Just as demonstration how can we present the equations

Laser ablation lacks a precise determination of the amount of ablated/transported material and hence of the concentration (mass/volume or mass/entire mass). By combining two linear regressions of two elements/isotopes it becomes evident that by knowing at least one concentration in the unknown sample, all other concentrations could be determined.

$$conc_1^{SAM} = cps_1^{SAM} \cdot \frac{conc_1^{STD}}{cps_1^{STD}} \cdot \frac{conc_2^{SAM} \cdot cps_2^{STD}}{cps_2^{SAM} \cdot conc_2^{STD}}$$

$$conc_1^{SAM} = cps_1^{SAM} \cdot \quad m_1 \quad \cdot \quad S_2$$

Abbreviation:

conc	concentration
cps	counts per second (counts/dwell time)
SAM	unknown Sample
STD	known Standard
1	unknown element 1
2	known element 2 = internal Standard Element
m	slope
S	SAM-STD matrix fractionation factor

The concentration is linearly related to cps. The transformation factor (slope) m_1 and the factor S_2 are related to characteristic fractionation processes during ablation in different matrices (glass, mineral, metal, fluid). Ideally this factor is near 1. In case of a volatile element normalized to a refractory element as internal standard or extreme differences in the matrices this factor easily exceeds 2 to 10 and even higher.

Because almost every tenth of a second there is a complete analysis of this particular time slice, we gain a chemical profile of the sample, which could be homogenous or not. In the latter case we struggle even with a variable concentration of the internal standard element in the unknown sample, the one point our quantification is correlated to. However, due to the fact that we are dealing with isotope ratios during analysis, the above calculus might be rearranged and calculated accordingly (ratioing for every time slice):

$$\left\langle \frac{conc_1^{SAM}}{conc_2^{SAM}} \right\rangle_t = \left\langle \frac{cps_1^{SAM}}{cps_2^{SAM}} \right\rangle_t \cdot \left\langle \left(\frac{cps_1^{STD}}{cps_2^{STD}} \right)^{-1} \right\rangle_{mean} \cdot \left\langle \frac{conc_1^{STD}}{conc_2^{STD}} \right\rangle_{mean}$$

$$R_{conc}^{SAM} = R_{cps}^{SAM} \cdot \left(R_{cps}^{STD}\right)^{-1} \cdot R_{conc}^{STD}$$

The cps-ratio in the standard is computed by ratioing every time slice and averaging the ratio over the time interval which should have a flat top over integration time. From all cps must be subtracted the gas-blank without lasering.

The total error of the method should be calculated from all individual errors, that is:

Cps in SAM: a measure for the error in every time slice is only related to SQR(counts)
Cps in STD: is an average with sigma error calculated from the STD file
Conc in STD: there are several data for the NBS glasses, average and stdev
Conc in SAM: the absolute concentration in the unknown sample is at least related to the (systematic?) error in the determination of the internal standard concentration.

$$\left(\frac{\sigma\left(R_{cps}^{SAM}\right)}{R_{cps}^{SAM}}\right)^2 = \left(\frac{\sqrt{cps_1^{SAM}}}{cps_1^{SAM}}\right)^2 + \left(\frac{\sqrt{cps_2^{SAM}}}{cps_2^{SAM}}\right)^2 \quad \Rightarrow \quad \sigma\left(R_{cps}^{SAM}\right) = \sqrt{\frac{1}{cps_1^{SAM}} + \frac{1}{cps_2^{SAM}}} \cdot R_{cps}^{SAM}$$

$$\left(\frac{\sigma\left(R_{cps}^{STD}\right)}{R_{cps}^{STD}}\right)^2 = \left(\frac{\sigma\left(cps_1^{STD}\right)}{cps_1^{STD}}\right)^2 + \left(\frac{\sigma\left(cps_2^{STD}\right)}{cps_2^{STD}}\right)^2 \quad \Rightarrow \quad \sigma\left(R_{cps}^{STD}\right) = \sqrt{\left(\frac{\sigma\left(cps_1^{STD}\right)}{cps_1^{STD}}\right)^2 + \left(\frac{\sigma\left(cps_2^{STD}\right)}{cps_2^{STD}}\right)^2} \cdot R_{cps}^{STD}$$

$$\left(\frac{\sigma\left(R_{conc}^{STD}\right)}{R_{conc}^{STD}}\right)^2 = \left(\frac{\sigma\left(conc_1^{STD}\right)}{conc_1^{STD}}\right)^2 + \left(\frac{\sigma\left(conc_2^{STD}\right)}{conc_2^{STD}}\right)^2 \quad \Rightarrow \quad \sigma\left(R_{cps}^{STD}\right) = \sqrt{\left(\frac{\sigma\left(conc_1^{STD}\right)}{conc_1^{STD}}\right)^2 + \left(\frac{\sigma\left(conc_2^{STD}\right)}{conc_2^{STD}}\right)^2} \cdot R_{conc}^{STD}$$

Combining every error contribution the equation becomes:

$$\left(\frac{\sigma(conc_1^{SAM})}{conc_1^{SAM}}\right)^2 = \left(\frac{\sigma(counts_1^{SAM}\cdot t_{dwell})}{counts_1^{SAM}\cdot t_{dwell}}\right)^2 + \left(\frac{\sigma\left(counts_2^{SAM}\cdot t_{dwell}\right)}{counts_2^{SAM}\cdot t_{dwell}}\right)^2 +$$

Poisson statistics for counts in every time slice SAM

$$\left(\frac{\sigma\left(counts_1^{STD}\cdot t_{dwell}\right)}{counts_1^{STD}\cdot t_{dwell}}\right)^2 + \left(\frac{\sigma\left(counts_2^{STD}\cdot t_{dwell}\right)}{counts_2^{STD}\cdot t_{dwell}}\right)^2 +$$

Average counts and standard deviation in time interval STD

$$\left(\frac{\sigma\left(conc_1^{STD}\right)}{conc_1^{STD}}\right)^2 + \left(\frac{\sigma\left(conc_2^{STD}\right)}{conc_2^{STD}}\right)^2 +$$

Error of STD concentrations

$$\left(\frac{\sigma\left(conc_2^{SAM}\right)}{conc_2^{SAM}}\right)^2$$

Error of internal STD element in unknown sample

Another detailed description of the calculus:

$$\frac{\sum_{t_1}^{t_2}\frac{Conc_{SAM}^{EL}(t_n)}{Conc_{SAM}^{IS}(t_n)}}{N_{(t_2-t_1)}} = \frac{\sum_{t_1}^{t_2}\left(\frac{Cps_{SAM}^{EL}(t_n)}{Cps_{SAM}^{IS}(t_n)} - \frac{\sum_N \frac{Blank^{EL}}{Blank^{IS}}}{N}\right)}{N_{(t_2-t_1)}} \cdot \left[\frac{\sum_{t_3}^{t_4}\left(\frac{Cps_{STD}^{EL}(t_n)}{Cps_{STD}^{IS}(t_n)} - \frac{\sum_N \frac{Blank^{EL}}{Blank^{IS}}}{N}\right)}{N_{(t_4-t_3)}}\right]^{-1} \cdot \frac{Conc_{STD}^{EL}}{Conc_{STD}^{IS}}$$

1. Average
2. Stdev
3. Confidence
4. Linearity check (first half/second half)
5. BEC, LOD, m_1, S_2
6. External STD comparison
7. Response curve
8. REE, Spider
9. Factor Analysis (interdependence of element concentrations)

Avoiding all the more or less constant parameters in the equation, then

$$conc_1^{SAM} \propto \frac{cps_1^{SAM}}{cps_2^{SAM}} \cdot conc_2^{SAM}$$

For best results (= lowest error of $conc_{SAM}$), the cps of the internal standard should be high, but the concentration low, that is good sensitivity: cps/conc/%abund. >> 1000

Input Files:

Blank cps	Elements x time slices, average over entire time
STD cps	Elements x time slices, average over part time
SAM cps	Elements x time slices, average over part time (homogeneous), for single time slice (heterogeneous, chemical gradient)
STD conc	Elements x concentration

Output File:

SAM conc
Statistics …

Everything in Matrix Notation:

1. STD and SAM cps-Matrix go through subtraction of average blank cps

$$conc_{IS}^{SAM}(t) = cps_{IS}^{SAM}(t) \cdot \left(cps_{IS}^{STD} \right)^{T} \cdot conc_{IS}^{STD}$$