



# Statistical Methods for use in Proficiency Testing

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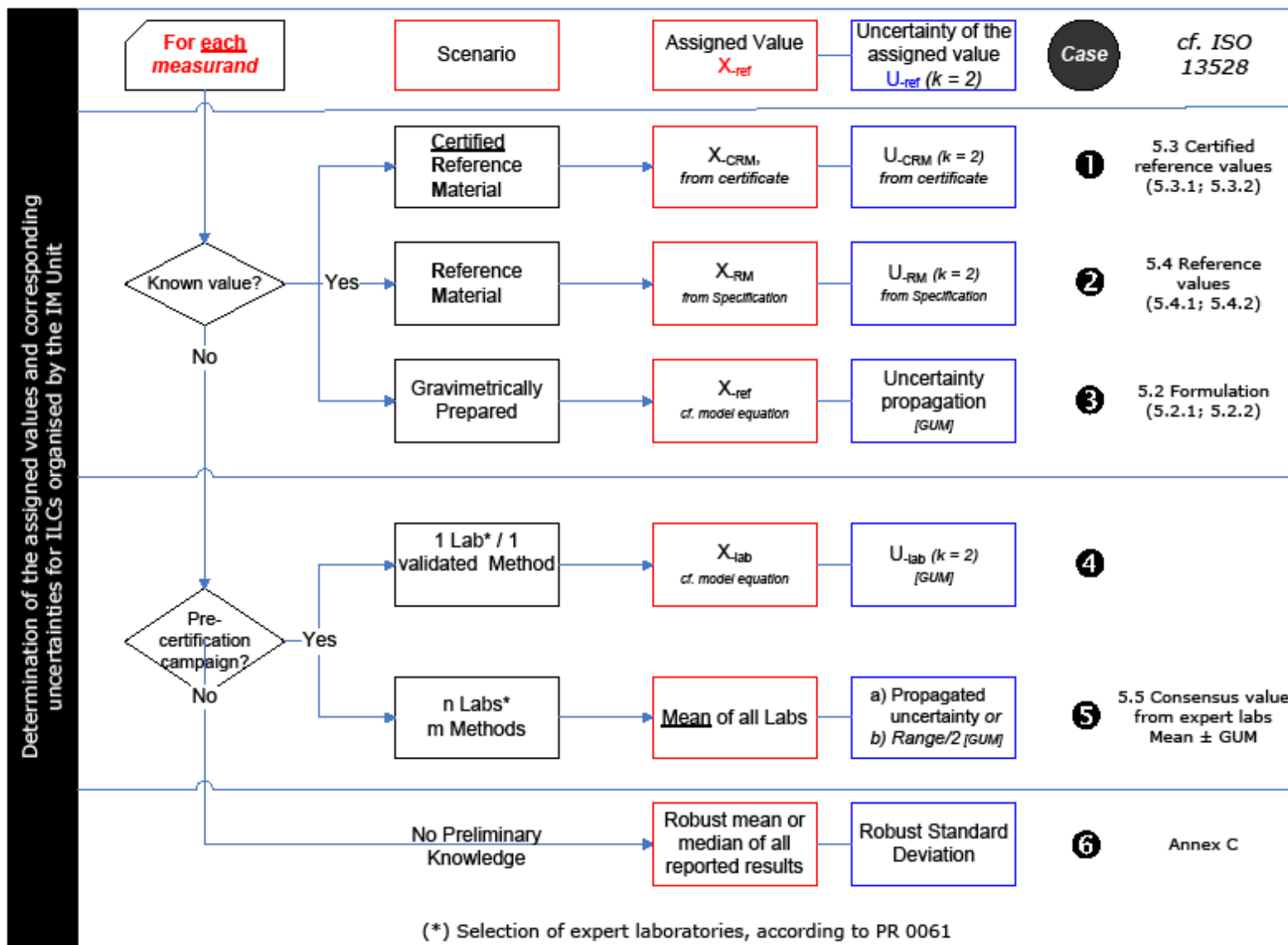
**Proficiency testing** by interlaboratory comparisons (**ILC**) is used to determine the performance of individual laboratories for specific tests or measurements, and to monitor the continuing performance of laboratories.

**Assigned value:** value attributed to a particular quantity and accepted, sometimes by convention, as having an uncertainty appropriate for a given purpose

**Standard deviation for proficiency assessment:** measure of dispersion used in the assessment of proficiency, based on the available information

**z-score (zeta-):** standardized measure of laboratory bias, calculated using the assigned value and the standard deviation for proficiency assessment

- ✓ **Formulation:** assigned value  $X_{Ref}$  is derived by calculation from the masses used.
- ✓ **CRM / RM:** certified reference value is used as the assigned value  $X$  (*RM calibrated against a CRM*)
- ✓ **Consensus value from participants:** robust average of the results reported by all the participants
- ✓ **Consensus from expert labs:** robust average
- ✓ **Measurement by a reference laboratory**



$$u_{ref} = \sqrt{u_{char}^2 + u_{bb}^2 + u_{sts}^2}$$

**$u_{ref}$  : standard uncertainty associated to the assigned value**

**$u_{char}$  : standard uncertainty of characterisation**

**$u_{bb}$  : standard uncertainty contribution for the between-bottle homogeneity**

**$u_{sts}$  : standard uncertainty contribution derived from the short-term stability study  
(usually 8 weeks at 4, 18 and 60 °C)**

**PT material should be “enough homogeneous”**

Between-sample standard deviation  $S_s$  and the standard deviation for proficiency assessment  $\underline{\sigma}$ .

$$S_s \leq 0.3 \sigma$$

**Uncertainty on the assigned value:**

$$u_X \leq 0.3 \sigma$$

**Enough Stability? (allow an appropriate time delay)**

$$\left| \overline{X_H} - \overline{Y_S} \right| \leq 0.3\sigma$$

If the data follow a normal distribution  
(by definition: no outliers)

- Evaluation by ANOVA:

$$s_{bb} = s_{among} = \sqrt{\frac{MS_{among} - MS_{within}}{n}}$$

- $MS_{among}$ ,  $MS_{within}$ : data from ANOVA table
- $n$ : number of replicates per bottle

## Cd in $\mu\text{g Kg}^{-1}$

	R 1	R 2	Diff	Diff <sup>2</sup>	ave Xi	Xi-ave
1	880.16	889.94	9.78	95.648	885.050	6894.645
2	869.04	876.81	7.77	60.373	872.925	5028.086
3	827.85	834.54	6.69	44.756	831.195	851.414
4	824.08	815.92	8.16	66.586	820.000	323.424
5	811.63	790.05	21.58	465.696	800.840	1.383
6	790.85	773.39	17.46	304.852	782.120	395.851
7	784.69	758.19	26.5	702.250	771.440	934.892
8	767.36	769.05	1.69	2.856	768.205	1143.184
9	754.31	754.91	0.6	0.360	754.610	2247.329
10	733.05	734.5	1.45	2.103	733.775	4656.834
	SUM =			1745.48	802.016	22477.04

<b>ISO approach</b>	$S_W =$	9.342	( $S_{an}$ = repeatability)
<b>(13528:2005)</b>	$S_x =$	49.974	(Sd of sample average)
	$S_S =$	49.536	
Criteria	38.497	( $0.3 \cdot \sigma$ )	( $\sigma = 15\%$ of mean)
Cochran's C =	0.40	critical 95 % = 0.60	
no duplicate result should be removed			
$S_S > 0.3 \sigma$			
hence not enough homogeneous			

## Scores and evaluation criteria:

$$z = \frac{x_{lab} - X_{ref}}{\sigma}$$

$$zeta = \frac{x_{lab} - X_{ref}}{\sqrt{u_{ref}^2 + u_{lab}^2}}$$

$x_{lab}$	Mean of the individual measurement results calculated by the ILC organiser
$X_{ref}$	Certified reference value (assigned value)
$u_{ref}$	Standard uncertainty of the reference value
$u_{lab}$	Standard uncertainty reported by a participant
$\sigma$	Standard deviation for proficiency assessment

$|z| \leq 2$

$2 < |z| \leq 3$

$|z| > 3$

satisfactory result

questionable result

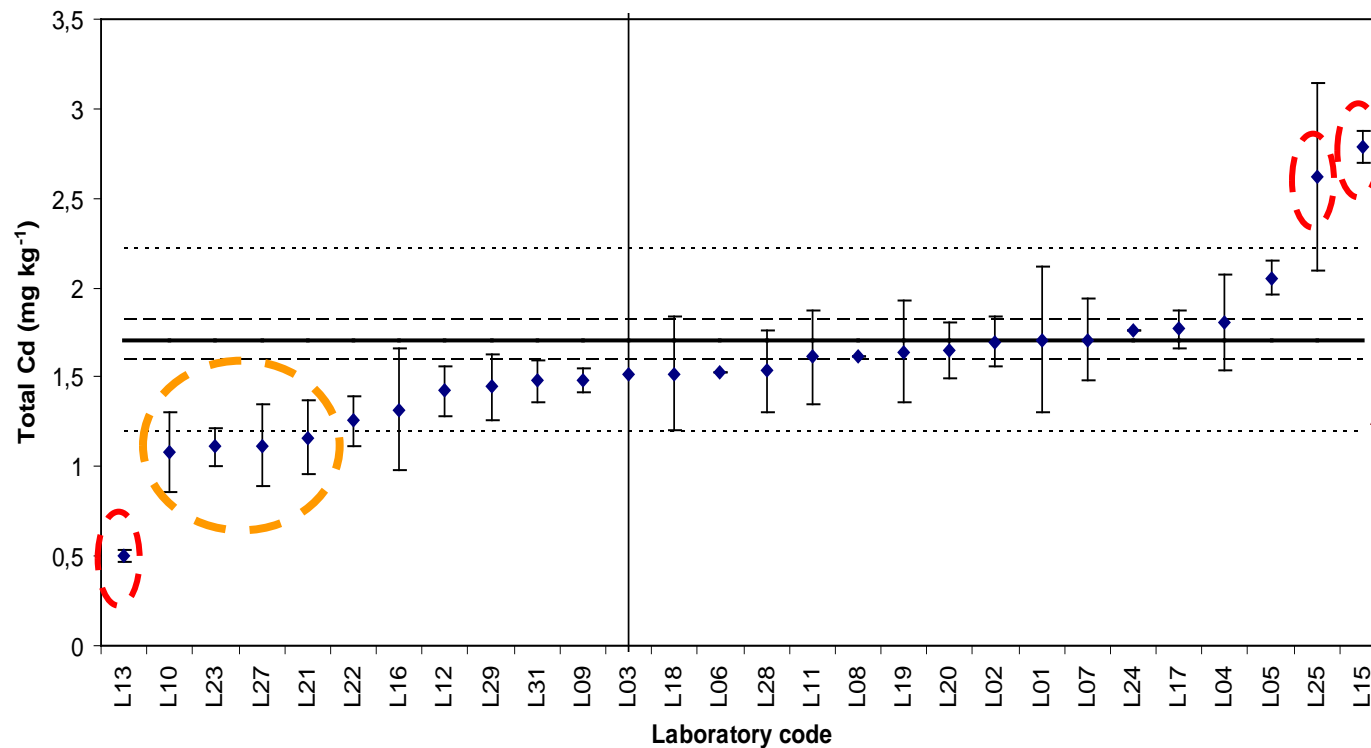
unsatisfactory result

- ✓  $\sigma$  describes the end-user's requirements (fitness for purpose). Set by legislation.
- ✓ It represents the amount of uncertainty in the result that is tolerable in relation to the purpose of the analysis
- ✓  $\sigma$  following the Horwitz function  
$$\sigma_H = 0.02 c^{0.8495}$$
  
(c in mass fraction,  $1.71 \text{ mg Kg}^{-1} = 1.71 \cdot 10^{-6}$ )

$$\text{RSD}_H = 15.0 \% \text{ (taking Tot Cd as } X_{\text{Ref}} \text{)}$$

ID	x1	x2	x3	x4	Ulab	k	Tot Cd	ulab	Xref	Uref	uref	sigma	Technique	z	zeta
L01	1.690	1.690	1.750		0.41	2	1.710	0.205	1.708	0.11	0.055	0.2562	ICP-MS	0.0	0.0
L02	1.649	1.748			0.141	2	1.699	0.0705	1.708	0.11	0.055	0.2562	ICP-MS	0.0	-0.1
L03	1.494	1.535	1.515		10	1.732051	1.515	5.773503	1.708	0.11	0.055	0.2562	AAS-GF	-0.8	0.0
L04	1.860	1.720	1.830		0.27	2	1.803	0.135	1.708	0.11	0.055	0.2562	ETAAS	0.4	0.7
L05	2.103	2.012	2.053		0.091	1.732051	2.056	0.052539	1.708	0.11	0.055	0.2562	ETAAS	1.4	4.6
L06	1.530	1.540	1.520		0	1.732051	1.530	0	1.708	0.11	0.055	0.2562	ICP-OE	-0.7	-3.2
L07	1.700	1.720			0.23	2	1.710	0.115	1.708	0.11	0.055	0.2562	ICP-OE	0.0	0.0
L08	1.620	1.610			0	1.732051	1.615	0	1.708	0.11	0.055	0.2562	ICP-MS	-0.4	-1.7
L09	1.513	1.444	1.483		0.064	2	1.480	0.032	1.708	0.11	0.055	0.2562	ETAAS	-0.9	-3.6
L10	1.084	1.187	0.975		0.227	2	1.082	0.1135	1.708	0.11	0.055	0.2562	ETAAS	-2.4	-5.0
L11	1.580	1.550	1.710		0.26	2	1.613	0.13	1.708	0.11	0.055	0.2562	ZETAAS	-0.4	-0.7
L12	1.400	1.310	1.560		0.14	2	1.423	0.07	1.708	0.11	0.055	0.2562	ICP-MS	-1.1	-3.2
L13	0.556	0.487	0.475		0.034	2	0.506	0.017	1.708	0.11	0.055	0.2562	FAAS	-4.7	-20.9
L15	2.810	2.740	2.820		0.09	1.732051	2.790	0.051962	1.708	0.11	0.055	0.2562	ETAAS	4.2	14.3
L16	1.310	1.310	1.340		0.34	2	1.320	0.17	1.708	0.11	0.055	0.2562	ICP-OE	-1.5	-2.2
L17	1.707	1.835			0.106	2	1.771	0.053	1.708	0.11	0.055	0.2562	ICP-MS	0.2	0.8
L18	1.520				0.32	2	1.520	0.16	1.708	0.11	0.055	0.2562		-0.7	-1.1
L19	1.690	1.520	1.720		0.28	2	1.643	0.14	1.708	0.11	0.055	0.2562	ICP-MS	-0.3	-0.4
L20	1.600	1.680	1.670		0.16	1.732051	1.650	0.092376	1.708	0.11	0.055	0.2562	ICP-MS	-0.2	-0.5
L21	1.010	1.120	1.360		0.21	1.732051	1.163	0.121244	1.708	0.11	0.055	0.2562	ETAAS	-2.1	-4.1
L22	1.228	1.298	1.241		0.137	1.732051	1.256	0.079097	1.708	0.11	0.055	0.2562	ICP-MS	-1.8	-4.7
L23	1.083	1.134	1.117		0.109	2	1.111	0.0545	1.708	0.11	0.055	0.2562	AAS	-2.3	-7.7
L24	1.770	1.760			0	2	1.765	0	1.708	0.11	0.055	0.2562	ETAAS	0.2	1.0
L25	2.676	2.498	2.680		0.524	2	2.618	0.262	1.708	0.11	0.055	0.2562	ETAAS	3.6	3.4
L27	1.100	1.140			0.23	1.732051	1.120	0.132791	1.708	0.11	0.055	0.2562	ICP-OE	-2.3	-4.1
L28	1.570	1.520	1.520		0.23	1.732051	1.537	0.132791	1.708	0.11	0.055	0.2562	FAAS	-0.7	-1.2
L29	1.450	1.500	1.400	1.430	0.18	2	1.445	0.09	1.708	0.11	0.055	0.2562	FAAS	-1.0	-2.5
L31	1.424	1.540	1.473		0.12	2	1.479	0.06	1.708	0.11	0.055	0.2562	ETAAS	-0.9	-2.8

Total Cd in mg Kg<sup>-1</sup>. Acceptance limits as  $X_{Ref} \pm 2 \sigma$  (1.20 – 2.22 mg Kg<sup>-1</sup>)



$X_{ref} = 1.708$

$U_{ref} = 0.110$

Acceptance limits

$2 \times 0.256$  (15 %)

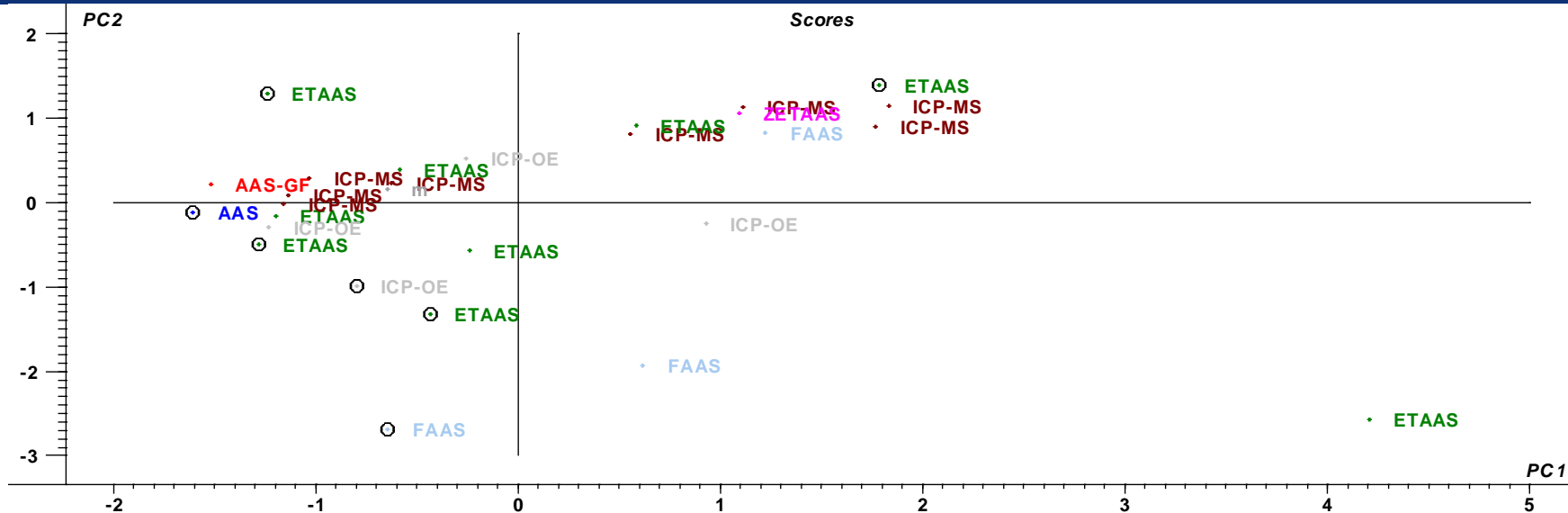
**11 % unsatisfactory, 14 % questionable and 75 % satisfactory results**

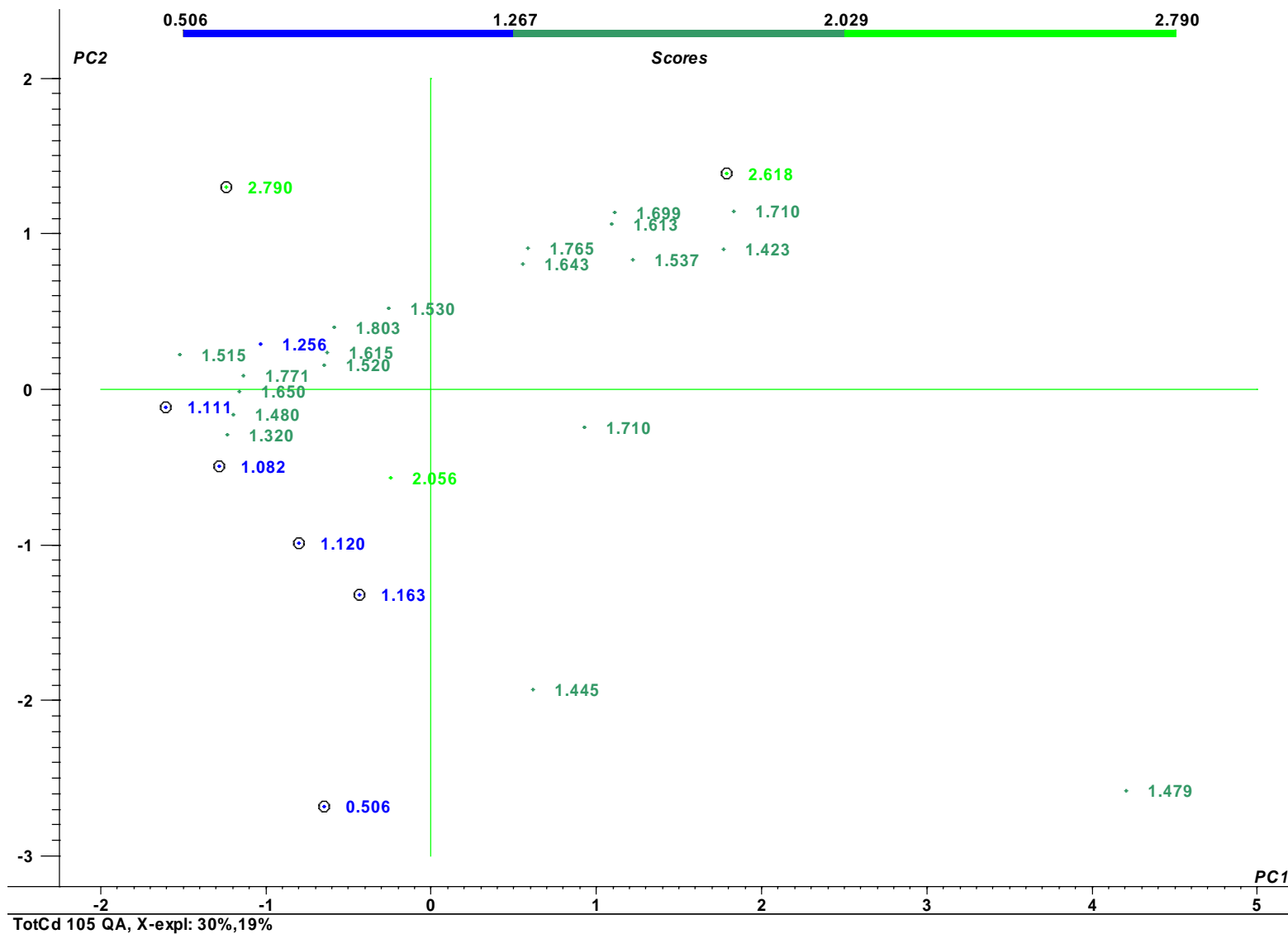
## Horwitz Reproducibility Relative Standard Deviation, $RSD_H$

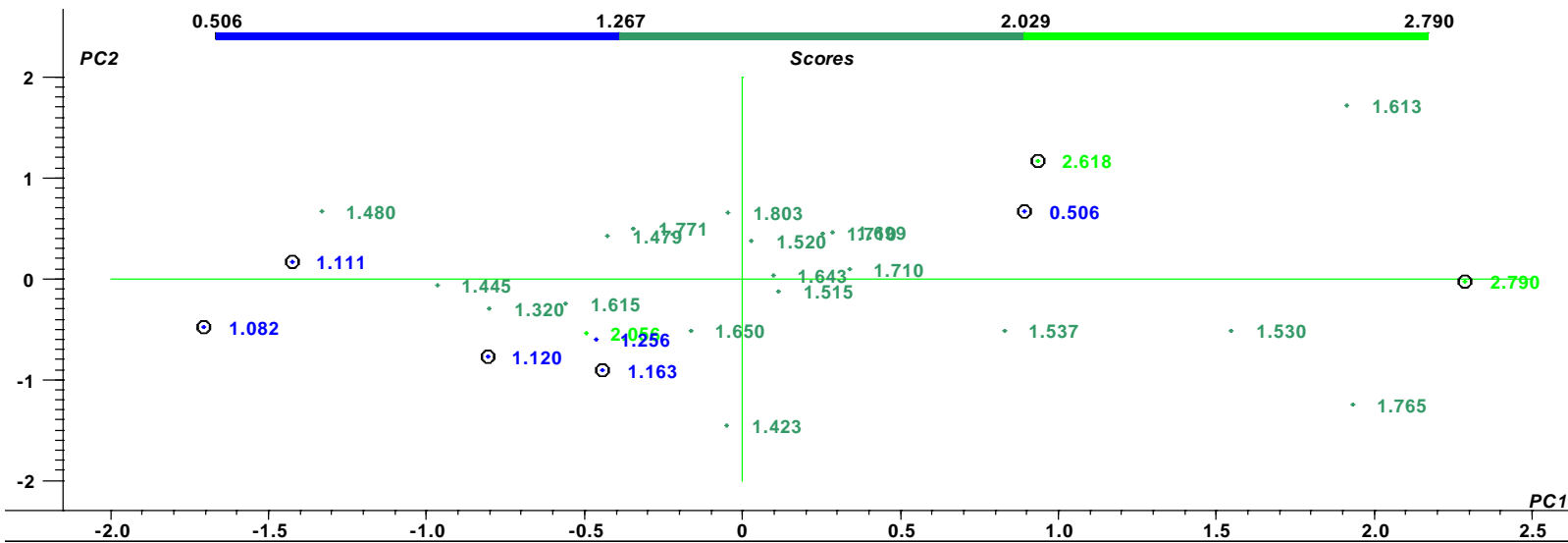
$$RSD_H = 15.0 \% \text{ (taking } X_{Ref}\text{)}$$

$$RSD_R = 25.6 \% \text{ (N = 28, ANOVA)}$$

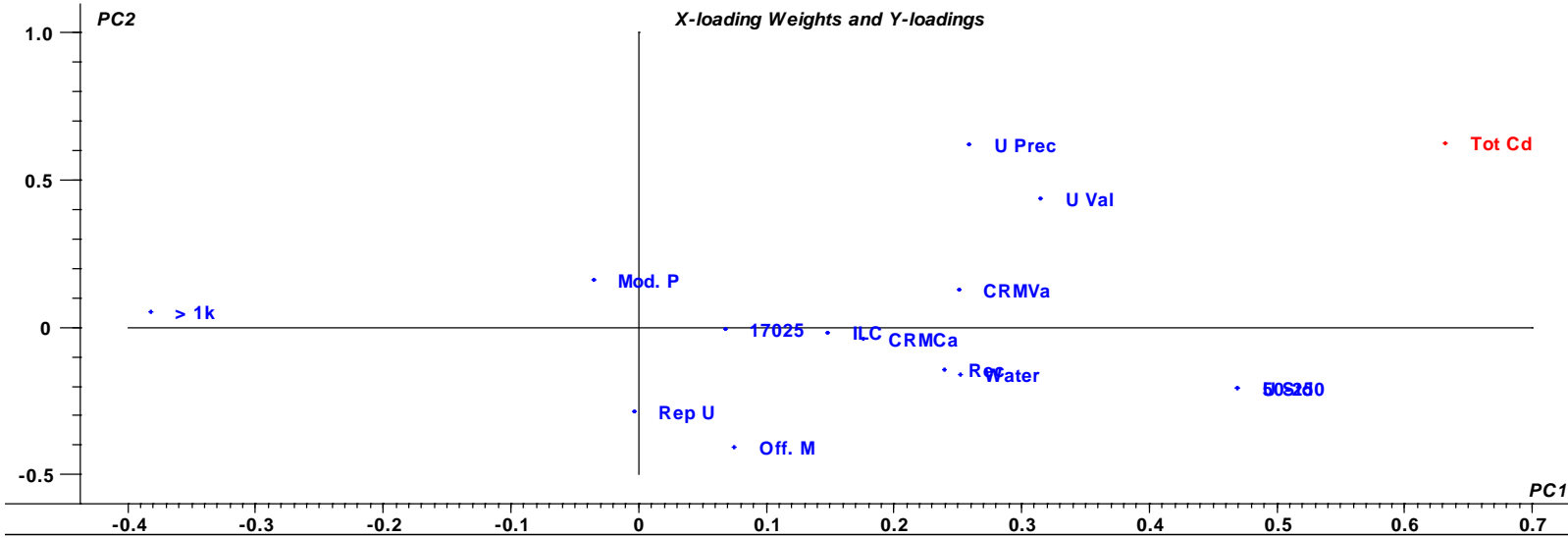
$$\text{Horrat ratio} = RSD_R / RSD_H = 1.7 \text{ (acceptable)}$$







TotCd 105 TS10, X-expl: 14%,8% Y-expl: 64%,22%



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