Appendix B
Equations

This appendix includes descriptions and equations for Calibration, Quantitation, SemiQuantitation and Averaging Repetition Files.

Calibration

Weighted Regression

When data with more than one repetition is used to create a calibration curve, weighted regression can be selected. The count error for data collected in this manner is represented as the standard deviation of the counts. Usually the count error for higher concentrations is larger than that for lower concentrations. When weighted regression is selected, lower concentrations are given more weight because it is more desirable that the curve pass through points having lower error than points having higher error.

The weight of each point is calculated as follows.

$$w_i = S_i^{-2} / \left(\sum_i S_i^{-2} / n \right)$$

where

S_i : standard deviation of each point
n : number of point

In case of 1/count, s_i changes to 1/count.
However, if a count0 level exists, weighting is not possible.
In case of 1/conc, s_i changes to 1/conc.
However, if 0 concentration exists in calibration levels, weighting is not possible.

Only linear regressions can be weighted.

Internal Standard

When an internal standard is selected, the count of each data point in the calibration curve is divided by the ratio of the count per concentration of the internal standard of the same level.

$$y = y_\sigma / (y_i / x_i)(y = y_\sigma \text{ if } x_i = 0)$$

where

x_i : concentration of internal standard
y_i : count of internal standard
y_σ : count of sample data

This value is used as the measured value of y in the following sections.

Correlation Coefficient

This value is calculated using the following formula.

$$\tau = \frac{\sum_i \{(x_i - \bar{x})(y_i - \bar{y})\}}{\left\{\left[\sum_i (x_i - \bar{x})^2\right]\left[\sum_i (y_i - \bar{y})^2\right]\right\}^{1/2}}$$

where

$\bar{x}$: average of x_i

$\bar{y}$: average of y_i

x_i : measured value of x

y_i : measured value of y

This is available only for linear regressions.

Coefficients of Calibration Curves

Coefficients are calculated as follows.

where

n: number of points

x_i: numbered value of x

y_i: measured value of y

w_i: weight of each point (w_i=1.0 in the case of unweighted regressions)

1 y = ax

$$a = \frac{\sum_i x_i y_i w_i}{\sum_i x_i^2 w_i}$$

2 y = ax + b

$$a = \frac{n\left(\sum_i x_i y_i w_i\right) - \left(\sum_i x_i w_i\right)\left(\sum_i y_i w_i\right)}{n\left(\sum_i x_i^2 w_i\right) - \left(\sum_i x_i w_i\right)^2}$$

$$b = \frac{\sum_i y_i w_i}{n} - a\frac{\sum_i x_i w_i}{n}$$

3 y = ax^2 + bx

$$a = \frac{\left(\sum_i x_i^3 w_i\right)\left(\sum_i x_i y_i w_i\right) - \left(\sum_i x_i^2 w_i\right)\left(\sum_i x_i^2 y_i w_i\right)}{\left(\sum_i x_i^3 w_i\right)^2 - \left(\sum_i x_i^2 w_i\right)\left(\sum_i x_i^4 w_i\right)}$$

$$b = \frac{\sum_i x_i y_i w_i - a\sum_i x_i^3 w_i}{\sum_i x_i^2 w_i}$$

4 y = ax^2 + bx + c

$$a = \frac{s_{(x^2y)}s_{(xx)} - s_{(xy)}s_{(xx^2)}}{s_{(xx)}s_{(x^2x^2)} - \{s_{(xx^2)}\}^2}$$

$$b = \frac{s_{(xy)}s_{(x^2x^2)} - s_{(x^2y)}s_{(xx^2)}}{s_{(xx)}s_{(x^2x^2)} - \{s_{(xx^2)}\}^2}$$

$$c = \frac{\sum_i y_i w_i}{n} - b\frac{\sum_i x_i w_i}{n} - a\frac{\sum_i x_i^2 w_i}{n}$$

where

$$s_{(xx)} = \left(\sum_i x_i^2 w_i\right) - \frac{\left(\sum_i x_i w_i\right)^2}{n}$$

$$s_{(xy)} = \left(\sum_i x_i y_i w_i\right) - \frac{\sum_i x_i w_i \sum_i y_i w_i}{n}$$

$$s_{(xx^2)} = \left(\sum_i x_i^3 w_i\right) - \frac{\left(\sum_i x_i w_i\right)\left(\sum_i x_i^2 w_i\right)}{n}$$

$$s_{(x^2 y)} = \left(\sum_i x_i^2 y_i w_i\right) - \frac{\left(\sum_i x_i^2 w_i\right)\left(\sum_i y_i w_i\right)}{n}$$

$$s_{(x^2 x^2)} = \left(\sum_i x_i^4 w_i\right) - \frac{\left(\sum_i x_i^2 w_i\right)^2}{n}$$

5 log (y) = a (log x) + b

$$a = \frac{n\left\{\sum_i (\log x_i \log y_i) w_i\right\} - \left(\sum_i \log x_i w_i\right)\left(\sum_i \log y_i w_i\right)}{n\left\{\sum_i (\log x_i)^2 w_i\right\} - \left(\sum_i \log x_i w_i\right)^2}$$

$$b = \frac{\sum_i \log y_i w_i}{n} - a\frac{\sum_i \log x_i w_i}{n}$$

6 y = ax + b + bkg (Standard Addition)

$$a = \frac{n\left(\sum_i x_i y_i w_i\right) - \left(\sum_i x_i w_i\right)\left(\sum_i y_i w_i\right)}{n\left(\sum_i x_i^2 w_i\right) - \left(\sum_i x_i w_i\right)^2}$$

$$b = \frac{\sum_i y_i w_i}{n} - a\frac{\sum_i x_i w_i}{n} y_{bkg}$$

where

y_{bkg} : count of the background

7 y = ax +[blank]

$$a = \frac{\sum_i x_i (y_i - Blk) w_i}{\sum_i x_i^2 w_i}$$

where

Blk : number of counts in the calibration blank

DL

DL refers to a concentration equivalent to 3σB.

The equation for DL varies depending on the calibration formula.

If a linear equation such as y = ax + b is used:

DL = 3σB/a

Where,

3σB: value three times the standard deviation of the count at the 0 concentration level.

a: a in y = ax + b

The unit set in the calibration should be used and must not be changed.

Quantitation

Internal Standard

When an internal standard is selected in the current calibration curve, the count of the target ion of the sample data is divided by the ratio of the count per concentration of the internal standard in the sample data. In this calculation, the concentration of the internal standard in the first level of the calibration curve is used as the concentration of the internal standard in the sample data. The count value for each element reported on a quantitative report is therefore a count ratio.

$$y = y_\sigma / (y_i / x_i) (y = y_\sigma \text{ if } x_i = 0)$$

where

x_i : concentration of the internal standard of the first level in the calibration curve
y_i : count of internal standard
y_σ : count of the target ion

This value is used as the measured value of y in the following sections.

Calculating Concentration

Concentration of the target ion of the sample data is calculated as follows.

where

x : concentration of the target ion
y : measured count of the target ion
a : coefficient "a" in the calibration curve
b : coefficient "b" in the calibration curve
c : coefficient "c" in the calibration curve

1 y = ax

$$x = \frac{y}{a}$$

2 y = ax + b

$$x = \frac{y - b}{a}$$

3 y = ax^2+ bx

$$x = \frac{-b + \sqrt{b^2 + 4ay}}{2a}$$

4 y = ax^2 + bx + c

$$x = \frac{-b + \sqrt{b^2 - 4a(c - y)}}{2a}$$

5 log y = a (log x) + b

$$x = \left(\frac{y}{10^b}\right)^{\frac{1}{a}}$$

6 y = ax + b + bkg (Standard Addition)

$$x = \frac{b}{a}$$

7 y = ax + [blank]

$$x = \frac{y - blk}{a}$$

where

Blk : number of counts in the calibration blank

Standard Deviation of the Concentration

When a linear regression is used, the standard deviation is calculated as follows.

$$SD = \sqrt{\frac{\sum_i x_i^2 - \frac{1}{n}\left(\sum_i x_i\right)^2}{n-1}}$$

where

n : number of sample repeats

x_i : concentration

Interpolation Formulas for Virtual-Internal-Standard Correction

These formulas are used to calculate the modification rates for all internal standards used for the latest calibration curve and the current sample data. The concentration level of the current data internal standards uses the value of level 1 of the calibration curve, as with the existing internal-standard correction. In the case of “Linear” and “Quadratic,” one formula is created from all internal-standard modification rates. In the case of “Point to Point,” a formula is created for every two internal standards.

$$Ri = \frac{Cps\_ci / Conc\_ci}{Cps\_si / Conc\_si}$$

where

Cps_ci, Conc_ci: CPS and concentration of the internal standard of the data last used to update the calibration curve

Cps_si, Conc_si: CPS and concentration of the internal standard of the current sample data (For the concentration, use the value set for level 1 of the calibration curve.)

Point to Point (Y = aX + b; Two adjacent internal standards are used; Default)

Linear (Y = aX + b; All internal standards are used.)

$$a = \frac{n\sum_i MiRi - \sum_i Mi \sum_i Ri}{n\sum_i Mi^2 - (\sum_i Mi)^2}$$

$$b = \frac{\sum_i Ri}{n} - a\frac{\sum_i Mi}{n}$$

$$Ra = aMa + b$$

where

Mi: Mass number of internal standards

n: Number of internal standards (two in the case of “Point to Point”)

Ri: Modification rate of the internal-standard CPS between the standard data and sample data

Ma: Mass number of the element to be quantitatively analyzed

Ra: Virtual-internal-standard correction coefficient for correcting the CPS of the element to be quantitatively analyzed

Quadratic (Y = aX^2 + bX + c; All internal standards are used.)

$$a = \frac{S_{(M^2R)}S_{(MM)} - S_{(MR)}S_{(MM^2)}}{S_{(MM)}S_{(M^2M^2)} - \{S_{(MM^2)}\}^2}$$

$$b = \frac{S_{(MR)}S_{(M^2M^2)} - S_{(M^2R)}S_{(MM^2)}}{S_{(MM)}S_{(M^2M^2)} - \{S_{(MM^2)}\}^2}$$

$$c = \frac{\sum_i Ri}{n} - b\frac{\sum_i Mi}{n} - a\frac{\sum Mi^2}{n}$$

$$Ra = aMaMa + bMa + c$$

where

Mi: Mass number of internal standards

n: Number of internal standards

Ri: Modification rate of the internal-standard CPS between the standard data and sample data

Ma: Mass number of the element to be quantitatively analyzed

Ra: Virtual-internal-standard correction coefficient for correcting the CPS of the element to be quantitatively analyzed

$$S_{(MM)} = \sum_i Mi^2 - \frac{(\sum_i Mi)^2}{n}$$

$$S_{(MR)} = (\sum_i MiRi) - \frac{\sum_i Mi \sum_i Ri}{n}$$

$$S_{(MM^2)} = \sum_i Mi^3 - \frac{\sum_i Mi \sum_i Mi^2}{n}$$

$$S_{(M^2R)} = \sum_i Mi^2 Ri - \frac{\sum_i Mi^2 \sum_i Ri}{n}$$

$$S_{(M^2M^2)} = \sum_i Mi^4 - \frac{(\sum_i Mi^2)^2}{n}$$

Correct the CPS of the element to be quantitatively analyzed using the virtual-internal-standard correction coefficient.

$$Cps\_na = Cps\_sa*Ra$$

where

Cps_na: Corrected CPS of the element to be quantitatively analyzed

Cps_sa: CPS of the element to be quantitatively analyzed

Ra: Virtual-internal-standard correction coefficient for the CPS of the element to be quantitatively analyzed

SemiQuantitation

The counts used in semiquantitation were the counts of the most abundant point of the mass specified in the semiquant parameters panel for a given element.

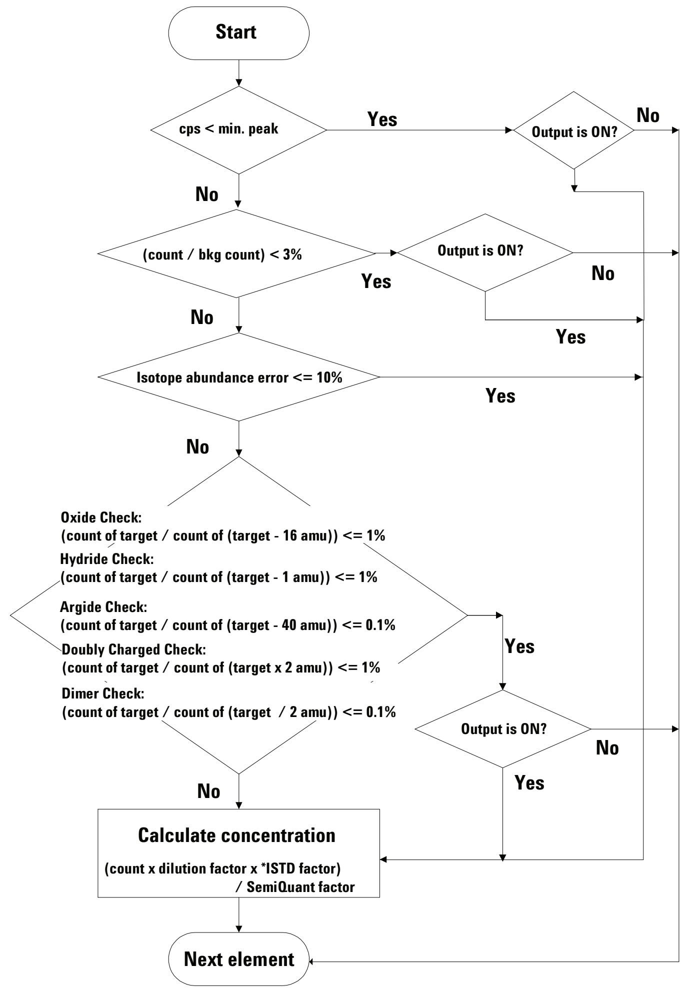
There are some exceptions to the execution of interference check protocol as follows:

Oxide check is not executed for ^{72}Ge.

Doubly charged ion check is not executed for ^{7}Li.

Dimer check is not executed for ^{7}Li, ^{24}Mg, ^{60}Ni, ^{72}Ge.

Argide check is not executed for ^{60}Ni, ^{72}Ge.



where

Auto Add Mode

* ISTD factor = (cps of ISTD in the STD) / (cps of ISTD in the sample)

Normal Mode

* ISTD factor = (concentration of ISTD in the sample) x (SemiQuant factor) / (cps of ISTD in the sample)

Averaging Repetition Files

When the repetition data files are averaged to create an average results file, the following formulas are used:

$$x_{avg} = \frac{\sum_i n_i x_i}{\sum_i n_i}$$

$$s_{avg} = \sqrt{\frac{\sum_i n_i \sum_i \bar{x}^2 - \left(\sum_i \bar{x}\right)^2}{\sum_i n_i \left(\sum_i n_i - 1\right)}}$$

where

$$\sum_i \bar{x} = \sum_i n_i x_i$$

$$\sum_i \bar{x}^2 = \sum_i \frac{n_i (n_i - 1) s_i^2 + (n_i x_i)^2}{n_i}$$

$\boldsymbol{x_{avg}}$: average count of the averaged results file

$\boldsymbol{s_{avg}}$: standard deviation of the averaged results file

$\boldsymbol{n_i}$: repetition number of the individual repetition file

$\boldsymbol{x_i}$: average count of the individual repetition file

$\boldsymbol{s_i}$: standard deviation of the individual repetition file