ASSESSMENT OF ACCURACY OF SINGLE AND REPLICATE ANALYSIS OF A CERTIFIED REFERENCE MATERIAL

APPLICATION NOTE: 23

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If replicate analysis (more than one analysis) has been done on a CRM within a batch of samples, then a statistical t-test (one-sample, two-tailed t-test) can be used for verification of the accuracy of CRM mean and the certified value of the CRM. However, in the case of a single assay of a certified reference material inserted into a batch of samples a different but related test is done. In this application note, the both approaches are discussed.

1. Statistical Test for Accuracy Evaluation of a Single CRM Result

Decisions on the accuracy of the analysis on a single CRM result (x) compared to the value of the certified reference material with its stated measurement uncertainty is given by:

$$|x - certified\ value| \leq 2\,u \qquad [1]$$

Where, x is the assayed value of the certified reference material, u is the standard uncertainty of the certified reference material (Skoog & West, 1982; Abzalov, 2011).

Example:

Single assay value obtained is 72.48 % Pb for CRM BMPb_Conc-1 Std. The certified value for Pb is 72.46 % with a standard deviation (1*s*) of 0.05 % (Table 1). In measurement uncertainty terminology, 1*s* is the 'standard uncertainty', or u. Using equation [1], the accuracy of the single assay value is verified as:

$$|x - certified\ value| \leq 2\ u$$

$$|72.48 - 72.46| \leq 2\ (0.05)$$

$$|0.020| \leq 0.1$$

Since 0.020 is less than 0.1, the value of 72.48 % demonstrates accuracy in relation to the certified value and its accompanying measurement of uncertainty.

Table 1. Extract from certificate of certified reference material BMPb_Conc-1. The certificate states that due to the reactive nature of the concentrate it should not be dried prior to analysis.

Element	**Certified Value**	**1*s***	**2*s* Low**	**2*s* High**
Pb wt. %	72.46	0.05	72.35	72.57

2. Statistical Test for Evaluation of Accuracy of a Replicate CRM Results

According to ERM (2005); Eurolab (2007) and Abzalov (2011), the validation of accuracy for a given mean and certified value requires the inclusion of the measurement uncertainty of the CRM in a t-test for statistical significance. The classical Student's t-test as shown in [2], does not take into account the measurement uncertainty of the CRM. To compensate for this, Eurolab Technical Report No.1/2007 recommends equation [3] for the validation of CRMs with stated measurement uncertainties.

$$t_{calc} = \frac{|\bar{x} - \mu|}{\frac{s}{\sqrt{n}}} \qquad [2]$$

$$t_{calc} = \frac{|\bar{x} - \mu|}{\sqrt{(u_\mu)^2 + \frac{s^2}{n}}} \quad [3]$$

Where, t_{calc} is the calculated t-statistic, $\bar{x}$ the mean of *n* replicates with a standard deviation of *s* for a CRM of μ certified value. The standard uncertainty *u* is the stated expanded uncertainty (*U*) of the CRM divided by the coverage factor (*k*) as stated on the certificate of analysis. Note that the | | bars indicate that the absolute value between the mean and the certified value is to be used, *i.e.* ignore the sign.

An example in which [3] is used for validation of accuracy is given below.

Example

AMIS0619 is a Certified Reference Material of Copper Concentrate, Black Mountain, Northern Cape, South Africa. AMIS0619 is analysed (replicated) nine times for % Cu concentration by EDTA titration, *i.e.* 9 individual titrations were done. A mean value of *n*=9 measurements is 24.86 % Cu, with a standard deviation of 0.022 %.

Table 2. Excerpt taken from AMIS0619 certificate of analysis giving the certified value and standard uncertainty u_c.

Analyte	Method	Certified (μ)[7]	*N*	n	k	% RSD	(u_c)[8]	(2s)[9] ±	(CI)[10] 95%	(U)[11] ±	Unit
Cu	Titration[1]	24.80	5	37	2.776	3	0.77	1.5	1.1	2	%

of the replicate data are shown with the certified value and standard uncertainty (in the certificate is denoted as u_c). Using the observed mean for the replicate data (*n*=9) obtained for the CRM and substituting into [3]:

$$t_{calc} = \frac{|\bar{x} - \mu|}{\sqrt{0.0356^2 + \frac{0.01015^2}{9}}} = \frac{|4.59 - 4.62|}{\sqrt{0.00126 + 0.00001145}} = 0.84$$

Therefore, t_{calc}= 0.84 and $t_{crit}(5\%, 8) = 2.31$ (*df* is 8, therefore, t_{crit}=2.31, (Table 3 gives a t-critical table) which is >0.84. Similarly, the *p*-value=0.43 which is >0.05. This is strong evidence in favour of accepting the null hypothesis that there is no significant statistical

difference between the certified value and the observed mean. Therefore, under the conditions that the uncertainty associated with the certified value is known the accuracy is validated for the CRM tested. If the null hypothesis is accepted that the mean obtained is not statistically different from the certified value, then the principle of traceability has been conformed to.

Table 3. T-distribution table for t-critical values (t crit.) for a two-tailed t-test at a 95% level of confidence.

df	**Two-tailed**	***df***	**Two-tailed**
1	12.71	23	2.06
2	4.30	24	2.06
3	3.18	25	2.06
4	2.78	26	2.05
5	2.57	27	2.05
6	2.44	28	2.04
7	2.36	29	2.04
8	2.30	30	2.04
9	2.26	35	2.03
10	2.22	40	2.02
11	2.20	45	2.01
12	2.17	50	2.00
13	2.16	55	2.00
14	2.14	60	2.00
15	2.13	70	1.99
16	2.12	80	1.98
17	2.11	90	1.98
18	2.10	100	1.98
19	2.09	120	1.98
20	2.08	Infinity	1.96
21	2.08		
22	2.07		

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