Appendix 1 – Low Concentrations: Limit on the Limit of Quantitation (LOQ)

Suppose raw mass estimates m_{raw} may be modeled as:

$$m_{raw} = m_{ref} \cdot (1 + bias) + m_{ref} \cdot \varepsilon[TRSD_{raw}] + \varepsilon_0[\sigma_{raw}],$$

where *bias* is specific to a low-concentration range, and where the εs are normally distributed random variables. Often at higher concentrations, ε_0 is negligible and the *relative* standard deviation is roughly constant over a concentration range. However, at low concentrations sampled, the standard deviation may become independent of the mass, hence the term ε_0 giving the limiting standard deviation σ_{raw}.

In evaluating the method many pairs of measurements m_{raw} and m_{ref} are made, yielding an estimate $bi\hat{a}s$:

$$bi\hat{a}s = \sum (m_{raw} - m_{ref}) / m_{ref} .$$

The bias-corrected mass estimate *m* is then

$$\begin{aligned} m &\equiv m_{raw} / (1 + bi\hat{a}s) \\ &= m_{ref} \frac{1 + bias}{1 + bi\hat{a}s} + m_{ref} \cdot \varepsilon[TRSD] + \varepsilon_0[\sigma] \end{aligned},$$

where the bias-corrected σ is:

$$\sigma = \sigma_{raw} / (1 + bi\hat{a}s),$$

needed for estimating an upper limit on the *limit of quantitation LOQ* given by

$$LOQ = 10 \times \sigma.$$

Thus, the corrected error is:

$$\begin{aligned} error &\equiv (m - m_{ref}) / m_{ref} \\ &\approx \varepsilon[TRSD] + \varepsilon_0[\sigma] / m_{ref} \end{aligned},$$

neglecting a term proportional to $bias - bi\hat{a}s$. Ignoring correlation between ε_0 and ε, the expected value:

$$E[error^2] \approx TRSD^2 + \sigma^2 \cdot m_{ref}^{-2} .$$

Thus, by approximating $error^2$ as normally distributed, through linear regression on m_{ref}^{-2}, the parameter σ^2 may be estimated and limits determined.

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Example – low-concentration XRF and ICP (reference) data

Twenty eight data points with m_{ref} between 5 μg and 15 μg were taken, with bias estimated at 6.4%. The data for $error^2$ are shown in the figure:

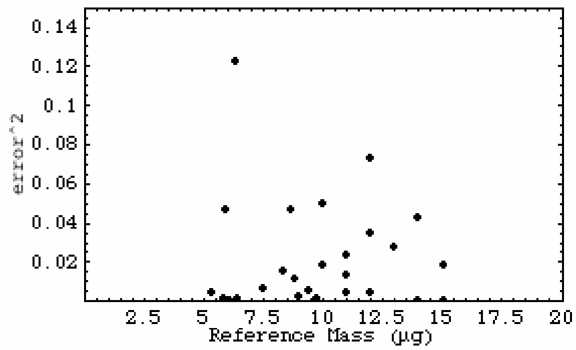

Figure A-1.

Though there is no obvious divergence proportional to m_{ref}^{-2} visible, limits on σ^2 may yet be determined through linear regression, the results of which are presented here:

{ANOVATable →

	DF	SumOfSq	MeanSq	FRatio	PValue
Model	1	0.0317432	0.0317432	1.46243	0.237427
Error	26	0.564352	0.0217058		
Total	27	0.596095			

ParameterCITable →

	Estimate	SE	CI
1	0.0507728	0.0503441	{-0.052711, 0.154257}
$\frac{1}{x^2}$	-3.66646	3.03187	{-9.89855, 2.56563}

ParameterConfidenceRegion → Ellipsoid[{0.0507728, -3.66646},
{7.87079, 0.072266}, {{-0.0138343, 0.999904}, {0.999904, 0.0138343}}]}

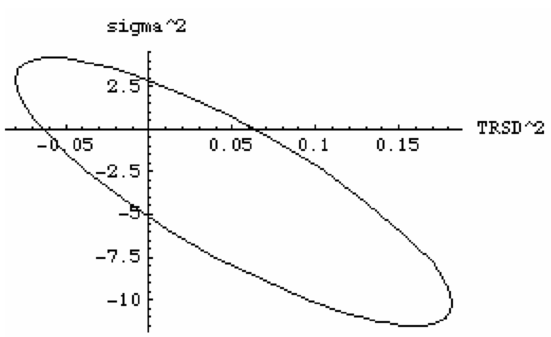

Figure A-2. 95% confidence region on the determined parameters.

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The confidence intervals given in the table are two-sided at the 95% confidence level, whereas we are interested in a single-sided interval $\sigma^2 < \sigma^2_{95\%}$:

$$\sigma^2_{95\%} = \hat{\sigma}^2 + SE \cdot t_{\upsilon \ \ 0.95},$$

where $t_{\upsilon \ \ 0.95}$ = 1.7056 is the 95% StudentT quantile at υ = 26 degrees of freedom. Thus,

$$\sigma^2_{95\%} = -3.66646 + 1.70562 \times 3.03187 = 1.505.$$

Finally,

$$LOQ_{95\%} = 10 \times \mathrm{Sqrt}[\sigma^2_{95\%}]$$

$$= 12.3\ \mu\mathrm{g}.$$

For this set of data, *LOQ* < 12.3 μg at the 95% confidence level.