

## Calibration by standard additions method – what, why and how

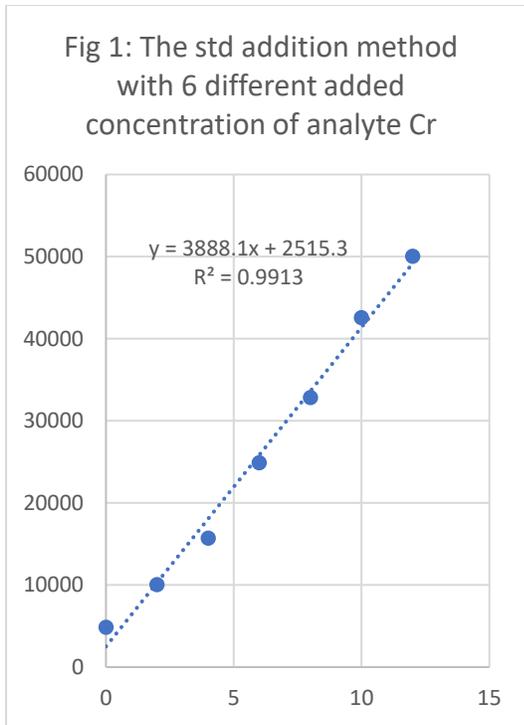
Imagine that we wish to determine the concentration of pollutant chromium in samples of treated waste water from a plating factory by inductively coupled plasma – optical emission spectrometry (ICP-OES). Commonly we calibrate the spectrometer with a series of working aqueous standard solutions of chromium, prepared by diluting a stock 1000 mg/L chromium standard solution with distilled water. We then use the resulting calibration graph in the determination of the chromium in test samples.

It is noted that this calibration method is valid only if a pure aqueous solution of chromium and the waste water sample containing the same concentration of chromium give the same spectrometric intensity values. In here, we have made an assumption that in using the pure standard solutions to establish the calibration graph, there is no reduction or enhancement of the chromium intensity signal caused by many other constituents present in the waste sample. Such assumption can be risky and, in many instance, this assumption is not valid at all because of serious matrix interfering effects which are normally proportional to the analyte signals, resulting in a change of the slope of the linear calibration curve.

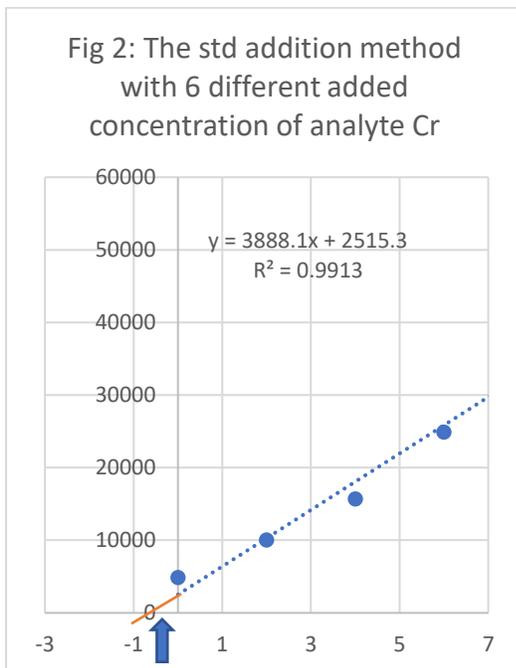
It is therefore important to note that in order to make a valid comparison between the calibration curve and test solutions, the  $y$ -intercept and sensitive of the calibration equation  $y=a+bx$  must match those we would observe in the sample matrix as much as possible. In practice, this does not work well for waste water samples with pure standard solutions used in establishing the calibration curve due to a noticeable difference between these two matrices.

To overcome this sensitivity due to the matrix, one may opt to use the standard addition method for calibration. This method however, does not overcome changes to the baseline of the signal but is to be applied to the net signal. That means it requires any baseline signal to be subtracted from the gross signal before the method can be applied.

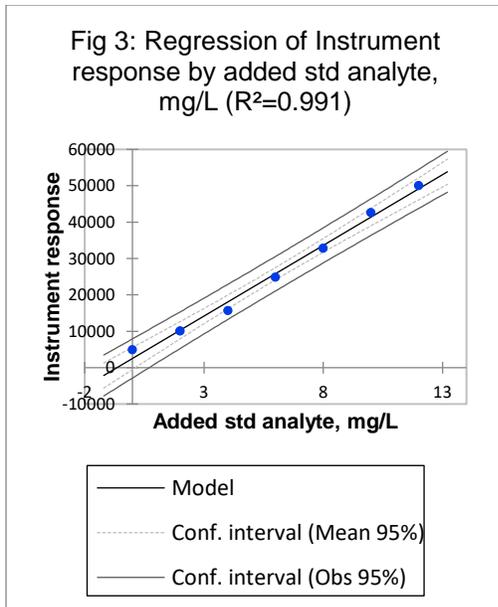
This standard addition method involves the addition to a test solution of several different exactly known amounts of the analyte, so that the matrix is identical in each added standard solution. The analytical response (corrected for a baseline shift) is measured for each solution and the line fitted to the points is extrapolated down to zero net response. See Figure 1.



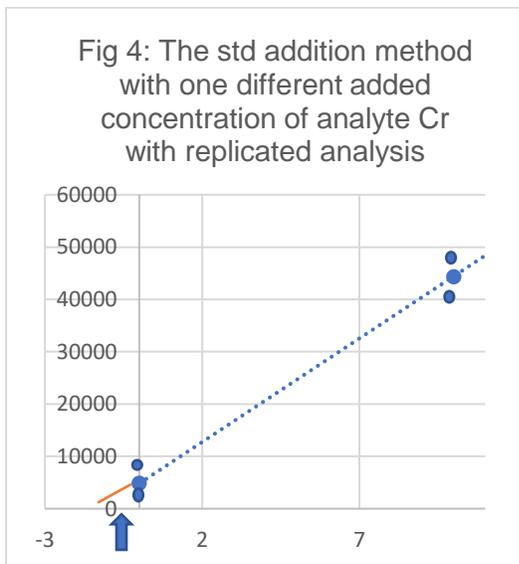
In fact, the negative reading on the concentration axis is the concentrated estimate of the actual sample solution. See Figure 2.



The extrapolation can be done graphically as above but the application of regression to estimating the original concentration is obvious. The resulting function  $y = a + bx$  with response ( $y$ ) set at zero gives  $x = -a/b$ . The variation to the slope is shown in Figure 3.



Note that standard addition method is valid only when the calibration is known to be linear. If we can assume linearity in such calibration, we can design a simpler experiment with only one level of added analyte, preferably with replicated measurements. In this case, the added level should be the highest possible concentration consistent with a linear calibration function. See Figure 4.



This design obviously cuts down the laboratory workload and also improves the precision of the final result for the same number of measurements. Moreover, regression is not needed in the calculations as a line passing through the means of the responses at both concentrations is identical with a regression line, whether simple or weighted.