

SUPPORTING INFORMATION

for the manuscript "Calibration of Mo isotope amount ratio measurements by MC-ICPMS using normalisation to an internal standard and improved experimental design" by D. Malinovsky, P.J.H. Dunn, and H. Goenaga-Infante

NOTES ON THE REGRESSION MODEL

Following the comments we received in a process of reviewing of the manuscript we find it useful to add some notes on the regression model, illustrating its independence from any assumption on a particular form of mass fractionation law used to represent instrumental isotope fractionation in MC-ICPMS.

It is worth noting out that although benefits of using regression analysis of simultaneously measured isotope ratios of analyte and internal standard for mass bias correction were known since the approach by Maréchal et al. (1999), the fact that the regression model is free from any aforementioned assumptions was explicitly shown only in subsequent works (Meija et al. 2009; Baxter et al. 2012). An inherent property of logarithms with the same base to produce a linear array when plotted against each other, e.g. as $\ln(r_{analyte})$ vs $\ln(r_{instd})$, is what makes the regression model free from the above assumptions. This advantage of the regression model was probably best illustrated in the derivation by Meija et al. (2009), which we reproduce here with additional details, omitted for the sake of brevity in the original work.

For calibration factors of analyte, $K_{analyte}$, and internal standard, K_{instd} , which relate measured value of isotope ratio, r , to its true value, R , the following can be written

$$\ln K_{analyte} = \ln\left(\frac{R_{analyte}}{r_{analyte}}\right) = \ln R_{analyte} - \ln r_{analyte} \quad (1)$$

$$\ln K_{instd} = \ln\left(\frac{R_{instd}}{r_{instd}}\right) = \ln R_{instd} - \ln r_{instd} \quad (2)$$

Once a ratio of the calibration factors of analyte and internal standard is considered the following re-arrangements can be made

$$\frac{\ln K_{analyte}}{\ln K_{instd}} = \frac{\ln R_{analyte} - \ln r_{analyte}}{\ln R_{instd} - \ln r_{instd}} \quad (3)$$

$$\ln K_{instd} \cdot (\ln R_{analyte} - \ln r_{analyte}) = \ln K_{analyte} \cdot (\ln R_{instd} - \ln r_{instd}) \quad (4)$$

$$\ln K_{instd} \cdot \ln R_{analyte} - \ln K_{instd} \cdot \ln r_{analyte} = \ln K_{analyte} \cdot \ln R_{instd} - \ln K_{analyte} \cdot \ln r_{instd} \quad (5)$$

from which it follows

$$\ln r_{analyte} = \ln r_{instd} \underbrace{\frac{\ln K_{analyte}}{\ln K_{instd}}}_{\text{slope, } b} + \underbrace{\ln R_{analyte} - \ln R_{instd} \frac{\ln K_{analyte}}{\ln K_{instd}}}_{\text{intercept, } a} \quad (6)$$

The eqn 6 is the form of a linear equation ($y=bx + a$), where

$$a = \ln R_{analyte} - b \cdot \ln R_{instd} \quad (7)$$

is the intercept. Solving eqn 7 for $R_{analyte}$ yields the formula used in the regression model

$$R_{analyte} = e^a \cdot R_{instd}^b \quad (8)$$

To illustrate the universal value of the formula used in the regression model further, we show below that it can also be derived even if one would prefer to assume that instrumental isotope fractionation is governed by popular mass fractionation “laws” such as exponential and power ones.

1. Derivation for the case of exponential law of Russel et al. (1978) governing mass fractionation

Baxter et al. (2006) were first to describe this derivation and showed that if the exponential model of Russell et al. (1978) was assumed the following could be written

$$K_{analyte} = \frac{R_{analyte}}{r_{analyte}} = \left(\frac{m_2}{m_1} \right)^{\beta_{analyte}} \quad (9)$$

$$K_{instd} = \frac{R_{instd}}{r_{instd}} = \left(\frac{m_4}{m_3} \right)^{\beta_{instd}} \quad (10)$$

where m_1, m_2, m_3 and m_4 are masses of isotopes making up isotope ratios. Re-arrangement of eqn 9 and 10 leads to

$$\beta_A = \frac{\ln(R_{analyte} / r_{analyte})}{\ln(m_2 / m_1)} \quad (11)$$

$$\beta_{instd} = \frac{\ln(R_{instd} / r_{instd})}{\ln(m_4 / m_3)} \quad (12)$$

After further re-arrangement the following equation is obtained

$$\ln r_{analyte} = \ln R_{analyte} - \frac{\beta_{analyte} \cdot \ln(m_2 / m_1)}{\beta_{instd} \cdot \ln(m_4 / m_3)} \cdot \ln R_{instd} + \frac{\beta_{analyte} \cdot \ln(m_2 / m_1)}{\beta_{instd} \cdot \ln(m_4 / m_3)} \cdot \ln r_{instd} \quad (13)$$

which is the form of a linear equation ($y=a+b \cdot x$)

$$\ln r_{analyte} = a + b \cdot \ln r_{instd} \quad (14)$$

where

$$b = \frac{\beta_{analyte} \cdot \ln(m_2 / m_1)}{\beta_{instd} \cdot \ln(m_4 / m_3)} \quad (15)$$

$$a = \ln R_{analyte} - \frac{\beta_{analyte} \cdot \ln(m_2 / m_1)}{\beta_{instd} \cdot \ln(m_4 / m_3)} \cdot \ln R_{instd} = \ln R_{analyte} - b \cdot \ln R_{instd} \quad (16)$$

are the slope and the intercept, respectively.

It is from eqn 16 the formula used in the regression model is readily obtained

$$R_{analyte} = e^a \cdot R_{instd}^b \quad (17)$$

2. Derivation for the case of power "law" governing mass fractionation

Once the power "law" is assumed to operate the calibration factors for analyte and internal standard can be written as follows

$$K_{analyte} = \frac{R_{analyte}}{r_{analyte}} = g_{analyte}^{(m_2 - m_1)} \quad (18)$$

$$K_{instd} = \frac{R_{instd}}{r_{instd}} = g_{instd}^{(m_4 - m_3)} \quad (19)$$

where g is the power-law mass fractionation coefficient. As isotope ratio data are expressed as logarithms, the following can be written

$$\frac{\ln K_{analyte}}{\ln K_{instd}} = \frac{\ln R_{analyte} - \ln r_{analyte}}{\ln R_{instd} - \ln r_{instd}} = \frac{(m_2 - m_1) \cdot \ln g_{analyte}}{(m_4 - m_3) \cdot \ln g_{instd}} \quad (20)$$

where m_1 and m_2 are masses making up isotope ratio of analyte; m_3 and m_4 are masses making up isotope ratio of internal standard. Further re-arrangement leads to

$$(\ln R_{analyte} - \ln r_{analyte}) \cdot (m_4 - m_3) \cdot \ln g_{instd} = (\ln R_{instd} - \ln r_{instd}) \cdot (m_2 - m_1) \cdot \ln g_{analyte} \quad (21)$$

and

$$\ln r_{analyte} = \ln R_{analyte} - \frac{(m_2 - m_1) \ln g_{analyte}}{(m_4 - m_3) \ln g_{instd}} \ln R_{instd} + \frac{(m_2 - m_1) \ln g_{analyte}}{(m_4 - m_3) \ln g_{instd}} \ln r_{instd} \quad (22)$$

which is the form of a linear equation ($y = a + b \cdot x$)

$$\ln r_{analyte} = a + b \cdot \ln r_{instd} \quad (23)$$

where

$$b = \frac{\beta_{analyte} \cdot \ln(m_2 / m_1)}{\beta_{instd} \cdot \ln(m_4 / m_3)} \quad (24)$$

$$a = \ln R_{analyte} - \frac{\beta_{analyte} \cdot \ln(m_2 / m_1)}{\beta_{instd} \cdot \ln(m_4 / m_3)} \cdot \ln R_{instd} = \ln R_{analyte} - b \cdot \ln R_{instd} \quad (25)$$

are the slope and the intercept, respectively.

It is from eqn 25 the formula used in the regression model is readily obtained

$$R_{analyte} = e^a \cdot R_{instd}^b \quad (26)$$

References

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