amc technical brief

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What should be done with results below the detection limit? Mentioning the unmentionable

What we should do when results of analytical measurements fall below the detection limit has long been a source of puzzlement. In fact the idea of a detection limit itself is puzzling: why else should we spend so much effort trying to define it once and for all, but never quite succeed! The common perception of detection limit as a kind of event horizon around a black hole, from which information cannot possibly emerge, is partly to blame for this difficulty.

Measuring zero

We tend to think that we should be working well above the detection limit if we are trying to make sensible measurements. That is a correct attitude in so far as it can be accomplished, but it simply ignores an obvious fact of life: many analytical scientists, unlike most other metrologists, are called on to measure concentrations that have a true value of zero. Let's consider an example: the concentration of a banned synthetic growth promoter in a sample of pig's liver. The true answer could be exactly zero, unless the pig has been given the substance illegally. Under these circumstances, and many others less extreme, we will encounter results that fall below the detection limit. Moreover, the problem of trying to measure zero will not go away with improved technology. How can we refine our ideas about reporting such results, and advise end-users of our data how to interpret them?

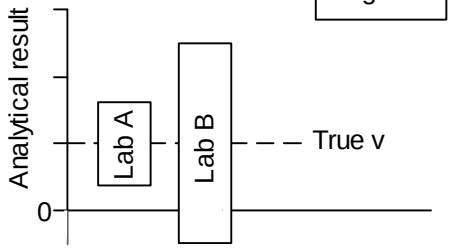
Reporting low concentrations

In the absence of a definitive answer, most of us have settled for reporting results below a detection limit c_L in one of the following possible ways.

- Not detected
- Less than c_L
- A value of zero
- An arbitrary fraction of c_L, e.g., $c_L/2$
- The result found, with a statement of its uncertainty.

Which of these is best? Clearly 'not detected' is the worst, as it contains hardly any information. A typical problem with 'not detected' is that of obtaining confirmatory results from a second laboratory. Suppose Laboratory A has the best available technology for the job in hand, with a detection limit of $c_{L,A}$, and detects a prohibited substance in the test material. Laboratory B, with older instrumentation and a higher detection limit $c_{L,B}$, tries to confirm the result but fails to detect the analyte. In Fig 1 the bars indicate the extended uncertainties around the two results.

Figure 1



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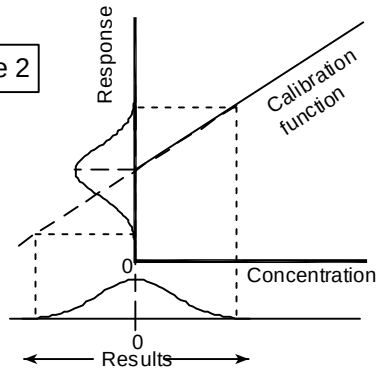
zero. Concentrations by definition can only be zero or greater, but we must remember that *analytical results are not concentrations but error-prone estimates of concentrations*.

Imagine a typical situation: we have a linear calibration and an unbounded analytical response, which is the usual case. In repeated measurements at zero concentration about half of the responses will be above the average and half below the average. Those below the average, when mapped onto the concentration axis, will give rise to negative results (Fig. 2). This effect is caused by random variations.

Figure 2



Systematic effects can also give rise to negative results. For example, over-correcting of interference effects is sometimes encountered in the determination of elements by atomic spectrometry and is one cause of the problem. Another common cause is lack of fit at the low end in a estimated calibration function (Fig. 3).