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Development of equations 8 and 9 from equation 7

$$bias^{\pm}_{CSam}(\%) = \frac{\left\{\frac{(S \pm e_S)}{[1-(S \pm e_S)]}\right\} - \left(\frac{S}{1-S}\right)}{\left(\frac{S}{1-S}\right)} \times 100\% \qquad (7)$$

It can be noticed (see equation 6) that the upper limit of e_S value will lead to the upper limit of e_C and concentration bias, e_C^+ and $bias^{+}_{CSam}$ respectively. Thus, equation 7 can be further developed as follows.

$$bias^{+}_{CSam}(\%) = \frac{\left\{\frac{(S + e_S)}{[1-(S + e_S)]}\right\} - \left(\frac{S}{1-S}\right)}{\left(\frac{S}{1-S}\right)} \times 100\%$$

$$bias^{+}_{CSam}(\%) = \frac{\left\{\frac{[(S+e_S)\times(1-S)]-[S\times(1-S-e_S)]}{(1-S-e_S)\times(1-S)}\right\}}{\left(\frac{S}{1-S}\right)} \times 100\%$$

$$bias^{+}_{CSam}(\%) = \frac{(S - S^2 + e_S - Se_S - S + S^2 + Se_S)}{(1-S-e_S)\times(1-S)} \times \frac{(1-S)}{S} \times 100\%$$

$$bias^{+}_{CSam}(\%) = \frac{e_S}{S(1-S-e_S)} \times 100\% \qquad (8)$$

The lower limit, $bias^{-}_{CSam}$, can be calculated analogously, resulting in equation 9.

$$bias^{-}_{CSam}(\%) = \frac{\left\{\frac{(S - e_S)}{[1-(S - e_S)]}\right\} - \left(\frac{S}{1-S}\right)}{\left(\frac{S}{1-S}\right)} \times 100\%$$

$$bias^{-}_{CSam}(\%) = \frac{\left\{\frac{[(S-e_S)\times(1-S)]-[S\times(1-S+e_S)]}{(1-S+e_S)\times(1-S)}\right\}}{\left(\frac{S}{1-S}\right)} \times 100\%$$

$$bias^{-}_{CSam}(\%) = \frac{(S - S^2 - e_S + Se_S - S + S^2 - Se_S)}{(1-S+e_S)\times(1-S)} \times \frac{(1-S)}{S} \times 100\%$$

$$bias^{-}_{CSam}(\%) = \frac{-e_S}{S(1 - S + e_S)} \times 100\% \qquad (9)$$

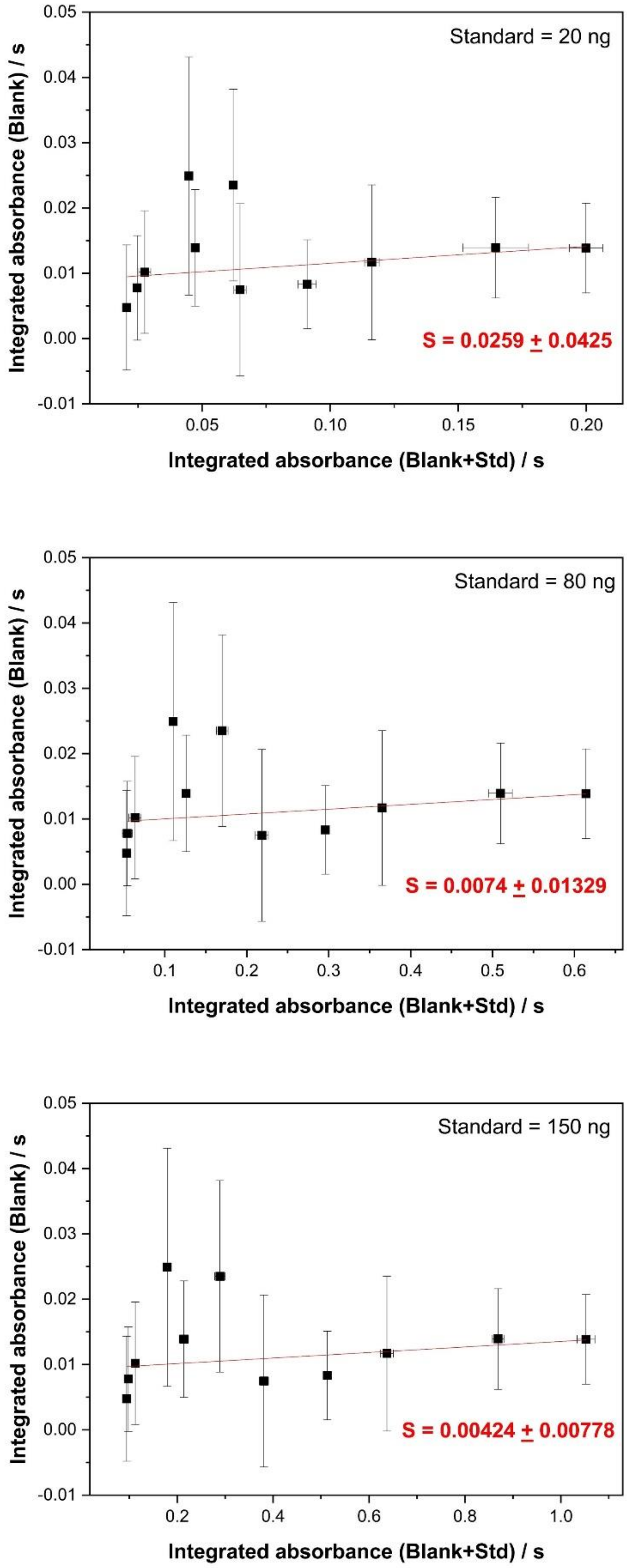

Figure S1. Blank measurements vs. 20, 80 and 150 ng Br spikes using MEC for calculating the LOD and LOQ, as described in equation 13.