Isobaric correction of mass-spectrometric isotope ratio measurements in O_2, CO, CO_2 and N_2O

Jan Kaiser[1] and Thomas Röckmann[2]

[1]School of Environmental Sciences, University of East Anglia, Norwich, United Kingdom
[2]Institute for Marine and Atmospheric Research Utrecht, Utrecht University, The Netherlands

University of East Anglia
School of Environmental Sciences

IMAU
Institute for Marine and Atmospheric research Utrecht

Rationale & Abstract

Gas isotope ratio mass spectrometers usually measure ion current ratios of molecules, not atoms. Often several isotopologues (i.e., isotopically substituted molecules) contribute to an ion current at a particular mass-to-charge ratio (m/z). Therefore, for data reduction purposes, corrections have to be applied to derive the desired atomic isotope ratios. The mathematical formulation of these corrections is usually made in terms of isotope ratios (R), but this does not reflect the practice of measuring the ion current ratios of the sample relative to those of a reference material. Correspondingly, the relative ion current ratio differences (expressed as δ values) are usually first converted to isotopologue ratios, then to isotope ratios and finally back to elemental δ values.

Here, we present a reformulation of this data reduction procedure entirely in terms of δ values and the 'absolute' isotope ratios of the reference material[6]. This also shows that not the 'absolute' isotope ratios of the reference material themselves, but only product and ratio combinations of them are required for the data reduction (Tables 1 & 2). These combinations can be and, for CO_2, have been measured by conventional isotope ratio mass spectrometers. The frequently implied use of 'absolute' isotope ratios measured by specially calibrated instruments is actually unnecessary.

We show reformulated data reduction equations for the species O_2, CO, CO_2 and N_2O, including position-dependent N isotope measurements using the NO^+ fragment of N_2O. Advantages of the new formulation in terms of δ values are listed below.

Advantages of new δ formulation

- mass spectrometers measure δ values, not isotope ratios R $\Rightarrow$ only δ values can be derived
- clarity about coefficients needed for data reduction (i.e., ratios of isotope ratios, not isotope ratios themselves)
- conversion coefficients can be determined by δ measurements alone!
- can be used for direct error propagation, no Monte-Carlo modelling required
- may help improve data reduction algorithms used by mass-spectrometer manufacturers

Notation

m/z mass-to-charge ratio

$^i\boldsymbol{R}$ sample isotopologue/isotope ratio for species of mass $i/(i-1)$

$^i\boldsymbol{R_r}$ reference isotopologue/isotope ratio for species of mass $i/(i-1)$

$\boldsymbol{\delta=^iR/^iR_r-1}$ relative ion current/isotopologue/isotope ratio difference

$\boldsymbol{^{17}\Delta=(1+^{17}\delta)/(1+^{18}\delta)^{0.528}-1}$ ^{17}O isotope excess[6]

B*, *C*, *D*, *E*, *F Coefficients for conversion of relative ion current to relative isotope ratio differences (see Table 2)

$\boldsymbol{R_1}$, $\boldsymbol{R_2}$, $\boldsymbol{R_{av}}$, $\boldsymbol{R_{sp}}$ $^{15}N/^{14}N$ isotope ratios for terminal N, central N, average N, site-preference N in N_2O analysis

$\boldsymbol{\zeta_{av}}$, $\boldsymbol{\zeta_{sp}}$ special "δ values" used in N_2O analysis; defined w.r.t. $R_{av,r}$

Table 1

Absolute isotope ratios (R) of international isotope measurement standards. For better comparison, some values are shown with more digits than justified by their precision.

		Latest value		IAEA recommended	
Ratio	**Standard**	**10^6R**	**Refs.**	**10^6R**	**Refs.**
$^{13}C/^{12}C$	VPDB-CO_2	11124±45	7	11237.2±30	1,3,8
$^{15}N/^{14}N$	Air-N_2	3675.8±0.7	4,5,6	3676±4	5
$^{17}O/^{16}O$	VSMOW	$382.7^{+1.7}_{-2.1}$	7	386.72±0.4	1,8
$^{17}O/^{16}O$	Air-O_2	$387.4^{+1.7}_{-2.1}$	7	—	
$^{17}O/^{16}O$	VPDB-CO_2	$391.1^{+1.7}_{-2.1}$	7	395.11±0.5	1,8
$^{18}O/^{16}O$	VSMOW	2005.20±0.45	2	2005.20±0.45	2
$^{18}O/^{16}O$	Air-O_2	2054.04±0.46	7	—	
$^{18}O/^{16}O$	VDPB-CO_2	2088.37±0.90	7	2088.35±0.47	8

Table 2

Coefficients for conversion of relative ion current to relative isotope ratio differences (R – reference isotope ratio R_r, R_{av} – average $^{15}N/^{14}N$ isotope ratio in the N_2O reference)

Species	Coeff.	Definition	Standards	10^3 Coeff.
O_2	B	$^{17}R^2/(2^{18}R)$	Air-O_2	$0.0365^{+0.0003}_{-0.0004}$
CO, CO_2	C	$^{17}R/^{13}R$	VPDB-CO_2	$35.16^{+0.05}_{-0.12}$
CO, CO_2	$D=B/C$	$^{13}R^{17}R/(2^{18}R)$	VPDB-CO_2	1.042±0.008
N_2O	E	$^{17}R/(2R_{av})$	Air-N_2/VPDB-CO_2	$53.2^{+0.2}_{-0.3}$
N_2O	$F=B/(2E)$	$R_{av}{}^{17}R/(2^{18}R)$	Air-N_2/VPDB-CO_2	0.358±0.002

Oxygen (O_2^+)

Mass-spectrometric ion current ratio measurements

m/z 32 $^{16}O_2^+$

m/z 33 $^{33}\delta$ $^{17}O^{16}O^+$

m/z 34 $^{34}\delta$ $^{18}O^{16}O^+$ $^{17}O_2^+$

Isotopologue and isotope ratio equations for sample and reference

$^{33}R=2^{17}R$ $^{33}R_r=2^{17}R_r$

$^{34}R=^{17}R^2+2^{18}R$ $^{34}R_r=^{17}R_r^2+2^{18}R_r$

δ value equations

$^{33}R_r{}^{33}\delta=2^{17}R_r{}^{17}\delta$

$^{34}R_r{}^{34}\delta=^{17}R_r^2(2^{17}\delta+^{17}\delta^2)+2^{18}R_r{}^{18}\delta$

Exact (direct) solution using δ measurements

$^{17}\delta=^{33}\delta$

$^{18}\delta=^{34}\delta+B(^{34}\delta-2^{33}\delta-^{33}\delta^2)$

Parameter

$B=^{17}R_r^2/(2^{18}R_r)\approx0.00004$ Air-O_2

Substituting numerical value for B

$^{17}\delta=^{33}\delta$

$^{18}\delta=1.00004^{34}\delta-0.00007^{33}\delta-0.00004^{33}\delta^2$

Carbon monoxide (CO^+)

Mass-spectrometric ion current ratio measurements

m/z 28 $^{12}C^{16}O^+$

m/z 29 $^{29}\delta$ $^{13}C^{16}O^+$ $^{12}C^{17}O^+$

m/z 30 $^{30}\delta$ $^{12}C^{18}O^+$ $^{13}C^{17}O^+$

Isotopologue and isotope ratio equations for sample and reference

$^{29}R=^{13}R+^{17}R$ $^{29}R_r=^{13}R_r+^{17}R_r$

$^{30}R=^{13}R^{17}R+^{18}R$ $^{30}R_r=^{13}R_r{}^{17}R_r+^{18}R_r$

δ value equations

$^{29}R_r{}^{29}\delta=^{13}R_r{}^{13}\delta+^{17}R_r{}^{17}\delta$

$^{30}R_r{}^{30}\delta=^{18}R_r{}^{18}\delta+^{13}R_r{}^{17}R_r(^{13}\delta+^{17}\delta+^{13}\delta{}^{17}\delta)$

Exact (iterative) solution using δ measurements and $^{17}\Delta$

$^{13}\delta=^{29}\delta+C(^{29}\delta-^{17}\delta)$

$^{18}\delta=^{30}\delta+2D[^{30}\delta-(1-C)^{17}\delta-(1+C)^{29}\delta(1+^{17}\delta)+C^{17}\delta^2]$

$^{17}\delta=(1+^{17}\Delta)(1+^{18}\delta)^{0.528}-1$

Parameters

$C=^{17}R_r/^{13}R_r\approx0.0352$ VPDB-CO_2

$D=^{13}R_r{}^{17}R_r/(2^{18}R_r)\approx0.0010$ VPDB-CO_2

Substituting numerical values for C and D, assuming $^{17}\Delta=0$

$^{13}\delta=1.0352^{29}\delta-0.0352^{17}\delta$

$^{18}\delta=1.0021^{30}\delta-0.0022^{29}\delta-0.0020^{17}\delta-0.0022^{29}\delta{}^{17}\delta+0.0001^{17}\delta^2$

$^{17}\delta=(1+^{18}\delta)^{0.528}-1$

Carbon dioxide (CO_2^+)

Mass-spectrometric ion current ratio measurements

m/z 44 $^{12}C^{16}O_2^+$

m/z 45 $^{45}\delta$ $^{13}C^{16}O_2^+$ $^{12}C^{17}O^{16}O^+$

m/z 46 $^{46}\delta$ $^{12}C^{18}O^{16}O^+$ $^{13}C^{17}O^{16}O^+$ $^{12}C^{17}O_2^+$

Isotopologue and isotope ratio equations for sample and reference

$^{45}R=^{13}R+2^{17}R$ $^{45}R_r=^{13}R_r+2^{17}R_r$

$^{46}R=2^{18}R+2^{13}R^{17}R+^{17}R^2$ $^{46}R_r=2^{18}R_r+2^{13}R_r{}^{17}R_r+2^{17}R_r{}^2$

δ value equations

$^{45}R_r{}^{45}\delta=^{13}R_r{}^{13}\delta+2^{17}R_r{}^{17}\delta$

$^{46}R_r{}^{46}\delta=2^{18}R_r{}^{18}\delta+2^{13}R_r{}^{17}R_r(^{13}\delta+^{17}\delta+^{13}\delta{}^{17}\delta)+^{17}R_r{}^2(2^{17}\delta+^{17}\delta^2)$

Exact (iterative) solution using δ measurements and $^{17}\Delta$

$^{13}\delta=^{45}\delta+2C(^{45}\delta-^{17}\delta)$

$^{18}\delta=^{46}\delta+D[(2+C)^{46}\delta-(2-2C)^{17}\delta-(2+4C)^{45}\delta(1+^{17}\delta)+3C^{17}\delta^2]$

$^{17}\delta=(1+^{17}\Delta)(1+^{18}\delta)^{0.528}-1$

Parameters

$C=^{17}R_r/^{13}R_r\approx0.0352$ VPDB-CO_2

$D=^{13}R_r{}^{17}R_r/(2^{18}R_r)\approx0.0010$ VPDB-CO_2

Substituting numerical values for C and D, assuming $^{17}\Delta=0$

$^{13}\delta=1.0703^{45}\delta-0.0703^{17}\delta$

$^{18}\delta=1.0021^{46}\delta-0.0022^{45}\delta-0.0020^{17}\delta-0.0022^{45}\delta{}^{17}\delta+0.0001^{17}\delta^2$

$^{17}\delta=(1+^{18}\delta)^{0.528}-1$

Nitrous oxide (N_2O^+)

NNO
1 2

Mass-spectrometric ion current ratio measurements

m/z 44 $^{14}N_2{}^{16}O^+$

m/z 45 $^{45}\delta$ $^{14}N^{15}N^{16}O^+$ $^{15}N^{14}N^{16}O^+$ $^{14}N_2{}^{17}O^+$

m/z 46 $^{46}\delta$ $^{14}N_2{}^{18}O^+$ $^{14}N^{15}N^{17}O^+$ $^{15}N^{14}N^{17}O^+$ $^{15}N_2{}^{16}O^+$

Define average (R_{av}) and site-preference (R_{sp}) $^{15}N/^{14}N$ ratios

$R_{av}=(^{15}R_2+^{15}R_1)/2$ $R_{sp}=(^{15}R_2-^{15}R_1)/2$

$R_{av,r}=(^{15}R_{2,r}+^{15}R_{1,r})/2$ $R_{sp,r}=(^{15}R_{2,r}-^{15}R_{1,r})/2$

Isotopologue and isotope ratio equations for sample and reference

$^{45}R=2R_{av}+^{17}R$ $^{45}R_r=2R_{av,r}+^{17}R_r$

$^{46}R=^{18}R+2R_{av}{}^{17}R+R_{av}{}^2-R_{sp}{}^2$ $^{46}R_r=^{18}R_r+2R_{av,r}{}^{17}R_r+R_{av,r}{}^2-R_{sp,r}{}^2$

Define average (ζ_{av}) and site-preference (ζ_{sp}) zeta values

$\zeta_{av}=R_{av}/R_{av,r}-1$ $\zeta_{sp}=R_{sp}/R_{av,r}-1$

$\zeta_{av,r}=R_{av,r}/R_{av,r}-1=0$ $\zeta_{sp,r}=R_{sp,r}/R_{av,r}-1$

δ and ζ value equations

$^{45}R_r{}^{45}\delta=2R_{av,r}\zeta_{av}+^{17}R_r{}^{17}\delta$

$^{46}R_r{}^{46}\delta=^{18}R_r{}^{18}\delta+2^{15}R_{av,r}{}^{17}R_r(\zeta_{av}+^{17}\delta+\zeta_{av}{}^{17}\delta)$
$+^{15}R_{av,r}{}^2(2\zeta_{av}+\zeta_{av}{}^2-\zeta_{sp}{}^2+\zeta_{sp,r}{}^2)$

Exact (iterative) solution using δ measurements and $^{17}\Delta$, ζ_{sp}, $\zeta_{sp,r}$

$\zeta_{av}=^{45}\delta+E(^{45}\delta-^{17}\delta)$

$^{18}\delta=^{46}\delta+F[(4+E^{-1})^{46}\delta-(6+4E+2E^{-1})^{45}\delta-(2-4E)^{17}\delta-(2+E+E^{-1})^{45}\delta^2\ldots$
$-(2+2E)^{45}\delta{}^{17}\delta+3E^{17}\delta^2+E^{-1}(\zeta_{sp}{}^2-\zeta_{sp,r}{}^2-^{46}\delta\zeta_{sp,r}{}^2)]$

$^{17}\delta=(1+^{17}\Delta)(1+^{18}\delta)^{0.528}-1$

Parameters

$E=^{17}R_r/(2R_{av,r})\approx0.0532$ VPDB-CO_2, Air-N_2

$F=R_{av,r}{}^{17}R_r/(2^{18}R_r)\approx0.00004$ VPDB-CO_2, Air-N_2

Substituting numerical values for E and F, assuming $^{17}\Delta=\zeta_{sp}=\zeta_{sp,r}=0$

$\zeta_{av}=1.0532^{45}\delta-0.0532^{17}\delta$

$^{18}\delta=1.0082^{46}\delta-0.0157^{45}\delta-0.0006^{17}\delta-0.0075^{45}\delta^2$
$-0.0008^{45}\delta{}^{17}\delta+0.0001^{17}\delta^2$

$^{17}\delta=(1+^{18}\delta)^{0.528}-1$

N_2O fragment analysis (NO^+)

Mass-spectrometric ion current ratio measurements

m/z 30 $^{14}N^{16}O^+$ 92 % $^{14}N^{16}O^+$ 8 % $(^{15}N_2{}^+)$

m/z 31 $^{31}\delta$ $^{15}N^{16}O^+$ $^{15}N^{16}O^+$ $^{14}N^{17}O^+$ $^{14}N^{17}O^+$

Isotopologue and isotope ratio equation for sample (s: scrambling)

$$^{31}R = sR_1 + (1-s)R_2 + {}^{17}R - \frac{s(1-s)(R_2-R_1)^2}{1+sR_2+(1-s)R_1}$$

$$= R_{av} + (1-2s)R_{sp} + {}^{17}R - \frac{4s(1-s)R_{sp}^2}{1+R_{av}-(1-2s)R_{sp}}$$

δ and ζ value equations

$$^{31}R_r\,{}^{31}\delta = R_{av,r}\left[\zeta_{av}+(1-2s)(\zeta_{sp}-\zeta_{sp,r})\right] + {}^{17}R_r\,{}^{17}\delta$$
$$-\frac{4s(1-s)R_{av,r}^2\zeta_{sp}}{1+R_{av,r}\left[1+\zeta_{av}-(1-2s)\zeta_{sp}\right]} + \frac{4s(1-s)R_{av,r}^2\zeta_{sp,r}^2}{1+R_{av,r}\left[1-(1-2s)\zeta_{sp,r}\right]}$$

Exact (iterative) solution using δ measurements and $^{17}\Delta$, $\zeta_{sp,r}$

$$\zeta_{sp} = \frac{^{31}\delta-{}^{45}\delta}{1-2s} + E\frac{2^{31}\delta-{}^{45}\delta-{}^{17}\delta}{1-2s} + \zeta_{sp,r}(1+{}^{31}\delta) + \frac{4s(1-s)R_{av,r}}{1-2s}\ldots$$
$$\left\{\frac{\zeta_{sp}^2}{1+R_{av,r}\left[1+{}^{45}\delta+E({}^{45}\delta-{}^{17}\delta)-(1-2s)\zeta_{sp}\right]} - \frac{\zeta_{sp,r}^2(1+{}^{31}\delta)}{1+R_{av,r}\left[1-(1-2s)\zeta_{sp,r}\right]}\right\}$$

Substituting numerical values for E and $R_{av,r}$, assuming s=0.08, $^{17}\Delta=0$

$\zeta_{av}=1.0532^{45}\delta-0.0532^{17}\delta$

$\zeta_{sp}\approx1.3171^{31}\delta-1.2538^{45}\delta+\zeta_{sp,r}-0.0633^{17}\delta\ldots$
$+0.0013\zeta_{sp}{}^2-0.0013\zeta_{sp,r}{}^2(1+{}^{31}\delta)$

$^{18}\delta=1.0082^{46}\delta-0.0157^{45}\delta-0.0006^{17}\delta-0.0075^{45}\delta^2$
$-0.0008^{45}\delta{}^{17}\delta+0.0001^{17}\delta^2$

$^{17}\delta=(1+^{18}\delta)^{0.528}-1$

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