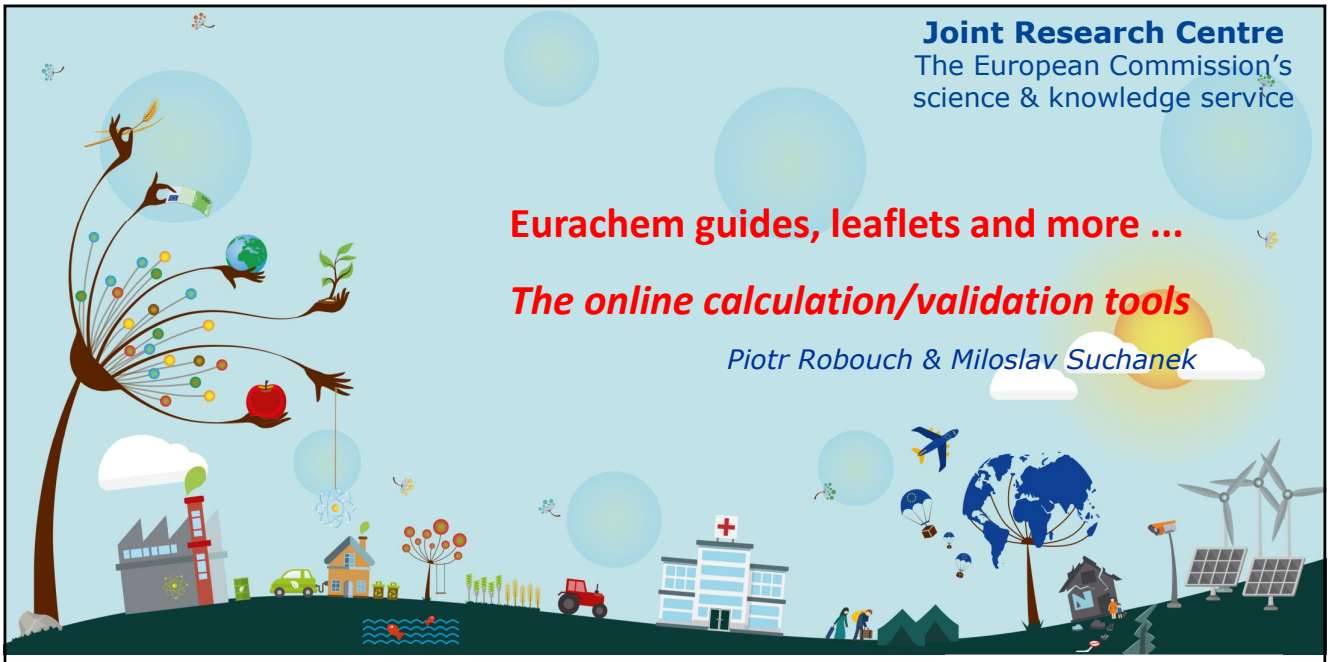


Joint Research Centre
The European Commission's science & knowledge service

Eurachem guides, leaflets and more ...

The online calculation/validation tools

Piotr Robouch & Miloslav Suchanek

European Commission

Eurachem – fact sheet

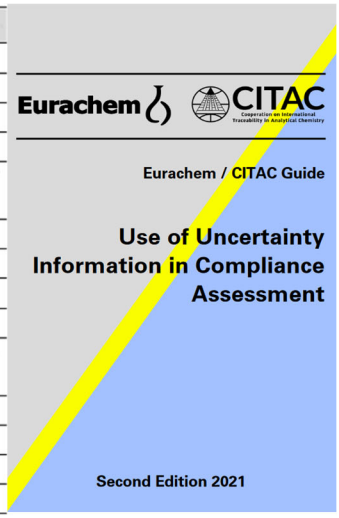
Establish a system for international traceability of chemical measurement results & promote of good quality practices.

- 35 member countries + EC
- 8 Working groups:
  MV; Edu; PT; RM; MU & Traceability;
  Qualitative; Sampling; EEE-PT
- Produce technical guides, leaflets
- Organise WS, contribute to conferences ...

European Commission

15+ ECH guides

WG		year
QA	Guide to Quality in Analytical Chemistry: An Aid to Accreditation	2016
	Accreditation for Microbiological Laboratories	2016
	Quality Assurance for R&D and non-routine Analysis	2013
	Terminology in Analytical Measurement: Introduction to VIM 3	2011
PT	Selection, Use and Interpretation of Proficiency Testing (PT) Schemes by Laboratories	(2021)
MU	Quantifying Uncertainty in Analytical Measurement (3rd ed.)	2012
	Measurement uncertainty arising from sampling (2nd ed.)	2019
	Use of uncertainty information in compliance assessment	2021
	Setting target measurement uncertainty	2015
MV	The Fitness for Purpose of Analytical Methods: A Laboratory Guide to Method Validation and Related Topics	(2021)
	Planning and reporting method validation studies (Supplement)	2019
	Blanks in method validation (Supplement)	2019
Trac.	Traceability in Chemical Measurement (2nd ed.)	2019
RM	The Selection and use of Reference Materials — *under revision*	
IUPAC	Harmonised Guidelines for the Use of Recovery Information in Analytical Measurements	1998



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17+ ECH leaflets

WG	Leaflet	year
Gen	You talk, we understand — The way out of the tower of Babel. An introduction to terminology in measurement	2015
QA	ISO/IEC 17025:2017 — A New Accreditation Standard	2018
PT	Proficiency Testing Schemes and other interlaboratory comparisons	2005
	Pre- and post-analytical proficiency testing	2009
	How can Proficiency Testing help my laboratory?	2013
	Selecting the right proficiency testing scheme for my laboratory	2015
	Proficiency testing — How much, and how often?	2017
	Use of surplus Proficiency Test items	2019
	How to investigate poor performance in proficiency testing	2019
	PT Schemes for sampling	2020
MU	Quality of chemical analyses for lab customers	2000
	Using repeated measurements to improve the standard uncertainty	2015
	Treatment of an observed bias	2017
	Setting target measurement uncertainty	2018
	Traceability of Analytical Results	2019
	What is the uncertainty factor?	2021
	Use of uncertainty information in compliance assessment	2021

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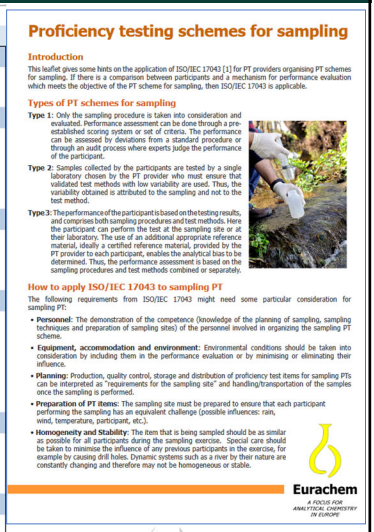
Translated in 22+ languages ...

Country	2005-PT	2009-Pre&Post	2013-Help	2015-Selection	2016-HowOften	2019-Surplus	2019-PoorPerform	2020-Sampling	2020-SpeakPT	Gd Total
EN	1	1	1	1	1	1	1	1	x	8
BG		1		1	1					3
CZ		1	1	1	1	1	1	1		7
DE	1	1	1	1	1	1	1	1		8
EE			1							1
ES	1	1	1	1						4
farsi			1		1	1	1			4
FI	1	1	1	1	x					4
FR	1	1	1	1	1	1	1	1		8
GA					1					1
HR			1							1
HU	1	1	1	1	x					4
IT	1	1	1	1	1	1	1	1		8
NL	1	1		1						3
PO	1	1								2
PT	1	1								2
RO		1								1
RU	1									1
SE	1	1	1	1	1	1	1	1		8
SI	1									1
SLK			1							1
SR		1	1		1					3
TK	1	1	1	1	1	1	1	1		8
UKR			1	1	1	1	1	1		6
Grand Total	**14**	**16**	**16**	**13**	**12**	**9**	**9**	**8**	**0**	**97**

PT leaflets



Proficiency testing schemes for sampling

Introduction

This leaflet gives some hints on the application of ISO/IEC 17043 [1] for PT providers organising PT schemes for sampling. If there is a comparison between participants and a mechanism for performance evaluation which meets the objective of the PT scheme for sampling, then ISO/IEC 17043 is applicable.

Types of PT schemes for sampling

Type 1: Only the sampling procedure is taken into consideration and evaluated. Performance assessment can be done through a pre-established scoring system or set of criteria. The performance can be assessed by deviations from a standard procedure or through an audit process where experts judge the performance of the participant.

Type 2: Samples collected by the participants are tested by a single laboratory chosen by the PT provider who must ensure that validated test methods with low variability are used. Thus, the variability obtained is attributed to the sampling and not to the test method.

Type 3: The performance of the participant is based on the testing results, and comprises both sampling procedures and test methods. Here the participant can perform the test at the sampling site or at their laboratory. The use of an additional appropriate reference material, ideally a certified reference material, provided by the PT provider to each participant, enables the analytical bias to be determined. Thus, the performance assessment is based on the sampling procedures and test methods combined or separately.

How to apply ISO/IEC 17043 to sampling PT

The following requirements from ISO/IEC 17043 might need some particular consideration for sampling PT:

- **Personnel:** The demonstration of the competence (knowledge of the planning of sampling, sampling techniques and preparation of sampling sites) of the personnel involved in organizing the sampling PT scheme.
- **Equipment, accommodation and environment:** Environmental conditions should be taken into consideration by including them in the performance evaluation or by minimising or eliminating their influence.
- **Planning:** Production, quality control, storage and distribution of proficiency test items for sampling PTs can be interpreted as "requirements for the sampling site" and handling/transportation of the samples once the sampling is performed.
- **Preparation of PT items:** The sampling site must be prepared to ensure that each participant performing the sampling has an equivalent challenge (possible influences: rain, wind, temperature, participant, etc.).
- **Homogeneity and Stability:** The item that is being sampled should be as similar as possible for all participants during the sampling exercise. Special care should be taken to minimise the influence of any previous participants in the exercise, for example by causing drill holes. Dynamic systems such as a river by their nature are constantly changing and therefore may not be homogeneous or stable.

Eurachem

A FOCUS FOR ANALYTICAL CHEMISTRY IN EUROPE

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24 workshops ... *since 2005*

mm/yy	Workshop	
10/22	10th International Workshop on Proficiency Testing	UK
05/21	Trends and challenges in ensuring quality in analytical measurements	CZ
07/20	Quality Assurance Elements for Analytical Laboratories in the University Curriculum	RO
02/20	Accreditation of analytical, microbiological & medical labs - ISO17025 & 15189	CY
11/19	Uncertainty from sampling and analysis for accredited laboratories	DE
05/19	Validation of targeted and non-targeted methods of analysis	EE
02/19	Critical Issues Of The Accreditation Standards - ISO17025 & 15189	CY
05/18	Data – Quality, Analysis and Integrity	IE
10/17	9th International Workshop on Proficiency Testing	SI
06/17	Uncertainty in Qualitative and Quantitative Analysis	CY
05/16	Method Validation - Current Practices and Future Challenges	BE
09/14	8th International Workshop on Proficiency Testing	DE
09/14	MU for food and feed analysis	DK
05/14	Quality in Analytical Measurements	PT
05/13	Quality Assurance of Measurements from Field to Laboratory	FI
10/12	Key Challenges in Internal Quality Control	DE
05/12	Validation, Traceability and Measurement Uncertainty	DE
10/12	7th Eurachem workshop on Proficiency Testing	TR
06/11	Recent developments in Measurement Uncertainty	PT
05/11	Key Quality Assurance Challenges for Analytical Measurements	RU
05/10	Analytical Results for Decisions	DK
10/08	6th Eurachem workshop on Proficiency Testing	IT
04/08	Measurement Uncertainty in Sampling and Compliance	DE
10/05	5th International Workshop on Proficiency Testing	SI

Eurachem
Prague 2021
17th May - 21st May 2021

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What else?

Just an example

Extract from QUAM 2012

From the calibration data.

The above formula for $var(x_{pred})$ can be written in terms of the set of n data points, (x_i, y_i), used to determine the calibration function:

$$var(x_{pred}) = var(y_{obs}) / b_1^2 + \frac{S^2}{b_1^2} \cdot \left(\frac{1}{\sum w_i} + \frac{(x_{pred} - \bar{x})^2}{\cdot (\sum (w_i x_i^2) - (\sum w_i x_i)^2 / \sum w_i)} \right)$$

Eq. E3.4

where $S^2 = \frac{\sum w_i (y_i - y_{fi})^2}{(n-2)}$, $(y_i - y_{fi})$ is the residual for the i^{th} point, n is the number of data points in the calibration, b_1 the calculated best fit gradient, w_i the weight assigned to y_i and $(x_{pred} - \bar{x})$ the difference between x_{pred} and the mean $\bar{x}$ of the n values x_1, x_2....

For unweighted data and where $var(y_{obs})$ is based on p measurements, equation E3.4 becomes

$$var(x_{pred}) = \frac{S^2}{b_1^2} \cdot \left(\frac{1}{p} + \frac{1}{n} + \frac{(x_{pred} - \bar{x})^2}{(\sum (x_i^2) - (\sum x_i)^2 / n)} \right)$$

Eq. E3.5

This is the formula which is used in example 5 with $S_{xx} = \left[\sum (x_i^2) - \left(\sum x_i \right)^2 / n \right] = \sum (x_i - \bar{x})^2$.

[…] and now you know …

or follow a training or buy a software

- ✓ Guides
- ✓ Leaflets
- ✓ Workshops
- ✓ Trainings
- ❑ **webtools**

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I Had A Dream

Use of uncertainty information in compliance assessment (2021)

- ❑ **Compliance** to requirements *v.s.* Producers', Consumers or Shared **Risks**
- ✓ Result ± $U_{rel,\%}$ (k=2)
- ✓ Upper limit or Lower limit or Both
- ✓ Level of max risk (normal or "0" tolerance)
- ✓ Guard band

Excellent tool @ https://**formeq.org**/avaliacao-automatica-de-conformidade/

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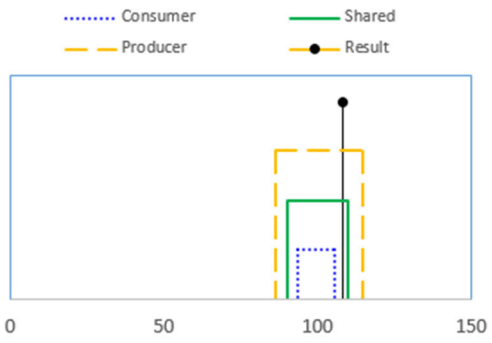
Goto https://pihin.eu/compliance

only yellow cells can be edited

Input			
	Result	108	
	unit	g/100g	
	LMR	5%	normal
Target MU (k=2)		10%	%
RU (k=2),% @ mL		5%	%
RU (k=2),% @ ML		5%	%
	mL	90	g/100g
	ML	110	g/100g
	gb	1.64	



piotr's Tools

Conformance according to ...		lower/min	upper/max	
Producers Risk	YES	86.31	114.51	g/100g
Shared Risk	YES	90	110	g/100g
Consumers Risk	NOT	93.69	105.49	g/100g

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... another example - Homogeneity

check é			
	F-test:	passed	$F < F_{crit}$?
	ISO-13528:	passed	$s_{sam} < 0.3 * s_{pt}$?
	IUPAC:	passed	$s_{sam}^2 < F1\ s_{all}^2 + F2*MSW$?
u* (ISO 35):	0.072072088	u* = sqrt(MSW/2)*(2/dfW)^0.25	
u(hom) =	0.072072088	1.5%	(= max(u*,Sb))

References
ISO 13528:2015
ISO 35
IUPAC - Pure Applied Chem. Vol 78, nr 1; p. 145-196

(vials) g = 10
(replicates) m = 2

ONE

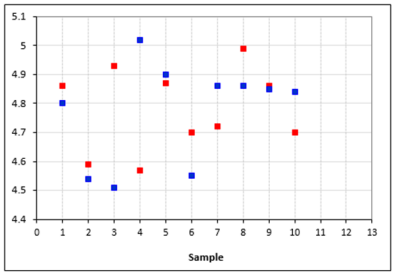
unit		ANOVA						
mean =	4.776		df	SS	MS	Variance	s	F
s_{pt} (%) =	11%	betw - B/sam	9	0.22858	0.025397778	0.001083889	0.032922468	1.093318027
s_{pt} =	0.539688	within - W/an	10	0.2323	0.02323	0.02323	0.15241391	3.020382947 *Fcrit*
$s_{all} = 0{,}3*s_{pt}$ =	0.1619064	total - T/x	19	0.46088		0.012698889	0.112689347	

0.026213682 $F1*s_{all}^2+F2*MSW$ = 0.049826752

TWO

outliers	Sample	x1	x2
	1	4.86	4.8
	2	4.59	4.54
	3	4.93	4.51
	4	4.57	5.02
	5	4.87	4.9
	6	4.7	4.55
	7	4.72	4.86
	8	4.99	4.86
	9	4.86	4.85
	10	4.7	4.84
	11		
	12		

var avg



piotr's Tools

Determination of the mass fractions of **total As in complete feed for fish EURL-HM-25, 2017**
https://europa.eu/!dd96ND

- ✓ 10 bottles, 2 replicates
- ✓ σ_{pt} = 11 %
- ✓ Suitable homogeneity
- ➢ u_{hom} = 1.5 % (**ISO guide 35**)
- ➢ Validated *v.s.* SoftCRM©

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How did I do this ?

- Defined the problem,
- Collected the model equations,
- ➢ Constructed the XLS file,
- Checked/Validated (i) using reference data or (ii) *vs.* reliable software,
- Protected all cells (excl. "input" ones),
- Saved the file one MS OneDrive (or MS SharePoint),
- Generated the "Embed" code,
- Pasted in blog/webpage,
- Checked with various **browsers/devices**,
- ❖ Drafted **instructions** & provided **validation data**.

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Pros & Cons

- ✓ Responsibility of the app owner
- ✓ Nothing to download/install
- ✓ No alterations possible
- ✓ Available everywhere
- ✓ Accessible to all
- ✓ Fairly easy
- ✓ Useful for training
- ✓ Useful for own tool validation

- ❖ Caution required when introducing data
- ❖ Page refresh = data lost ☹
- ❖ Not possible to use Copy/Paste to introduce data (*anymore*)
- ❖ ???

Just try it

European Commission

Available apps on www.pihin.eu

feedback friendly

Proficiency Testing
- RSD_R(Horwitz)
- Homogeneity
- *(stability)*
- PT evaluation ($D_{\%}$, z, ζ, MU)
- *(Naji2 Plot)*

- ECH-Compliance (ISBN 978-0-948926-38-9)
- LOQ/LOD (doi: 10.2787/8931)
- GMO-MU (doi:10.2760/738565)
- (*FCM-compliance*)

SUGGESTION

Eurachem could launch a "call" (1/y)
for a specific **calculation app**
"*simple & effective*"
later available from the ECH www
(after formal selection by ECH panel)

Reward
- Free Registration* @ next ECH workshop
- Invited presentation

* *Sponsored by* pihin.eu

European Commission

Thank you for your attention

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Miloslav Suchanek

European Commission