Assessment of Laboratory Performance with CCRMP Certified Reference Materials

1.0 Repeatability (Precision) of a Method or Laboratory

To assess the repeatability (precision) of an analytical method, or the laboratory using that method by the analysis of a certified reference material, the average within-laboratory standard deviation (σ_{Rm}) of the certification measurements must be known. If not provided in the certificate, σ_{Rm} is usually available in the certification report, or will be provided by CCRMP on request. To determine repeatability, the parameter is measured in replicate, and the mean (X_L) and standard deviation (S_{wL}) are determined.

The analytical method or laboratory applying the method is accepted with regard to **repeatability** if:

$$(S_{wL}/\sigma_{Rm})^2 \leq F_c \qquad \text{Eq. 1}$$

where:

S_{wL} = the standard deviation of the replicate results,
σ_{Rm} = the within-laboratory standard deviation of the certified value, and
F_c = critical F value at 95 percentage points for n-1 results in this investigation and the number -1 of laboratories in the interlaboratory measurement program. If the latter is unknown, use 60.

Note: It is recommended that this test be performed with at least five (5) replicates.

2.0 Accuracy of a Method or Laboratory

To assess the accuracy of an analytical method, or the laboratory using that method by the analysis of a certified reference material, the between-laboratories standard deviation (σ_{Lm}) of the certification measurements must be known. If not provided on the certificate, σ_{Lm} is usually available in the certification report, or will be provided by CCRMP on request.

A method or laboratory performing a method should be assessed with respect to accuracy on the basis of the mean value of two or more replicate results. Although such an assessment is possible with a single result, the difference between the certified value of the reference material and the single result that is permitted could be too large to make the assessment meaningful.

2.1 Accuracy Assessment

The analytical method or laboratory applying that method is accepted with regard to **accuracy** if:

$$| X_C - X_L | \leq 2\sqrt{\sigma_{Lm}^2 + S_{wL}^2 / n} \qquad \text{Eq. 2}$$

X_C = the certified value,
σ_{Lm} = the between-laboratories standard deviation of the certified value,
X_L = mean value of the n replicates,
S_{wL} = standard deviation of the replicates,
n = the number of replicates (n must be ≥ 2).

2.1.1 Recommended minimum replication for validity of accuracy test

To be valid, the accuracy test should be designed to minimize the contribution of S_{wL} in Equation 2. The contribution of the S_{wL}^2 in Equation 2 depends on its magnitude relative to σ_{Lm}^2 and the size of n. The contribution of the S_{wL}^2 term can be regarded as insignificant when it contributes less than 5% to the test value. Table 1 shows the relationship between the ratio S_{wL} / σ_{Lm} and the minimum required value of n to achieve this.

Table 1

S_{wL} / σ_{Lm}	minimum n
≤0.33	1
0.5	3
0.67	5
1	10
1.5	22

Where the conditions of Table 1 are maintained for the accuracy test, Equation 2 becomes:

$$| X_C - X_L | \leq 2\,\sigma_{Lm} \qquad \text{Eq. 3}$$

2.1.2 Relationship between 95% confidence interval for the recommended value and parameters σ_{Lm} and σ_{Rm}

The 95% confidence interval for a CCRMP material (±CI) is calculated as:

$$\pm CI = t(0.05, N_C\text{-}1)\,\sigma_C \qquad \text{Eq. 4}$$

where:

t = the value of the two-sided Student's t distribution at 95% probability for N_C-1 degrees of freedom,
N_C = the number of laboratories in the certification program,
σ_C = the statistically estimated standard uncertainty of the recommended value:

$$\sigma_C = \sqrt{(\sigma_{Lm}^2 + \sigma_{Rm}^2 / n_c) / N_C} \qquad \text{Eq. 5}$$

where n_c is the average number of in-laboratory replicates in the certification program.

Note that σ_C is the standard uncertainty estimate for reproducibility of the recommended mean in an interlaboratory certification program of similar magnitude and composition, and is not the parameter recommended for testing sufficient accuracy in the use of CCRMP reference materials. The relevant parameter for the accuracy test is instead σ_{Lm} . Approximately,

$$\sigma_C \sim \sigma_{Lm} / \sqrt{N_C} \qquad \text{Eq. 6}$$

Since N_C typically varies from 10 to 40 in CCRMP programs, σ_{Lm} may be 3 to 6 times σ_C.

Provided N_C is known, σ_{Lm} is estimable from the ± confidence interval Equations 4 and 6:

$$\sigma_{Lm} \sim \pm CI \sqrt{N_C} \ / \ t(0.05, N_C\text{-}1) \qquad \text{Eq. 7}$$

3.0 References

R. Sutarno and H.F. Steger, 'The use of certified reference materials in the verification of analytical data and methods.', Talanta Vol. 32, No. 6 pp 439-445, 1985.

ISO Guide 33 Uses of Certified Reference Materials

EXAMPLE 1

Laboratory A analyzed CCRMP Gold Reference Material MA-1b.

Parameter for MA-1b	Value	Notes
X_C, Certified Value	17.0 μg/g Au	
± 95% CI	0.26 μg/g Au	
N_C	33	$\sigma_{Lm} \approx$ 0.7, Eq. 7
n_C	5	
σ_{Lm}	0.70 μg/g Au	from certification ANOVA
σ_{Rm}	0.42 μg/g Au	

Laboratory A	Test Data
Results	17.8 μg/g
	16.5 μg/g
	16.8 μg/g
	17.4 μg/g
	17.1 μg/g
Mean Value, X_L	17.12 μg/g
Std. Dev., S_{wL}	0.51 μg/g

Test Calculations			Notes
Eq. 1	$(S_{wL}/\sigma_{Rm})^2$	1.46	
Eq. 1	Fc	2.53	Estimated with $N_C \sim 60$; for N_C=33, F_C = 2.67
Eq. 1		1.46 <2.53	Repeatability accepted.
Eq. 2	$\lvert X_C - X_L \rvert$	0.12 μg/g	
Eq. 2	$2\sqrt{\sigma_{Lm}^2 + S_{wL}^2/n}$	1.47 μg/g	
Eq. 2		0.12< 1.47	Accuracy accepted.
Table 1	S_{wL} / σ_{Lm}	0.73	Eq. 3 valid for n≥5
Eq. 3	$2\ \sigma_{Lm}$	1.4	
Eq. 3		0.12 < 1.4	Accepted for accuracy with effect of S_{WL} minimized.

Laboratory A is accepted with respect to repeatability and accuracy relative to the measurements of the CRM certification program.

EXAMPLE 2

Laboratory B analyzed CCRMP Gold Reference Material CH-3.

Parameter for CH-3	Value	Notes
X_C, Certified Value	1.40 μg/g Au	
± 95% CI	0.03 μg/g Au	
N_C	29	$\sigma_{Lm} \approx 0.08$, Eq. 7
n_C	5	
σ_{Lm}	0.07 μg/g Au	from certification ANOVA
σ_{Rm}	0.11 μg/g Au	

Laboratory B	Test Data
Results	1.70 μg/g
	1.88 μg/g
	1.76 μg/g
Mean Value, X_L	1.78 μg/g
Std. Dev., S_{wL}	0.09 μg/g

Test Calculations			Notes
Eq. 1	$(S_{wL}/\sigma_{Rm})^2$	0.68	0.68 < 3.15
Eq. 1	Fc	3.15	Estimated with $N_C \sim 60$ For N_C=28, F_C = 3.34
Eq. 1		0.68 < 3.15	Repeatability accepted
Eq. 2	$\lvert X_C - X_L \rvert$	0.38 μg/g	
Eq. 2	$2\sqrt{\sigma_{Lm}^2 + S_{wL}^2/n}$	0.18 μg/g	
Eq. 2		0.38>0.18	Accuracy not accepted
Table 1	S_{wL} / σ_{Lm}	1.3	n > 10 required for Eq. 3 to be valid. Replication n=3 possibly inadequate for accuracy test at this S_{wL}.

Laboratory B is accepted with respect to repeatability but is found unsatisfactory with respect to accuracy relative to the measurements of the CRM certification program.