Appendix 8. Practical calculation of critical levels: Examples.

Here, we briefly consider four examples of LA-ICPMS background measurements; in each case, the goal is to estimate the critical level. The first example describes a hypothetical, though practically important situation when the whole measurement yields zero counts. The remaining three examples are based on real background measurements described in Electronic Appendix 1. In all cases, the nominal level of false positive errors is set to 5%.

Example (i); input: $N_b=I_b=0$, $t_b=t_s=1$ s. Each of the sweeps constituting the background measurement returns zero counts (per second). Standard deviation estimates $s(N_b)$ and $s(I_b)$ according to eqn (28,30-32) are all equal to zero (in the absence of empirical manipulations with the background). L_c will be estimated using four decision rules:

(a) for the sample signal to be detected, the mid-*p* adjusted version of the binomial rule, eqn 69, requires at least 4 counts to be registered during the signal measurement, provided $t_b=t_s$:

$$p_{cumulative}^{mid-adjusted} = 0.5 \times p(N_b = 0,\ N_s = 4) = 0.5\left(\frac{1}{2}\right)^4 = 3.125\% < 5\%$$

At t_s=1 s, L_c=3/1-0/1=3 cps; detection occurs when $I_{s\,net}=I_s-I_b>L_c$, i.e., when $I_{s\,net}$=4/1-0/1=4 cps.

(b) rule based on the square root transform, d=0.4, eqn (65,90), as recommended in the main text:

$$L_c = (I_s - I_b)_c = 0.4\left(\frac{1}{1}-\frac{1}{1}\right) + 0.677\left(\frac{1}{1}+\frac{1}{1}\right) + 1.645\sqrt{(0+0.4)\frac{1}{1}\left(\frac{1}{1}+\frac{1}{1}\right)} = 2.825\ cps$$

(c) $\surd 2N_b$ rule, eqn (63,72): $L_c = (I_s - I_b)_c = 1.645\sqrt{0\left(\frac{1}{1}+\frac{1}{1}\right)} = 1.645 \times 0 \times \sqrt{1+\frac{1}{1}} = 0\ cps$

(d) $\surd 2N_b$ rule empirically corrected for an 'empty' background by adding one count to one of the sweep readings constituting the background measurement, eqn (64,73):

assuming the ordinary Poisson distribution, eqn (32): $s(I_b) = \sqrt{\frac{1}{1}} = 1\ cps$

assuming any distribution of uncorrelated sweep readings (eqn 31):

$s(I_b) = \sqrt{\frac{(100-1)^2 + 99(0-1)^2}{100*99}} = 1\ cps$, number of sweeps arbitrarily set to 100 (10 ms dwell time);

$s(I_b) = \sqrt{\frac{(50-1)^2 + 49(0-1)^2}{50*49}} = 1\ cps$, number of sweeps arbitrarily set to 50 (20 ms dwell time), etc.

Accordingly, $L_c = (I_s - I_b)_c = 1.645\sqrt{1\left(\frac{1}{1}+\frac{1}{1}\right)} = 1.645 \times 1 \times \sqrt{1+1} = 2.326\ cps$

Conclusions. The highest L_c value was returned by the mid-*p* adjusted version of the binomial rule. It amounts to 3 cps, i.e., 3 counts in the signal are not yet detected, while 4 counts are detected. From the size modelling for this rule, we know that it can be conservative ($\overline{N}_b$ limiting to zero) or robust ($\overline{N}_b > 4$, $t_b=t_s$). Since the probability to obtain a zero background estimate at $\overline{N}_b > 4$ is small, it can be safely concluded that the mid-*p* adjusted version of the binomial rule returned a conservative decision (which would become even more conservative when using the canonical formulation of this rule, see section 2.3 of the main text). Using the square root transform (d=0.4) returns an L_c value of 2.825 cps: 3 counts in the signal are already detected. From the size modelling for this rule, we know that it can be conservative ($\overline{N}_b$ limiting to zero) or robust ($\overline{N}_b > 1.1$). As the mean background count number is unknown, we cannot provide more details. Still, we are sure that the liberal decision is excluded: if we repeat our paired analysis many times, the rate of false detections will be lower than the declared level of 5%, or close to this level. Using the $\surd 2N_b$ decision rule in its original formulation, we have to accept that the rate of false detections will be much higher than declared, although an L_c value of zero returned by this rule can, at first glance, look attractive: any positive sample signal is detected. Empirically correcting this rule for an 'empty' background partly repairs the situation, provided the background estimate is happened to contain zero counts. At N_b>0, liberal detection decisions are taken, as no correction is applied; the overall behaviour of this decision rule remains liberal. Even if one count is added to any outcome of the background measurement, including the non-zero outcomes, the $\surd 2$ rule continuous to behave liberally (see Ref. 5 from the main text).

Example (ii); input: N_b=3 counts, t_b=1.8 s (90 sweeps x 20 ms dwell time per sweep), t_b/t_s=3. The corresponding statistics can be found in Table 1 from Electronic Appendix 1, see time-resolved data for ^{93}Nb. $s(N_b)$ and $s(I_b)$ are estimated as follows:

assuming the ordinary Poisson model, eqn (30,32):

$$N_b = 3 \ counts; \ s(N_b) = \sqrt{3} = 1.732 \ counts$$

$$I_b = \frac{3}{1.8} = 1.667 \ cps; \ s(I_b) = \sqrt{\frac{1.667}{1.8}} = 0.962 \ cps$$

assuming any distribution of uncorrelated sweep readings (eqn 28,31):

$$N_b = 3 \ counts; \ \overline{N}_{sw} = 3/90 = 0.033 \ counts; \ s(N_b) = \sqrt{\frac{90}{89}\left[3(1-0.033)^2 + 87(0-0.033)^2\right]} = 1.712 \ counts$$

$$I_b = \frac{3}{1.8} = 1.667 \ cps; \ s(I_b) = \sqrt{\frac{3(50-1.667)^2 + 87(0-1.667)^2}{90*89}} = 0.951 \ cps$$

As the background value is very small, assuming it to be part of an ordinary Poisson distribution does not require a dedicated study. Still, this assumption is confirmed by the close match between the standard deviation values above and proved by the Chi-square goodness-of-fit test presented in Table 2 from Electronic Appendix 1.

L_c will be estimated using three decision rules:

(a) for the sample signal to be detected, the mid-*p* adjusted version of the binomial rule, eqn 69, t_b/t_s=3, requires at least 4 counts to be registered during the signal measurement. This example is partly described in the main text (section 2.4). The *max* number of counts in the signal measurement, when the signal is not yet detected is equal to 3. At t_s=0.6 s, L_c=3/0.6-3/1.8=3.333 cps; detection occurs when $I_{s\ net}=I_s-I_b>L_c$, i.e., when $I_{s\ net}$=4/0.6-3/1.8=5 cps.

(b) rule based on the square root transform, d=0.4, eqn (65,90), as recommended in the main text:

$$L_c = (I_s - I_b)_c = 0.4\left(\frac{1}{1.8} - \frac{1}{0.6}\right) + 0.677\left(\frac{1}{0.6} + \frac{1}{1.8}\right) + 1.645\sqrt{(1.667*1.8+0.4)\frac{1}{1.8}\left(\frac{1}{0.6} + \frac{1}{1.8}\right)} = 4.431 \ cps$$

(c) $\sqrt{2N_b}$ rule, eqn (64) and (73), respectively:

$$L_c = (I_s - I_b)_c = 1.645\sqrt{1.667\left(\frac{1}{0.6} + \frac{1}{1.8}\right)} = 3.166 \ cps; \ L_c = (I_s - I_b)_c = 1.645 \times 0.951\sqrt{1+\frac{3}{1}} = 3.129 \ cps$$

Conclusions. The mid-*p* adjusted version of the binomial rule and the square root transform (d=0.4) return the same result: 3 counts in the signal are not yet detected, while 4 counts are detected. From the size modelling for these rules, we know that they can be conservative ($\overline{N}_b/3$ limiting to zero) or robust ($\overline{N}_b/3 > 2$ for the mid-*p* adjusted version of the binomial rule, $\overline{N}_b/3 > 0.5$ for the square root transform). As the mean background count number is unknown, we cannot provide more details. The liberal behaviour is excluded anyway. The $\sqrt{2N_b}$ rule returns a smaller L_c value that implies, contrary to the above rules, that 3 counts in the signal are already detected. From the size modelling, we know that this decision is liberal: the $\sqrt{2N_b}$ rule demonstrates a liberal behaviour for all $\overline{N}_b/3$ values that could yield an estimate of $N_b = 3$ counts with a non-negligible probability.

Example (iii); input: N_b=3373 counts, t_b=0.90 s (90 sweeps x 10 ms dwell time per sweep), t_b/t_s=2. The corresponding statistics can be found in Table 1 from Electronic Appendix 1, see time-resolved data for ^{23}Na. $s(N_b)$ and $s(I_b)$ are estimated as follows:

assuming the ordinary Poisson model, eqn (30,32):

$$N_b = 3373 \ counts; \ s(N_b) = \sqrt{3373} = 58.078 \ counts$$

$$I_b = \frac{3373}{0.9} = 3747.778 \ cps; \ s(I_b) = \sqrt{\frac{3747.778}{0.9}} = 64.531 \ cps$$

assuming any distribution of uncorrelated sweep readings (eqn 28,31):

$$N_b = 3373 \ counts; \ \overline{N}_{sw} = 3373/90 = 37.478 \ counts; \ s(N_b) = \sqrt{\frac{90}{89}\sum_{i=1}^{k}\left(N_{sw\,i} - 37.478\right)^2} = 58.709 \ counts$$

$$I_b = \frac{3373}{0.9} = 3747.778 \ cps; \ s(I_b) = \sqrt{\frac{1}{90 \times 89}\sum_{i=1}^{k}\left(I_{sw\,i} - 3747.778\right)^2} = 65.266 \ cps$$

The background intensity is relatively high, and the presence of an excess variance, i.e., an over-dispersion of counts compared to the prediction from the ordinary Poisson distribution, cannot be ruled out *a priori*. Still, the standard deviation values above are closely matched; moreover, the Chi-square goodness-of-fit test presented in Table 3 from Electronic Appendix 1 shows that both the ordinary Poisson distribution and the Gauss distribution are acceptable proxies for the statistics observed in the background measurement studied.

L_c will be estimated using three decision rules:

(a) rule based on the square root transform, d=0.4, eqn (65,90), as recommended in the main text:

$$L_c = (I_s - I_b)_c$$

$$= 0.4\left(\frac{1}{0.9} - \frac{1}{0.45}\right) + 0.677\left(\frac{1}{0.45} + \frac{1}{0.9}\right) + 1.645\sqrt{(3747.778 * 0.9 + 0.4)\frac{1}{0.9}\left(\frac{1}{0.45} + \frac{1}{0.9}\right)} = 185.685 \ cps$$

(b) $\sqrt{2N_b}$ rule, eqn (64) and (73), respectively:

$$L_c = (I_s - I_b)_c = 1.645\sqrt{3747.778\left(\frac{1}{0.45} + \frac{1}{0.9}\right)} = 183.862 \ cps$$

$$L_c = (I_s - I_b)_c = 1.645 \times 65.266\sqrt{1 + \frac{2}{1}} = 185.957 \ cps$$

(c) extension of the square root transform for data that may contain an excess variance, eqn (78), as recommended in the main text:

$$L_c = (I_s - I_b)_c = \left[\frac{\sqrt{I_b} + \sqrt{I_b - ab}}{a}\right]^2 - I_b = 188.300 \ cps$$

where: $I_b = 3747.778 \ cps$

$$a = \left[1 - \frac{\left(t_b s^2(I_b) - I_b\right)k_\alpha^2}{4 t_b I_b^2}\right] = \left[1 - \frac{\left(0.9 \times 65.266^2 - 3747.778\right)1.645^2}{4 \times 0.9 \times 3747.778^2}\right] = 0.99999540 \ (unitless)$$

$$b = \left[I_b - \frac{k_\alpha^2}{4}\left(\frac{1}{t_b} + \frac{t_b s^2(I_b)}{t_s I_b}\right)\right] = \left[3747.778 - \frac{1.645^2}{4}\left(\frac{1}{0.9} + \frac{0.9 \times 65.266^2}{0.45 \times 3747.778}\right)\right] = 3745.488519 \ cps$$

Conclusions. All decision rules from this example yield similar critical values. In all cases, the detection is expected to be robust, given the large number of counts contained in the studied background measurement. Any of the above rules can be used for the practical estimation of critical levels, provided large background count numbers are handled and the ordinary Poisson model is still relevant.

Example (iv); input: N_b=120273 counts, t_b=0.90 s (90 sweeps x 10 ms dwell time per sweep), t_b/t_s=2. The corresponding statistics can be found in Table 1 from Electronic Appendix 1, see time-resolved data for ^{29}Si. $s(N_b)$ and $s(I_b)$ are estimated as follows:

assuming the ordinary Poisson model, eqn (30,32):

$$N_b = 120273\ counts;\ s(N_b) = \sqrt{120273} = 346.8\ counts$$

$$I_b = \frac{120273}{0.9} = 133636.7\ cps;\ s(I_b) = \sqrt{\frac{133636.7}{0.9}} = 385.3\ cps$$

assuming any distribution of uncorrelated sweep readings (eqn 28,31):

$$N_b = 120273\ counts;\ \overline{N}_{sw} = 120273/90 = 1336.4\ counts;\ s(N_b) = \sqrt{\frac{90}{89}\sum_{i=1}^{k}\left(N_{sw\,i} - 1336.4\right)^2} = 567.7\ counts$$

$$I_b = \frac{120273}{0.9} = 133636.7\ cps;\ s(I_b) = \sqrt{\frac{1}{90\times 89}\sum_{i=1}^{k}\left(I_{sw\,i} - 133636.7\right)^2} = 630.7\ cps$$

The background intensity is high: the presence of an excess variance, i.e., an over-dispersion of counts compared to the prediction from the ordinary Poisson distribution, can be suspected. The standard deviation values above are mismatched, with the values obtained assuming the ordinary Poisson model being smaller. The Chi-square goodness-of-fit test presented in Table 4 from Electronic Appendix 1 indeed shows that the ordinary Poisson distribution cannot be applied to describe the studied background measurement. The Gauss distribution is applicable. Decision rules for ordinary Poisson distributed data cannot be employed; they will underestimate L_c values.

L_c will be estimated using two decision rules applicable for the description of data with an excess variance:

(**a**) eqn (73): $L_c = (I_s - I_b)_c = 1.645\times 630.7\sqrt{1+\frac{2}{1}} = 1797.0\ cps$

(**b**) extension of the square root transform for data that may contain an excess variance, eqn (78), as recommended in the main text:

$$L_c = (I_s - I_b)_c = \left[\frac{\sqrt{I_b} + \sqrt{I_b - ab}}{a}\right]^2 - I_b = 1805.6\ cps$$

where: $I_b = 3747.778\ cps$

$$a = \left[1 - \frac{\left(t_b s^2(I_b) - I_b\right)k_\alpha^2}{4 t_b I_b^2}\right] = \left[1 - \frac{\left(0.9\times 630.7^2 - 133636.7\right)1.645^2}{4\times 0.9\times 133636.7^2}\right] = 0.99999056\ (unitless)$$

$$b = \left[I_b - \frac{k_\alpha^2}{4}\left(\frac{1}{t_b} + \frac{t_b s^2(I_b)}{t_s I_b}\right)\right] = \left[133636.7 - \frac{1.645^2}{4}\left(\frac{1}{0.9} + \frac{0.9\times 630.7^2}{0.45\times 133636.7}\right)\right] = 133631.920955\ cps$$

Conclusions. Both decision rules from this example yield similar critical values. In all cases, the detection is expected to be robust, given the large number of counts contained in the studied background measurement. Any of the above rules can be used for the practical estimation of critical levels, provided very large background count numbers are handled and the ordinary Poisson model is not applicable.