Electronic Supplementary Information

Multispecies calibration: A novel application for inductively coupled plasma tandem mass spectrometry

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Calculation of limits of detection in multispecies calibration

In multispecies calibration (MSC), the instrumental limit of detection (LOD) is calculated from the analyte concentration determined for a blank solution (or most likely the signal fluctuation perceived as analyte signal). Ten replicates of S1 (3.00 mL of 1% v/v HNO_3 plus 3.00 mL of a standard solution containing 20.0 μg L^{-1} of each analyte), and ten replicates of S2 (1% v/v HNO_3) were run separately to determine the LODs for As, Co and Mn. In this case, 1% v/v HNO_3 is the sample. The ten resulting MSC plots provided the values of ten distinct analyte concentrations in the blank. The LODs were then calculated as 3 times the standard deviation (n = 10) of the analyte concentrations in the blank. Figs. S1, S2 and S3 show the MSC plots for one of the replicates used to estimate the LODs for As, Co and Mn, respectively. From these MSC plots, one can find the blank concentrations of 0.024, 0.092, and 0.257 μg L^{-1} (see eqn (7) in the main article). The standard deviation values for ten replicates (the other MSC plots are not shown) were calculated as 0.022, 0.010, and 0.0236 μg L^{-1} for As, Co and Mn, respectively. Finally, the LODs (3 times the standard deviation of the analyte concentrations) were estimated as 0.07, 0.03, and 0.07 μg L^{-1}, respectively.

According to the IUPAC, "*The limit of detection, expressed as the concentration, c_L, or the quantity, q_L, is derived from the smallest measure, x_L, that can be detected with reasonable certainty for a given analytical procedure*".[1] By multiplying the standard deviation of the blank concentration by three, one can ensure "*reasonable certainty*". As discussed by Winefordner and Long,[2] concentration values at or above the LODs calculated in this manner have only an 11 % chance to be a result of signal fluctuations due to the blank.[2]

Similar to any other method, the LODs calculated for MSC are based on noise and analyte sensitivity. The MSC slope contains the analyte sensitivity and incorporates signal fluctuations (as it is determined using least squares regression). Noise is further estimated by calculating the standard deviation of the blank concentrations determined with MSC. On the other hand, several analyte species are evaluated at once, rather than separately as would be the case with a traditional calibration method. Therefore, the LODs reported for MSC represent the smallest concentration that can be detected with reasonable certainty involving all analyte species evaluated at once.

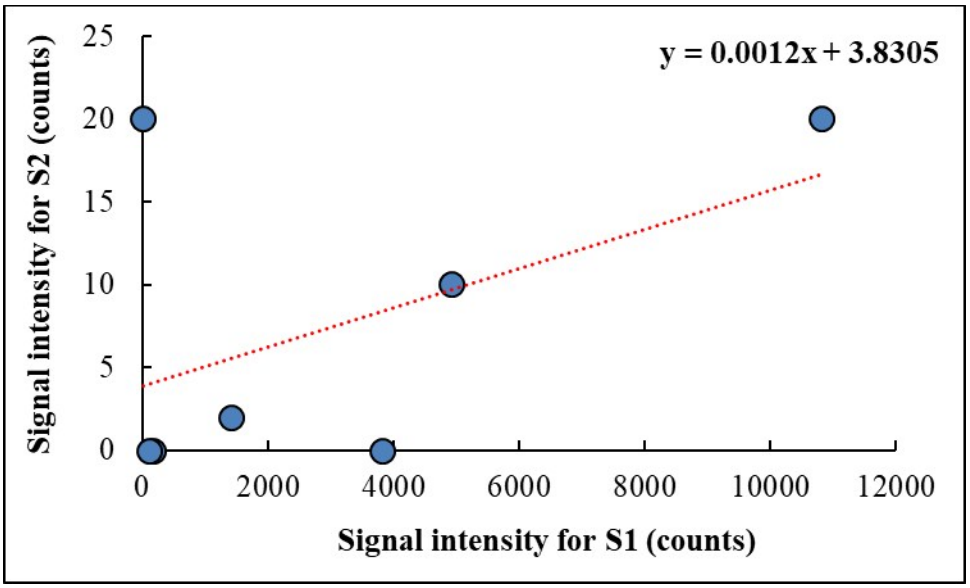

Fig. S1. MSC plot of one of the replicates used to calculate the LOD for As.

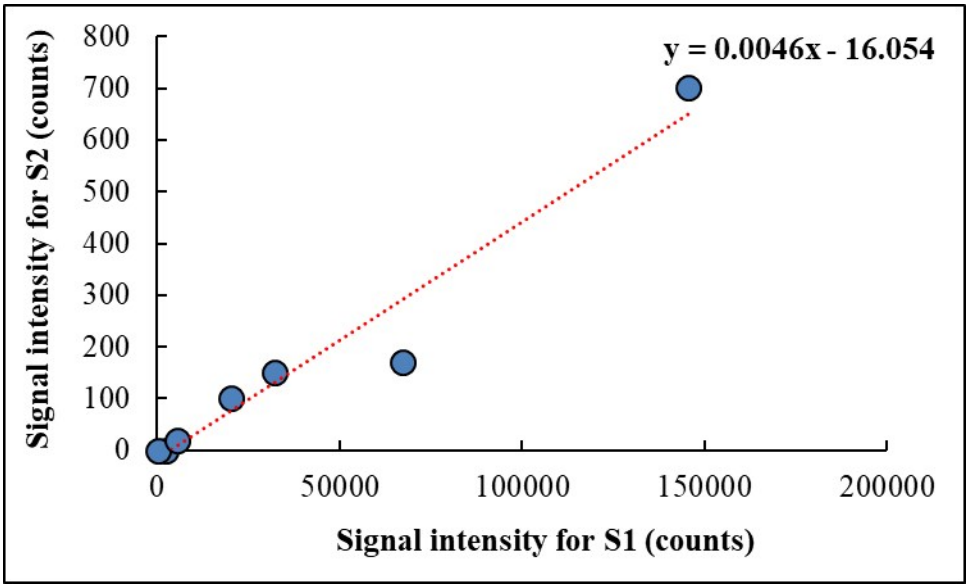

Fig. S2. MSC plot of one of the replicates used to calculate the LOD for Co.

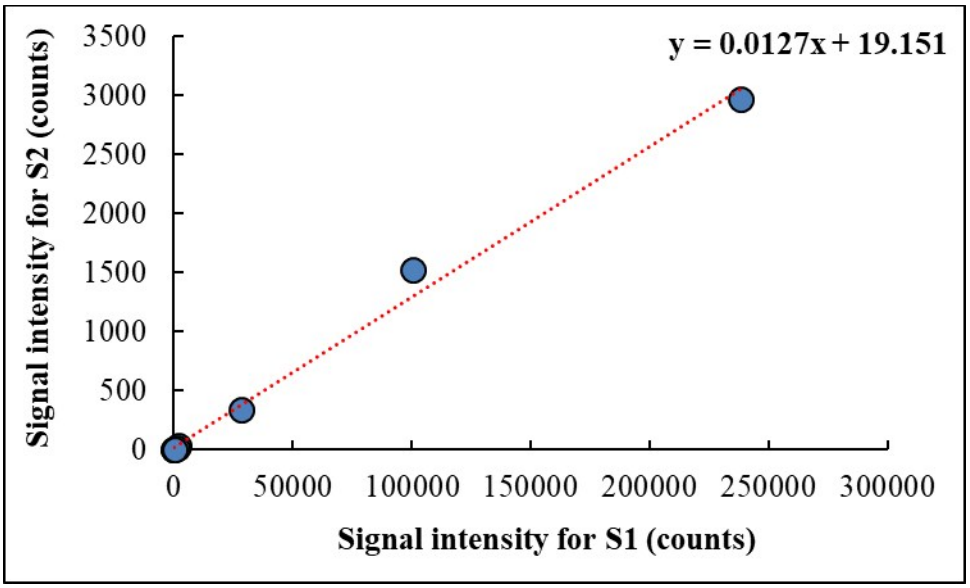

Fig. S3. MSC plot of one of the replicates used to calculate the LOD for Mn.

References

1. IUPAC, Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"). Compiled by A. D. McNaught and A. Wilkinson. Blackwell Scientific Publications, Oxford, 1997. XML on-line corrected version: http://goldbook.iupac.org (2006-) created by M. Nic, J. Jirat, B. Kosata; updates compiled by A. Jenkins.

2. J. D. Winefordner and G. L. Long, *Anal. Chem.*, 1983, **55**, 712A-724A.