Atomic Absorption

Sensitivity Versus Detection Limit

The earliest atomic absorption (AA) spectrometers provided results in terms of percent absorption (%A = 100 – %T). Those early instruments were significantly less stable than today's modern equipment, and virtually all analyses were performed with no scale expansion. For most elements, the smallest concentration which could be detected was that which produced a percent absorption signal of about 1%A (0.0044 absorbance units) which became accepted as a rough measurement of performance known as "sensitivity", a term used with emission spectroscopy and other techniques. However, improvements in AA systems soon permitted the use of high degrees of scale expansion, allowing the determination of concentrations much lower than that represented by the sensitivity value. The term "detection limit" was coined to mean the lowest concentration that could be detected by atomic absorption.

The change in the terminology used to describe the smallest detectable quantity by AA had an unfortunate side effect – the frequent (and erroneous) inter-changeable use of the terms "sensitivity" and "detection limit".

The difference between sensitivity and detection limit

Sensitivity is a measure only of signal magnitude, the solution concentration or weight of an element that produces a signal of 0.0044A (1%A) for continuous or peak height measurements or 0.0044 A•s for integrated peak area. It is also known as characteristic concentration with flame AA or characteristic mass with furnace AA.

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Detection limit is a measure of the smallest concentration which can be determined with a specified precision or reproducibility. Most frequently, the specified precision is defined in terms of the concentration producing a signal equivalent to three times the standard deviation of a series of blank (baseline) readings or readings for a standard with a concentration close to the anticipated detection limit. This definition is equivalent to a 99% confidence level. That is, the answer obtained under these conditions will be correct 99 times out of 100.

As defined, the detection limit is a function of both signal strength (or sensitivity) and signal stability.

For a visual representation of the difference between sensitivity and detection limit, refer to the signals below. Signals A and B represent the same concentration and give comparable absorbances or signal (S). The sensitivities are, therefore, the same. However, the better signal stability or lower "noise" level (N) of signal B will provide better reproducibility (precision) and allow smaller concentrations to be accurately measured. Signal B will provide better precision and detection limits because it has a better (i.e., higher) signal-to-noise ratio (S/N).

Greater sensitivity alone will not provide better detection limits or precision as illustrated by signals C and D, which again are for the same concentration. The system which produced signal C provided twice the signal or sensitivity of that which produced signal D but also generated twice the noise level. The signal-to-noise ratios for the two signals are therefore the same (S/N = 8 for each). As a result, performance should also be the same for the two systems.

Sensitivity alone cannot be related to system performance, since it is only an indication of signal strength. Detection limits are direct indicators of system performance, since both detection limits and performance are functions of the signal-to-noise ratio.

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