QUALITY MATTERS

Is your spectrometer in calibration?

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A question that was easily answerable you might think, especially if you have used a certified reference material traceable to NIST, for example. After all it comes with a certified value with an expanded measurement uncertainty doesn't it?

So when you measure this CRM on your spectrometer, what are your acceptance limits? A good question because the expanded measurement uncertainty relates to the certified reference standard itself, not to the value measured on your spectrometer. So how do you establish acceptance limits for your spectrometer for your type of calibration?

The answer is somewhat buried in manufacturers' and NIST publications. You could carry out an uncertainty budget exercise. An example of this approach has been given recently.[1] Here an uncertainty budget calculation is used to show that the mean value of the measured value lies within the combined uncertainty. In other words, the difference between the certified value and the measured value of 0.0042 absorbance units is within the combined uncertainty of 0.0058 absorbance units and hence within calibration.

However, as many laboratories would like to use simple acceptance limits, is there another way?

Some manufacturers and CRM suppliers use a simple acceptance limits statement contained in the NIST SRM 1930 Glass filters certificate:

> "An acceptable level of agreement between the user's measurements and the certified value and its expanded uncertainty overlaps any part of the user's tolerance band defined by the measured mean and the user-defined level of acceptability"[2]

This has been interpreted as "Add the SRM expanded uncertainty to the manufacturer's tolerance and make those the acceptance limits for satisfactory calibration performance". Let us see if this works, as it is very easy to calculate and apply. Even QA will be able to understand it.

By way of an example consider an SRM absorbance value which has an expanded uncertainty (U) of ±0.0049 absorbance units. The actual certified value does not matter as you will see. The instrument manufacturer's specification (A), at that absorbance value, is ±0.005 absorbance units. Hence, simple addition gives Acceptance Limits of ±0.0099 absorbance units from the certified value. Note that in the NIST statement it uses the term "measurement mean" implying that the user measures the standard more than once and takes the mean value. In other words, the difference between the measurement mean and the certified value must not exceed ±0.0099 absorbance units for the instrument to be deemed in calibration.

We can test this approach by running a Monte Carlo Simulation (MCS) model,[3] using Minitab Devize software and assuming that the SRM standard deviation is 0.00245 (i.e. half the expanded uncertainty) and that the manufacturer's specification has a uniform or rectangular distribution. When we run this simulation, the result is shown in Figure 2 for 50,000 iterations of the model and set the acceptance limits (specification limits) as ±0.0099.

As can be seen, more than 99.6% of the results would lie within the acceptance limits. So this would appear to be a reasonable approach.

Can this be applied to wavelength accuracy also? Yes indeed. This time let us assume that SRM has a standard devi-

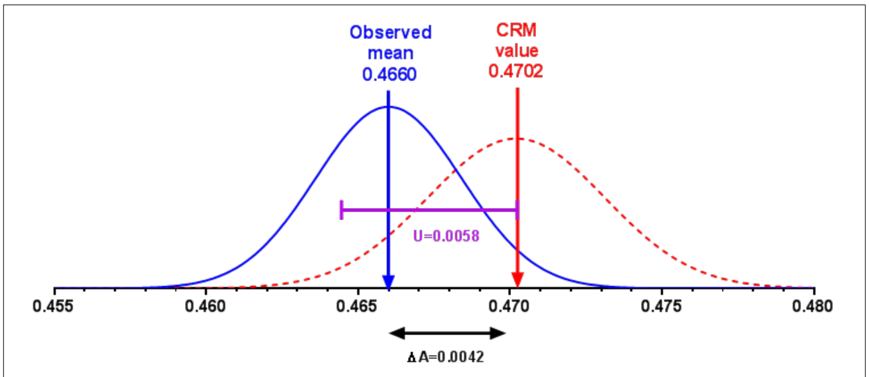

Figure 1. An example of a mean measured absorbance value lying inside the combined measurement uncertainty of the measurement and the CRM.[1]

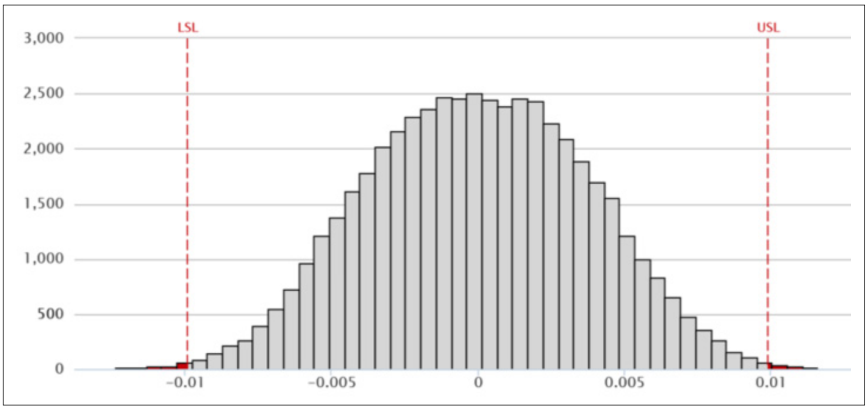

Figure 2. Minitab Devize MCS model output for absorbance accuracy acceptance limits of ±0.0099 for $N = 50{,}000$.

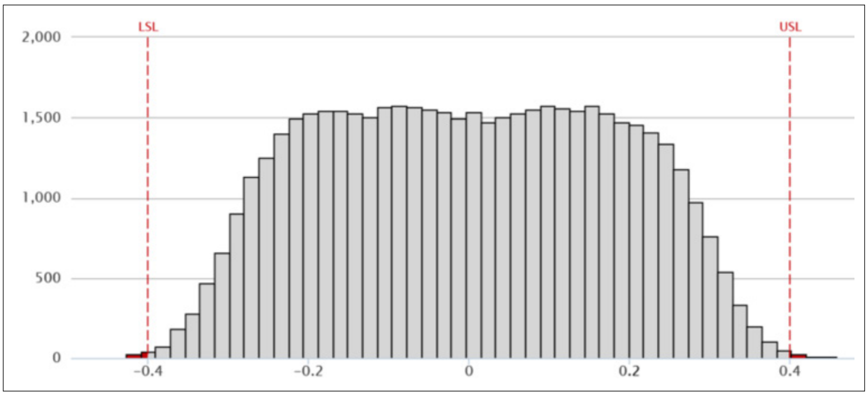

Figure 3. Minitab Devize MCS model output for wavelength accuracy acceptance limits of ±0.4 nm for $N = 50{,}000$.

ation of 0.05 nm (expanded uncertainty is 0.10 nm) and the manufacturer's specification is ±0.3 nm. In this instance, the acceptance limits would be (0.1 + 0.3) i.e. 0.4 nm. The result of the MCS model is shown in Figure 3. This time more than 99.8% of the results would lie within the acceptance limits.

Does this simple acceptance limit method sound a bit too good to be true? Yes it is, because this method ignores the metrological uncertainty of the mean itself!

Careful reading of NIST Special Publication 829 reveals that, in section E3a, the statistically correct calculation for the acceptance limits (AL) required is given by:

$$AL = \pm t_{(0.05,n-1)} \frac{s}{\sqrt{n}} + (U + A))$$

These acceptance limits include the above mentioned approach for the acceptance limits ($U + A$) and, in addition, the standard error of the measured mean corrected for the number of determinations. These correct limits will be a little larger than the acceptance limits based on just ($U + A$) which are more conservative. From a compliance perspective the acceptance limits based on just ($U + A$) are "fail safe", so would be acceptable.

References

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2. D. Becker *et al.*, *Use of NIST Standard Reference Materials for Decisions on Performance of Analytical Chemical Methods and Laboratories*. NIST Special Publication 829 (1992). http://www.nist.gov/mml/csd/inorganic/upload/NIST_SpecialPub829.pdf
3. C. Burgess, "Measurement uncertainty without the math", *Pharmaceut. Technol.* **40(2),** 36–40 (2016). http://www.pharmtech.com/measurement-uncertainty-without-math