EURL-HM 2006–2017
What did we learn
25 PTs later?
Piotr Robouch
on behalf of the EURL team

The European Commission's science and knowledge service

Joint Research Centre

European Commission

Mandate - Regulation (EC) No 882/2004

[…] Coordinate application by NRLs of analytical methods, in particular by organising **comparative test (PTs)** and by ensuring an appropriate follow-up of such PTs in accordance with internationally accepted protocols, when available […]

- EURL for Heavy Metals in Food (of non-animal origin), Feed and wild caught fish

- As, iAs; Cd; Hg; MeHg; Pb
  + optional *(Trace elements)*

- 51 NRLs from all MS + CH, IS, NO & RS
  (IS-CY 4700 km apart)

➔ 23 PTs + 2 ring-trial validated methods

2

CRL EURL

European Commission

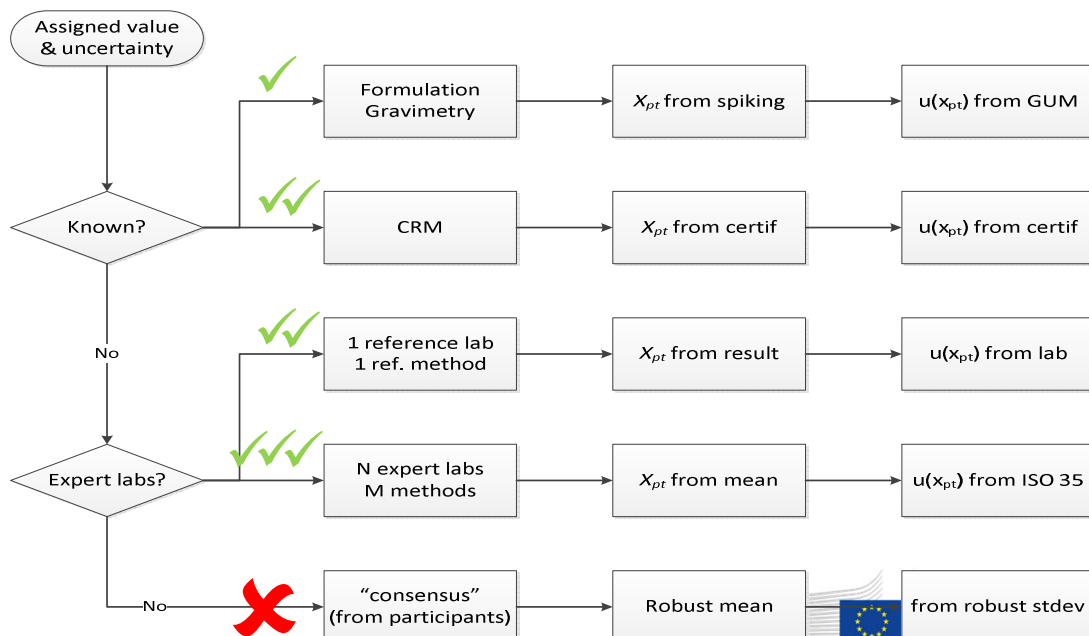## A rigorous approach *"à la IMEP"* (since 1989)

- Benefited of the **processing facility** of the Reference Material Unit
- **Independent assigned value &** corresponding **MU**
- Request systematically **measurement uncertainties**
- Z (& Z') scores
- Zeta scores
- MU evaluation
- Review "***truncated values***" (less than)
- **Compliance** assessment
- Thorough "discussion" in report to participants & during annual WS
- Fully compliant with ISO 17043:2010 & ISO 13528:2015

268-PT Accredited by the
Belgian Accreditation Body (BELAC)

European Commission

3

Assigned value & uncertainty

| Known? | ✓ | Formulation Gravimetry | → | X_{pt} from spiking | → | $u(x_{pt})$ from GUM |
| | ✓✓ | CRM | → | X_{pt} from certif | → | $u(x_{pt})$ from certif |

No

| Expert labs? | ✓✓ | 1 reference lab 1 ref. method | → | X_{pt} from result | → | $u(x_{pt})$ from lab |
| | ✓✓✓ | N expert labs M methods | → | X_{pt} from mean | → | $u(x_{pt})$ from ISO 35 |

No ✗ "consensus" (from participants) → Robust mean → from robust stdev

4

Uncertainty of assigned value, $u(x_{pt})$

✓ Characterisation (u_{char}), (1 or n) expert lab(s)

✓ Homogeneity (balanced design) ➔ u_{hom} = max(s_{bb} , u^*), cf. ISO 35

✓ Stability (classical or isochronous) ➔ u_{st} = 0 (?)

$$➔ u(x_{pt}) = \sqrt{u_{char}^2 + u_{hom}^2 + \cancel{u_{st}^2}}$$

European Commission

EURL-HM 25 HM in complete feed for fish

	As	iAs	Cd	Pb	Hg
Expert 1	3.98 ± 0.38	0.0263 ± 0.0031			
Expert 2	4.40 ± 0.31	0.041 ± 0.0041			0.0879 ± 0.0088
Expert 3	3.65 ± 0.55	0.0239 ± 0.0044			0.0924 ± 0.0114
Expert 4	4.33 ± 0.77	0.0327 ± 0.0034			0.0892 ± 0.0238
Expert 5	4.57 ± 0.22				0.0953 ± 0.0123
Expert 6			0.4549 ± 0.0067	2.603 ± 0.026	0.0908 ± 0.0014
x_{pt}	4.19	0.0309	0.4549	2.603	0.0911
u_{char}	0.17	0.0037	0.0033	0.013	0.0013
u_{hom}	0.03	0.0002	0.0023	0.042	0.0017
u_{st}	0	0	0	0	0
$u(x_{pt})$	0.17	0.0037	0.0040	0.044	0.0022
$U(x_{pt})$	0.34	0.0074	0.0081	0.087	0.0044
σ_{pt}	0.54	0.0068	0.0819	0.364	0.0200
σ_{pt} (% x_{pt})	13%	22%	18%	14%	22%
$u(x_{pt})/\sigma_{pt}$	0.3	0.5	0.1	0.1	0.1

European Commission

Report of the evaluation

Lab Code	x_lab	±	k	technique	u_lab	z-score	zeta	unc.
L01	3.9	0.86	2	AAS	0.430	-0.5	-0.6	a
L02	4.4	1.1	2	ICP-MS	0.550	0.4	0.4	c
L03	4.1	0.7	2	ICP-MS	0.350	-0.2	-0.2	a
L04	3.89	0.58	2	ICP-MS	0.290	-0.5	-0.9	a
L05	4.5	0.7	2	ICP-MS	0.350	0.6	0.8	a
L06	4.3	0.3	2	ICP-MS	0.150	0.2	0.5	b
L07	4.5	0.9	2	ICP-MS	0.450	0.6	0.7	a
L08	5.116	1.099	2	ICP-MS	0.550	1.7	1.6	c
L09	5.03	0.25	2	ICP-MS	0.125	1.6	3.9	b
L10	3.93	1.06	2	ICP-MS	0.530	-0.5	-0.5	a
L12	4.89	0.979	2	ICP-MS	0.490	1.3	1.4	a
L14	7.29	1.5	2	ICP-MS	0.750	5.7	4.0	c
L15	5.328	1.332	2	ICP-MS	0.666	2.1	1.7	c
L16	5.471	1.335	2	AAS	0.668	2.4	1.9	c
L17	5.28	0.4	2	HG-GFAAS	0.200	2.0	4.1	a
L18	4.43	0.76	2	ICP-MS	0.380	0.5	0.6	a
L19	5.2	2.09	2	ICP-MS	1.045	1.9	1.0	c

(watermark: example)

- **Not reported uncertainties are set to ZERO !**

- $\sqrt{3}$ is set by the ILC coordinator when no coverage factor k is reported.
  The reported uncertainty assumed to have a rectangular distribution

- score evaluation colours: satisfactory, questionable, unsatisfactory,

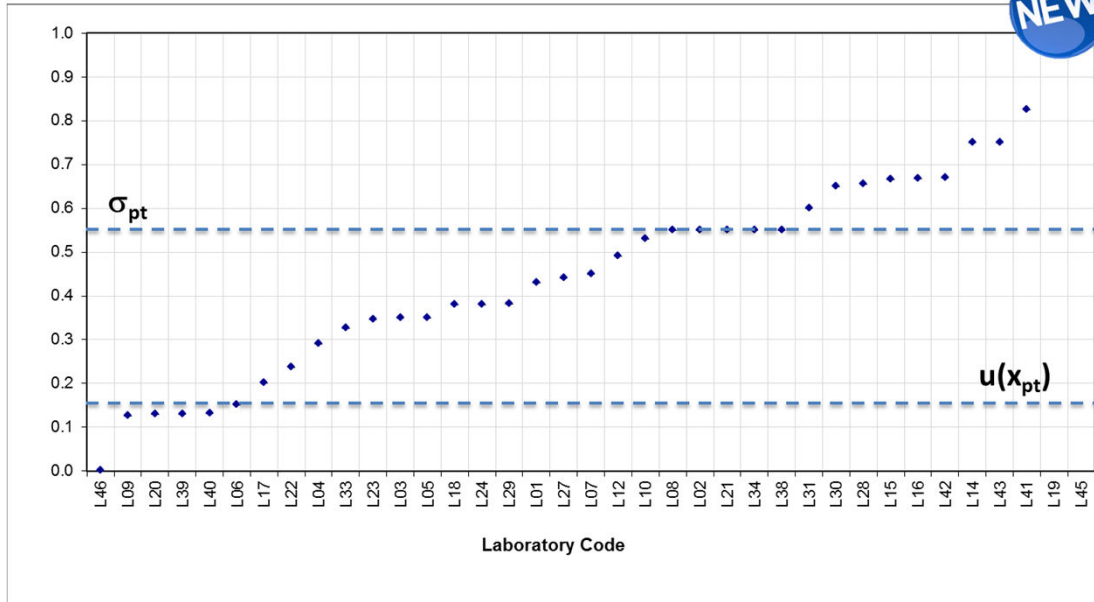- ^{c} Case "a": $u(x_{pt}) \leq u(x_i) \leq \sigma_{pt}$; Case "b": $u(x_i) < u(x_{pt})$; and Case "c": $u(x_i) > \sigma_{pt}$

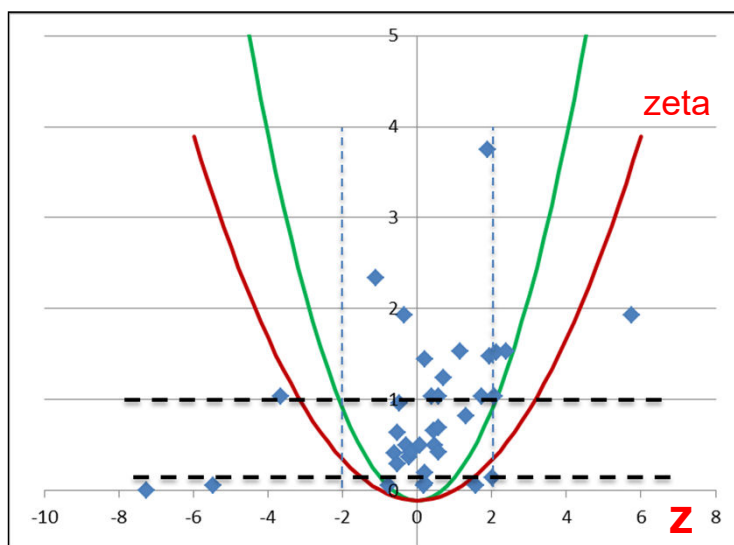---

EURL-HM 25: totAs in complementary feed
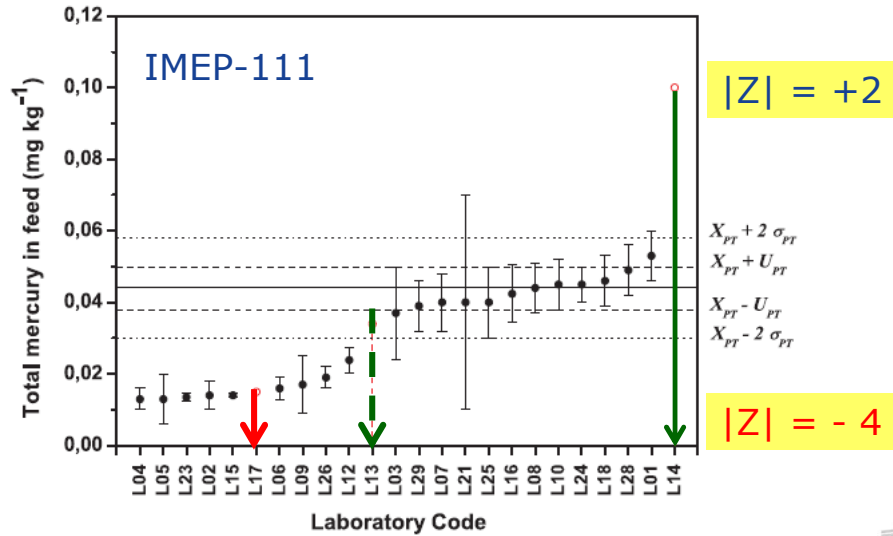

Assigned value (x_{pt}): solid black line; Assigned range ($x_{pt} \pm U_{pt}$ (k=2)): dashed blue lines; Acceptance range ($x_{pt} \pm 2\ \sigma_{pt}$): dotted red lines.

European Commission
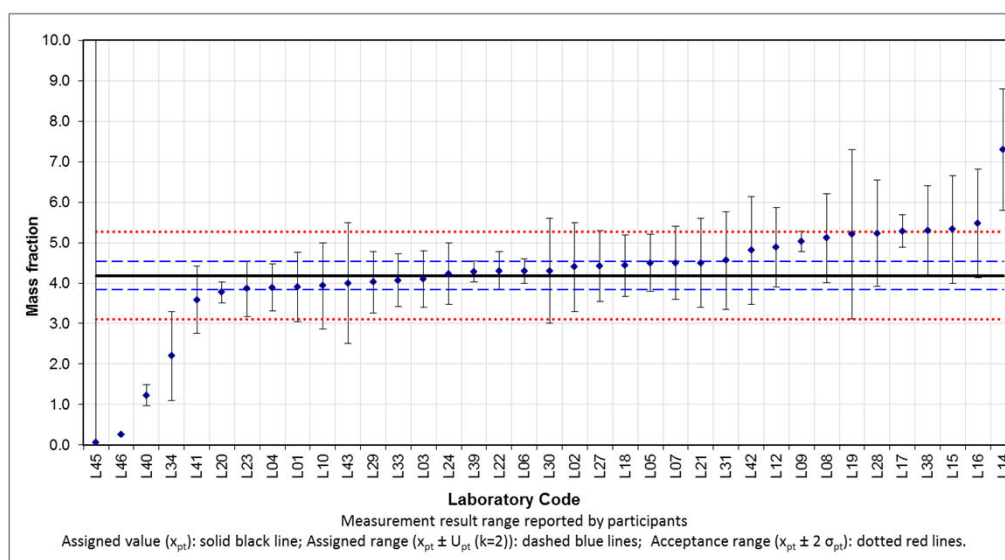
EURL-HM 25: reported MU

Naji Plot *(since 2002)*: $[u_i / \sigma_{pt}]^2 = f(z)$

Truncated values ("*less than*")

IMEP-111

$|Z| = +2$

$X_{PT} + 2\,\sigma_{PT}$
$X_{PT} + U_{PT}$

$X_{PT} - U_{PT}$
$X_{PT} - 2\,\sigma_{PT}$

$|Z| = -4$

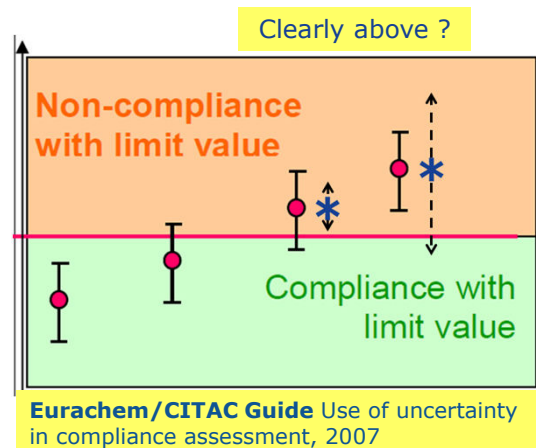11   (Fig.E.5 ISO 13528:2015)

An additional "*measurand*": "Compliance"

<u>HYP</u>: **the test item is non-compliant**

Consider the following three components:

- compliance statement by laboratory
  (Compliant or Non-Compliant)

- laboratory measurement results:
  reported (or not) for the relevant analyte);
  $X_i - U_i > ML?$

- laboratory justification
  (correct, incorrect or partially incorrect).

Clearly above ?

Non-compliance with limit value

Compliance with limit value

Eurachem/CITAC Guide Use of uncertainty in compliance assessment, 2007

12

Yet another concern: **Rounding**

- $u(x_{pt}) < 0.3\ \sigma_{pt}$ [in XLS: up to 0.349]

- |scores| > 2.0   [in XLS: up to 2.050]
  |scores| ≥ 3.0   [in XLS: up to 3.050]

European Commission

EURL-MeNiCoFF

Thank you