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Absolute calibration of the intramolecular site preference of 15N fractionation in tropospheric N2O by FT-IR spectroscopy

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Abstract
Nitrous oxide (N2O) plays important roles in atmospheric chemistry both as a greenhouse gas and in stratospheric ozone depletion. Isotopic measurements of N2O have provided an invaluable insight into understanding its atmospheric sources and sinks. The preference for 15N fractionation between the central and terminal positions (the “site preference”) is particularly valuable because it depends principally on the processes involved in N2O production or consumption, rather than the 15N content of the substrate from which it is formed. Despite the value of measurements of the site preference, there is no internationally recognized standard reference material of accurately known and accepted site preference, and there has been some lack of agreement in published studies aimed at providing such a standard. Previous work has been based on isotope ratio mass spectrometry (IRMS); in this work we provide an absolute calibration for the intramolecular site preference of 15N fractionation of working standard gases used in our laboratory by a completely independent technique—high-resolution Fourier transform infrared (FT-IR) spectroscopy. By reference to this absolute calibration, we determine the site preference for 25 samples of tropospheric N2O collected under clean air conditions to be 19.8‰ ± 2.1‰. This result is in agreement with that based on the earlier absolute calibration of Toyoda and Yoshida (Toyoda, S. and Yoshida, N. Anal. Chem. 1999, 71, 4711–4718) who found an average tropospheric site preference of 18.7‰ ± 2.2‰. We now recommend an interlaboratory exchange of working standard N2O gases as the next step to providing an international reference standard.

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Absolute calibration of the intramolecular site preference of $^{15}$N fractionation in tropospheric N$_2$O by FTIR spectroscopy.

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Abstract

Nitrous oxide (N$_2$O) plays important roles in atmospheric chemistry both as a greenhouse gas and in stratospheric ozone depletion. Isotopic measurements of N$_2$O have provided an invaluable insight into understanding its atmospheric sources and sinks. The preference for $^{15}$N fractionation between the central and terminal positions (the “site preference”) is particularly valuable because it depends principally on the processes involved in N$_2$O production or consumption, rather than the $^{15}$N content of the substrate from which it is formed. Despite the value of measurements of the site preference, there is no internationally-recognised standard reference material of accurately known and accepted
site preference, and there has been some lack of agreement in published studies aimed at
providing such a standard. Previous work has been based on Isotope Ratio Mass
Spectrometry (IRMS); in this work we provide an absolute calibration for the
intramolecular site preference of $^{15}$N fractionation of working standard gases used in our
laboratory by a completely independent technique – high resolution FTIR spectroscopy.
By reference to this absolute calibration, we determine the site preference for 25 samples
of tropospheric N$_2$O collected under clean air conditions to be 19.8 ± 2.1‰. This result is
in agreement with that based on the earlier absolute calibration of Toyoda et al $^1$, who
found an average tropospheric site preference of 18.7 ± 2.2‰. We now recommend an
inter-laboratory exchange of working standard N$_2$O gases as the next step to providing an
international reference standard.

**Keywords**

Nitrous oxide, tropospheric chemistry, isotopomers, $^{15}$N site preference, FTIR
spectroscopy, isotopic analysis
Introduction

Nitrous oxide plays two major roles in the chemistry of the atmosphere – it is an important greenhouse gas and it is the principal source of NO which catalytically destroys ozone in the stratosphere. Its atmospheric mixing ratio is currently near 320 nmol mol\(^{-1}\) and has increased at 0.2 - 0.3% per year for the past few decades. This increase is thought to be due mainly to increased microbial production in soils following increased use of nitrogen fertilisers in agriculture. Resolving the significant uncertainties in the global N\(_2\)O budget is aided by isotopic measurements of atmospheric N\(_2\)O. Moore and Kim and Craig first recognized that the bulk \(^{15}\)N and \(^{15}\)O fractionation in tropospheric N\(_2\)O (+7‰ and +21‰ relative to atmospheric N\(_2\) and O\(_2\) respectively) represents a balance between isotopically light sources at the surface and isotopically heavy back-flux from the stratosphere.

With the structure N=N=O, N\(_2\)O has two chemically distinct and non-interchangeable N-atoms, and the difference between \(^{15}\)N fractionations at the central and terminal positions (called the intramolecular \(^{15}\)N site preference and defined in the next section) provides an additional and independent isotopic signal to the bulk or average \(^{15}\)N fractionation. The site preference is particularly useful because it depends principally on the processes which form (or deplete) N\(_2\)O, rather than the \(^{15}\)N composition of the substrate from which it is formed. Thus the site preference has been used to characterise the mechanisms of formation (for example nitrification and denitrification in soils) and destruction (photolysis and photo-oxidation in the stratosphere) of N\(_2\)O.

An international standard N\(_2\)O reference material of accurately known mean \(^{15}\)N amount and site preference is highly desirable to ensure all site preference measurements from different laboratories are on the same scale, but to date no such standard exists. In the late
1990s two laboratories independently developed an Isotope Ratio Mass Spectrometry (IRMS) technique to allow the measurement of site preference in N₂O through analysis of both the parent molecular ion and the NO⁺ fragment ion \(^1, 12\). At the same time, we developed a high resolution Fourier Transform InfraRed (FTIR)-based method which determines the individual \(^{15}\)N isotopomers independently \(^8, 13\). Both IRMS laboratories provided an independent absolute calibration of their standard working gases. Toyoda et al. \(^1\) prepared an absolute N₂O standard by thermal decomposition of NH₄NO₃ of known isotopic composition – NH₄NO₃ is known to decompose with the NH₄⁺ -N exclusively in the terminal position, and the NO₃⁻ -N in the central position \(^14\). Kaiser et al. used a standard addition technique using doubly-labelled \(^{15}\)N₂O \(^15\) to calibrate their working standard. Based on their respective calibrations, Toyoda et al. and Kaiser et al. found average northern hemisphere tropospheric N₂O to have a mean site preference of 18.7 ± 2.2‰ and 46.3 ± 1.4‰ respectively, a difference of around 27‰. However, due to its long lifetime (>100 years\(^4\)) and effective global-scale mixing, we expect tropospheric N₂O to have a similar site preference everywhere in the troposphere, allowing its use as a de facto transfer standard. The 27‰ discrepancy remained unresolved until Westley et al. \(^16\) revisited both methods and found that the standard addition method of Kaiser et al. was subject to non-reproducible variations in instrument-dependent ion chemistry in the ionization source. They obtained results consistent with the NH₄NO₃-based calibration of Toyoda et al., but made no case to recommend any change to the Toyoda standard pending independent confirmation.

Both Toyoda et al. and Westley et al. recommended calibration by an independent method, and optical techniques such as high resolution FTIR \(^8, 13, 17, 18\) and laser spectroscopy \(^19\) provide such an opportunity. These techniques naturally distinguish the isotopologues of N₂O as separate species because the different mass and geometry of
substitution slightly changes vibrational and rotational energy levels and absorption frequencies in the IR spectrum. Quantitative analysis of high resolution N₂O gas phase spectra thus provides an analytical method for determining complete isotopic composition of N₂O. In our previous work with FTIR spectroscopy⁸,¹³, measurement precision for the site preference was around 1–2 ‰, but recent instrument improvements in our laboratory now allow precision of 0.3-0.4‰ for the determination of individual ¹⁵N isotopomer fractionations and 0.1‰ for the site preference. In this paper we provide an absolute calibration of our working laboratory standard N₂O gas which is completely independent of those of Toyoda, Kaiser and Westley et al. Absolute measurements of tropospheric N₂O site preference based on this calibration are consistent with those of Toyoda et al. and Westley et al.

**Methods**

**Definitions**

We use the common spectroscopic shorthand notation for isotopologues of N₂O: 446 = ¹⁴N¹⁴N¹⁶O, 456 = ¹⁴N¹⁵N¹⁶O, 546 = ¹⁵N¹⁴N¹⁶O, etc. Thus 456 represents N₂O with ¹⁵N substitution of the α- or 2-position and 546 refers to substitution at the β- or 1-position. FTIR spectroscopy naturally determines absolute concentrations or partial pressures of individual species, rather than ratios as in IRMS. We follow 2008 IUPAC draft recommendations²⁰,²¹ with symbol X referring to isotopic abundances and R referring to isotopic ratios to define

\[
X^{456} = \frac{[456]}{[\Sigma N_2O]} \quad X^{546} = \frac{[546]}{[\Sigma N_2O]} \\
R^{456} = \frac{[456]}{[446]} \quad R^{546} = \frac{[546]}{[446]} \quad R^{\alpha} = \frac{[456]}{[546]}
\]  

(1)
In delta notation, the bulk $^{15}\text{N}$ and site preference of 456 relative to 546 are respectively

$$\delta^{15}\text{N} = \left( \frac{R^{456} + R^{546}}{R_{std}^{15}} \right) \frac{2}{1} - 1 \quad \text{and} \quad \delta^{sp} = \left( \frac{R^{sp}}{R_{std}^{sp}} - 1 \right) \quad (2)$$

where the square brackets represent the concentration or amount of an isotopomer or isotopologue in a sample, and $[\Sigma N_2O]$ is the sum of all isotopologues in that sample. (For simplicity we ignore the contribution of the 556 isotopologue.) $R_{std}^{15}$ is the $^{15}\text{N}/^{14}\text{N}$ ratio in a reference standard, here taken to be atmospheric N$_2$. Implicit in equation (2) is the assumption that the reference isotopic ratio for site preference is unity, i.e. $R_{std}^{sp} = 1$, or equivalently $\delta_{std}^{sp} = 0$. In this paper, $R^{sp}$ and $\delta^{sp}$ will be used interchangeably as the context requires.

**FTIR spectroscopy and sample handling**

Sample handling and spectroscopic methods were similar to those in our previous work with several improvements. The sample gas to be measured was contained in a small multipass White cell with 100 mL volume and 2.4m pathlength adapted from a commercially available cell (2.4PA Ultra-mini, IR Analysis, Anaheim CA) in the FTIR spectrometer beam. The cell was evacuated and filled through a brass and copper manifold with several valved side-arms. Sample pressures in the cell were measured by a capacitance manometer (Baratron 622A, 0-100 torr, MKS Instruments, Massachusetts, USA) which had a linear response from <1 to 100 torr as detailed below. The sample cell, pressure gauge and manifold were pumped by a small turbomolecular pump (TMH071P, Pfeiffer, New Hampshire, USA) to <0.001 hPa, water-jacketed and kept at 25±0.05ºC. All spectra used for quantitative analysis were run at sample pressure of 1 torr (1.33 hPa, approximately 5 µmol) unless specified otherwise.
A fixed volume of the sample manifold was used as an expansion volume to reduce pressure in the cell during dilutions. To check the linearity of the pressure gauge and calibrate the expansion volume, a series of expansions was carried out. Starting with 100 hPa of gas in the cell, the manifold was evacuated, the cell contents expanded into the expansion volume, and the pressure measured. The expansion and pressure measurement was repeated until the pressure was < 1 hPa. After the \( n \)th expansion the pressure \( P_n \) is

\[ P_n = P_0 \gamma^n \]

where \( \gamma \) is the volume expansion ratio. A plot of \( \log(P_n) \) vs \( n \) showed no measurable deviation from linearity over the range 100-1 hPa. Thus the pressure gauge can be assumed linear over this range, and the volume expansion ratio from the slope of the \( \log(P_n) \) vs \( n \) regression line was \( \gamma = 0.77929 \pm 0.00006 \). This expansion ratio was used for calculations in the serial dilution experiments described below.

All spectra were measured on a high resolution FTIR spectrometer (IFS125, BrukerOptik, Ettlingen, Germany) at 0.011 cm\(^{-1}\) resolution (optical path difference 90 cm) using a globar source, KBr beamsplitter, 1950-2600 cm\(^{-1}\) bandpass filter, and liquid-nitrogen cooled InSb detector. Fifteen scans were coadded for a total measurement time of approximately 10 minutes per sample. Sample spectra were ratioed to a spectrum of the evacuated cell to provide transmittance spectra. The spectrometer was evacuated to <1 hPa to remove interference from atmospheric CO\(_2\) and H\(_2\)O absorption.

**Quantitative analysis of FTIR spectra**

Each FTIR spectrum was analysed by computing a best fit to a region of the measured spectrum using a computer model and a database of absorption line parameters for all N\(_2\)O isotopologues. The computer model (MALT - Multiple Atmospheric Layer Transmission) is described in detail by Griffith, but in this work uses an iterative non-linear least squares algorithm instead of Classical least Squares (CLS) to achieve best fit.
This method offers good precision (<0.5‰) for the retrieval of individual isotopologue concentrations, but for absolute accuracy requires calibration by comparison to known standards.

The spectroscopic line parameters for N$_2$O used in the MALT calculation were provided by R.A Toth (private communication). They are the same as those provided by Toth for the HITRAN 2004 database but extended to include weaker absorption lines of singly and doubly-substituted isotopologues which are measurable in our $^{15}$N-enriched spectra but below the intensity cut-off for inclusion in the HITRAN database. The extended set includes the singly-substituted isotopologues 446, 456, 546, 448 and 447, and the doubly-substituted 556, 458 and 548. Small residuals in the fitted spectra due to the missing isotopologues 457 and 547 are also evident but these species are not included in the line parameters. Their exclusion from the calculation does not significantly affect the precision of the analysis. All other molecular line parameters (CO$_2$, H$_2$O interferences) are taken from HITRAN 2004.

In the iterative non-linear-least-squares fitting routine, the spectrum is initially calculated from the best estimate of all input parameters and compared to the measured spectrum. The input parameters include the individual isotopologue amounts as well as instrumental parameters representing wavenumber shift, linewidth and line asymmetry to fit the measured lineshapes accurately. The Levenberg-Marquardt algorithm is then used to iteratively update the best estimates of the input parameters to improve the fit until convergence to a minimum residual (i.e. least mean-squared difference between measured and calculated spectra) is obtained. The concentrations (or partial pressures) of the individual isotopologues are obtained as their values in the best-fit calculation. The spectra were fitted in the region 2170-2220 cm$^{-1}$, in the strong $\nu_3$ vibration band of N$_2$O.
This region includes the R-branch of 456 and the P-branch of 546, covering a range of absorption lines with similar intensity distribution and temperature dependence in both isotopomers, and was chosen to minimize the potential for different systematic errors in analyzing the 456 and 546 isotopomers. Figure 1 illustrates a typical fit to a measured spectrum.

Replicate measurements of the same sample show a 1-σ repeatability for the determination of isotopomer ratios for 456, 546 and the site preference of 0.3‰, 0.4‰ and 0.1‰ respectively. Absolute accuracy for the site preference is better than 3%, limited by inaccuracies in the line parameters and the inability to fit imperfect spectra due to instrumental effects. Absolute concentrations of isotopomers were therefore determined by calibration against mixtures of known composition as described further below.

190 **N₂O gases**

Two N₂O gases of unknown site preference were calibrated in this work. Both were working standards used for relative determinations of site preference in normal laboratory measurements. Working standard 1 (WS1) was industrial grade N₂O (BOC Gases) with a stated purity of >99%. Subsamples from the cylinder were purified by freeze-pump-thaw cycles to remove non-condensable gases, and the FTIR spectrum did not show any other IR-absorbing contaminants. This is the same working gas described by Turatti 18 with all isotopes in natural abundance (bulk ¹⁵N isotopic abundance of 0.366 %) and bulk $\delta^{15}N$ of -1.8 ‰ relative to atmospheric N₂. Subsamples of this standard have been stored over 5 years and show no change in isotope ratios relative to recent samples from the main tank.

The second N₂O working standard (WS2) was high purity (>99.9%) N₂O sourced from
Scott-Marin Specialty Gases (California, USA). Turatti showed this N$_2$O to be enriched in 456 relative to 546 with a $\delta^{15}N$ value of $+29.8 \pm 1.8$ ‰ relative to WS1. This N$_2$O is produced as a by-product of adipic acid production, whereas WS1 is prepared from ammonium nitrate.

Isotopically "pure" samples of 456, 546, 556 and $^{15}$N-depleted 446 N$_2$O were obtained from Cambridge Isotope Labs Inc. (Massachussetts, USA). We refer to these gases as CIL-456, CIL-546 etc. Each gas was purified by several freeze-pump-thaw cycles and expanded into a storage bulb for use. The isotopic composition of each gas was measured by FTIR spectroscopy as described below.

The isotopic purity of the CIL isotopologue gases is quoted by the manufacturers to be $>98\%$ for CIL-456, -546 and -556, and $>99.9\%$ for CIL-446. These uncertainties are too large to enable preparation of a standard mixture with a site preference of $\pm 1\%$ accuracy. However FTIR spectroscopy provides a convenient method to measure the isotopic purity of each gas, since each isotopologue can be determined independently from quantitative analysis of the FTIR spectrum. We determined the full isotopic composition of each N$_2$O gas in two ways – by direct analysis of the FTIR spectrum, and in the case of the isotopic purity of 456 in CIL-456 and 546 in CIL-546 by standard addition of up to 4% of BOC working standard (WS1) to determine the total amount of all minor isotopologues. The two methods agree in each case to better than 0.1% for the isotopic fraction of the major component. Table 1 summarises the isotopic composition of all N$_2$O gases as determined by these analyses. The relative uncertainty ($1\sigma$) of each value in Table 1 is $<0.1\%$ based on the repeatability of replicate analyses and the agreement between the two methods. 

CO$_2$ used for standard dilution experiments was industrial N$_2$O-free grade obtained from BOC gases with stated purity of $>99\%$. It was purified by several freeze-pump-thaw
cycles and its IR spectrum showed no interfering absorptions from impurity gases.

**Preparation of the absolute standard**

The calibration method hinged on the preparation of an N₂O standard with an accurately known site preference $\delta^{sp}$. We prepared such a standard manometrically by mixing nominally pure isotopologues using the thermostatted FTIR measurement cell and pressure gauge as a standard mixing volume. The standard was made at 10 atom % $^{15}$N using accurately measured pressures of CIL-456 (10 hPa), CIL-546 (10 hPa), CIL-556 (1 hPa) and natural abundance BOC N₂O (WS1, 79 hPa). The high concentrations of $^{15}$N (10 atom %) were required to ensure that the accuracy of the pressure measurement did not limit the accuracy of the calculated 456/546 ratio. Each standard was prepared by first adding a 10 hPa aliquot of CIL-456 to the standard volume, closing off the volume and evacuating the manifold, then trapping the aliquot of 456 into a valved side-arm of the manifold with liquid nitrogen. This process was repeated with the other components of the mixture (CIL-546, CIL-556 and WS1 N₂O) until all components were co-trapped in the sidearm. This mixture was then warmed and expanded into a storage bulb, allowed to mix, and used for a series of calibration experiments.

The isotopic composition of the standard was calculated from the measured pressures of the added components and their isotopic compositions. Both 456 and 546 were measured at the same nominal pressure, so any non-linearity in the pressure gauge which would lead to systematic errors is insignificant for calculating the ratio $R^{sp}$ of the standard. Individual pressure measurements are precise to approximately 0.002 hPa; for an aliquot of any component (which requires two pressure measurements), we assign an uncertainty of 0.003 hPa, or 0.03% for a 10hPa aliquot of 456 or 546. Adding an uncertainty in the temperature of 0.05 in 298K (<0.02%) in quadrature gives a relative error of 0.04%
The isotopic composition of the 10 atom % $^{15}$N reference standard was calculated to be $10.034 \pm 0.011\%$ 456, $10.112 \pm 0.011\%$ 546 and $\delta^{sp} = -7.8 \pm 1.4\‰$ by summing the individual contributions to each isotopologue amount from each source gas in the synthesized mixture. The uncertainties were calculated allowing relative uncertainties of 0.04% for each aliquot amount, and 0.1% for each isotopologue fraction value, and are dominated by the uncertainties in the isotopic composition of the individual CIL isotopologues; a 0.1% error in the isotopic composition is equivalent to an error of approx. 1‰ in $\delta^{sp}$.

Outline of the calibration method

The $\delta^{sp}$ calibration was a two step process conceptually similar to the common analytical technique of standard addition of a reference standard to an unknown, but in reverse:

1. A reference standard of N$_2$O of accurately known absolute site preference and approximately 10 atom % $^{15}$N was prepared.

2. The N$_2$O reference standard was serially diluted with the N$_2$O of unknown site preference and the site preferences $R^{sp}$ (equivalently $\delta^{sp}$) of the resulting mixtures were determined. Extrapolation of the dilution curve of measured $\delta^{sp}$ against composition of the mixture to the pure unknown axis provided the required site preference of the unknown as the Y-intercept.

The reference standard was prepared as described in the previous section. The dilution sequence proceeded by first filling the measurement cell to 1.33 hPa with pure reference standard (10 atom % $^{15}$N) and measuring the FTIR spectrum. The cell contents were then expanded into the calibrated expansion volume of the vacuum manifold so that the total
pressure dropped to 0.77929 times its value before expansion, then made up to 1.33 hPa
with the unknown gas being analysed. The pressure was recorded and the spectrum
measured. This expansion-dilution-measurement sequence was repeated 15-25 times until
the cell contents approached pure unknown

**Results and data analysis**

To interpret the serial dilution results, we require a suitable (ideally linear) algebraic
equation for \( R^{\delta p} \) or \( \delta^{\delta p} \) of the mixture as the standard is diluted with the unknown. Let

\[ p_{456}^{546} = \text{the partial pressure of } 456(546) \text{ in the mixture} \]

\[ p_{\text{std}} = \text{the partial pressure of reference standard in the mixture} \]

\[ p_u = \text{the partial pressure of unknown in the mixture} \]

\[ p_T = \text{total pressure of the mixture} \]

\[ Y_{\text{std}} = p_{\text{std}}/p_T = \text{the mole fraction of standard in the mixture} \]

With definitions of isotopic fractions and ratios given in (1) and (2), the \([456]/[546]\) ratio

of the mixture \( R^{\delta p} \) is

\[
R^{\delta p} = \frac{D^{456}}{D^{546}} = \frac{X_{\text{std}}^{456}Y_{\text{std}} + X_u^{456}(1 - Y_{\text{std}})}{X_{\text{std}}^{546}Y_{\text{std}} + X_u^{546}(1 - Y_{\text{std}})} \quad (3)
\]

Substituting \( X_{\text{std}}^{456} = R_{\text{std}}^{\delta p} \cdot X_{\text{std}}^{546} \) and \( X_u^{456} = R_u^{\delta p} \cdot X_u^{546} \) we obtain an expression for \( R^{\delta p} \) as a

function of \( Y_{\text{std}} \) and the site preference ratios of the standard and unknown gases:

\[
R^{\delta p} = \frac{(R_{\text{std}}^{\delta p}Y_{\text{std}} - R_{\text{std}}^{\delta p}X_{\text{std}}^{546})Y_{\text{std}} + R_u^{\delta p}X_u^{546}}{(X_{\text{std}}^{546} - X_u^{546})Y_{\text{std}} + X_u^{546}} \quad (4)
\]

However this expression is strongly non linear as \( Y_{\text{std}} \to 0 \) in the present case where
$X^{546}_{std} \gg X^{546}_{u}$ – their values are approximately 0.1 and 0.0036 respectively. By substituting $X^{546} = p^{546} / p_T$ for standard and unknown and rearrangement we obtain

$$R^{sp} = R^{sp}_{std} Y^{546}_{std} + R^{sp}_{u} (1 - Y^{546}_{std})$$

where

$$Y^{546}_{std} = \frac{p^{546}_{std}}{p^{546}_{std} + p^{546}_{u}}$$

is the mole fraction of 546 in the dilution mixture which is derived from the known standard. Equation (5) provides the desired linear relationship, with the $Y^{546}_{std} = 1$ intercept equal to the known $R^{sp}_{std}$ and the $Y^{546}_{std} = 0$ intercept equal to the desired unknown quantity, $R^{sp}_{u}$. $Y^{546}_{std}$ can be calculated for each dilution step from the measured pressures and the known values of $R^{546}_{std}$ and $R^{546}_{u}$ – with sufficient accuracy, $R^{546}_{std}$ and $R^{546}_{u}$ are the bulk $^{15}$N abundances of the standard (ca. 10%) and the unknown (natural abundance, ca. 0.366%). The transformation from $Y_{std}$ to $Y^{546}_{std}$ linearises the dilution curve of $R^{sp}$ vs mole fraction (equation 5). $Y_{std}$ and $Y^{546}_{std}$ are related by

$$Y^{546}_{std} = \frac{Y_{std}}{1 - \frac{X^{546}_{u}}{X^{546}_{std}}} \frac{Y^{546}_{std} + X^{546}_{u}}{Y^{546}_{std}} \approx Y_{std} + 0.963 \cdot Y_{std} + 0.037$$

We ran duplicate dilutions of the 10 atom % $^{15}$N reference standard with working gas WS1 and one dilution with WS2. For each expansion-dilution, the value of $Y^{546}_{std}$ was calculated using equation (6 $Y^{546}_{std} = \frac{p^{546}_{std}}{p^{546}_{std} + p^{546}_{u}}$) from the measured initial pressure, calibrated expansion ratio, and the known values of $X^{546}_{std}$ and $X^{546}_{u}$. $\delta^{sp}$ of the mixture was determined from analysis of the 456 and 546 concentrations in the
FTIR spectrum using equation (5). Figure 2(a) shows the raw values of \( \delta^{sp} \) as a function of \( Y_{std}^{546} \) for the three runs. In the absence of systematic error these plots should be linear, with the \( Y_{std}^{546} = 1 \) intercept of the linear regression equal to the (known) value of \( \delta_{std}^{sp} \) and the \( Y_{std}^{546} = 0 \) intercept providing the desired quantity, \( \delta_{u}^{sp} \) in each case. In reality instrument effects lead to a significant \( Y_{std}^{546} \)-dependent calibration offset in the raw \( \delta^{sp} \) values and non linearity in the plots, especially above \( Y_{std}^{546} = 0.9 \). These effects and their correction are described next.

During the dilution sequences shown in Figure 2(a), the partial pressure of the 456 and 546 isotopomers in the sample decrease by a factor of 25 from 10% to 0.4% of the total pressure, ie approximately 0.13 to 0.005 hPa. It therefore becomes necessary to calibrate the FTIR analysis to quantify the calibration offset in \( \delta^{sp} \) and its \( p^{546} \) dependence. The ideal way to provide such a \( p^{546} \)-dependent calibration would be the FTIR analysis of a serial dilution of the reference standard of known \( \delta^{sp} \) with \( ^{15} \)N-free N\(_2\)O (446 only) – in this way the true value of \( \delta^{sp} \) is known and does not change, and any apparent a \( p^{546} \)-dependent variation in the measured value of \( \delta^{sp} \) must be due to instrumental effects. This variation could then be used to correct the FTIR response as a function of \( p^{546} \) during the dilution of the unknown mixtures. Unfortunately such truly \( ^{15} \)N-free N\(_2\)O is not available. The \( ^{15} \)N-depleted N\(_2\)O CIL-446 had \( ^{15} \)N reduced below 0.1% as specified by the supplier, but the fractions of 456 and 546 were approximately 0.06 and 0.09% (Table 1), with an effective \( \delta^{sp} \) of -330‰. This gas was therefore not suited to the task of determining any instrument effects.

We therefore quantified the instrument effect in two less ideal ways – by carrying out a dilution sequence of the reference standard with pure CO\(_2\), and by reducing the total
pressure of pure reference standard from 1.33 hPa, to cover the same range of total $^{15}$N amount as in the dilutions with unknown N$_2$O. Neither is ideal because the amount of infrared absorption by 446 decreases during the dilution sequence, whereas it increases slightly in the "real" case of dilution with natural abundance N$_2$O. For ideal spectra, the MALT quantitative analysis should account for this effect exactly, but inevitable inaccuracies in line parameters or non-ideal instrument lineshapes can cause small cross-sensitivities which may affect the retrieved concentrations at the levels of precision required. During dilution with CO$_2$ the total pressure remains at 1.33 hPa throughout the dilution sequence, and if CO$_2$ (with the same mass as N$_2$O) has a similar pressure-broadening effect to that of N$_2$O, spectroscopic effects connected with lineshapes and linewidths should be minimised. However the line broadening coefficients for N$_2$O by CO$_2$ are not known, and we used N$_2$O self-broadening coefficients in the MALT calculation, with consequent uncertainty. During pressure reduction there is no such uncertainty in using self-broadened linewidths - pressure broadening of the absorption lines decreases through the dilution sequence, and while the MALT calculation in principle accurately accounts for this, the result may be susceptible to small errors in line parameters and instrument lineshapes.

Figure 3 shows the results of these instrumental effect measurements, where the raw measured values of $\delta^{sp}$ of the reference standard (which is in reality -7.8‰ and constant) are plotted against the partial pressure of 546 ($p^{546}$) in the sample for pressure reduction sequences (filled squares) and dilution with CO$_2$ (open circles). There is a large overall offset of the raw measured $\delta^{sp}$ of approximately -20 to -28‰ from the known value of -7.8‰ due to these systematic errors. The CO$_2$ and pressure reduction series agree within 2‰ over the entire range. From these data we generated 6$^{th}$ order polynomial correction...
functions (shown as solid and dotted curves in Figure 3) for $\delta^{546}$ as a function of $p^{546}$ for both the CO$_2$ dilution and the pressure reduction separately. These were applied to the raw data for dilutions with unknown working standards WS1 and WS2 shown in Figure 2(a). The difference in final result for the two corrections provides an estimate of the uncertainty introduced by this correction.

Figure 2(b) shows the corrected results for the three dilutions using the CO$_2$ dilution correction; the results using the pressure reduction correction are similar. The nonlinearity evident in Figure 2(a) is largely corrected. The “kick” in the curve at $Y_{std}^{546} > 0.9$ corresponds to $p^{546} > 0.03$ hPa in Figure 3 but does not affect the Y-intercepts significantly. Table 2 shows the values of corrected $\delta^{546}$ from linear regressions to the data at $Y_{std}^{546} = 0$ and $Y_{std}^{546} = 1$ in each case. The $\delta^{546}$ values at $Y_{std}^{546} = 0$ provide the desired results, i.e. $\delta^{546}$ for the unknown working standards WS1 and WS2. The mean of all determinations for WS1 is -0.93 ‰ and for WS2 +28.16‰. The difference, 29.09‰ is in excellent agreement with the value of 29.8‰ determined independently for these same working gases in 2000 by Turatti$^{18}$.

The standard errors of the $Y_{std}^{546} = 0$ intercepts are 0.2‰, to which should be added the uncertainty in the determination of the 10 atom % $^{15}$N standard (-7.8 ± 1.4‰). The uncertainty in the instrument correction function is harder to define. The differences in $\delta^{546}$ values derived using the two corrections are < 0.8‰. The correction shown in Figure 3 is most uncertain at values of $p^{546} > 0.03$ hPa, corresponding to $Y_{std}^{546} > 0.9$ because of the non-linearity of the Y mole fraction scale (Equation 7). Thus the instrument correction uncertainty is high only near the right hand axis of Figure 2(b), as is evident in the plotted points. The $Y_{std}^{546} = 0$ intercept is less sensitive to this uncertainty; we allow a conservative
1.0‰ for this source of error. Adding the three values (0.2, 1.4, 1.0‰) in quadrature gives a total error estimate of 1.8‰ for $\delta^{sp}$ of the working standards.

In the absence of error the $\delta^{sp}$ values at $Y_{std}^{546} = 1$ should all equal the calibrated value of $\delta^{sp}$ for the 10 atom % $^{15}$N reference standard, -7.8 ‰. The measured values differ by 0.5 to 1.2 ‰ from this value and reflect the systematic error in applying the $p^{546}$- dependent corrections, which as noted above is greatest near $Y_{std}^{546} = 1$.

**Comparison of working standard gases**

In 2001, the University of Wollongong (UoW) and Max Planck Institute (MPI) laboratories exchanged N$_2$O working standards, making comparative measurements of $\delta^{sp}$ by FTIR and IRMS techniques. Turatti 18 measured the $\delta^{sp}$ values of three laboratory working standards relative to WS1 by FTIR spectroscopy: WS2 from the present work, MPI-1 from the Max Plank Institute for Chemistry 15, and SNOW, the Standard Nitrous Oxide Working gas of Rahn et al. 27. From these relative measurements and the absolute value of $\delta^{sp}$ determined in this work, we deduce absolute $\delta^{sp}$ values for WS2, MPI-1 and SNOW as +28.2, +2.7 and -4.6‰ respectively. (SNOW is included for completeness because it was the standard gas used in all earlier work at the Scripps Institution of Oceanography.) The relative precision of these values is 1-2‰ due to the older, less precise FTIR spectrometer used at that time. The absolute value of $\delta^{sp}$ for the MPI working gas, +2.7‰ is 22.5‰ lower than the value determined by Kaiser et al. using their isotopic standard addition method, +25.2% 15. This result is discussed further below in the context of tropospheric N$_2$O measurements.

As part of the 2001 intercomparison of working gases, Kaiser also determined the bulk $\delta^{15}N$ of WS1 and WS2 to be -1.8‰ and -0.7‰ relative to atmospheric N$_2$. 

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The $^{15}$N site preference for tropospheric N$_2$O

In the absence of an international standard for the site preference in N$_2$O, tropospheric N$_2$O has acted as the de facto “transfer standard” for site preference intercomparisons since its bulk $\delta^{15}$N and site preference in clean air are expected to be fairly constant in time and space $^{28}$. Table 3 collects published measurements of the site preference of N$_2$O from several laboratories. In addition, we include 13 new measurements of tropospheric N$_2$O collected in relatively clean air at Wollongong and in rural Victoria $^{29}$. In the data from MPI and UC Berkeley, based on the Kaiser et al. calibration, the values marked “corrected” have been adjusted from the published values by -22.5‰ to set them to the absolute calibration scale determined in this work. The results from UoW and Tokyo Institute of Technology (TITech) calibrations are consistent within their uncertainties, while those from the corrected MPI calibration remain systematically higher by 3-4‰. It is more likely that this difference lies in the inaccuracy of the calibration and correction determined from the less precise 2001 FTIR standards intercomparison than that it is due to a real difference in tropospheric isotopic composition.

Conclusions

Using high resolution FTIR spectroscopy, we have derived an absolute calibration of the intramolecular site preference for $^{15}$N fractionation in two working standard gases used in our laboratory. This measurement technique and calibration strategy is completely independent of existing calibrations, which rely on isotope ratio mass spectrometry for the measurement technique. With recent instrument improvements, the FTIR technique provides precision of around 0.1-0.2‰ for the site preference for a 10 minute
measurement. Standard WS1, produced from ammonium nitrate decomposition and provided by BOC gases, had an absolute site preference of -0.9 ± 1.8‰ and, from previous measurement by Kaiser at the Max Planck Institute for Chemistry, a bulk δ^{15}N of -1.8‰ relative to atmospheric N\textsubscript{2}. WS2, produced as a byproduct of adipic acid manufacture and provided by Scott Marrin Specialty gases, had an absolute site preference of +28.2 ± 1.8‰ and a bulk δ^{15}N of -0.7‰ relative to atmospheric N\textsubscript{2}.

Based on this absolute calibration, we obtain an average value of 19.8 ± 2.1‰ for the site preference of N\textsubscript{2}O in 25 samples of N\textsubscript{2}O collected from clean tropospheric air near the ground in SE Australia from 2000 to 2006. Using tropospheric N\textsubscript{2}O as a de facto transfer standard, our calibration is consistent with the original standard of Toyoda et al. \textsuperscript{1}, who found a mean tropospheric site preference of 18.7 ± 2.2‰. Our results support the detailed analysis of Westley et al. \textsuperscript{16} which suggests that the calibration of Kaiser et al. \textsuperscript{15} is in error due to variations in ion chemistry in the IRMS source. We now recommend an inter-laboratory exchange of working standard N\textsubscript{2}O gases as the next step towards providing an international reference standard.

**Acknowledgements**

We wish to thank Fred Turatti for earlier studies on which much of the technique development is based, and Jan Kaiser for his participation in the the 2001 intercomparison of working gas standards. Bob Toth is gratefully acknowledged for providing the extended N\textsubscript{2}O line parameters. This work was supported by the Australian Research Council under grants DP0211606 and LE0668470.
References


(14) Friedman, L.; Bigeleisen, J. *Journal of Chemical Physics* 1950, 18, 1325-1331.


Figure captions

Figure 1. Example fit of a typical N2O spectrum. Lower trace - measured spectrum; dots – fitted spectrum; upper trace - residual (measured-fitted) spectrum. The residual is symmetrical about zero and on the same scale but shifted for clarity.

Figure 2. (a) Raw δ¹⁵N values as a function of Y₅₄₆std for dilution of 10 atom % ¹⁵N reference standard with working gases WS1 (two runs, open and closed circles) and WS2 (crosses). (b) The same data corrected for instrumental effects (see Figure 3 and text). The 1-σ random error in each value of δ¹⁵N is approximately 0.1‰, as described in the text.

Figure 3. Raw values and apparent change in δ¹⁵N as a function of partial pressure of 546 during CO₂ dilution (open circles) and pressure reduction sequences (filled squares) of the 10 atom % ¹⁵N reference standard.
Table 1. Isotopic composition of all N₂O gases used. All isotopologues are measured from the FTIR spectra except 457 and 547, which are not included in the line parameter list used to analyse the spectra. These amounts are assumed to be equal to the fraction of the 456 or 546 isotopologue respectively, multiplied by the natural abundance of $^{17}$O, 0.04%.

<table>
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<tr>
<th>Source gas</th>
<th>446</th>
<th>456</th>
<th>546</th>
<th>448</th>
<th>447</th>
<th>456</th>
<th>458</th>
<th>457</th>
<th>547</th>
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<tr>
<td>CIL-456</td>
<td>0.79</td>
<td>98.49</td>
<td>0.03</td>
<td>0.00</td>
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<td>0.45</td>
<td>0.20</td>
<td>0.00</td>
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<td>0.01</td>
<td>98.93</td>
<td>0.00</td>
<td>0.00</td>
<td>0.42</td>
<td>0.00</td>
<td>0.19</td>
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<tr>
<td>CIL-556</td>
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<td>0.03</td>
<td>-</td>
<td>-</td>
<td>99.74</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CIL-446</td>
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<td>0.09</td>
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<td>-</td>
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<td>-</td>
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</table>
Table 2. Calculated $\delta^{15}P$ values (‰) for the two working standards.

<table>
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<th>$Y_{\text{std}}^{s46} = 0$ intercept</th>
<th>$Y_{\text{std}}^{s46} = 1$ intercept</th>
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<tr>
<td></td>
<td>$\delta^{15}P$ (WS1)</td>
<td>$\delta^{15}P$ (WS1)</td>
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<tr>
<td></td>
<td>#1</td>
<td>#2</td>
</tr>
<tr>
<td>CO$_2$ correction</td>
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<td>Pressure reduction correction</td>
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<td>-1.46</td>
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<tr>
<td>Mean</td>
<td>-0.81</td>
<td>-1.05</td>
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Table 3. Site preference measurements of tropospheric N$_2$O. The quoted uncertainties are the standard deviations of each set of measurements.

* The corrected values for MPI and UC Berkeley has been reduced by 22.5‰ following the recalibration in this work.

<table>
<thead>
<tr>
<th>Laboratory</th>
<th>Tropospheric N$_2$O $\delta^{15}$O /‰</th>
<th>Number of samples (year of measurement)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TITech $^{30}$</td>
<td>+18.7 ± 2.2</td>
<td>17 (1997 – 1999)</td>
</tr>
<tr>
<td>UoW $^{18}$</td>
<td>+19.4 ± 2.0</td>
<td>13 (2000 – 2001)</td>
</tr>
<tr>
<td>UoW – this work</td>
<td>+20.2 ± 2.1</td>
<td>13</td>
</tr>
<tr>
<td>MPI $^{15}$ corrected*</td>
<td>+46.3 ± 1.4</td>
<td>&gt;50 (1998 – 2000)</td>
</tr>
<tr>
<td></td>
<td>+23.8 ± 1.4</td>
<td></td>
</tr>
<tr>
<td>UC Berkley $^{15}$ Corrected*</td>
<td>+45.6 ± 1.4</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td>+23.1 ± 1.4</td>
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</tr>
<tr>
<td>Michigan State $^{31}$</td>
<td>+21.5 ± 2.4</td>
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</tr>
</tbody>
</table>
Figure 1
Figure 2
Figure 3