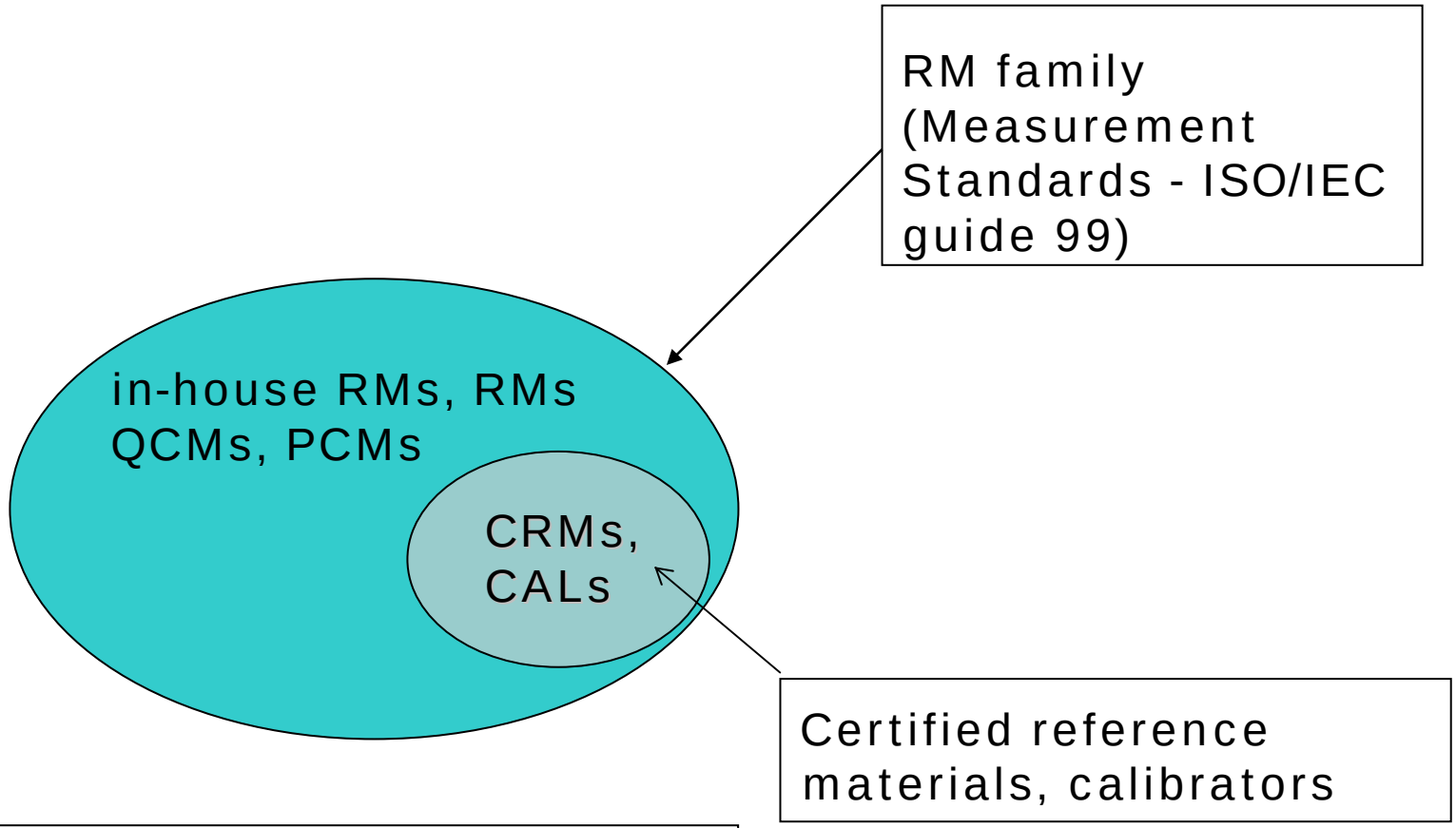
ILAC G13:2007

Test Item

- ***"sample, product, artefact, reference material, piece of equipment, measurement standard or data set provided to one or more participants, or submitted by participants, in a proficiency testing round"***

ISO-IEC CD 17043: March 2008

Test item in analytical chemistry



H. Emons et. al., 2006, AQUAL 10, 576

Quality of test items

- **Matrix matching**
- **Homogeneity**
- **Stability**
- **Assigned values**

Test item - Matrix matching

1993

Pure & Appl. Chem. Vol.65 n°9 (IUPAC Protocol)

Qualitative definition

2008

ISO/IEC CD 17043

Matrix Matching

- ***"Matrix proficiency test items should, were practicable, have the same or nearly the same matrix as routine test materials in order to simulate the measurement process as close as possible"***

ILAC-G13:2007

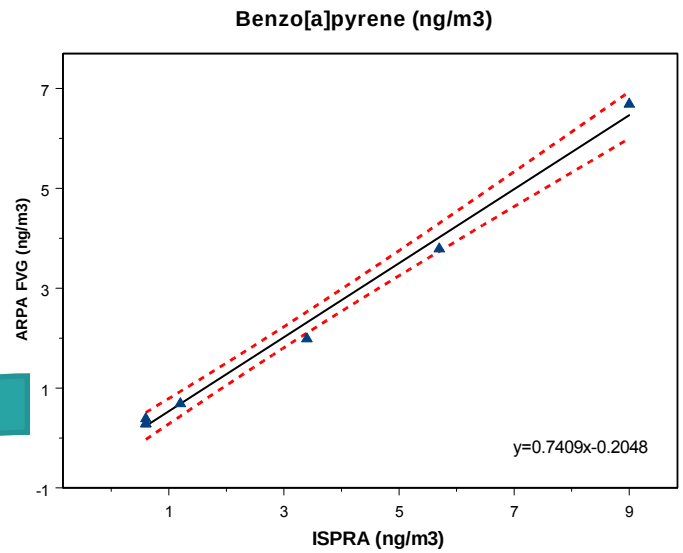
Commutability

- ISO Guide 99 gives the definition of commutability of reference material
- ISO Dguide 34 reports a method to assess commutability of reference material:

  “If the ratio between the results on reference material with 2 measurement procedures is the same as the ratio for routine samples, the reference material is commutable”

Commutability

PAH in PM10

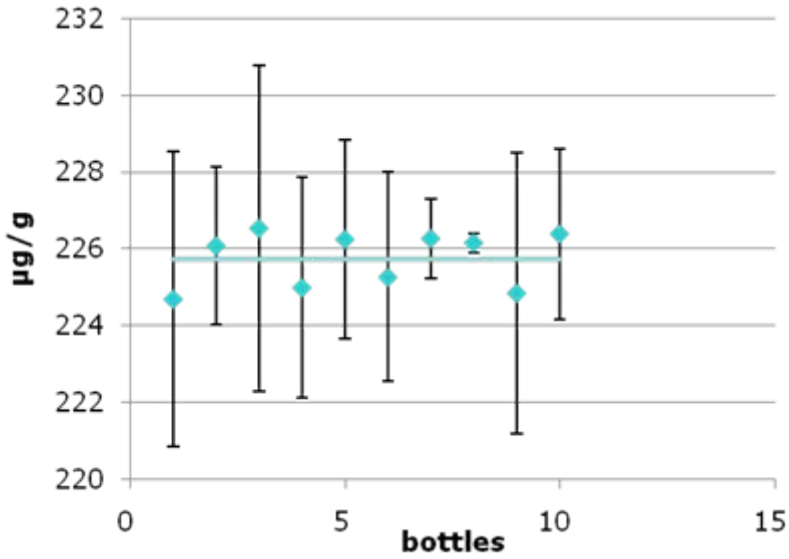


Procedures	CRM	ratio
GC-MS/HPLC	BCR 535 sediment	1.6
GC-MS/HPLC	BCR088 sludge	1.3
GC-MS/HPLC	NIST1650b	0.6

Procedures	ratio
GC-MS/HPLC	1.7±0.2

Homogeneity

APAT RM014 - Ni – between bottles homogeneity



Homogeneity study results are affected by:

- ***measurement repeatability***
- ***between bottles variability***

Homogeneity Study – Standards and Guidelines requirements

Standards/Guidelines	How*
IUPAC Harm. Protocol (1993)	10 test items - 2 replicates ANOVA $s_{bb}/\sigma_{PT} < 0.3$
ISO Guide 43-1:1997	Cross reference to IUPAC (1993)
ISO 13528:2005 Statistical methods in PT	10 test items - 2 replicates $s_{bb}/\sigma_{PT} < 0.3$
IUPAC Harm. Protocol (2006)	10 test items - 2 replicates $\sigma^2_{samp} < F_1 0.3\sigma^2_{PT} + F_2 s^2_{an}$ ANOVA to obtain σ^2_{samp} e s^2_{an} Recommendation $\sigma_{an}/\sigma_{PT} < 0.5$
ILAC G13:08/2007	Where appropriate

*** Measurements in repeatability conditions**

Homogeneity Study – Standards and Guidelines requirements

Standards/Guidelines	How*
ISO/IEC CD 17043:2008 Conformity assessment – General requirement for PT	As above, but cross reference to ISO 13528 IUPAC (2006), ISO Guide 34 and ISO Guide 35
ISO Guide 35:2006 RM-General and Statistical principles for certification	10 or more test items – 3 replicates - ANOVA to assess the uncertainty contribution for residual heterogeneity
ISO DGuide 34:2008 General requirements for the competence of RM producers	Always RM producers shall carry out homogeneity study in compliance with ISO 17025
ISO CD Guide 80:2008 Guidance for production of RM for precision control (PCMs)	10 test items – 2 replicates ANOVA to assess homogeneity between bottles

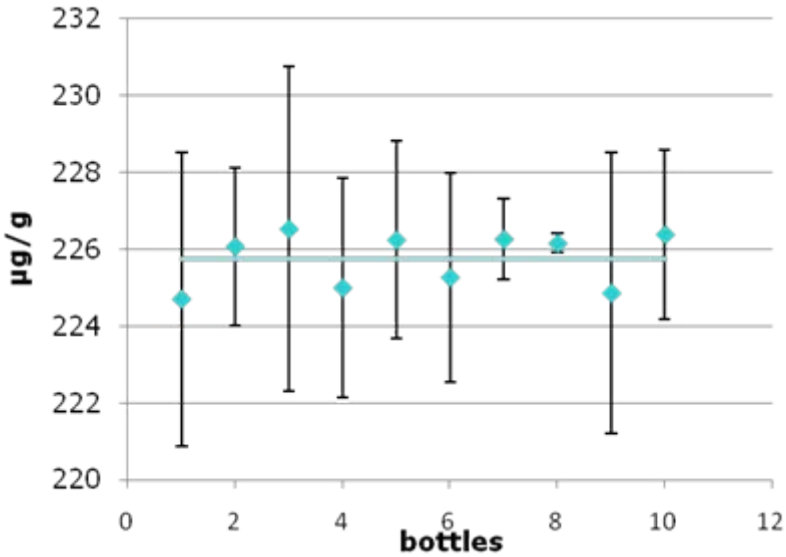
***measurements in repeatability conditions are always required**

APAT RM014 – Ni homogeneity

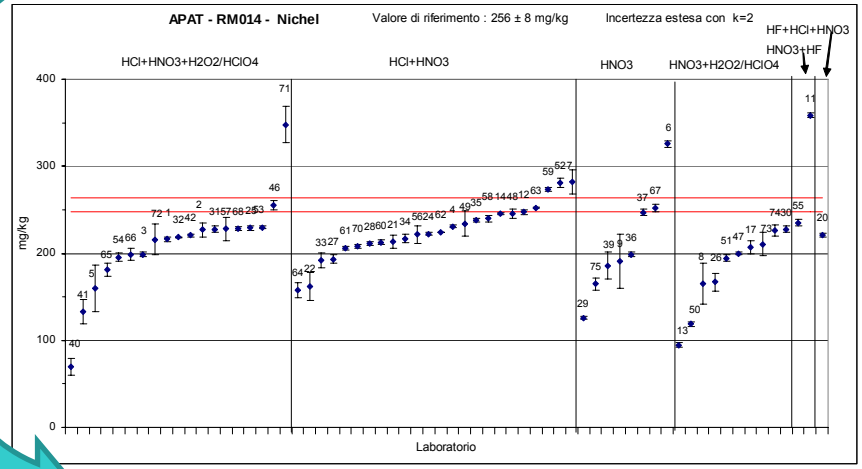
Before the PT

ISO Guide 35:2006

u_{bb}= 1.2 µg/g



After the PT

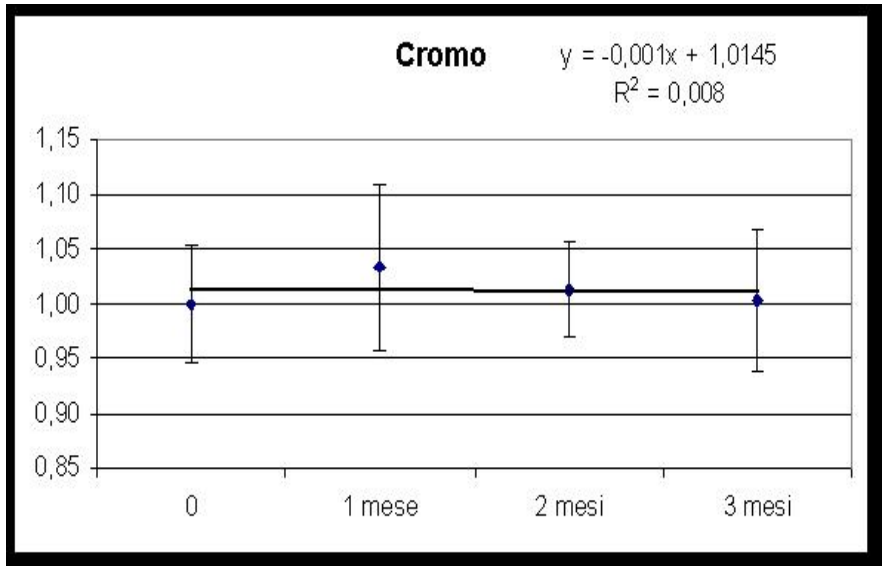


σ_{PT}=31.8 µg/g

U_{bb}<9.5 µg/g

ISO 13528:2005

Stability



Stability study results are affected by:

- ***measurement repeatability***
- ***between bottles variability***

Stability Study – Standards and Guidelines requirements

Standards/Guidelines	How*
IUPAC Harm. Protocol (1993)	Stability of the matrix and analytes must be determined
ISO Guide 43-1:1997	Where possible the coordinator should provide evidence of stability of the test items during the PT
ISO 13528:2005 Statistical methods in PT	Test items of the hom. test≥3 2 replicates measured at the end of PT $\lvert x_{mh}-y_{ms} \rvert \leq 0.3\sigma_{PT}$
IUPAC Harm. Protocol (2006)	Isochronous stability study for the PT period
ILAC G13:08/2007	Where appropriate

*** Measurements in repeatability conditions**

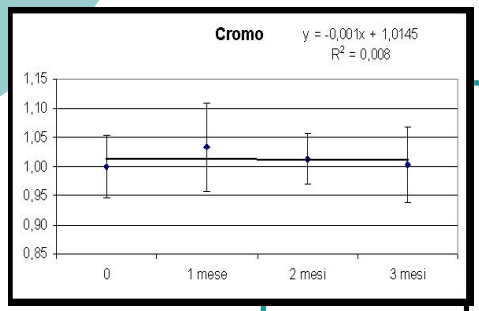
Stability Study – Standards and Guidelines requirements

Standards/Guidelines	How*
ISO/IEC CD 17043:2008 Conformity assessment – General requirement for PT	As above, but cross reference to ISO 13528 IUPAC (2006), ISO Guide 34 and ISO Guide 35
ISO Guide 35:2006 RM-General and Statistical principles for certification	Short term stability by isochronous; long term stability by classical method
ISO DGuide 34:2008 General requirements for the competence of RM producers	Always RM producers shall carry out stability study in compliance with ISO 17025
ISO CD Guide 80:2008 Guidance for production of RM for precision control (PCMs)	isochronous method

*** Measurements in repeatability conditions**

APAT RM014 – stability

- **Isochronous method 3 months**
- **Effects at +20°C**
- **Reference group at – 18°C**
- **Measurements under repeatability condition**



By Linear Regression

$$|b_1| \leq t_{0,95;n-2} \cdot s(b_1)$$

b_1 = slope;
$s(b_1)$ = slope uncertainty;
$t_{0,95}$ = t-Student.

Assigned values

- **All standards and guidelines agree on methods to determine the assigned values and their associated uncertainties:**
  - **Reference values**
  - **Consensus from participants**
  - **Consensus from expert laboratories**
  - **By formulation**

Conclusions

- **Production of test items is not an easy activity**
- **Laboratories in charge for their preparation shall demonstrate competence in the measurement of properties being determined**
- **Is the ISO 17025 accreditation enough for test items production?**