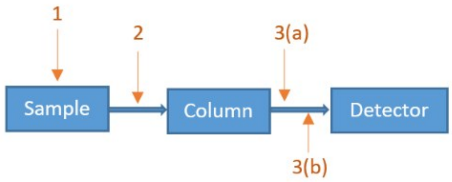
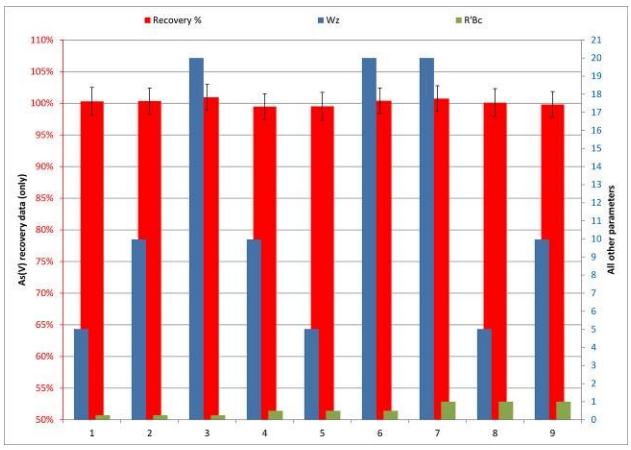
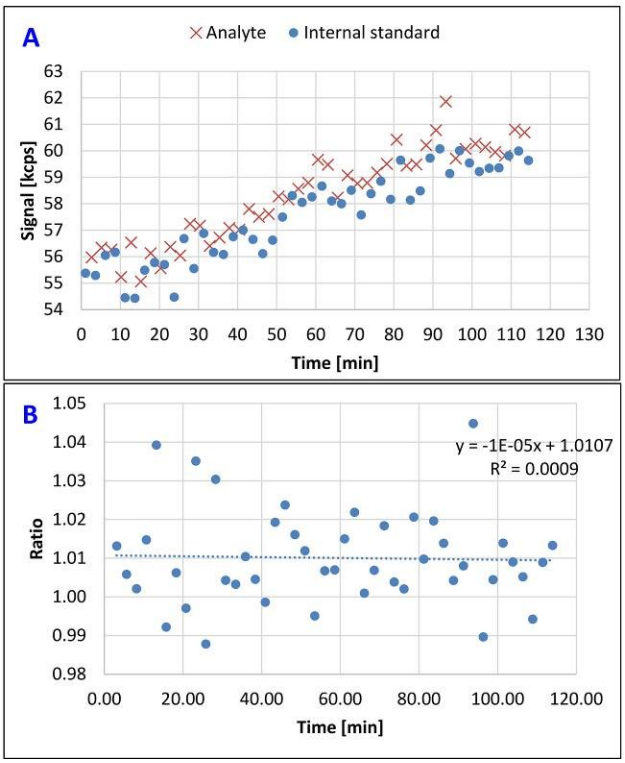
ESI:



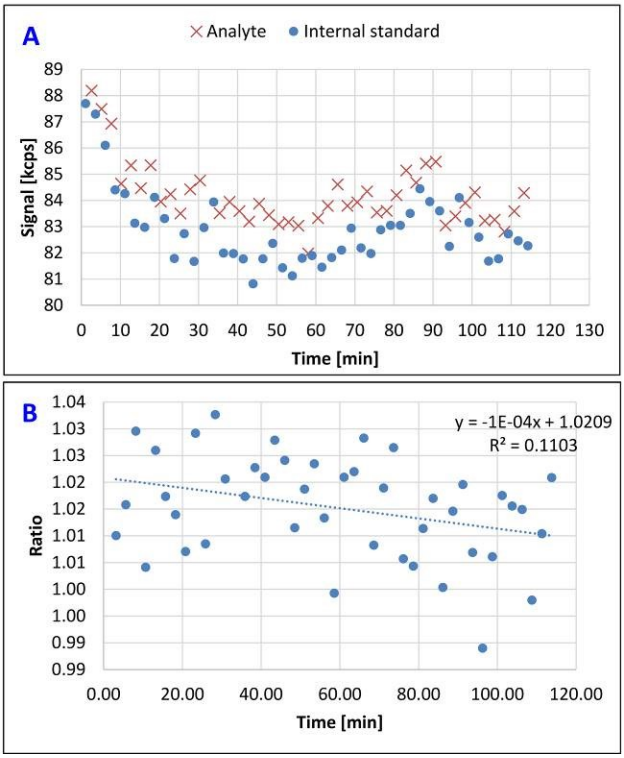
ESI Diagram 1. Schematic diagram of the different IS types by point of introduction: 1 – in the sample; internal standard species or surrogate compound. 2 – Pre-column IS approach proposed in this study. 3(a) – discrete post-column IS; the internal standard is introduced trough injection loop or syringe injection. 3(b) continuous post-column IS; internal standard continuously introduced through a pump with fixed flow rate.



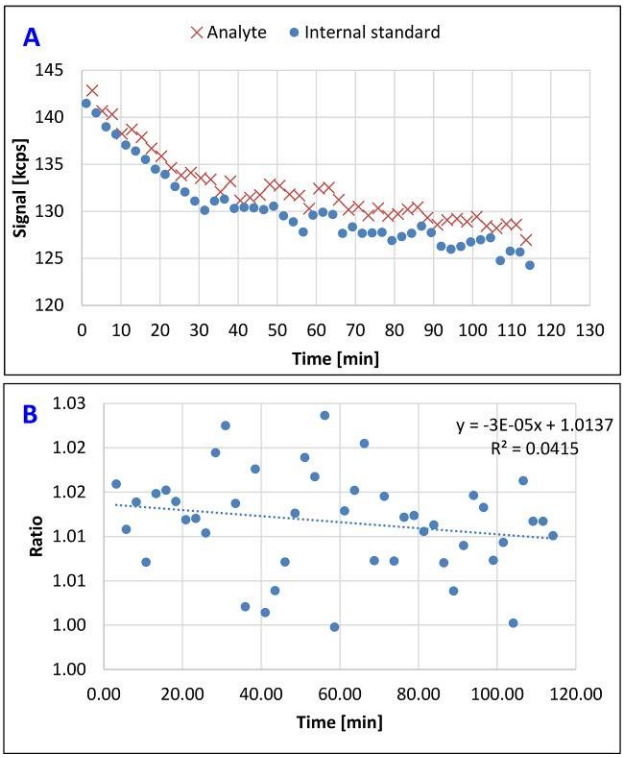
ESI Figure 1. As(V) standards recoveries using Pre-column IS calibration. Wz – mass fraction of the As(V) standard, R'Bc – ratio of the standard and IS peak areas.



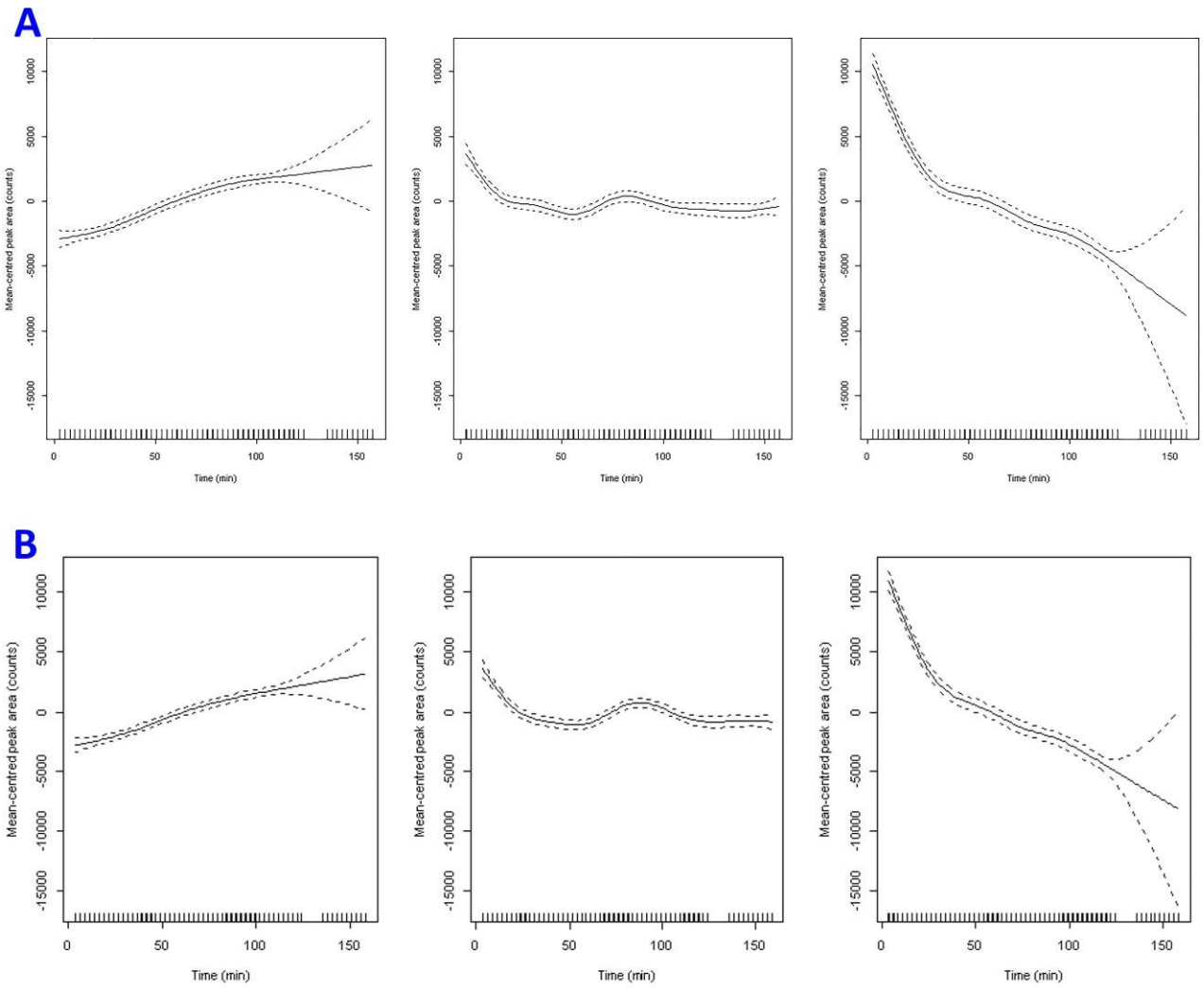
ESI Figure 2. A – As(V) and IS As(V) signal vs. time showing positive signal drift. B – As(V)/IS As(V) ratios providing efficient drift correction.



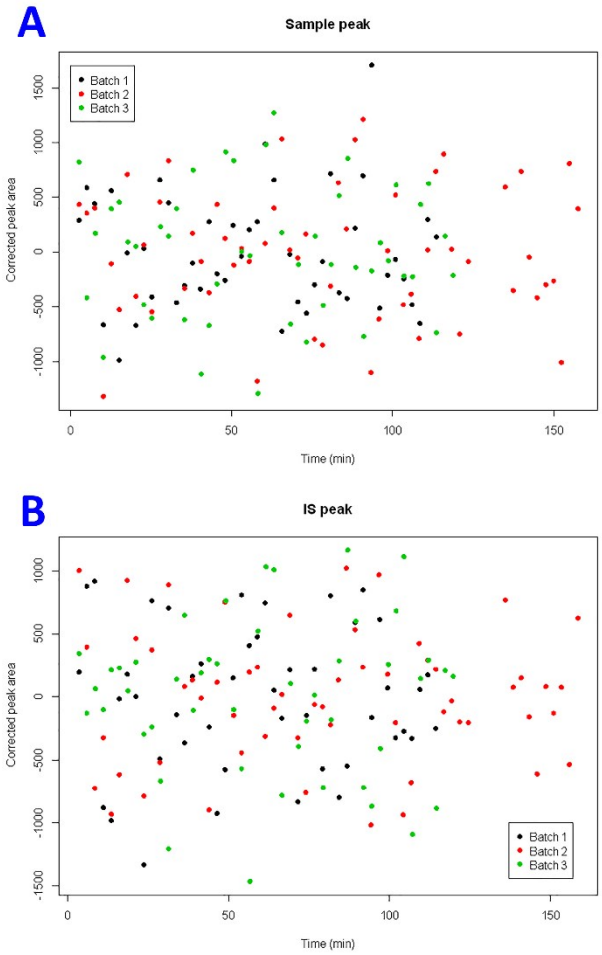
ESI Figure 3. A – As(V) and IS As(V) signal vs. time showing variable signal drift. B – As(V)/IS As(V) ratios providing efficient drift correction.



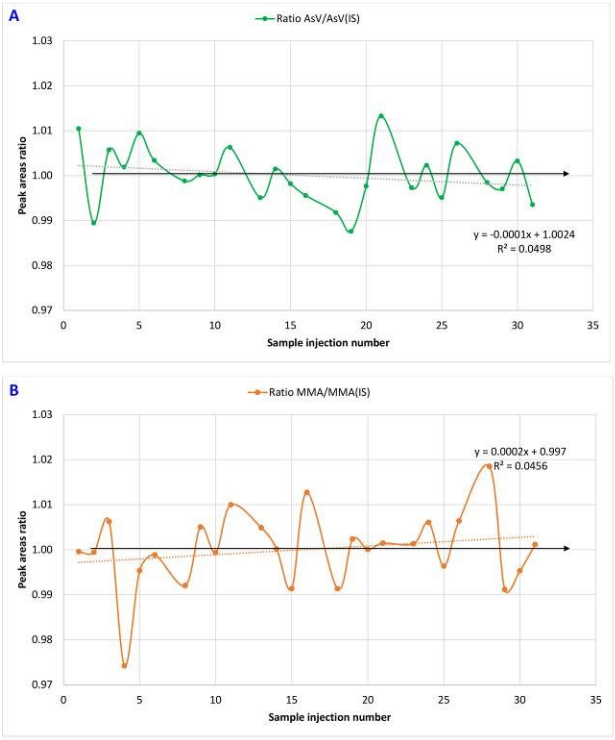
ESI Figure 4. A – As(V) and IS As(V) signal vs. time showing negative signal drift. B – As(V)/IS As(V) ratios providing efficient drift correction.



ESI Figure 5. Example of additive models used for trend removal prior to calculating the within-run variability: A) for the sample injection and B) for the IS injection. Solid lines show the model, dotted lines (not used for trend removal) define the uncertainty in the model.



ESI Figure 6. Absolute peak areas variation (in counts) around the mean for A) sample injections and B) IS injections, both at 2.5 µg.kg^{-1} As(V) level. The sample and IS mean peak areas were 9.13.10^4 count and 8.99.10^4 count, respectively.



ESI Figure 7. Stability of the peak area ratios of standards to the same species IS for A) As(V) and B) methylarsonate (MA) at 2.5 µg.kg^{-1} level, each. Methanol in water 5% V/V was introduce to the plasma between the samples