Statistical Methods for use in Proficiency Testing

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Definitions

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

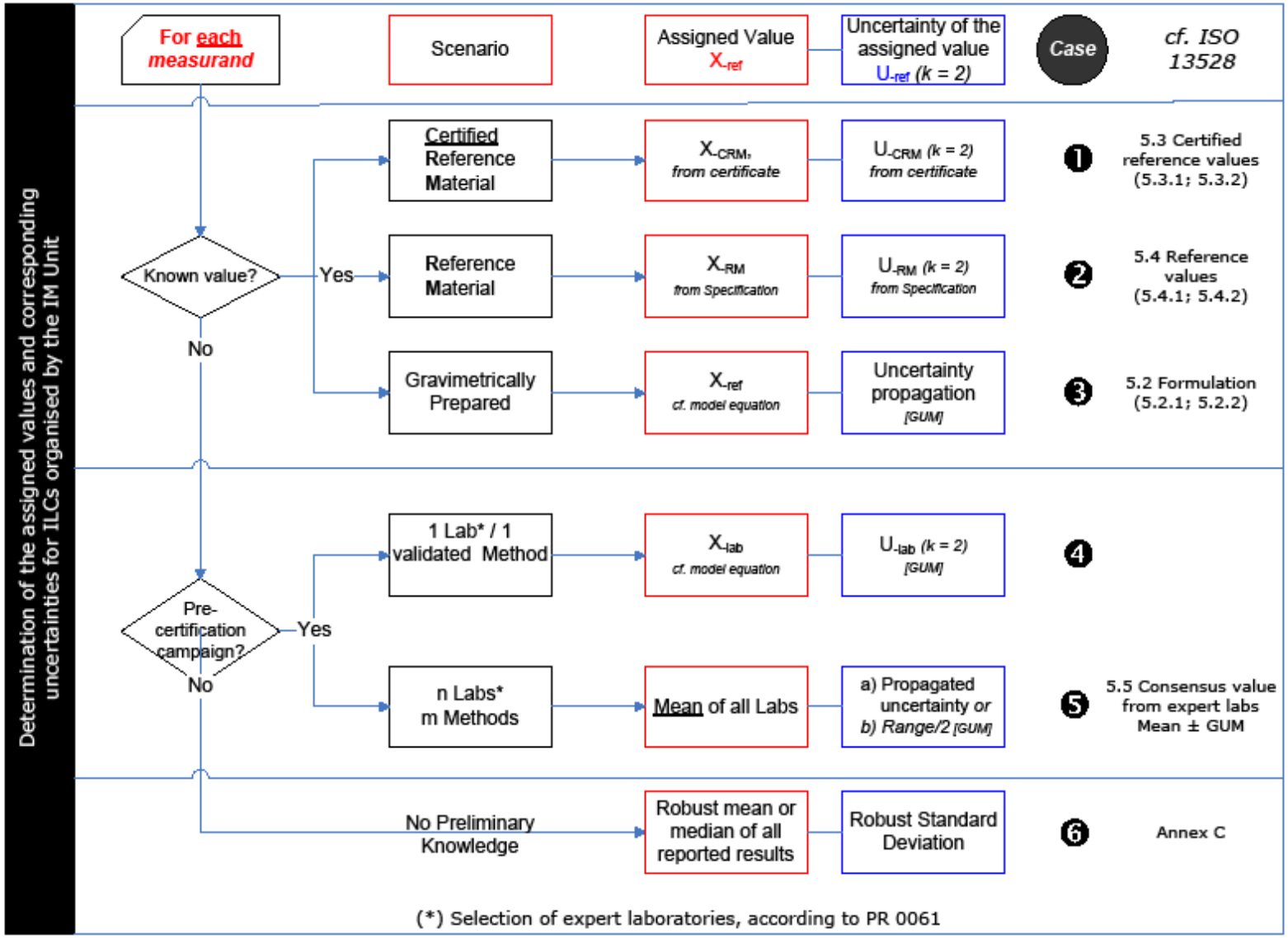
Standard deviation for proficiency assessment: measure of dispersion used in the assessment of proficiency, based on the available information

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

The Assigned Value X

- ✓ **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**

ILC Strategy Flow Chart



Uncertainty on The Assigned Value

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

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 (Analytical) Requirements

PT material should be "enough homogeneous"

Between-sample standard deviation S_s and the standard deviation for proficiency assessment σ.

$$S_S \leq 0.3\ \sigma$$

Uncertainty on the assigned value:

$$u_X \leq 0.3\,\sigma$$

Enough Stability? (allow an appropriate time delay)

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

Quantification of heterogeneity

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

Homogeneity, Cd in Feed (ANOVA)

Cd in µg Kg^{-1}

	R 1	R 2	Diff	Diff ^{2}	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

ISO approach (13528:2005)

S_W = 9.342 (San = repeatability)

Sx = 49.974 (Sd of sample average)

S_S = 49.536

Criteria 38.497 (0.3*σ) (σ = 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
σ	Standard deviation for proficiency assessment

$\lvert z \rvert \leq 2$	**satisfactory result**
$2 < \lvert z \rvert \leq 3$	**questionable result**
$\lvert z \rvert > 3$	**unsatisfactory result**

SD for Proficiency Assessment (σ)

- ✓ **σ 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**

- ✓ **σ following the Horwitz function**

$$\sigma_H = 0.02\ c^{0.8495}$$

(c in mass fraction, 1.71 mg Kg^{-1} = $1.71.10^{-6}$)

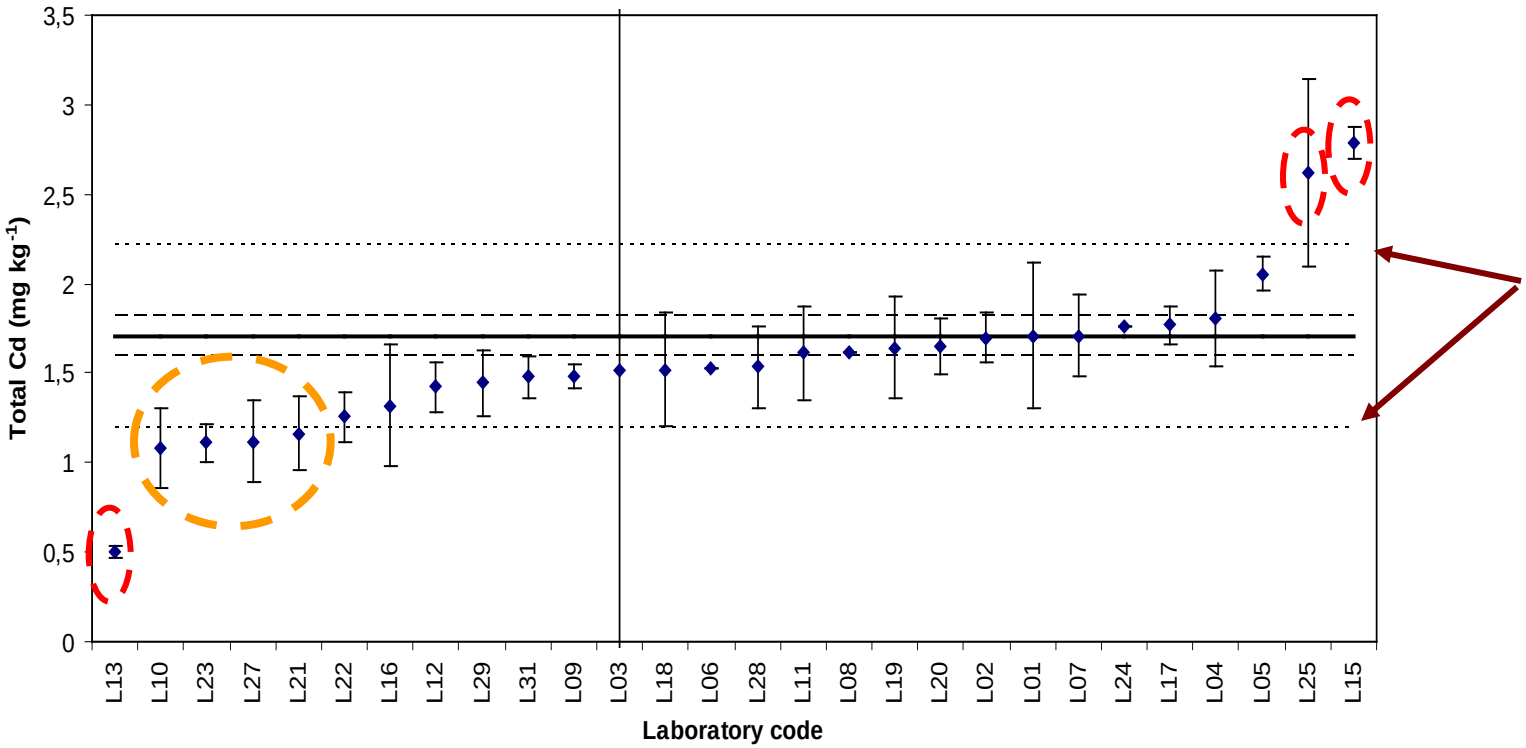
$$RSD_H = 15.0\ \%$$ **(taking Tot Cd as X_{Ref})**

ILC Results (Tot Cd /mg Kg^{-1})

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^{-1}. Acceptance limits as $X_{Ref} \pm 2\,\sigma$ (1.20 – 2.22 mg Kg^{-1})

Report results ± U (k = 2)



X_{ref} = 1.708
U_{ref} = 0.110

Acceptance limits

2x 0.256 (15 %)

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

Overall Performance

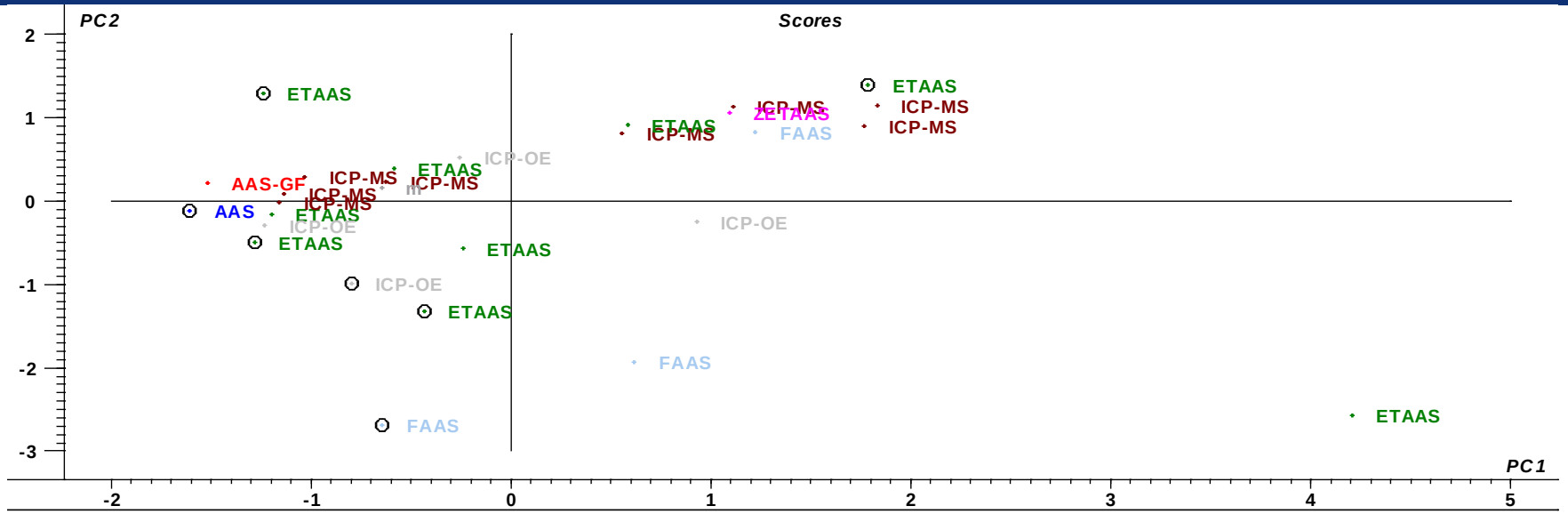
Horwitz Reproducibility Relative Standard Deviation, RSD_H

RSD_H = 15.0 % (taking X_{Ref})

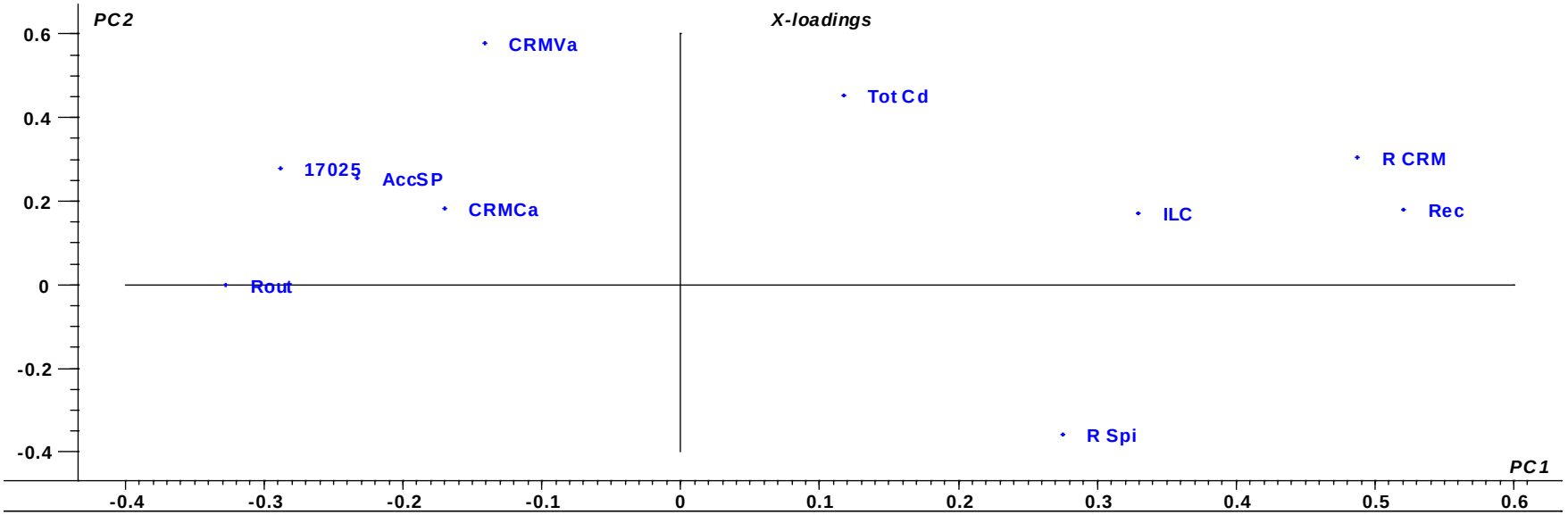
RSD_R = 25.6 % (N = 28, ANOVA)

Horrat ratio = RSD_R/RSD_H = 1.7 (acceptable)

Overall Performance (MVDA, PCA)

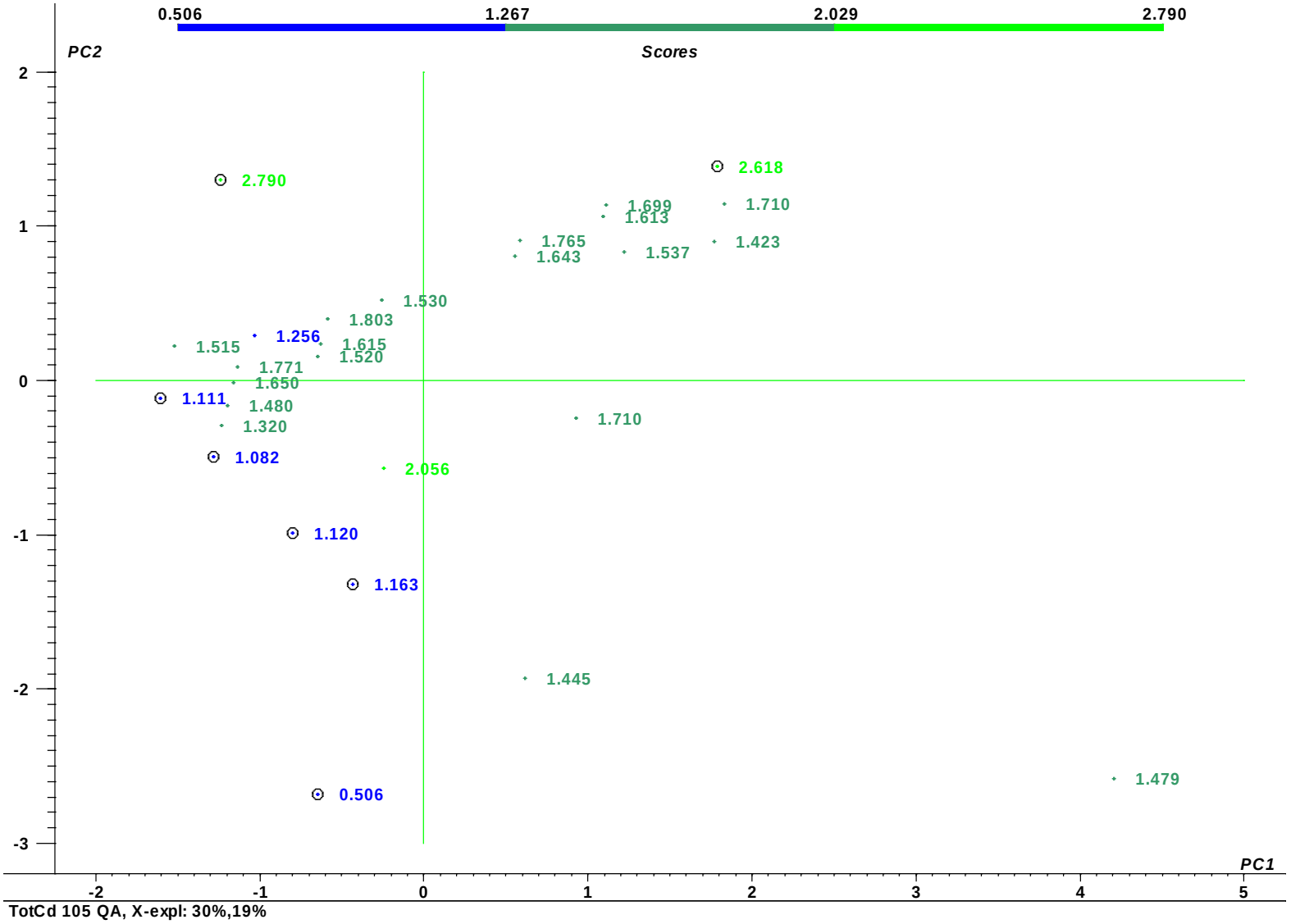


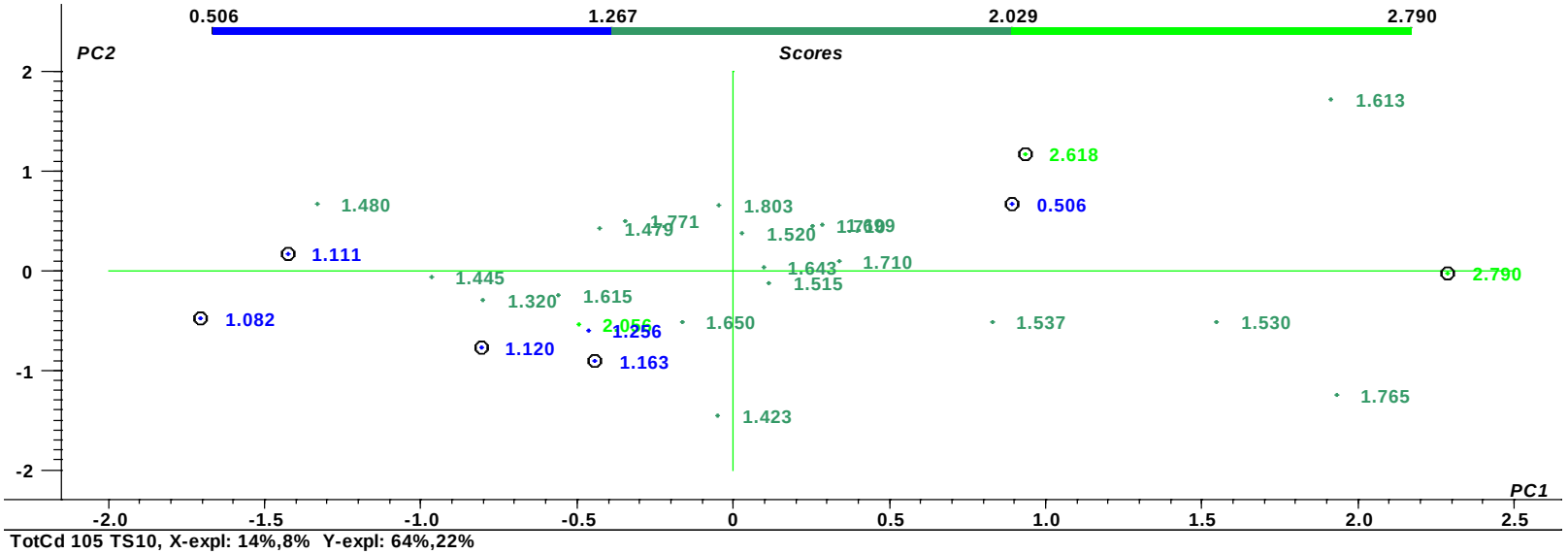
TotCd 105 QA, X-expl: 30%,19%

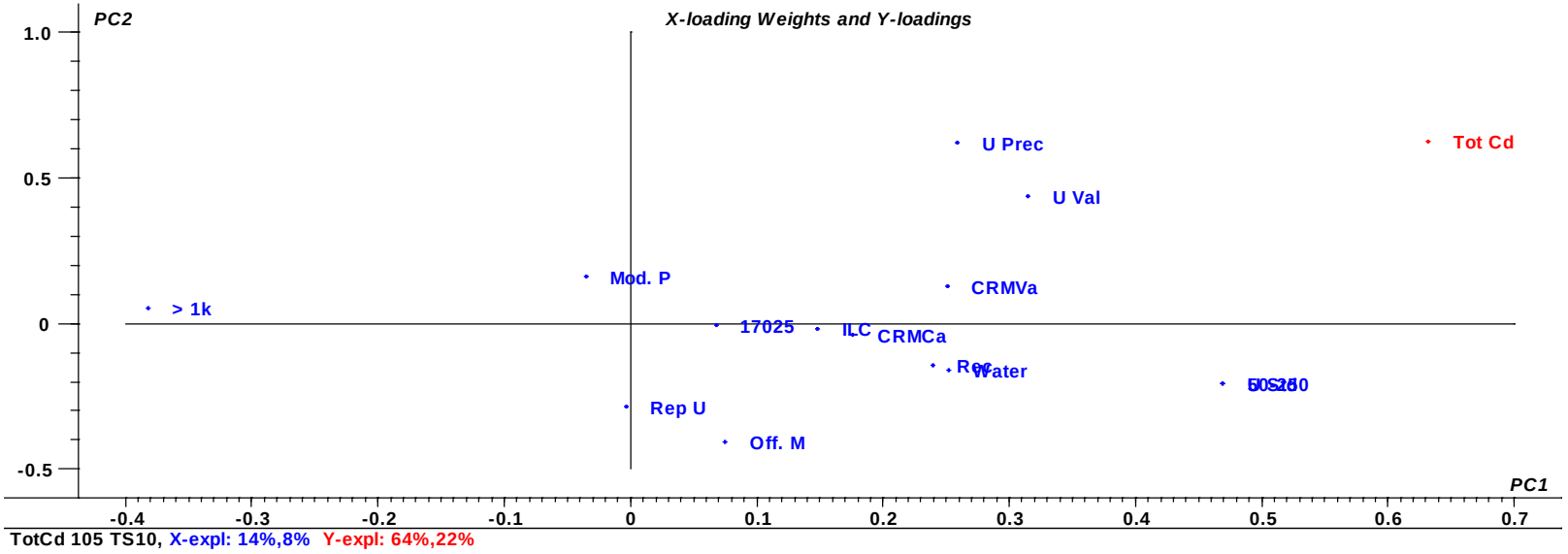


TotCd 105 QA, X-expl: 30%,19%

Principal Component Analysis (PCA)




0.506
1.267
2.029
2.790
PC2
Scores
1.613
2.618
1.480
1.803
0.506
1.771
1.479
1.520
1.111
1.643
1.710
1.445
1.515
2.790
1.320
1.615
1.082
1.650
1.537
1.530
1.256
1.120
1.163
1.765
1.423
PC1
TotCd 105 TS10, X-expl: 14%,8% Y-expl: 64%,22%


PC2
X-loading Weights and Y-loadings
U Prec
Tot Cd
U Val
Mod. P
CRMVa
> 1k
17025
ILC
CRMCa
Water
Rep U
Off. M
PC1
TotCd 105 TS10, X-expl: 14%,8% Y-expl: 64%,22%