

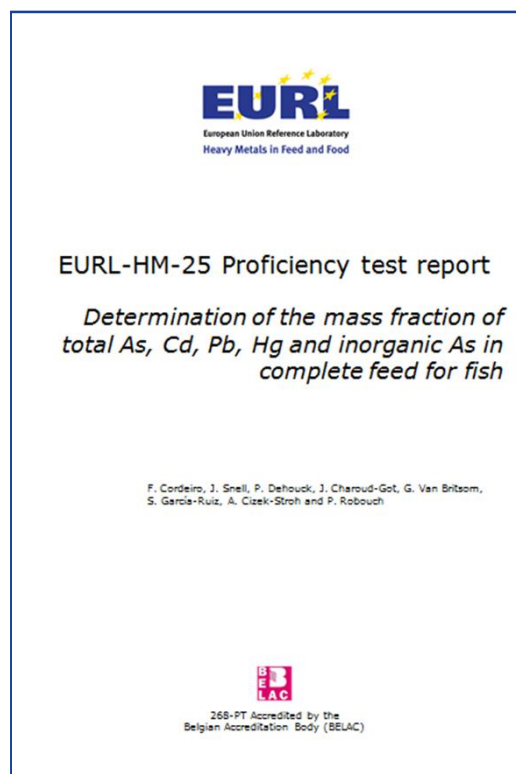


EURL-HM-25: Determination of As, Cd, Pb, Hg and iAs, Co, Cu, Fe, Mn, Se and Zn in complete feed for fish

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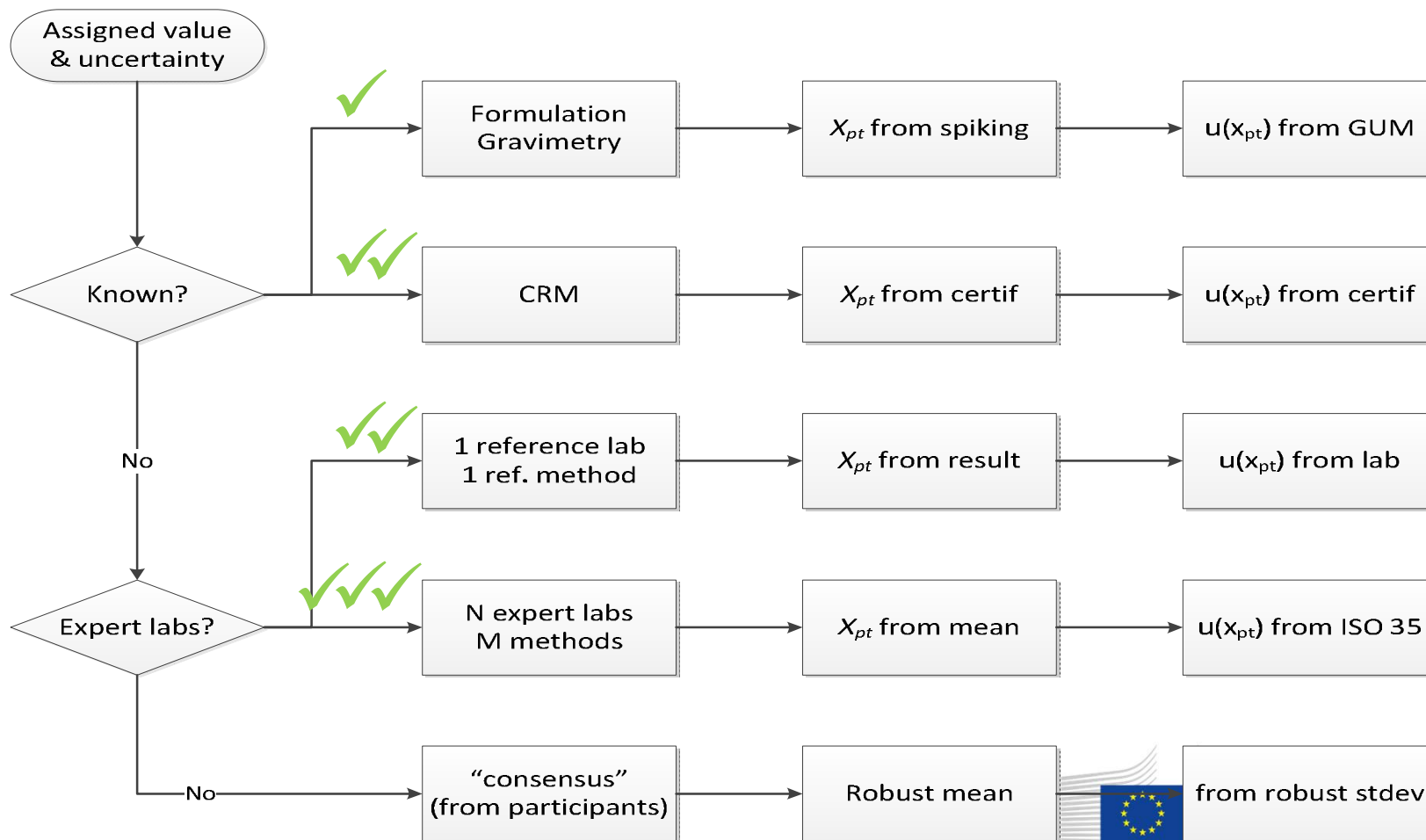
The test item & PT organisation



JRC Report 108471 (2017)

- Complete feed for fish **provided by CReAA**
- **Composition:** 50 % (m/m) fishmeal, 10 % soybean protein
10 % soybean extraction flour, 10 % corn gluten
+ cod liver oil + vitamins and minerals
- Processed @ JRC-Geel (**spiked** with As, Pb and Hg)
- Produced 200 vials (5 g each)
- Water content 1.7 % m/m
- Particle size below 196 nm X_{90}
- Sample dispatch: 11-12/06/2017
- Deadline for reporting: 30/06/2017
- Preliminary Report: 28/07/2017





Relevant parameters (for As, iAs, Hg, Cd* & Pb*)

- ✓ Homogeneity: 10 bottles, 2 replicates, u_{hom} (As, Cd, Hg, Pb)
minimal sample intake: 0.4 g
- ✓ Stability (8 weeks); start & end; no trends: $u_{stab} = 0$
- ✓ Characterisation, u_{char} : up to 5 expert labs
related to 12 % moisture !!

$$u_{hom} = \sqrt{\frac{1}{n} \sum_{i=1}^n (x_i - \bar{x})^2}$$

- ✓ σ_{pt} (Horwitz)

$$\text{IF } u(x_{pt})/\sigma_{pt} = 0.3 \Rightarrow z'_i = \frac{x_i - x_{pt}}{\sqrt{\sigma_{pt}^2 + u^2(x_{pt})}}$$

- ✓ ELSE z score

Assigned values & Co. (mandatory)

	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_{stb}	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
$\sigma_{pt} (\% x_{pt})$	13%	22%	18%	14%	22%
$u(x_{pt})/\sigma_{pt}$	0.3	0.5	0.1	0.1	0.1

Assigned values & Co. (optional)

	Co	Cu	Fe	Mn	Se	Zn
x_{pt}	0.339	15.3	289	37.2	0.952	93.5
$s^* = \sigma_{pt}$	0.046	2.8	27	4.1	0.163	10.3
n	15	21	20	15	16	21
$u(x_{pt})$	0.014	0.7	7.2	1.3	0.047	2.9
$U(x_{pt})$	0.028	1.5	14	2.6	0.094	5.7
$\sigma_{pt} (\% x_{pt})$	14%	18%	9%	11%	17%	11%
$u(x_{pt})/\sigma_{pt}$	0.3	0.3	0.3	0.3	0.3	0.3

- ✓ x_{pt} = robust mean (Alg.A, ISO 13528:2015)
- ✓ σ_{pt} = robust stdev = s^*
- ✓ $u(x_{pt}) = 1.25 s^* / \sqrt{n}$

Reported results (example: Se)

Assigned range: $x_{pt} = 0.952$; $U(x_{pt})$ ($k = 2.0$) = 0.094; $\sigma_{pt} = 0.163$
(all values in mg kg⁻¹)

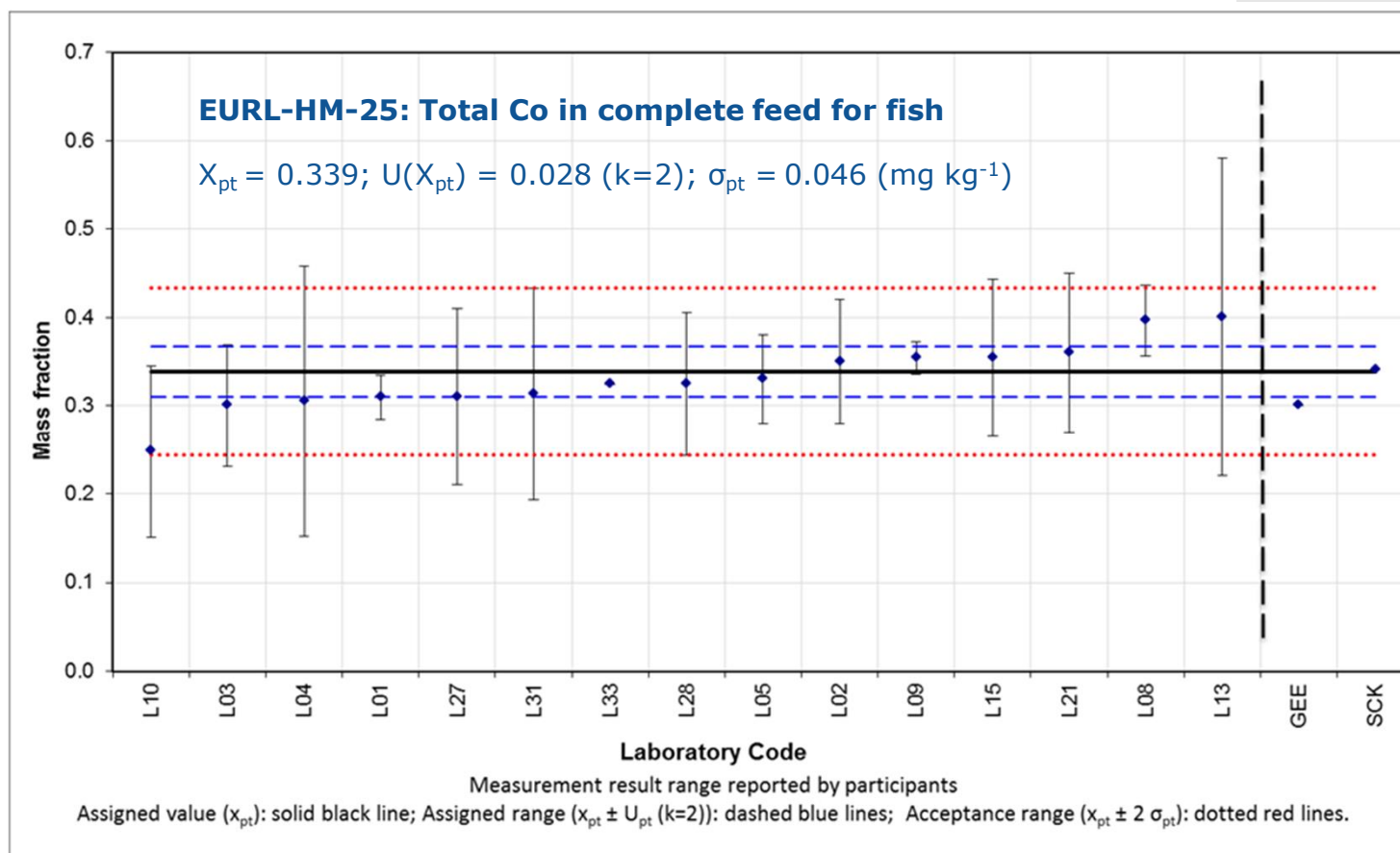
Lab	x_i	U_i	k	u_i	Technique	z score ^a	ζ score ^a
L01	< 0.75				ICP-MS		
L03	0.83	0.27	2	0.135	ICP-MS	-0.75	-0.85
L04	0.891	0.134	2	0.067	ICP-MS	-0.38	-0.75
L05	1.2	0.3	2	0.15	ICP-MS	1.53	1.58
L06	0.85	0.07	2	0.035	ICP-MS	-0.63	-1.74
L07	0.8	0.2	2	0.1	ICP-MS	-0.94	-1.38
L08	1.046	0.188	2	0.094	ICP-MS	0.58	0.89
L09	1.25	0.06	2	0.03	ICP-MS	1.84	5.34
L10	0.788	0.26	2	0.13	ICP-MS	-1.01	-1.19
L15	1.374	0.344	2	0.172	ICP-MS	2.61	2.37
L18	0.915	0.198	2	0.099	ICP-MS	-0.23	-0.34
L19	0.98	0.49	2	0.245	ICP-MS	0.17	0.11
L21	0.9	0.2	2	0.1	ICP-MS	-0.32	-0.47
L22	0.879	0.132	2	0.066	ICP-MS	-0.45	-0.90
L28	1.07	0.27	2	0.135	ICP-MS	0.73	0.83
L31	0.977	0.26	2	0.13	ICP-MS	0.15	0.18
L33	0.871			0	ICP-MS	-0.50	-1.72

- ✓ N = 16 (quantified)
- ✓ L01: truncated value
- ✓ L33: no MU
- ✓ "k" reported?

Cobalto (N = 15; ICP-MS)

CIR 131/2014

ML = 1 mg/kg (total)
12 % moisture

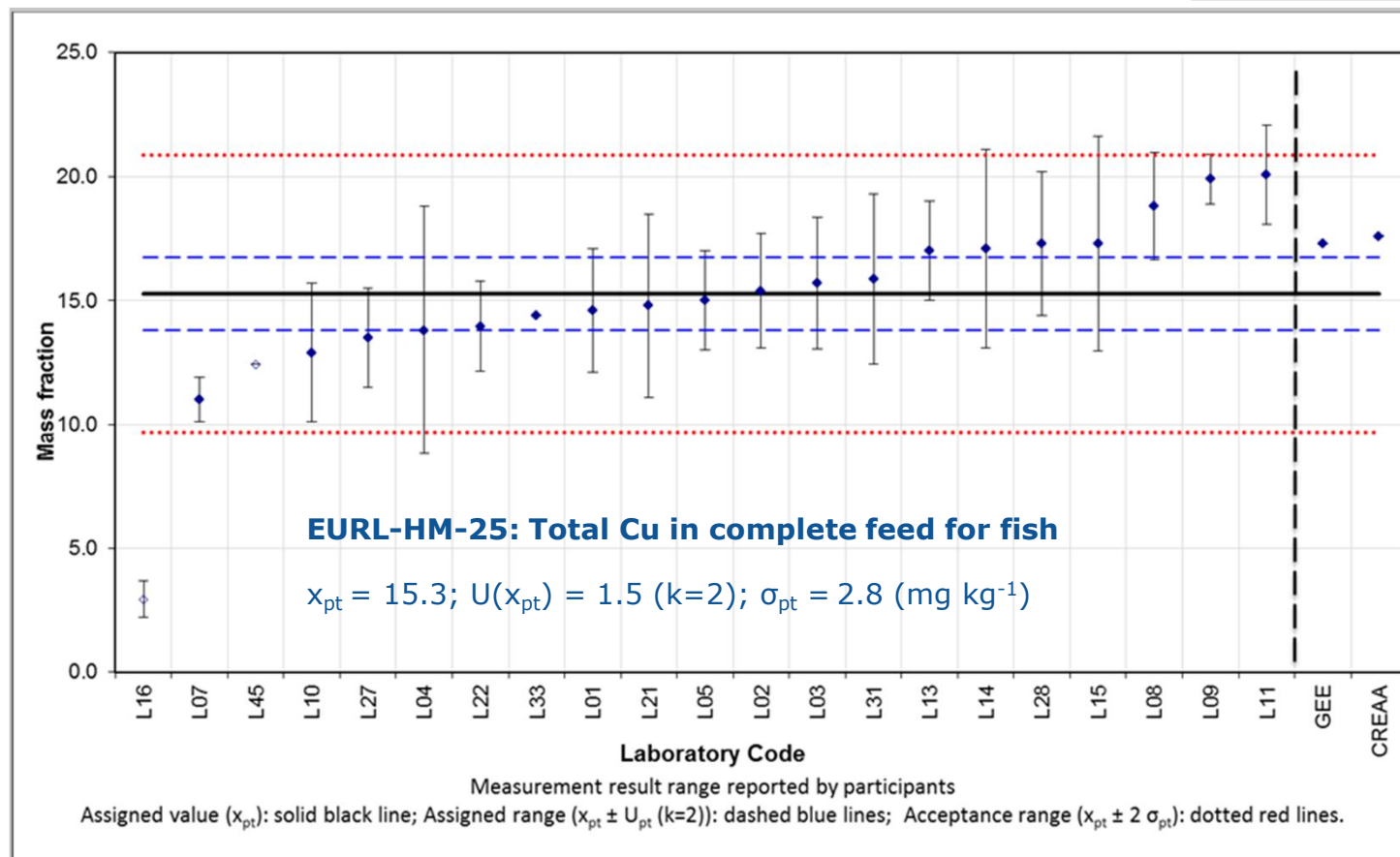


Rame (N = 21; AAS, ICP-MS, ICP-OES)

CIR 2016/2261

ML = 25 mg/kg (total)

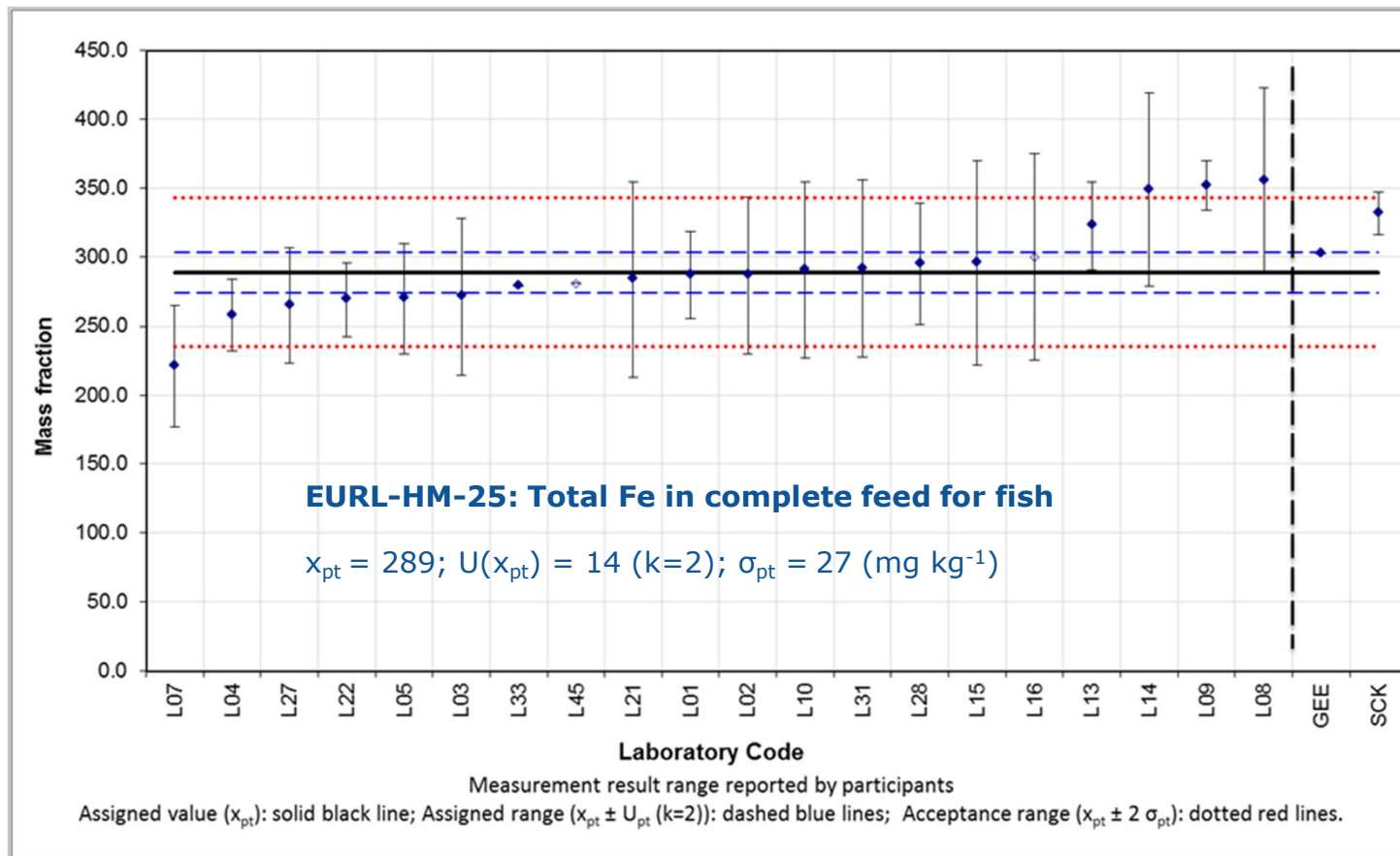
12 % moisture



Ferro (N = 20; AAS, ICP-MS, ICP-OES)

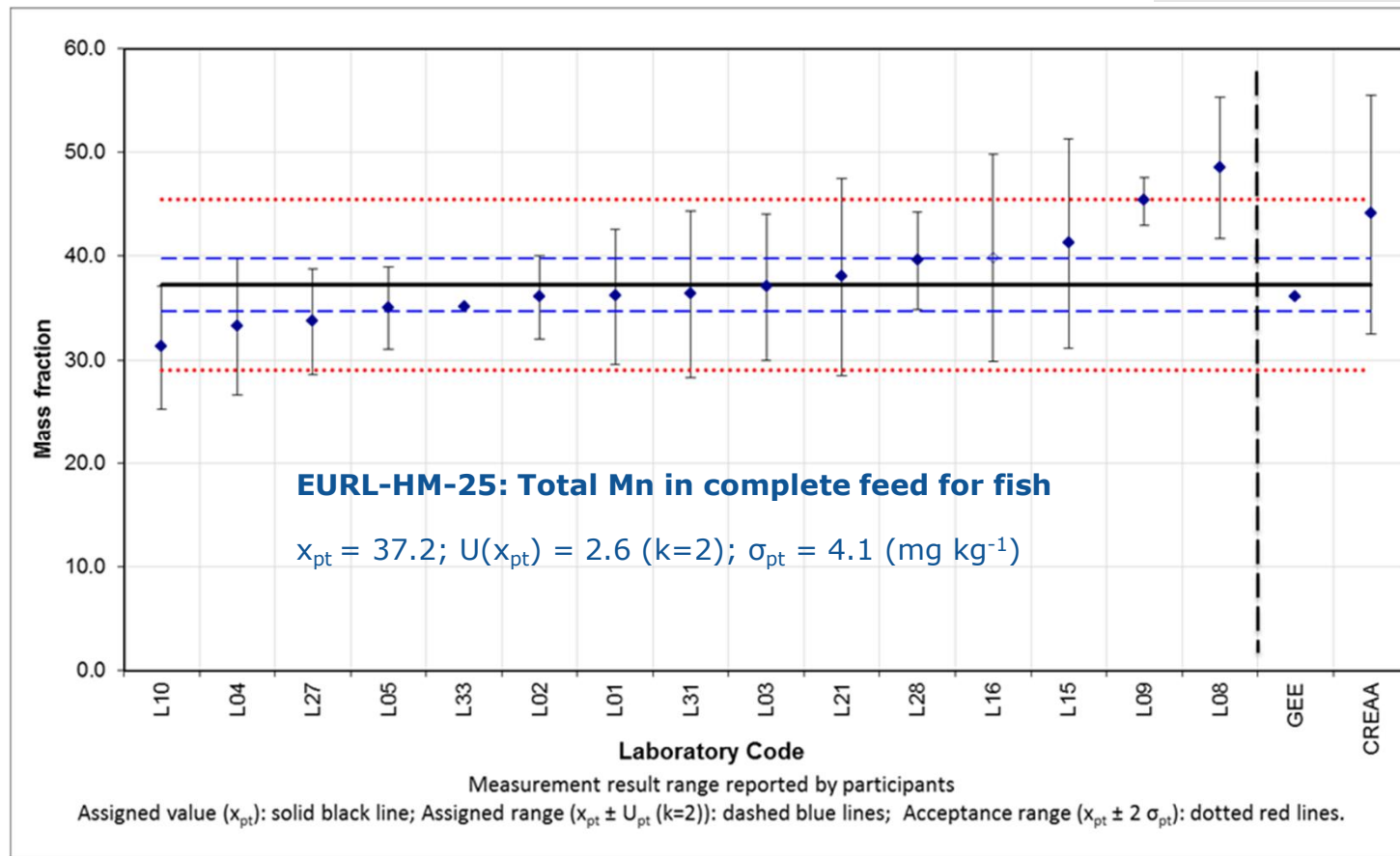
CIR 2016/896

ML = 750 mg/kg (total)
~~12 % moisture (not yet)~~



Manganese (N = 15; AAS, ICP-MS, ICP-OES)

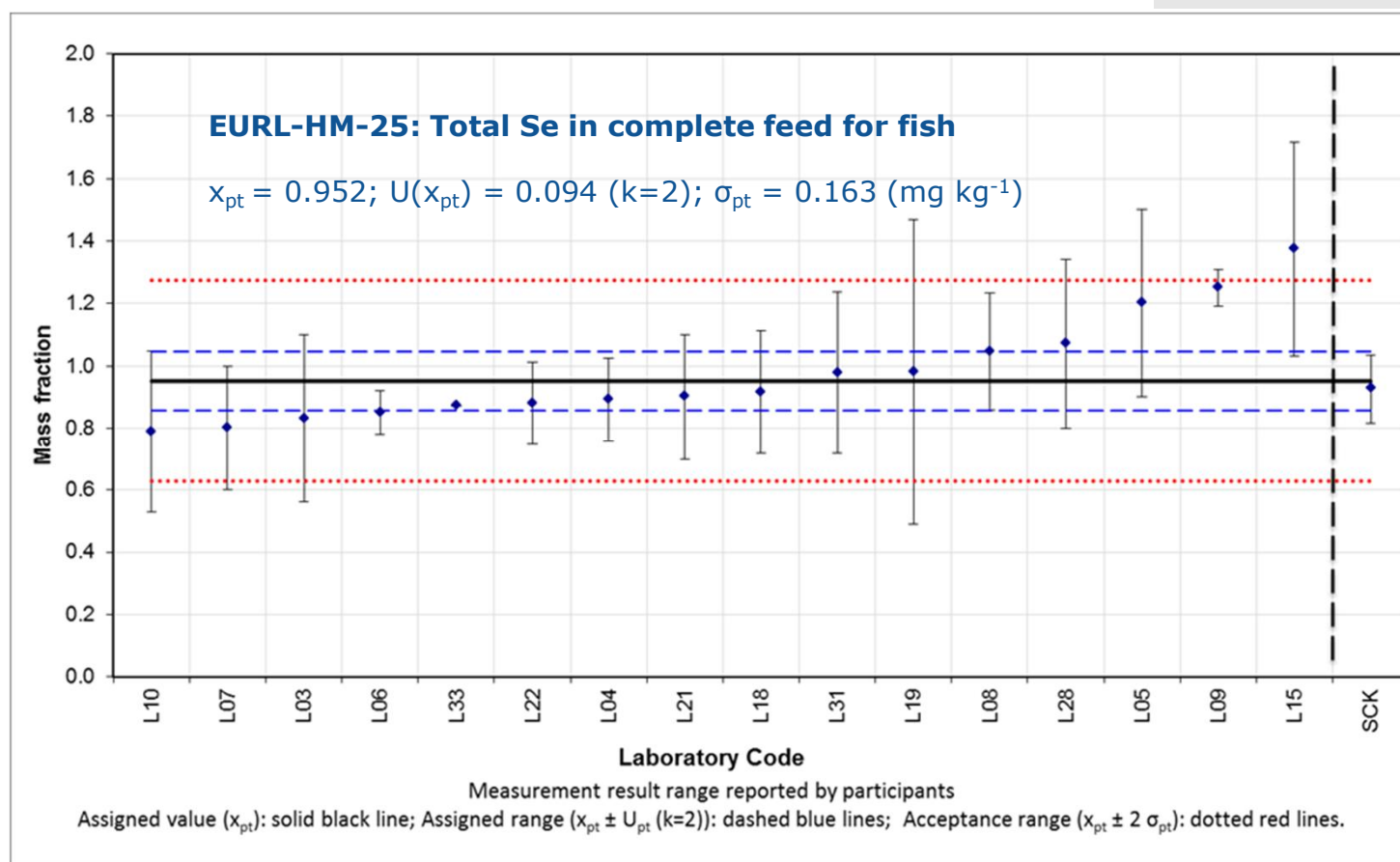
Com.Reg 350/2010
ML = 100 mg/kg (total)
12 % moisture



Selenio (N = 16; ICP-MS)

CIR 427/2013

ML = 0.50 mg/kg (total)
12 % moisture

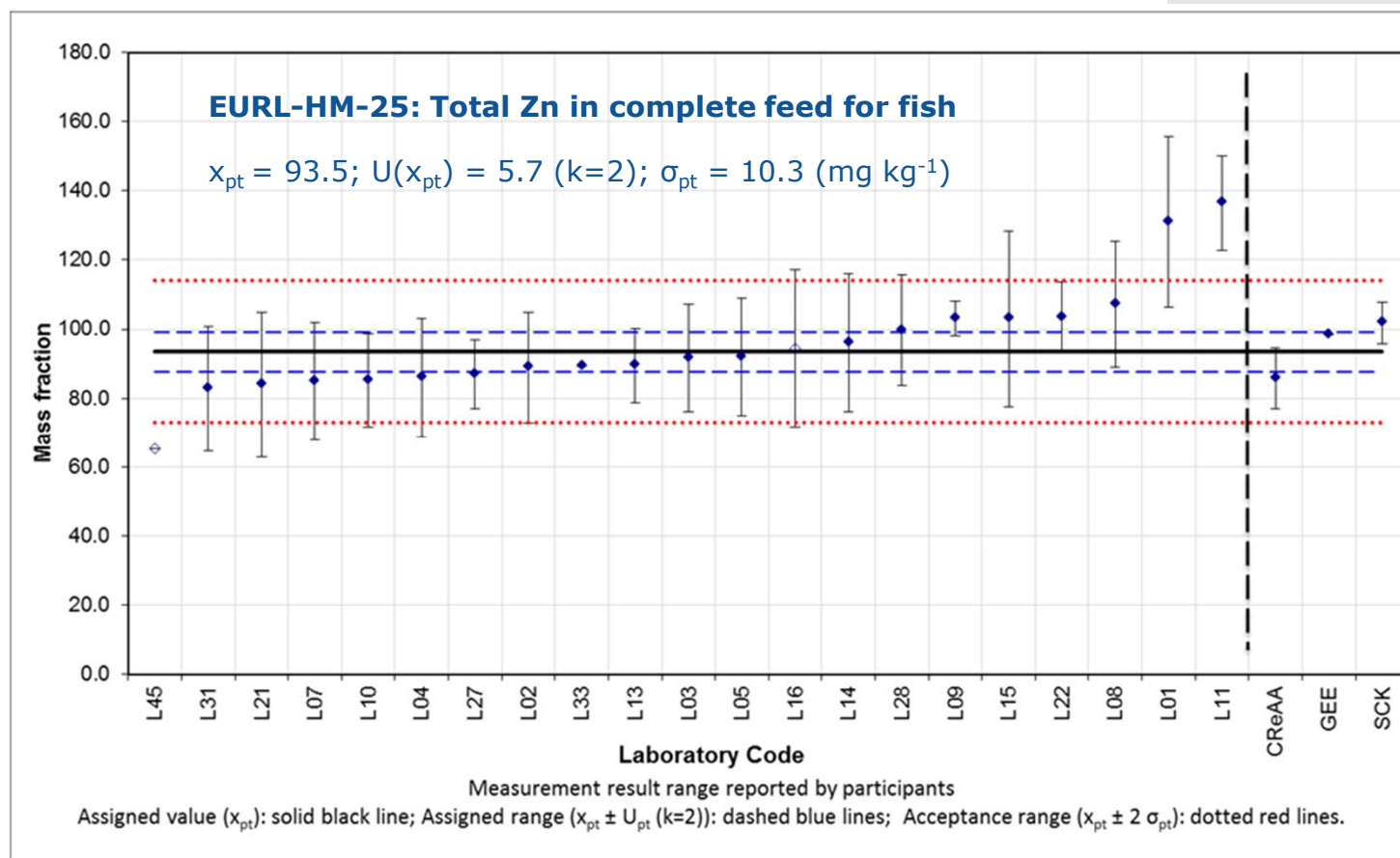


Zinco (N = 21; AAS, ICP-MS, ICP-OES)

CIR 2016/1095

ML = 120 mg/kg (total)

12 % moisture



Compliance?

$$\text{Se } (x_{pt}) = 0.95 \pm 0.09 \text{ mg/kg } (k = 2)$$

Max. Content = 0.50 mg Se/kg feed (total)

Maximum content of element (Se) in mg/kg of complete feed with a **moisture content of 12 %** (cf. CIR 427/2013)

beyond reasonable doubt **above** ML?

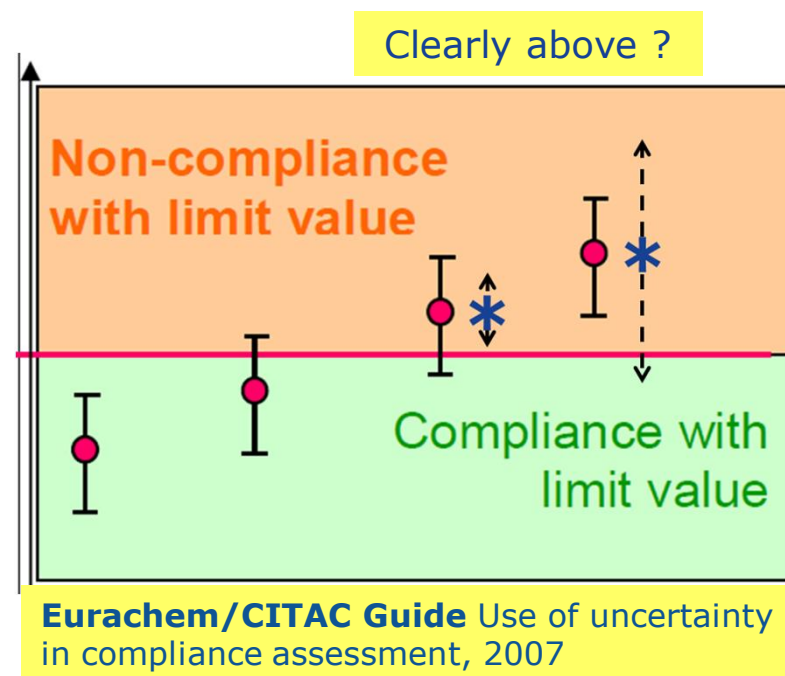
**NOT
Compliant**

An additional "*measurand*": "Compliance"

HYP: the test item is non-compliant

Consider the following **three components**:

- Å compliance statement by laboratory
(Compliant or Non-Compliant)
- Å laboratory measurement results:
reported (or not) for the relevant analyte);
 $X_i - U_i > ML?$
- Å laboratory justification
(correct, incorrect or partially incorrect).



Grazie per la Vostra attenzione



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