Data correction scheme for Sigman Mass Spectrometry Lab

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0.1 Purpose

The aim of this document is to familiarize the end user with the current data correction scheme for the denitrifier method as performed in the Sigman Lab.

0.2 $\delta^{15}NO_3^-$ corrections

From the Mass Spec output file we get: area, uncorrected $\delta^{15}N\left(d\frac{45}{44}\right)$, and uncorrected $\delta^{18}O\left(d\frac{46}{44}\right)$. You will also need the injection volume from the MS or injection log sheet. Warning: due to the use of the delta convention there will be many 1000s and +1s, be not affraid.

We first correct for the mass 17 anomaly:

$$\delta^{15}N(1) = d\frac{45}{44} + \left[\frac{\frac{^{17}O}{^{16}O})_{SMOW}}{2 * \frac{^{15}N}{^{14}N})_{N_2}} * \left[d\frac{45}{44} - \left[\left[1 + \frac{d\frac{46}{44}}{1000}\right]^{0.52} - 1\right] * 1000\right]\right] \tag{1}$$

where k = 0.52 and the accepted values for isotopic ratios are

$\frac{^{18}O}{^{16}O})_{SMOW}$	0.0020052	[Baertschi, 1976]
$\frac{^{17}O}{^{16}O})_{SMOW}$	0.0003799	[Li et al., 1988]
$\frac{^{15}N}{^{14}N})_{N2}$	0.0036782	[De Bievre et al., 1996]

$$\delta^{18}O(1) = d\frac{46}{44} + \left[\frac{\frac{^{15}N}{^{14}N}_{N2}^{\;2}}{\frac{^{18}O}{^{16}O}_{SMOW}} * \left[d\frac{46}{44} - 2 * \delta^{15}N(1) - \frac{\delta^{15}N(1)^2}{1000} + 2 * \frac{^{15}N}{^{14}N}_{N2} * \frac{^{17}O}{^{16}O}_{SMOW} * \frac{1}{\frac{^{18}O}{^{16}O}_{SMOW}} * d\frac{46}{44} - 1 + \delta^{15}N(1)\left[\left[1 + \frac{d\frac{46}{44}}{1000}\right]^{0.52} - 1\right] * 1000\right]\right] \tag{2}$$

This is then repeated with the updated $\delta^{15}N(1)$ for $\delta^{15}N$

$$\delta^{15}N(2) = d\frac{45}{44} + \left[\frac{\frac{^{17}O}{^{16}O})_{SMOW}}{2 * \frac{^{15}N}{^{14}N})_{N_2}} * \left[d\frac{45}{44} - \left[\left[1 + \frac{\delta^{18}O(1)}{1000}\right]^{0.52} - 1\right] * 1000\right]\right] \tag{3}$$

and $\delta^{18}O$

$$\delta^{18}O(2) = d\frac{46}{44} + \left[\frac{\frac{^{15}N}{^{14}N}{}^{2}_{N2}}{\frac{^{18}O}{^{16}O}_{SMOW}} * \left[d\frac{46}{44} - 2 * \delta^{15}N(2) - \frac{\delta^{15}N(2)^2}{1000} + 2 * \frac{^{15}N}{^{14}N}_{N2} * \frac{^{17}O}{^{16}O}_{SMOW} * \frac{1}{\frac{^{18}O}{^{16}O}_{SMOW}} * d\frac{46}{44} - 1 + \delta^{15}N(2)\left[\left[1 + \frac{d\frac{46}{44}}{1000}\right]^{0.52} - 1\right] * 1000\right]\right] \tag{4}$$

next we need to do a blank correction

$$\delta^{15}N_{blank} = \delta^{15}N(2) * (s + b)/b \tag{5}$$

where

$$s = samplesize(i.e.20nmols) \tag{6}$$

$$b = Area(blank)/(\Sigma Area_{IAEAN3}/n) \tag{7}$$

next tranform $\delta^{15}N_{IAEA-N3}$ vs. tank to $\delta^{15}N_{tank}$ vs. IAEA-N3 for all IAEA-N3 standards

$$\delta^{15}N_{tank}^{IAEAN3} = \frac{-\delta^{15}N_{blank} * 1000}{\delta^{15}N_{blank} + 1000} \tag{8}$$

$$\delta^{15}N_{NO_3^-}^{IAEAN3} = ((((\frac{\delta^{15}N_{blank}}{1000}) + 1) * m + b) - 1) * 1000 \tag{9}$$

m and b are slope and intercept from a fitted line through measured MS IAEAN3 and USGS34 vs. Bohlke reported values

$$m = \frac{R_{IAEAN3} - \frac{(\delta^{15}N_{NO_3^-}^{USGS}/1000+1)}{(\delta^{15}N_{NO_3^-}^{IAEAN3}/1000+1)}}{Average(\delta^{15}N_{IAEA-N3}) - Average(\delta^{15}N_{USGS34})} \tag{10}$$

with

$$R_{IAEAN3} = 1 \;, \delta^{15}N_{NO_3^-}^{IAEAN3} = 4.7permil \;, \delta^{15}N_{USGS34} = -1.8permil \tag{11}$$

and

$$b = R_{IAEAN3} - Average(\delta^{15}N_{IAEA-N3}) * m \tag{12}$$

and finally

$$\delta^{15}N^{air}_{NO_3^-} = ((\frac{\delta^{15}N^{IAEAN3}_{NO_3^-}}{1000} + 1) * (\frac{\delta^{15}N^{air}_{IAEAN3}}{1000} + 1) - 1) * 1000 \tag{13}$$

where

$$\delta^{15}N^{air}_{IAEAN3} = -4.7 permil \tag{14}$$

0.3 $\delta^{18}O$ corrections

... and now for the more complicated stuff.

Column W is the average $\delta^{18}O_{H20}$ of each sample. For the USGS-34 standards this is simply -5.1 permil. For most ocean samples $\delta^{18}O_{sample}$ will be 0 permil.

$$avg.\delta^{18}O_{H20} = \frac{V_{med} * \delta^{18}O_{med} + V_{s.w.} * \delta^{18}O_{s.w.} + V_{inject} * \delta^{18}O_{sample}}{V_{med} + V_{s.w.} + V_{inject}} \tag{15}$$

it is very important that you make sure this is correct for each individual sample (row). Jumping back to column R.

$$\delta^{18}O^{IAEA}_{NO3} = \frac{(\frac{P}{1000} + 1) - ((\frac{average\delta^{18}O_{H20}}{1000} + 1) * x)}{(1 - x)} * m + b) - 1) * 1000 \tag{16}$$

where P is

$$P = \delta^{18}O^{tank}_{NO3} = \frac{\delta^{18}O(2) - \epsilon * 1000}{1 + \epsilon}, \qquad \epsilon = 0.04 \tag{17}$$

and finally

$$\delta^{18}O^{SMOW}_{NO3} = ((\frac{\delta^{18}O^{IAEA}_{NO3}}{1000} + 1) * (\frac{\delta^{18}O_{NO3}(IAEA)}{1000} + 1) - 1) * 1000, \quad \delta^{18}O_{NO3}(IAEA) = 25.61 permil \tag{18}$$

care should be used to ensure that bad standards do not skew the correction of you samples.