

Guide for Determining ICP/ICP-MS Method Detection Limits and Instrument Performance

Vanaja Sivakumar, Laszlo Ernyei and Ralph H. Obenauf • Spex CertiPrep, Metuchen, NJ 08840

As the term itself implies, one cannot make a measurement below the detection limit. But not everyone has a complete understanding of what the true detection limit is or how it is determined. So what is the method detection limit (MDL)?

Standard Methods defines the MDL as: “constituent concentration that, when processed through the complete method, produces a signal with a 99% probability that it is different from the blank”¹. The EPA defines it as: “the minimum concentration that can be determined, with 99% confidence, that the true concentration is greater than zero”². The MDL depends on the equipment, chemicals, methodology, materials, sample composition and even the analysts.

The MDL is different from the instrument detection limit (IDL). The instrument manufacturer’s manuals often contain numbers that can only be achieved under optimal conditions. But instruments often cannot be run under optimum conditions. For example in the case of ICP and ICP-MS, there may be matrix interferences; the sample introduction system may be contaminated by earlier samples, ICP-MS cones (for ICP-MS) may not be in perfect condition or the torch and injector tube may have deposits. Instrument detection limits are useful for comparison of different techniques (such as polarography, atomic absorption, ICP, ICP-MS) or different versions of the same type of instrument.

One of the procedures outlined in 40 CFR 136 for determining the MDL is to prepare the analyte concentration at a level one to five times the estimated detection limit and run multiple determinations. The standard deviation is then calculated and the MDL computed based on the following formula: MDL = Student’s t-value times the standard deviation. (MDL = t x sd) Here we determined the MDL for Nickel using an Elan 3300 ICP Spectrometer. The estimated detection limit for this element was determined, based on seven replicate analyses of a blank, to be 0.0025 ppm. We selected a concentration (0.01 ppm) four times higher than the IDL and ran seven replicates of this solution. We obtained an average of 0.0098 ppm with a standard deviation (sd) of ± 0.00048 ppm.

- MDL = Student’s t x standard deviation = 3.707 x 0.00048 ppm = 0.0018 ppm
- MDL is a useful parameter to determine the lowest concentration at which an analyte can be observed. Based on the MDL that we calculated for nickel, above, the lowest level that we can determine with certainty (using this particular instrument) is 2.5 times the MDL or 0.0045 ppm.³

Common sense goes a long way in determining if your system is working properly. For example, one might conclude that the calibration standard was faulty if the calibration curve had a negative slope. In one case, the blank had zero intensity and the standard had just one count (intensity) instead of a number in the thousands. Here the sample introduction system was not working properly. This could be due to a number of problems such as a partially blocked nebulizer, broken capillary or pump tubing or other hardware related problem. In the case of ICP, a negative calibration curve (slope) could be due to interference from a background wavelength.

Reviewing the relative standard deviation from samples periodically can help detect errors. If the relative standard deviation is not between 0.5 and 2%, one should look for a possible instrument problem. Check the signal. In the case of low signals, reported values may be near to the detection limit and hence will not be accurate. In the case of high signals, (higher than 100,000 counts), check the sample introduction system and sample concentration.

Another extreme case is a standard deviation of ZERO. Your relative standard deviation should not be zero. If so, it could be due to a saturated detector or non-working detector. Both of these conditions require operator intervention – dilute the solution in the case of a saturated detector or check the power to the detector.

Use of an internal standard can eliminate many problems as well as point out other issues. Internal standard use eliminates or reduces variations such as power fluctuations, temperature changes, differences in solution parameters such as density, viscosity, or surface tension, and changes in the sample introduction system.

To summarize, an operator can improve the accuracy and confidence in measurements by a proper understanding of detection limits, looking at parameters such as the sd and MDL to see if they make sense and the use of internal standards. Importing instrument data into a spreadsheet can make this review easier.

References:

1. Standard Methods for the Examination of Water and Waste Water, 20th Edition, 1-3
2. EPA document 40 CFR 136
3. Tim Loftus, “Method Detection Limits, New Jersey Effluents, Winter 2005, page 39