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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.

Keywords

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Absolute calibration of the intramolecular site preference of ^{15}N fractionation in tropospheric N_2O by FTIR spectroscopy.

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Abstract

Nitrous oxide (N_2O) plays important roles in atmospheric chemistry both as a greenhouse gas and in stratospheric ozone depletion. Isotopic measurements of N_2O 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_2O 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_2O 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_2O 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 [2] and it is the principal source of NO which catalytically destroys ozone in the stratosphere [3]. 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 [4]. This increase is thought to be due mainly to increased microbial production in soils following increased use of nitrogen fertilisers in agriculture [4]. Resolving the significant uncertainties in the global N_2O budget is aided by isotopic measurements of atmospheric N_2O. Moore [5] and Kim and Craig [6, 7] first recognized that the bulk ^{15}N and ^{18}O fractionation in tropospheric N_2O (+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_2O 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_2O, 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_2O [8-11]

An international standard N_2O 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 N_2O 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 N_2O standard by thermal decomposition of NH_4NO_3 of known isotopic composition – NH_4NO_3 is known to decompose with the NH_4^+ -N exclusively in the terminal position, and the NO_3^- -N in the central position [14]. Kaiser et al. used a standard addition technique using doubly-labelled $^{15}N_2O$ [15] to calibrate their working standard. Based on their respective calibrations, Toyoda et al. and Kaiser et al. found average northern hemisphere tropospheric N_2O 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 N_2O 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 NH_4NO_3-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 N_2O 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 N_2O gas phase spectra thus provides an analytical method for determining complete isotopic composition of N_2O. In our previous work with FTIR spectroscopy[8, 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 ^{15}N isotopomer fractionations and 0.1‰ for the site preference. In this paper we provide an absolute calibration of our working laboratory standard N_2O gas which is completely independent of those of Toyoda, Kaiser and Westley et al. Absolute measurements of tropospheric N_2O 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 N_2O: 446 = $^{14}N^{14}N^{16}O$, 456 = $^{14}N^{15}N^{16}O$, 546 = $^{15}N^{14}N^{16}O$, etc. Thus 456 represents N_2O with ^{15}N 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 recommendations [20, 21] with symbol *X* referring to isotopic abundances and *R* referring to isotopic ratios to define

$$X^{456} = \frac{[456]}{[\Sigma N_2O]} \quad X^{546} = \frac{[546]}{[\Sigma N_2O]}$$
$$R^{456} = \frac{[456]}{[446]} \quad R^{546} = \frac{[546]}{[446]} \quad R^{sp} = \frac{[456]}{[546]} \qquad (1)$$

In delta notation, the bulk ^{15}N and site preference of 456 relative to 546 are respectively

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

where the square brackets represent the concentration or amount of an isotopomer or isotopologue in a sample, and [ΣN_2O] is the sum of all isotopologues in that sample. (For simplicity we ignore the contribution of the 556 isotopologue.) R^{15}_{std} is the $^{15}N/^{14}N$ 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. $R^{sp}_{std} = 1$, or equivalently $\delta^{sp}_{std} = 0$. In this paper, R^{sp} and δ^{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 [8, 13] 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 nth expansion the pressure P_n is $P_n = P_0\gamma^n$ where γ 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_2O 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_2O isotopologues. The computer model (MALT - Multiple Atmospheric Layer Transmission) is described in detail by Griffith [22], 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_2O 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 [23-25] 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_2O 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 [26] 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 ν_3 vibration band of N_2O.

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.

N_2O gases

Two N_2O 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 N_2O (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 ^{15}N isotopic abundance of 0.366 %) and bulk $\delta^{15}N$ of -1.8 ‰ relative to atmospheric N_2. 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 N_2O working standard (WS2) was high purity (>99.9%) N_2O sourced from

Scott-Marin Specialty Gases (California, USA). Turatti showed this N_2O to be enriched in 456 relative to 546 with a δ^{sp} value of +29.8 ±1.8 ‰ relative to WS1. This N_2O 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_2O 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 ±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_2O 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_2O gases as determined by these analyses. The relative uncertainty (1σ) 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_2O-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 N_2O 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 N_2O (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 N_2O) 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%

(0.4‰) for aliquot amounts.

The isotopic composition of the 10 atom % ^{15}N reference standard was calculated to be 10.034 ± 0.011% 456, 10.112 ± 0.011% 546 and δ^{sp} = -7.8 ± 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 δ^{sp}.

Outline of the calibration method

The δ^{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_2O of accurately known absolute site preference and approximately 10 atom % ^{15}N was prepared.
2. The N_2O reference standard was serially diluted with the N_2O of unknown site preference and the site preferences R^{sp} (equivalently δ^{sp}) of the resulting mixtures were determined. Extrapolation of the dilution curve of measured δ^{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^{sp} or δ^{sp} of the mixture as the standard is diluted with the unknown. Let

$p^{456(546)}$ = the partial pressure of 456(546) in the mixture

p_{std} = the partial pressure of reference standard in the mixture

p_u = the partial pressure of unknown in the mixture

p_T = total pressure of the mixture

Y_{std} = p_{std}/p_T = 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^{sp} is

$$R^{sp} = \frac{p^{456}}{p^{546}} = \frac{X_{std}^{456}.Y_{std} + X_u^{456}.(1-Y_{std})}{X_{std}^{546}.Y_{std} + X_u^{546}.(1-Y_{std})} \qquad (3)$$

Substituting $X_{std}^{456} = R_{std}^{sp} \cdot X_{std}^{546}$ and $X_u^{456} = R_u^{sp} \cdot X_u^{546}$ we obtain an expression for R^{sp} as a function of Y_{std} and the site preference ratios of the standard and unknown gases:

$$R^{sp} = \frac{(R_{std}^{sp}.X_{std}^{546} - R_u^{sp}.X_u^{546}).Y_{std} + R_u^{sp}.X_u^{546}}{(X_{std}^{546} - X_u^{546}).Y_{std} + X_u^{546}} \qquad (4)$$

However this expression is strongly non linear as $Y_{std} \to 0$ in the present case where

$X_{std}^{546} >> X_u^{546}$ – 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

$$R^{sp} = R_{std}^{sp}.Y_{std}^{546} + R_u^{sp}.(1-Y_{std}^{546}) \quad (5)$$

where

$$Y_{std}^{546} = \frac{p_{std}^{546}}{p_{std}^{546} + p_u^{546}} \quad (6)$$

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 $Y_{std}^{546} = 1$ intercept equal to the known R_{std}^{sp} and the $Y_{std}^{546} = 0$ intercept equal to the desired unknown quantity, R_u^{sp}. Y_{std}^{546} can be calculated for each dilution step from the measured pressures and the known values of R_{std}^{546} and R_u^{546} – with sufficient accuracy, R_{std}^{546} and R_u^{546} 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_{std}^{546} linearises the dilution curve of R^{sp} *vs* mole fraction (equation 5). Y_{std} and Y_{std}^{546} are related by

$$Y_{std}^{546} = \frac{Y_{std}}{\left(1-\frac{X_u^{546}}{X_{std}^{546}}\right)Y_{std} + \frac{X_u^{546}}{X_{std}^{546}}} \approx \frac{Y_{std}}{0.963 \cdot Y_{std} + 0.037} \quad (7)$$

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_{std}^{546} was calculated using equation (6 $Y_{std}^{546} = \frac{p_{std}^{546}}{p_{std}^{546} + p_u^{546}}$ $Y_{std}^{546} = \frac{p_{std}^{546}}{p_{std}^{546} + p_u^{546}}$) from the measured initial pressure, calibrated expansion ratio, and the known values of X_{std}^{546} and X_u^{546}. δ^{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 δ^{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 δ_{std}^{sp} and the $Y_{std}^{546} = 0$ intercept providing the desired quantity, δ_{u}^{sp} in each case. In reality instrument effects lead to a significant Y_{std}^{546}–dependent calibration offset in the raw δ^{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 δ^{sp} and its p^{546} (or Y_{std}^{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 δ^{sp} with ^{15}N-free N_2O (446 only) – in this way the true value of δ^{sp} is known and does not change, and any apparent a p^{546}-dependent variation in the measured value of δ^{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_2O is not available. The ^{15}N-depleted N_2O 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 δ^{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 1.33hPa, to cover the same range of total ^{15}N amount as in the dilutions with unknown N_2O. 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_2O. 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_2O) has a similar pressure-broadening effect to that of N_2O, spectroscopic effects connected with lineshapes and linewidths should be minimised. However the line broadening coefficients for N_2O by CO_2 are not known, and we used N_2O 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 δ^{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 δ^{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 6th order polynomial correction

functions (shown as solid and dotted curves in Figure 3) for δ^{sp} 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 δ^{sp} from linear regressions to the data at $Y_{std}^{546} = 0$ and $Y_{std}^{546} = 1$ in each case. The δ^{sp} values at $Y_{std}^{546} = 0$ provide the desired results, i.e. δ^{sp} 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 δ^{sp} 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 δ^{sp} of the working standards.

In the absence of error the δ^{sp} values at $Y_{std}^{546} = 1$ should all equal the calibrated value of δ^{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_2O working standards, making comparative measurements of δ^{sp} by FTIR and IRMS techniques. Turatti [18] measured the δ^{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 δ^{sp} determined in this work, we deduce absolute δ^{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 δ^{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_2O 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.

The ^{15}N site preference for tropospheric N_2O

In the absence of an international standard for the site preference in N_2O, tropospheric N_2O 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_2O from several laboratories. In addition, we include 13 new measurements of tropospheric N_2O 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 $\delta^{15}N$ of -1.8‰ relative to atmospheric N_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 $\delta^{15}N$ of -0.7‰ relative to atmospheric N_2.

Based on this absolute calibration, we obtain an average value of 19.8 ± 2.1‰ for the site preference of N_2O in 25 samples of N_2O collected from clean tropospheric air near the ground in SE Australia from 2000 to 2006. Using tropospheric N_2O as a de facto transfer standard, our calibration is consistent with the original standard of Toyoda et al. [1], who found a mean tropospheric site preference of 18.7 ± 2.2‰. Our results support the detailed analysis of Westley et al. [16] which suggests that the calibration of Kaiser et al. [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_2O gases as the next step towards providing an international reference standard.

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Figure captions

Figure 1. Example fit of a typical N_2O 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 δ^{sp} values as a function of Y_{std}^{546} for dilution of 10 atom % ^{15}N 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 δ^{sp} is approximately 0.1‰, as described in the text.

Figure 3. Raw values and apparent change in δ^{sp} as a function of partial pressure of 546 during CO_2 dilution (open circles) and pressure reduction sequences (filled squares) of the 10 atom % ^{15}N reference standard.

Tables

Table 1. Isotopic composition of all N_2O 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%.

Source gas	446	456	546	448	447	556	458	548	457	547
CIL-456	0.79	98.49	0.03	0.00	0.00	0.45	0.20	0.00	(0.04)	-
CIL-546	0.41	0.01	98.93	0.00	0.00	0.42	0.00	0.19	-	(0.04)
CIL-556	0.00	0.23	0.03	-	-	99.74	-	-	-	-
CIL-446	99.85	0.06	0.09	-	-	-	-	-	-	-

Table 2. Calculated δ^{sp} values (‰) for the two working standards.

	$Y_{std}^{546} = 0$ intercept			$Y_{std}^{546} = 1$ intercept		
	δ^{sp} (WS1) #1	δ^{sp} (WS1) #2	δ^{sp} (WS2) #3	δ^{sp} (10 atom % ^{15}N ref standard) #1	#2	#3
CO_2 correction	-0.45	-0.64	+28.50	-9.25	-9.46	-9.92
Pressure reduction correction	-1.17	-1.46	+27.83	-8.29	-8.45	-8.96
Mean	-0.81	-1.05	+28.16	-8.77	-8.95	-9.44

Table 3. Site preference measurements of tropospheric N_2O. 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 re-calibration in this work.**

Laboratory	Tropospheric N_2O δ^{sp} / ‰	Number of samples (year of measurement)
TITech [30]	+18.7 ± 2.2	17 (1997 – 1999)
UoW [18]	+19.4 ± 2.0	13 (2000 – 2001)
UoW – this work	+20.2 ± 2.1	13
MPI [15] corrected*	+46.3 ± 1.4 +23.8 ± 1.4	>50 (1998 – 2000)
UC Berkley [15] Corrected*	+45.6 ± 1.4 +23.1 ± 1.4	75
Michigan State [31]	+21.5 ± 2.4	3

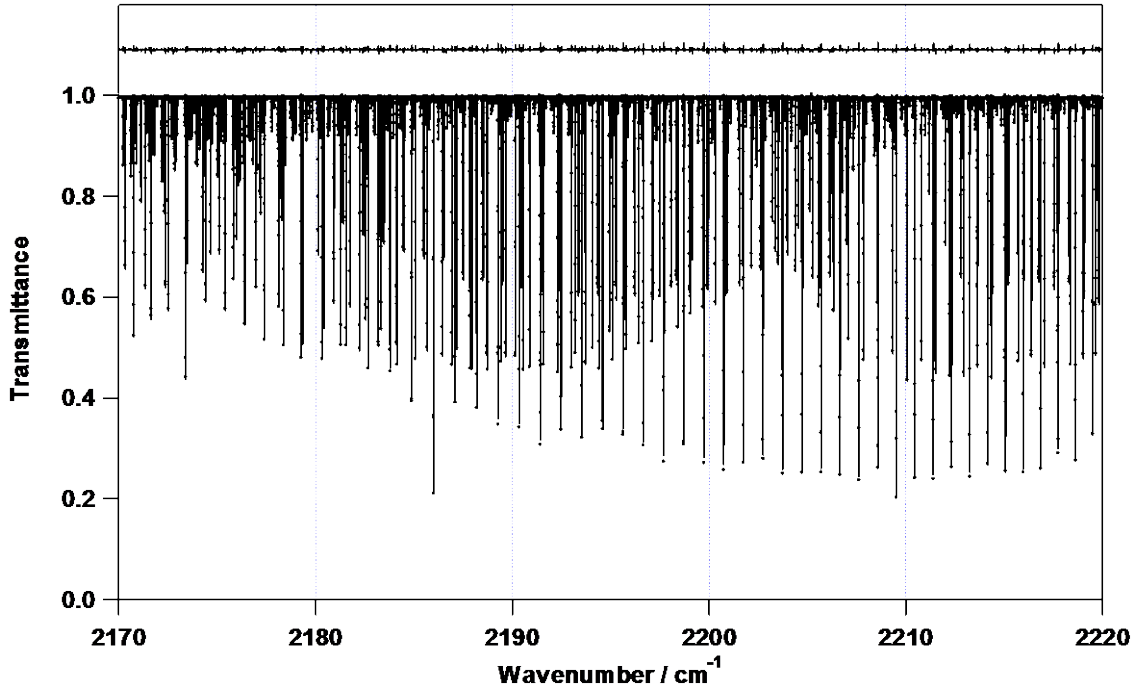
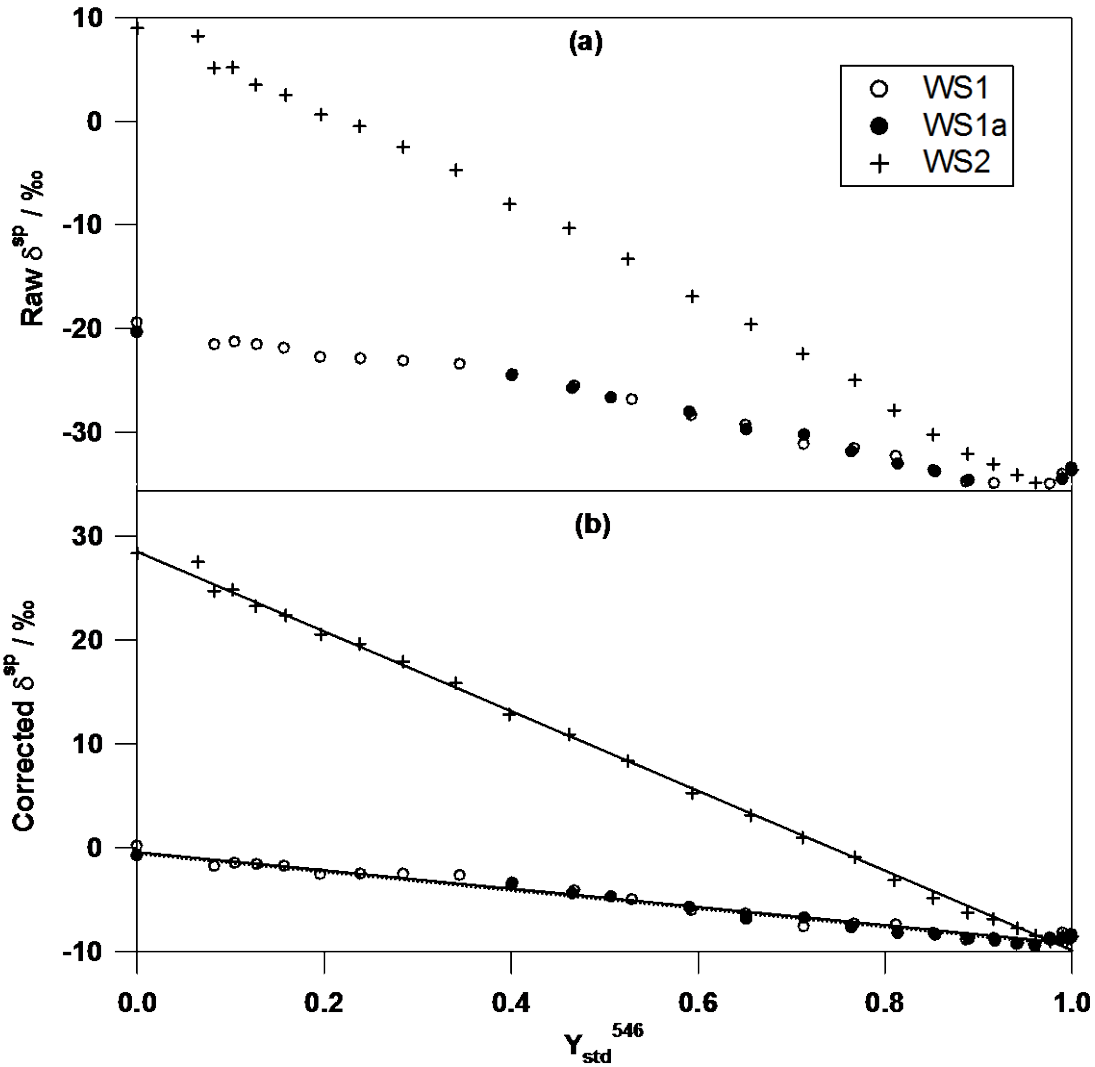

1.0
0.8
0.6
0.4
0.2
0.0
Transmittance
2170
2180
2190
2200
2210
2220
Wavenumber / cm-1

Figure 1


(a)
WS1
WS1a
WS2
Raw δ^sp / ‰
10
0
-10
-20
-30
(b)
Corrected δ^sp / ‰
30
20
10
0
-10
0.0
0.2
0.4
0.6
0.8
1.0
Y_std^546

555

Figure 2

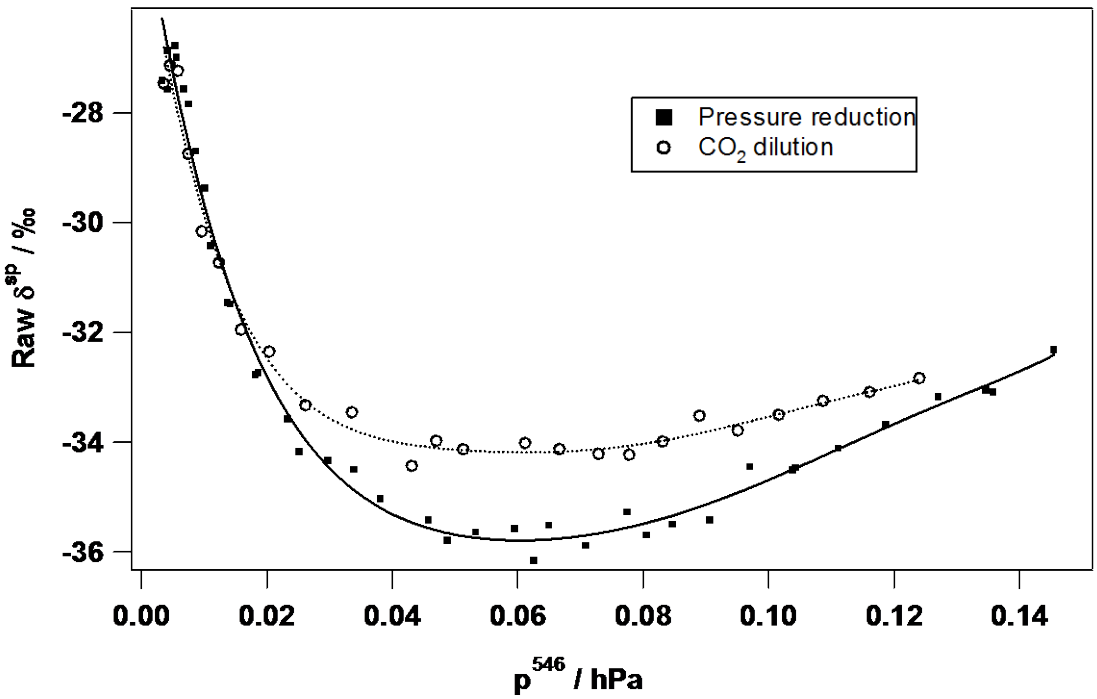

Pressure reduction
CO2 dilution
Raw δ^sp / ‰
-28
-30
-32
-34
-36
0.00
0.02
0.04
0.06
0.08
0.10
0.12
0.14
p^546 / hPa

Figure 3