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

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ISPRA environmental metrology activities

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

Contents

- Definitions
- ISO REMCO Guides
- Quality of test items
  - Commutability
  - Homogeneity
  - Stability

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"*

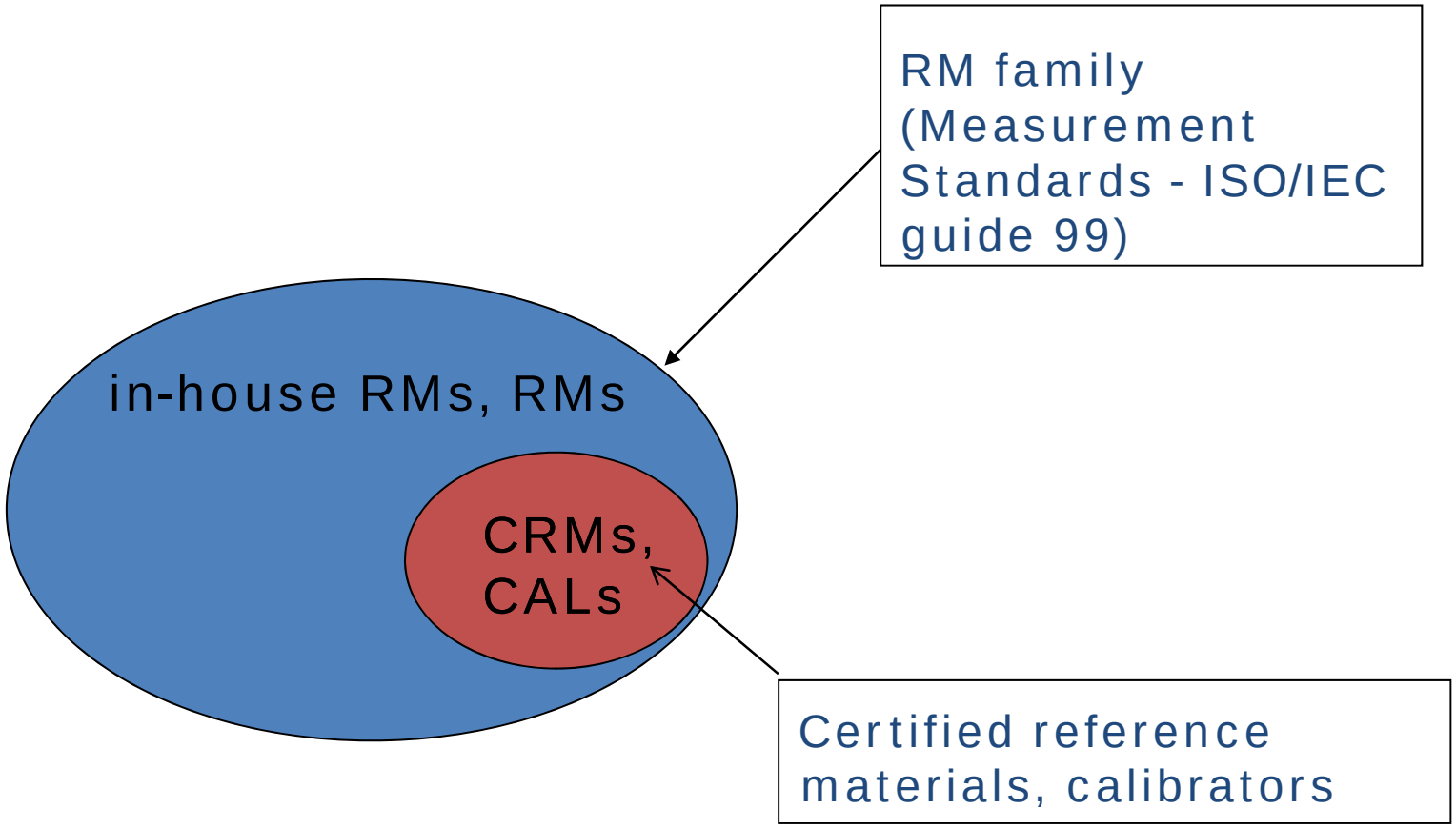
ILAC G13:2007

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

ISO Guide 34 – covering the required 'competence of RM producers'

The accreditation standard !

ISO Guide 80

on 'minimum requirements for in-house preparation of in-house used RMs for quality control '

ISO Guide 79

on production of RMs for qualitative analysis (testing of nominal properties)

ISO Guide 35 on 'characterisation and certification of RMs'

ISO Guide 33 on uses of RMs

(incl. calibration, method validation & verification, control charts, value transfer, PTs…)

ISO Guide 31 on accompanying documentation for RMs (content of certificates / RM labels / statements / transport docs, etc.)

ISO Guide 30 on definitions & terminology related to RMs (incl. a thesaurus)

Status of ISO REMCO Guides after the 32nd REMCO meeting– July 2009

- ISO DGuide 34 – Documents submitted to ISO/CS to proceed to publication
- ISO/REMCO confirms the need for CD Guide 80 and endorses the WG8 decision to limit the scope of ISO Guide 80 to materials prepared and used in-house for quality control

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

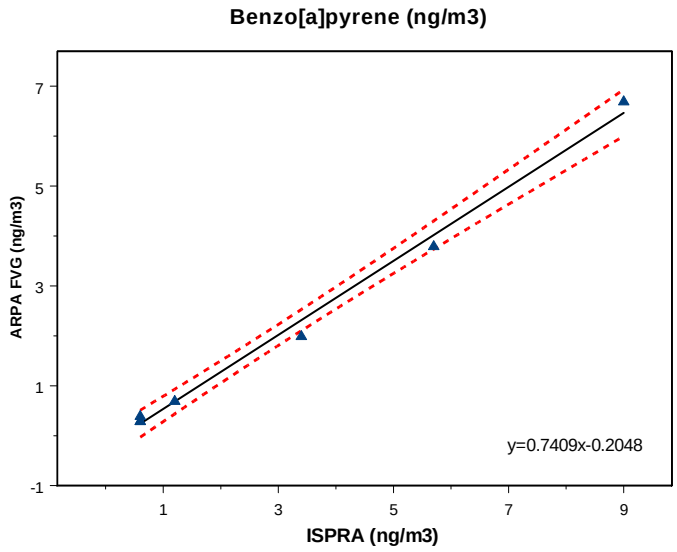
Commutability

- ISO Guide 99 gives the definition of commutability of reference material
- ISO D Guide 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"
- ISO D Guide 34 requires the assessment of commutability (where appropriate)

Commutability

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

PAH in PM10



Procedures	ratio
GC-MS/HPLC	1.7±0.2

Homogeneity

APAT RM014 - Ni – between bottles homogeneity

SERVIZIO DI TARATURA IN ITALIA

ATTESTATO DI ACCREDITAMENTO

Centro di taratura n. 211

Il Responsabile del SIT attesta che il laboratorio metrologico della ditta

Servizio di Metrologia Ambientale
dell'Istituto Superiore per la Protezione e la Ricerca Ambientale (ISPRA)
Sede: Via di Castel Romano, 100
00128 ROMA

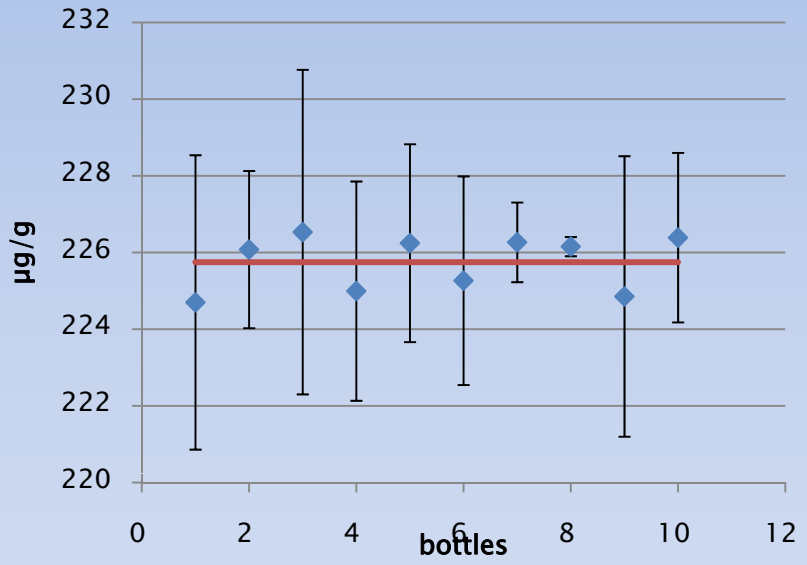
è accreditato quale Centro di taratura SIT per le grandezze, i campi e le incertezze di misura riportati nella tabella allegata al certificato di accreditamento. Il laboratorio accreditato è conforme ai requisiti della norma UNI CEI EN ISO/IEC 17025:2005 e della ISO Guide 34.

Il presente attestato è valido dal 29 Gennaio 2009 al 28 Gennaio 2013.

Torino, 29 Gennaio 2009

Il Responsabile del SIT
(Dott. Ing. M. Mosca)

This laboratory is accredited in accordance with the recognised International Standard ISO/IEC 17025:2005. This accreditation demonstrates technical competence for a defined scope and the operation of a laboratory quality management system (refer joint ISO-ILAC-IAF Communiqué dated January 2009).



Homogeneity study results are affected by:

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

Homogeneity study requirements

Standards/Guidelines	Experimental design*
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 requirements

Standards/Guidelines	Experimental design*
ISO/IEC CD 17043:2009 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 CD Guide 80:2008 Guidance on RM for precision control	10 test items – 2 replicates ANOVA to assess homogeneity between bottles
ISO DGuide 34:2009 General requirements for the competence of RM producers	Always RM producers shall carry out homogeneity study in compliance with ISO 17025 or ISO 15189 for medical field

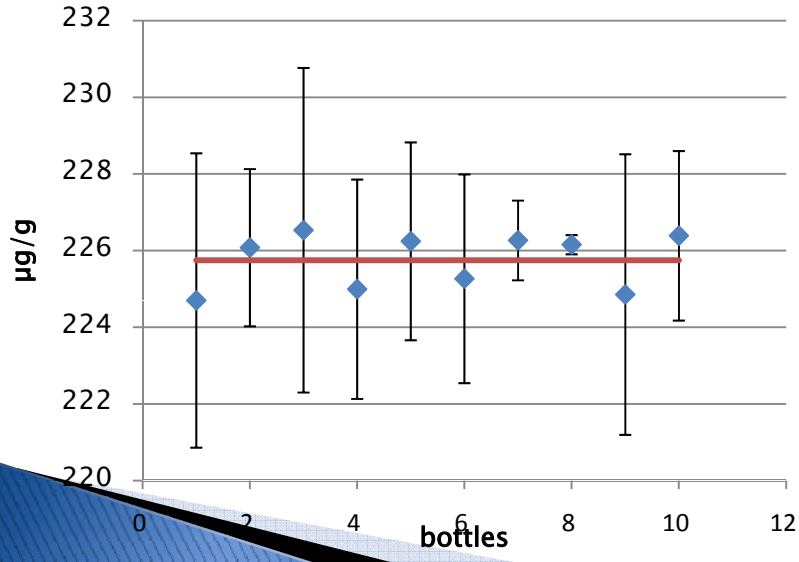
***measurements in repeatability conditions are always required**

APAT RM014 – Ni homogeneity

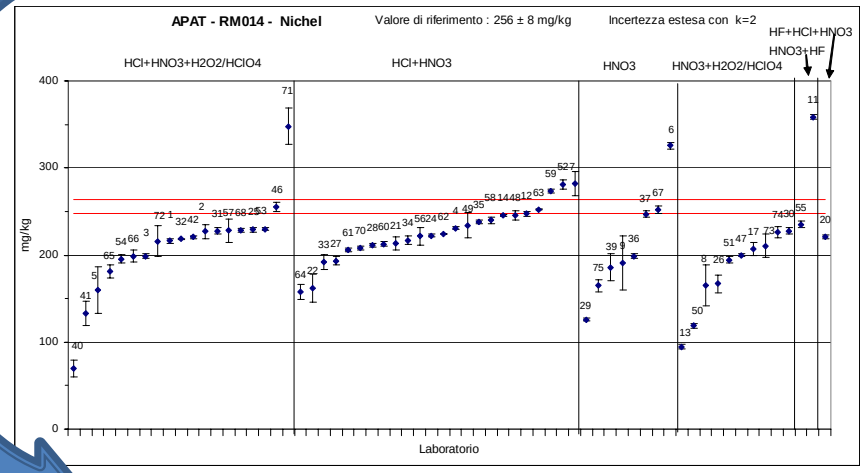
Before the PT

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

SIT

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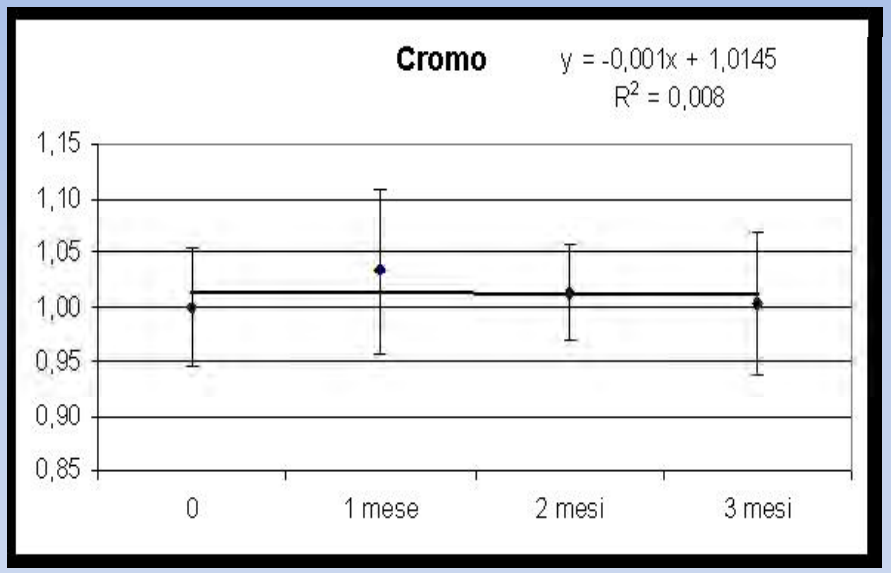


Stability study results are affected by:

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

Stability study requirements

Standards/Guidelines	Experimental design*
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**

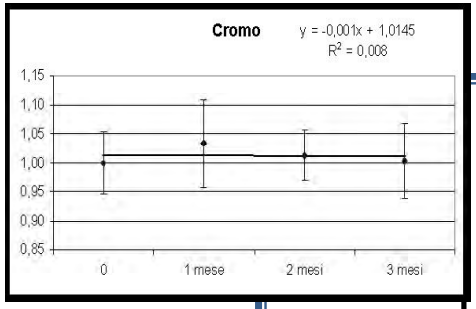
Stability study requirements

Standards/Guidelines	Experimental design*
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 CD Guide 80:2008 Guidance for production of RM for precision control (PCMs)	isochronous 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 or ISO 15189 for medical field

*** 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 through accreditation (ISO 17025 or ISO 15189 for medical field)
- Is the ISO 17025 or 15189 accreditation enough for test items production?