The NOAA nitrous oxide standard scale for atmospheric observations

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[1] A new nitrous oxide (N_2O) calibration scale has been developed for atmospheric observations. The NOAA-2006 N_2O scale is based on gravimetrically prepared compressed gas standards. This scale supercedes the NOAA-2000 scale, which was accepted by the community of experts within the World Meteorological Organization Global Atmosphere Watch program (GAW) as the GAW reference standard. The new scale is defined by thirteen "daughter" standards with dry air mole fractions ranging from $261-371$ parts-per-billion (nmol mol^{-1}, ppb). These were derived from four part-per-million (mmol mol^{-1}, ppm) level "parents". Standards were evaluated using gas chromatography with electron capture detection. The daughter standards are internally consistent with a standard deviation of residuals of 0.33 ppb, and there is essentially no detectable difference among "cousins" (standards prepared from different parents). The NOAA-2006 scale is 0.19 ppb lower than the NOAA-2000 scale at 320 ppb. The global mean N_2O mixing ratio (dry air mole fraction), calculated from in situ observations at five monitoring sites was 318.46 ppb in 2004 on the new scale. The NOAA-2006 scale compares well with other scales based on comparisons of compressed gas standards. The NOAA-2006 scale is, on average, 0.23% higher than that defined by NIST Standard Reference Materials 2608 and 2609, and an average of 0.01% lower than the Scripps Institution of Oceanography SIO-98 scale over the range $298-319$ ppb.

1. Introduction

[2] Nitrous oxide (N_2O) is a long-lived trace gas that plays important roles in stratospheric ozone chemistry and climate forcing. It has a global warming potential that is 300 times that of CO_2 over a 100-yr timescale [*Intergovernmental Panel on Climate Change (IPCC)*, 2001]. The atmospheric abundance has increased markedly from $\sim$270 ppb in pre-industrial times to nearly 320 ppb today [*Battle et al.*, 1996] and continues to increase at a rate of $0.2-0.3\%$ yr^{-1} [*Prinn et al.*, 2000; *Thompson et al.*, 2004]. At this rate the atmospheric abundance would reach $\sim$400 ppb by 2100.

[3] The dominant source of N_2O is microbial activity. The increase in tropospheric N_2O from the preindustrial era to present is thought to be related to changes in agricultural practices (food production) [*Nevison and Holland*, 1997; *Kroeze et al.*, 1999]. Other sources include biomass burning, oceanic production, gas-phase oxidation of NH_3, and industrial sources such as adipic acid and nitric acid production. The dominant sinks are photo-dissociation (90%) and reaction with O(^{1}D) (10%) in the stratosphere. Although recent studies [*IPCC*, 2001; *Kroeze et al*, 1999]

suggest that the atmospheric growth rate can be explained by known sources and sinks, the distribution of sources is difficult to quantify. Furthermore, the impacts of climate change on N_2O sources are uncertain.

[4] Tropospheric measurements performed by numerous laboratories around the world are key to understanding the distribution and behavior of N_2O sources. Through precise, calibrated measurements, inverse studies are beginning to shed light on key features in the N_2O budget [*Prinn et al.*, 1990; *Hirsch et al.*, 2006]. Thus far, however, inverse studies have been based on limited data obtained through isolated networks. Integrated data sets from multiple institutions have been underutilized primarily for lack of harmonized calibration scales.

[5] The first step in obtaining a global, integrated database is the establishment of a stable and consistent calibration scale. The NOAA-2000 N_2O scale, developed by the Global Monitoring Division (GMD) (formerly the Climate Monitoring and Diagnostics Laboratory) of the NOAA Earth System Research Laboratory was accepted by the community of experts within the World Meteorological Organization (WMO) Global Atmosphere Watch (GAW) program as the GAW N_2O mole fraction scale. NOAA/GMD serves as the GAW Central Calibration Laboratory for nitrous oxide, carbon dioxide, carbon monoxide, and methane. Here we describe the development and maintenance of the NOAA-2000 N_2O scale and conversion to the recently developed NOAA-2006 scale. We also present comparison results between the NOAA-2006 scale and two existing

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Table 1. Five ppm-Level Standards Prepared From Reagent-Grade N_2O

Number	Cylinder	Year	N_2O, ppm	Uncertainty[a], %
1	FF-30132	1990	1229.1	0.12
2	FF-30500	2000	2349.1	0.30
3	FF-39460	2000	1625.7	0.47
4	FA-2128	2002	1460.7	0.08
5	FA-2553	2005	1570.5	0.08

[a]Propagated weighing uncertainty (1σ).

scales: the SIO-98 scale developed by the Scripps Institution of Oceanography (SIO), and Standard Reference Materials 2608 and 2609 (no longer available), developed by the National Institute for Standards and Technology (NIST).

2. Experiment

2.1. Preparation of Compressed Gas Standards

[6] Most trace gas measurements made by GMD (CO_2 and ozone are two exceptions) are referenced to gravimetrically prepared compressed gas standards [*Novelli et al.*, 1991; *Montzka et al.*, 1993; *Thompson et al.*, 2004, *Dlugokencky et al.*, 2005, see also http://www.cmdl.noaa.gov/hats/standard/index.html]. We define gravimetrically prepared standards as primary standards. Secondary standards are those that are related to primary standards through analysis. Standards that are related to secondaries through analysis are tertiary standards, and so on. We define a scale by a unique set of primary standards. Thus, a change in the set of standards used to define the scale constitutes a change in scale.

[7] The preparation of compressed gas N_2O standards by static gravimetric dilution is similar to that described by *Dlugokencky et al.* [2005] and *Novelli et al.* [1991]. Briefly, aliquots of N_2O were transferred to aluminum cylinders and diluted to ppm levels with ultra-pure synthetic (zero) air. Subsequent dilution to ppb levels was performed. The sizes and surface treatments of cylinders have varied over the years. All standards prepared since 2000 have been prepared in 5.9-L aluminum cylinders (Luxfer, Riverside, CA; Scott-Marrin Inc., Riverside, CA) with brass, packless valves with metal seats and metal stems (Ceodeux, Luxembourg).

[8] In 2000, two ppm-level primary standards were prepared from 99.9+% N_2O (Scott Specialty Gases, Plumsteadville, PA) by static dilution (Table 1). Aliquots of N_2O (2−3 g) were transferred to 150-cm^3 stainless steel tubes with all-metal (Nupro) valves. Each tube was first weighed evacuated (~15 mtorr), and then with the added N_2O, on a dual-pan analytical balance (Voland, 0.001 g readability) relative to a tare tube of similar construction. The contents of the tubes were transferred using a vacuum manifold to evacuated cylinders which had also been weighed on the Voland relative to a tare cylinder of similar volume and density. Synthetic zero air (no argon) was used to transfer the N_2O from the single-valve tubes into the evacuated cylinder by alternately pressurizing and depressurizing the tubes, thus flushing the contents into the evacuated cylinder. The transfer efficiency of this technique was evaluated by measuring the N_2O remaining in the tube. We measured the transfer efficiency for a 50-cm^3 tube filled with 2.2 g 1571 ppm N_2O in air to be 99.99998%. The efficiency for a 150-cm^3 tube was not measured, but was assumed to be similar. Following the addition of the N_2O, 800−900 g of synthetic zero air was added. Impurities in the zero air were removed by passing it through synthetic activated carbon (Ambersorb) and molecular sieve 13X. The molecular weight of the zero air was determined by measuring the oxygen content with a Beckman E2 oxygen analyzer. Since 1986, all measurements made using this device have been referenced to a single synthetic zero air mixture (21.55% O_2), which in turn was calibrated against dry natural air (20.95% O_2) [*Seinfeld and Pandis*, 1998].

[9] The purity of the N_2O was examined by GC-MS. No significant impurities were detected other than a trace of O_2 (approximately 30 ppm). We tested for the presence of noncondensables by freezing the N_2O aliquot (−197°C) and pumping off the noncondensable vapors. Any fraction of noncondensables likely was negligible since we were unable to detect a change in mass during this procedure. The concentrations (dry air mole fraction) of the ppm-level standards were computed based on the masses of N_2O and air added, assuming that the N_2O was pure. Buoyancy corrections were applied, although these corrections are small (−0.012%) [*Schoonover and Jones*, 1981].

[10] Several ppb-level standards (daughters) were prepared from the ppm-level parents. In 2000, 13 daughters were prepared from two of the three existing ppm-level standards. Carbon dioxide (Airco) and sulfur hexafluoride (Scott Specialty Gases) were added to these standards. CO_2 was added to reduce the effects of chromatographic interaction between N_2O and CO_2 (discussed later). SF_6 was added because we typically analyze N_2O and SF_6 on the same instrument. Each daughter standard was prepared by weighing 0.1−0.2 g of ppm-level N_2O in a 5-cm^3 stainless steel tube fitted with a single Nupro valve. Weighing was performed on an electronic balance (Mettler AE201, 0.00001-g readability). Aliquots of N_2O, CO_2, and SF_6 were transferred to evacuated 5.9-L cylinders in a similar manner to that described above. The purity of the pure CO_2 was assessed by GC-MS. No significant impurities were found. Because the amount of CO_2 added was large compared to the amount of N_2O, even small levels of N_2O in the CO_2 would bias the results. The mixing ratio of N_2O in the pure CO_2 was determined (by GC-ECD) to be <3 ppb, which is not enough to affect the results.

[11] Prior to 2000, the zero air used to prepare the ppb-level standards was scrubbed using Ambersorb and molecular sieve 13× (at 20°C). In 2000, a second set of scrubbers (molecular sieve 13× and activated charcoal, at 0°C) was added. The zero air was sourced from Air Products (Phoenix, AZ) and Linweld (Lincoln, NE). In general, the Linweld zero air was cleaner than the Air Products air. The Linweld zero air typically contained <0.3 ppb N_2O, while the Air Products zero air often contained 0.5−1.0 ppb N_2O. These small amounts of N_2O were easily removed by the scrubbers, in most cases. We have attempted to prepare standards in ultrapure natural air instead of synthetic air, but we have been unable to consistently remove all residual N_2O from natural air. Even highly purified natural air (Scott-Marrin, Inc.) typically contains 3−10 ppb N_2O and this amount can break through scrubbers and bias the results. We have no reason to believe the absence of argon in the primary standards would affect the results, but we have not tested for such an effect.

Table 2. Characteristics of 17 Gravimetric Standards That Define the NOAA-2000 N_2O Scale

Daughter Standard	Parent No.[a]	Year	N_2O, ppb	Uncertainty[b], %	CO_2, ppm	Response[c]	Standard Deviation, %	Assigned[d], ppb	Residual, ppb
ALM-38408[e]	1	1993	96.2	0.75	337	0.3944	0.37	96.3	0.1
ALM-26738[e]	1	1993	172.2	0.52	355	0.6196	0.04	171.9	−0.3
ALM-26743[e]	1	1993	330.7	0.48	370	1.0362	0.03	328.2	−2.5
ALM-26737[e]	1	1993	359.9	0.50	403	1.1063	0.08	357.2	−2.7
FA-1861	2	2000	261.0	0.31	360	0.8653	0.10	261.1	0.1
FA-1856	2	2000	123.2	0.48	253	0.4733	0.16	122.2	−1.0
FA-1878	2	2000	314.2	0.31	363	1.0015	0.06	314.2	0.0
FA-1843	3	2000	331.1	0.48	377	1.0448	0.12	331.7	0.6
FA-1850	3	2000	315.7	0.48	370	1.0050	0.10	315.6	−0.1
FA-1851	3	2000	301.9	0.48	362	0.9715	0.15	302.2	0.3
FA-1865	3	2000	288.0	0.47	363	0.9372	0.10	288.8	0.8
FF-30512	3	2000	333.8	0.47	359	1.0537	0.06	335.4	1.6
FF-30501	3	2000	344.2	0.48	334	1.0757	0.09	344.4	0.2
FF-30498	3	2000	242.5	0.48	330	0.8159	0.09	242.5	0.0
FF-32812	3	2000	290.8	0.47	342	0.9450	0.02	291.8	1.0
FF-30505	3	2000	300.6	0.48	333	0.9682	0.08	300.9	0.3
FF-30499	3	2000	312.9	0.48	333	0.9997	0.05	313.5	0.6

[a]From Table 1.
[b]Propagated weighing uncertainty (1σ).
[c]Mean response (N_2O peak height normalized to that of a 313.45-ppb secondary standard).
[d]Based on least squares regression of mean response versus prepared mixing ratio.
[e]29.5-L Aculife-treated aluminum cylinder (Scott Specialty Gases, Plumsteadville, PA).

[12] Seventeen parts-per-billion level N_2O standards (13 prepared in 2000 along with 4 prepared in 1993) were used to define the NOAA-2000 N_2O scale (Table 2). By 2003, some of these 17 standards were nearing the end of their useful lives and needed to be replaced. Two additional ppm-level standards were prepared in 2002 and 2005. For these more recent standards, 50-cm^3 tubes were used for the N_2O aliquots. These tubes were weighed using electronic balances (Mettler Toledo PM400 and PR1200, 0.001 g readability) instead of the Voland balance. The precision of mass determinations using the Voland balance, used to prepare FF-30500 and FF-39460, was the determining factor in the uncertainties for these standards and their offspring (Tables 1 and 2). By using the electronic balances instead of the Voland, we were able to reduce the weighing uncertainties of this dilution step by a factor of three to six compared to the 2000 standards. Although the readability of the Voland is 0.001 g, the actual weighing precision (1 SD) is typically 0.004 g. Thus the

uncertainty in determining the mass of N_2O in this first step in the dilution process is 0.3–0.5%. With the electronic balances this uncertainty is <0.1%. Seven daughter standards were prepared in 2003 and 2005 from the newer ppm-level parents (Table 3). In 2003 and 2005, the secondary scrubbers were held at −78°C, which greatly enhances their ability to hold N_2O and SF_6.

2.2. Analysis

[13] Analysis of nitrous oxide was performed using an Agilent 6890 gas chromatograph with an electron capture detector (Agilent Technologies, Santa Clara, CA). Separation was achieved using a Porapak-Q packed column (80/100 mesh, Waters Associates, Milford, MA) (2 m × 3.7 mm I.D., 3/16 in. O.D. precolumn, 3 m × 3.7 mm I.D. main column). The carrier gas was ultrahigh purity nitrogen, purified using activated charcoal (to remove hydrocarbons and SF_6) and a heated cartridge (to remove oxygen) (Supelco, Bellefonte,

Table 3. Characteristics of 13 Gravimetric Standards That Define the NOAA-2006 N_2O Scale

Daughter Standard	Parent No.[a]	Year	N_2O[b], ppb	Uncertainty[c], %	CO_2, ppm	Response[d]	Standard Deviation, %	Assigned[e], ppb	Residual, ppb
FA-1861	2	2000	261.30	0.31	360	0.85410	0.040	261.20	−0.10
FA-1878	2	2000	314.66	0.31	363	0.98985	0.027	314.04	−0.62
FA-1843	3	2000	331.34	0.48	377	1.03363	0.038	331.57	0.23
FA-1850	3	2000	315.98	0.48	370	0.99396	0.040	315.68	−0.30
FA-1851	3	2000	302.12	0.48	362	0.95997	0.041	302.22	0.10
FA-1865	3	2000	288.29	0.48	363	0.92591	0.055	288.88	0.59
FA-2205	4	2003	315.39	0.10	364	0.99327	0.024	315.40	0.01
FA-2207	4	2003	333.01	0.10	362	1.03852	0.032	333.54	0.53
FA-2208	4	2003	357.33	0.10	361	1.09716	0.037	357.46	0.13
FA-2557	5	2005	291.36	0.10	367	0.93236	0.026	291.39	0.03
FA-2567	5	2005	320.98	0.11	380	1.00740	0.041	321.04	0.06
FA-2569	5	2005	336.08	0.10	377	1.04412	0.046	335.81	−0.27
FA-2585	5	2005	371.37	0.10	380	1.13049	0.023	371.27	−0.10

[a]From Table 1.
[b]2000 standards have been corrected for error in calculation (see text).
[c]Propagated weighing uncertainty (1σ).
[d]Mean response (N_2O peak area normalized to that of a 318.08-ppb secondary standard).
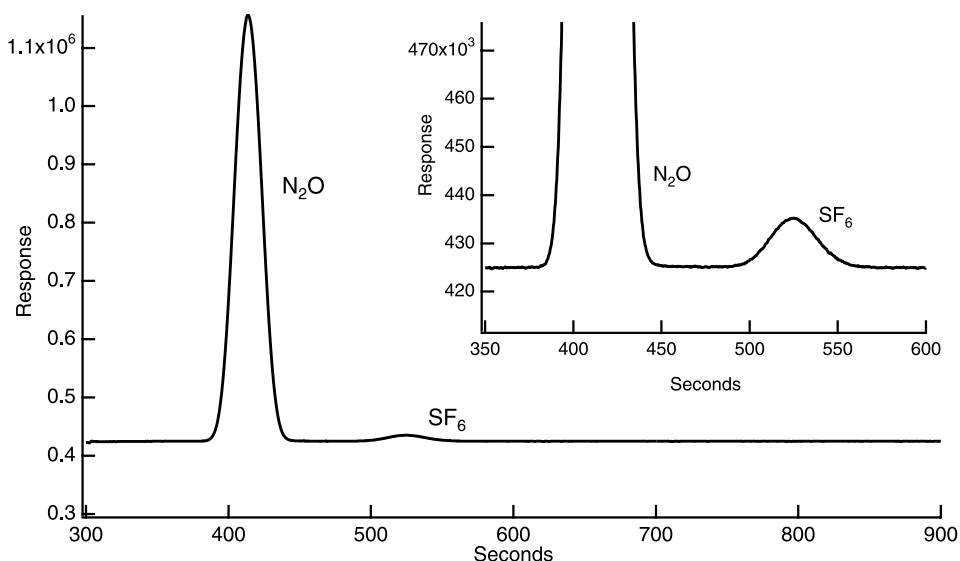[e]Based on orthogonal distance regression of mean response versus prepared mixing ratio.

Figure 1. Typical chromatogram showing detection of N_2O and SF_6 by electron capture detection.

PA). A small flow ($\sim$0.1 cm^3/min) of CO_2 (99.99%, Scott Specialty Gases) was added to the main column flow upstream of the ECD. The CO_2 acts as a dopant and takes the place of CH_4 when N_2 is used as a carrier gas instead of the customary 5% CH_4 in argon (P5) [*Moore et al.*, 2003]. Without a dopant added to the N_2 carrier gas, the ECD response to N_2O would be minimal [*Fehsenfeld et al.*, 1981]. The CO_2 flow rate was controlled using a pressure regulator and a restriction (a crimped stainless steel tube, 1.59 mm O.D. (1/16 in.), 0.127 mm I.D.). The CO_2 flow rate was set by maximizing the N_2O response as a function of the pressure on the restriction. The crimped tube was mounted inside a 2.16-mm I.D. tube and placed in the column oven to ensure thermal and mechanical stability. Previous GC-ECD systems used for N_2O analysis in our laboratory employed P5 as carrier gas. Although the P5-based systems performed well at times, the quality of the P5 limited the long-term performance of these systems. We often observed large changes in the ECD response to N_2O following a change in P5. These changes could be "calibrated out" to a large degree, but contributed to higher uncertainties for these instruments. Over the last 3 years, the current system has performed exceptionally well using CO_2-doped N_2 carrier gas.

[14] A 12-port gas sample valve (Valco Instrument Company Inc., Houston, TX) was used to inject the samples onto the columns in front-cut mode such that the air peak did not elute to the ECD [*Elkins et al.*, 1996]. The column oven temperature was 56°C and the ECD temperature was 340°C. Main and backflush carrier gas flows were 40 cm^3 min^{-1}. The sample volume was 9 cm^3. Sample volumes this large are not necessary for N_2O (1–2 cm^3 is sufficient); they were used to obtain sufficient signals for SF_6. The typical precision (one standard deviation) for a 320-ppb sample (eight injections) was 0.037%, or 0.12 ppb.

[15] In this configuration, N_2O elutes at 410 s followed by SF_6 at 515 s (Figure 1). Carbon dioxide elutes prior to N_2O (355 s), and is well separated from N_2O. Interferences between CO_2 and N_2O are minimized through CO_2 doping. The noninterference of CO_2 and N_2O was confirmed on the current GC and on an older GC that used P5 carrier gas by

comparing air with and without CO_2 (removed using Ascarite). The effect of CO_2 on N_2O is negligible in the current system. On the P5-based system, it was 0.005 ppb N_2O per ppm CO_2, which would amount to 0.25 ppb N_2O for a 50-ppm difference in CO_2 between an unknown and a secondary standard.

3. Discussion
3.1. Scale Definitions

[16] We define a calibration scale by a specific set of standards and their assigned mixing ratios. The set of 17 standards that define the NOAA-2000 scale is shown in Table 2. The response of each standard was measured relative to a secondary standard consisting of dried, natural air, obtained at Niwot Ridge, Colorado, in a 29.5-L aluminum cylinder. A second order polynomial (response curve) was fitted to the normalized peak height. From the least squares fit, we assigned mixing ratios to each standard. The differences between the assigned mixing ratios and the prepared mixing ratios provide an indication of how well we can prepare gravimetric standards. The standard deviation of residuals is 1.15 ppb for the standards that define the NOAA-2000 scale. Although the propagated weighing uncertainties of many of the standards prepared in 1993 and 2000 are large, the residuals are relatively small. This suggests that the propagated weighting uncertainties are a conservative estimate of the total uncertainty associated with standard preparation. Two of the 1993 standards do not agree with the others, however. The assigned values of ALM-26743 and ALM-26737 are 2.5 and 2.7 ppb lower than the prepared values. These standards are also inconsistent with other related standards for other gases, such as CCl_2F_2, suggesting that there may have been some inconsistencies in their preparation.

[17] Three other standards (FF-30512, FF-32812, and FA-1856) also show relatively poor agreement with the others, although the residuals for both of these are within the uncertainties. One potential source of bias is the possibility of N_2O in the synthetic zero air. Samples of zero air were taken off the manifold before and after the preparation
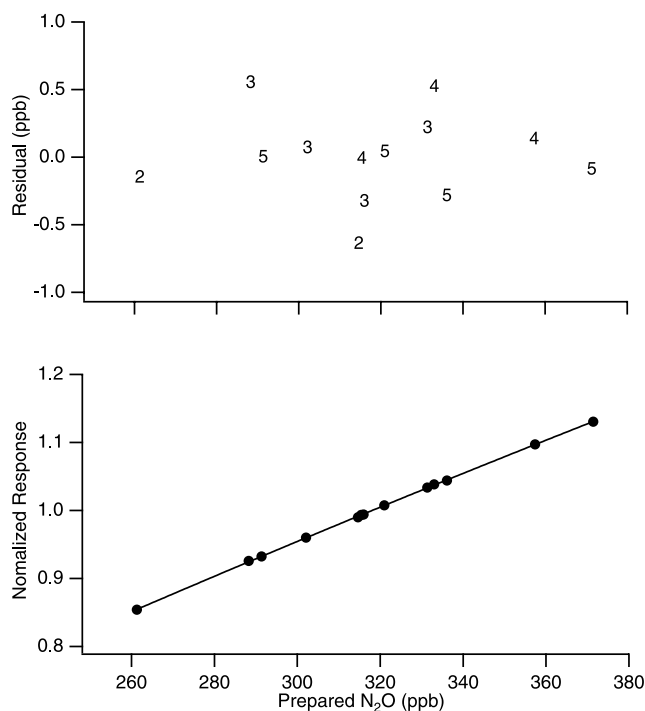
Figure 2. Response of thirteen primary standards relative to a 318.08 ppb secondary standard (lower plot) and residuals from a second order least squares fit (upper plot). Symbols in upper plot correspond to each standard's parent (Table 1). Residuals are evenly distributed among "cousins", suggesting that that all ppm-level primaries are equivalent.

of each standard. While the initial samples typically showed less than 0.1 ppb N_2O in the zero air, the final samples sometimes contained as much as 1.0 ppb N_2O. In particular, the zero air added to FF-30512 and FF-32812 may have contained as much as 1.0 and 0.6 ppb N_2O, respectively. Final samples associated with other 2000 standards contained less than 0.3 ppb. Testing of the zero air was not documented in 1993. Applying corrections to the prepared mixing ratio standards is difficult; however, because we cannot be sure that the zero air added to the cylinders contained this amount of N_2O during the entire transfer. It may have contained more N_2O near the end of the transfer than at the beginning. Therefore corrections were not applied.

[18] Because of these inconsistencies and also because the 1993 standards and some of the 2000 standards were nearing the end of their useful lives, a new scale was developed. Thirteen standards (Table 3) were selected to comprise the NOAA-2006 scale (seven new standards and six from the NOAA-2000 scale). In addition, an error was discovered in the way in which mixing ratios were calculated in 2000. The added CO_2 was not properly included in the calculation. This resulted in a mean increase of 0.10% in prepared mixing ratios for standards prepared in 2000. For standards prepared in 2003 and 2005, samples of the zero air collected before and after preparation typically contained <0.1 ppb N_2O. In two cases (FA-2207 and FA-2208), 0.5 ppb N_2O was detected in the zero air after preparation. Again,

corrections were not applied because we cannot be certain that the zero air contained 0.5 ppb during the entire transfer process.

[19] The range of the NOAA-2006 scale (260–370 ppb) is smaller than that of the NOAA-2000 scale (100–340 ppb). A smaller range was selected for two reasons. First, the vast majority of standards we analyze are used for measurements of N_2O in the remote troposphere, lowermost stratosphere, and firn air, for which N_2O mole fractions range from ~270–320 ppb. Second, better agreement among the standards is achieved within a smaller range. It is more difficult to fit a response curve over a large range. We have observed that the ECD response exhibits slightly different behavior below 200 ppb, and is better described by a power law in this range. We have also noticed this effect at higher mixing ratios (0.5–10 ppm). The best agreement among standards (i.e., lowest standard deviation of residuals) is achieved when the 0–250 and 250–370 ppb regions are treated separately. We have not ascertained whether this behavior is a function of the chromatography, the ECD, or our ability to prepare standards over a large range. We can easily extend the range to 50 ppb or lower (for example, for measurements of stratospheric air) by analyzing other standards prepared in 2005.

[20] The 13 standards that comprise the NOAA-2006 scale were analyzed in 2005 and 2006 (Figure 2). The response of each standard (peak area relative to that of a 318.08 ppb natural air secondary standard) was fitted to the prepared mixing ratios with a second order polynomial using orthogonal distance regression (ODR) [*Press et al.*, 1992]. Results are insensitive to the fitting tool used (FORTRAN ODR routine or Microsoft Excel curve fit). They are, however, somewhat sensitive to whether response is computed using peak area or peak height. The value assigned to the 318.08 ppb standard is consistently 0.05–0.1 ppb lower using peak height compared with using peak area. Although we cannot rule out the possibility of a coeluting peak, this difference is probably related to the nonlinear nature of the ECD, which would make peak area the prudent choice [*Carr*, 1980].

[21] The standard deviation associated with 16 replicate analyses of each standard ranged from 0.02–0.06%. The propagated weighing uncertainties associated with the 2003 and 2005 standards are much smaller than those of the 1993 or 2000 standards. Both improved analysis and improved standard preparation resulted in a set of standards that are internally consistent with a standard deviation of residuals of 0.33 ppb. This is much smaller than the 1.15-ppb associated with the 2000 scale. Furthermore, there is little difference between "cousins", i.e., daughters from different parents (Figure 2). All 13 standards are consistent even though they were derived from four parents over a period of 5 years.

[22] Although many of the standards that comprise the NOAA-2006 scale are different to those that comprise the NOAA-2000 scale, the scales are quite similar (Figure 3). The NOAA-2006 scale is only 0.19 ppb lower than the 2000 scale at 320 ppb. The largest difference between the scales occurs above 330 ppb, for which the 2000 scale was not well defined. At 320 ppb, the 2000 scale can be converted to the 2006 scale by the factor 0.999402. Over the range
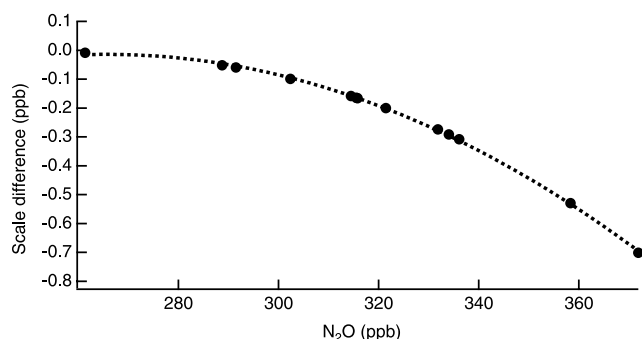
Figure 3. Difference (ppb) between the NOAA-2006 N_2O scale and the NOAA-2000 N_2O scale as a function of dry air mole fraction (ppb).

260–370 ppb, the scales can be converted according to the polynomial

$$y = -2.20205 \cdot 10^{-7}x^3 + 1.20704 \cdot 10^{-4}x^2 + 0.98343x \quad (1)$$

where y is N_2O mole fraction on the NOAA-2006 scale, and x is the mole fraction on the NOAA-2000 scale. For completeness, we offer a conversion for mole fractions between 50 and 260 ppb:

$$y = 6.5445 \cdot 10^{-7}x^3 - 2.8411 \cdot 10^{-4}x^2 + 1.0287x \quad (2)$$

[23] However, scale conversions below 260 ppb are based on standards that are not officially part of the NOAA-2006 scale and are subject to larger uncertainties (~1 ppb). Conversion from the NOAA-2000 scale to the NOAA-2006 scale has a negligible affect on the N_2O growth rate determined from measurements based on NOAA standards.

3.2. Maintaining the Scale

[24] In order for data from multiple instruments to be combined in a meaningful way, the instruments must be intercalibrated to the highest degree possible. An interlaboratory comparability of 0.1 ppb was recommended at the thirteenth WMO/IAEA Meeting of Experts on Carbon Dioxide Concentration and Related Tracers Measurement Techniques (19 to 22 September, 2005 in Boulder, CO). The first step toward this goal is to establish a calibration scale that can be maintained and propagated at this level.

[25] A single secondary standard (318.08 ppb) is used as a reference to which all other standards are compared. The 2006 scale was defined relative to this standard. The 2006 scale was then transferred to five secondary standards (mixtures of natural air and synthetic air in aluminum cylinders: 261.83, 289.28, 313.45, 332.77, and 347.05 ppb). These five standards are analyzed twice each month to establish the response curve of the ECD. A sixth secondary (318.55 ppb) is analyzed every few days as a quality control check. The ECD response curve usually remains steady for months at a time.

[26] We use the term reproducibility as a measure of how well the scale can be maintained. Reproducibility is the closeness of the agreement between results of measurements of the same quantity carried out under changed conditions of measurement [*International Organization for Standardization*, 1993]. Reproducibility can be assessed in two ways: (1) as the variability of secondary standards analyzed repeatedly over the last few years, and (2) as the difference between mixing ratios assigned to tertiary standards before and after they are used in our measurement programs. Figure 4 shows the range of values assigned to the 313.45-ppb secondary when it is treated as an unknown. The variability is generally less than ±0.2 ppb (shown as dashed lines in Figure 4). Although there is some indication of long-term drift, the slope is not significant at the 95% confidence level. The standard deviation of all measurements of this secondary standard is 0.09 ppb. Similar variability is observed for the 289.3- and 332.8-ppb standards, while the 261.8- and 347.1-ppb stand-
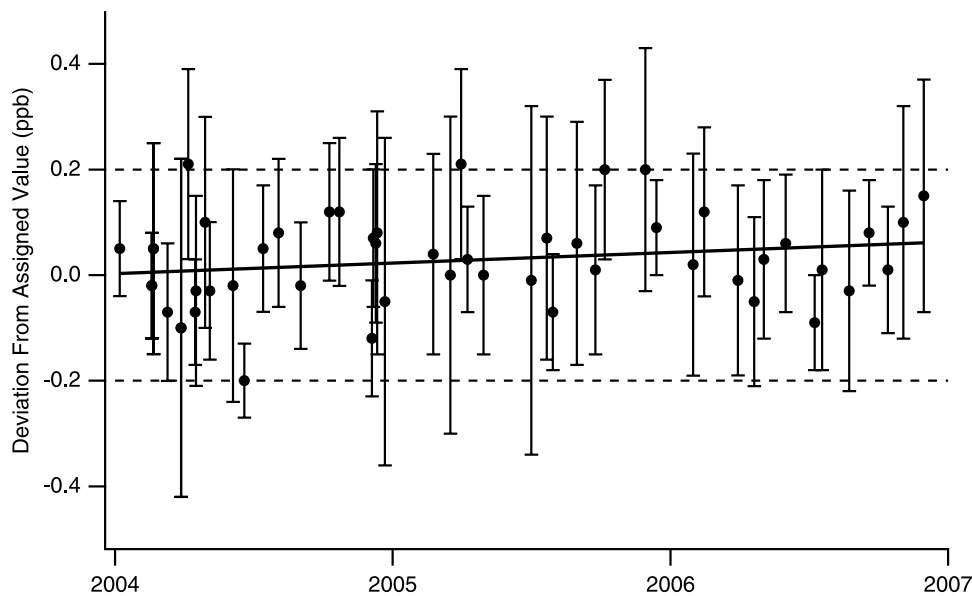

Figure 4. Reproducibility of the N_2O calibration instrument expressed as the variability of results for a 313.45-ppb secondary standard analyzed approximately every 3 weeks (eight aliquots) (error bars are 95% C.L.). Dashed lines show ±0.2 ppb for reference. Solid line is a least squares fit to the data with slope 0.016 ± 0.020 ppb yr^{-1}.

ards show slightly more variability (SD 0.15 ppb). Higher variability near the end points of the response curve is to be expected. Prior to 2003, when a different instrument was used for N_2O calibrations, the standard deviation of measurements of a similar secondary standard was 0.31 ppb. The higher variability of this earlier instrument is attributed to (1) variability in the quality of P5 carrier gas, (2) less precise ECD temperature control, and (3) less frequent comparisons among secondary standards.

[27] Another measure of reproducibility is captured by comparing results from tertiary standards measured several months or years apart. Tertiary standards are typically analyzed prior to deployment (at a pressure of $1.4 \cdot 10^5$ hPa) and again at the end of their terms ($1.4 \cdot 10^4$ hPa), typically 1–2 years later. This is, perhaps, a better way to gauge reproducibility because it more closely resembles how tertiary standards used by different laboratories would be calibrated and it is the variability over these timescales that would be transferred to other networks. Since mid-2003, when the Agilent instrument was brought on-line for N_2O calibrations, eight tertiary standards used in GMD programs have been calibrated before and after use. The mean difference between assigned values for these eight standards is 0.08 ppb. The maximum absolute difference is 0.20 ppb. Although this is a small sample, it is important because these standards have only been analyzed on two occasions and differences are in-line with those shown in Figure 4. Both the infrequent analysis of tertiary standards and the routine analysis of secondary standards suggest that a reproducibility of less than 0.2 ppb has been achieved since mid-2003.

[28] The signal to noise of the current instrument provides an indication of the feasibility of 0.1 ppb reproducibility under present operating conditions. In order to achieve a reproducibility of 0.1 ppb (at the 95% C.L.) the precision of the instrument would have to be at least a factor of two better (0.05 ppb) on a signal corresponding to 320 ppb. This would require a s/n of 6400, or a noise level of 0.016%. Under current conditions the ECD baseline noise is typically 0.01%. Thus, under ideal conditions with no other factors influencing the precision other than electronic noise, a reproducibility of 0.1 ppb is possible. At times, the actual precision of the instrument is on the order of 0.05 ppb (1 SD), but this does not usually hold over the long term. In order to meet the challenge of 0.1-ppb reproducibility, additional sources of variability will need to be identified and controlled.

3.3. Tropospheric Observations

[29] Nitrous oxide is measured in situ by GC-ECD at four NOAA/GMD baseline observatories (Point Barrow, AK; Mauna Loa, HI; Cape Matatula American Samoa; and South Pole). Air measurements are made once per hour and calibrated against two tertiary standards (one at ambient N_2O and the other ~290 ppb) every 2 hours. All GC-ECDs employ packed columns similar to those previously described. All use P5 carrier gas and Valco or Shimadzu (Kyoto, Japan) ECDs installed in custom-built temperature-controlled ovens. The characteristics of the chromatograms are similar to those described previously. Each of these instruments measures 13 trace gases in addition to N_2O.

Therefore the analysis time and calibration sequence are a compromise among the requirements for all 14 gases. The global mean N_2O mixing ratio, calculated from monthly median observations weighted by cosine latitude, was 318.46 ppb in 2004 (NOAA-2006 scale) based on in situ observations at five monitoring sites (four baseline observatories plus Niwot Ridge, Colorado).

[30] Daily mean N_2O mixing ratios (dry air mole fraction) measured at Point Barrow (BRW) are shown in Figure 5a. Monthly median mixing ratios observed at the four NOAA baseline observatories are shown in Figure 5b. Although the BRW measurements involved the use of 14 tertiary standards (seven pair), the record is nearly continuous, with no significant discontinuities resulting from changes in tertiary standards. A latitudinal gradient is observed in Figure 5b with higher mixing ratios in the Northern Hemisphere. The growth rate on a global basis from 2000–2005 is 0.73 ppb yr^{-1}. This growth rate is similar to those reported by *Prinn et al.* [2000] from mid-1978 to mid-1998 (0.69–0.74 ppb yr^{-1}). A key feature of these data is that they were collected using four different instruments and involved a total of 68 tertiary standards (34 pair) with an average of eight pair used at each site during this period. All tertiary standards were calibrated in Boulder. A large seasonal cycle is observed at Point Barrow while a smaller seasonal cycle is observed at South Pole. Seasonal cycles are less apparent at American Samoa and Mauna Loa. Seasonality in N_2O has been linked to seasonal variability of surface fluxes and seasonal changes in transport, such as stratosphere-troposphere exchange [*Jiang et al.*, 2007; *Nevison et al.*, 2004; *Morgan et al.*, 2004]. These data (Figure 5b) also show characteristics similar to those obtained by discrete sampling (flasks) followed by analysis on a single instrument [*Hirsch et al.*, 2006].

3.4. Comparisons With Other Scales

[31] Comparisons between the NOAA-2006 scale and two other scales have been made through the exchange of secondary and tertiary standards. We compared our scale to one developed at NIST in the mid-1980s and distributed as 300 and 330 ppb Standard Reference Materials (SRMs). Although the SRMs are ~20 years old, they appear to be very consistent, and differ by less than 1 ppb from the NOAA-2006 scale (Table 4). Average differences were 0.22% at 300 ppb, and 0.24% at 330 ppb. A scale defined by these SRMs would be 0.23% lower than the NOAA scale at 320 ppb. These results are at odds with those of *Rhoderick and Dorko* [2004], which suggested that NOAA and NIST scales differ by more than 1% (NIST higher than NOAA). It is likely that the new NIST scale described by *Rhoderick and Dorko* [2004] is not consistent with SRMs. The discrepancy may be the result of CO_2 interference during recent N_2O analysis by NIST (J. Rhoderick, personal communication, 2006).

[32] A comparison between NOAA and the Scripps Institution of Oceanography (SIO) was conducted in 2006 through the exchange of three tertiary standards (blends of natural air and zero air in 5.9-L aluminum cylinders). The NOAA-2006 scale compares extremely well with the SIO-98 scale [*Weiss et al.*, 1981; *Prinn et al.*, 2000], with an average difference of 0.01% (NOAA lower) over the range 299–319 ppb. At ambient N_2O (319 ppb) the NOAA-2006
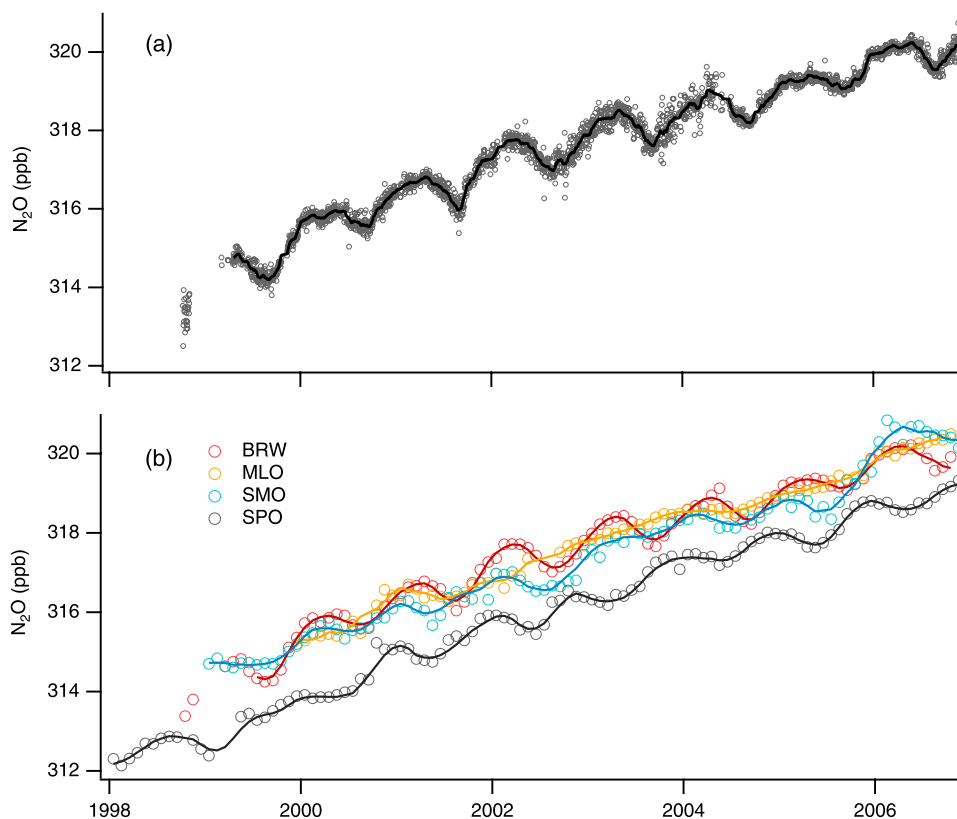
Figure 5. (a) Daily mean in situ N_2O observations at Point Barrow, Alaska and (b) monthly median in situ N_2O observations at four NOAA observatories (BRW: Barrow, Alaska; MLO: Mauna Loa, Hawaii; SMO: Cape Matatula, American Samoa, SPO: South Pole). Solid lines are smooth fits to the data: (a) 25-pt. moving average, (b) second order *Savitzky and Golay* [1964].

and SIO-98 scales are essentially equivalent. This result is consistent with comparisons based on in situ measurements obtained by both groups at Cape Matatula, American Samoa. The fact that a larger difference was observed at 310 ppb compared to 299 and 319 ppb suggests that resolving differences of <0.1% remains a difficult task. While a difference of 0.23 ppb is statistically significant based on the standard deviations associated with these analyses, it is not unexpected given that the reproducibilities of both NOAA and SIO calibrations are 0.2 ppb (95% C.L) (C. Harth, personal communication, 2006). Upon further analysis the difference observed for this cylinder could be smaller.

[33] Although comparisons between NOAA, NIST, and SIO revealed only minor scale differences, one should exercise caution when combining data sets from measurements based on multiple scales. The comparisons shown in Table 4 were based on results from first tier instrumentation, i.e., instruments linked closely to the scales, or in the NOAA case the instrument upon which the scale was developed. Different instruments, linked through tertiary standards, may introduce additional bias. For example, two nearly identical instruments at NOAA have shown a consistent offset of 0.2 ppb relative to each other, even though they are calibrated with the same set of tertiary standards. Furthermore, differences may vary with time, depending on how well a particular instrument is main-

Table 4. Comparison of NOAA-2006, SIO-98, and NIST SRM Scales (SRMs 2608 and 2609)[a]

Cylinder	NIST, ppb	NOAA, ppb	NOAA-NIST, ppb	NOAA-NIST, %
16-25-B	301.14 (0.23)	301.81 (0.11)	0.67	0.22
16-33-B	300.91 (0.37)	301.66 (0.11)	0.75	0.25
16-22-B	301.38 (0.33)	301.95 (0.15)	0.57	0.19
17-25-B	333.41 (0.32)	334.28 (0.13)	0.87	0.26
17-28-B	333.23 (0.26)	333.98 (0.10)	0.75	0.22
17-26-B	333.54 (0.40)	334.37 (0.15)	0.83	0.25
	SIO, ppb	NOAA, ppb	NOAA-SIO, ppb	NOAA-SIO, %
FA-2200	298.65 (0.13)	298.81 (0.10)	0.16	0.05
FA-2199	310.43 (0.13)	310.20 (0.14)	−0.23	−0.07
FA-2209	318.76 (0.11)	318.73 (0.15)	−0.03	−0.01

[a]Standard deviations are shown in parenthesis. Assignments are based on 24-26 Aliquots (NOAA), 29-36 Aliquots (SIO), and 4-6 Aliquots (NIST).

tained and operated. Researchers should attempt to bring multiple sources of comparative information to bear when combining data sets.

4. Summary

[34] An N_2O calibration scale for atmospheric observations was developed on the basis of gravimetrically prepared compressed gas standards. Thirteen internally consistent standards are used to define the NOAA-2006 scale over the range 260–370 ppb. The new scale is 0.059% lower than the NOAA-2000 scale at 320 ppb. The scale was transferred to five secondary standards for routine calibrations. Routine analysis of secondary standards suggests that the scale can be maintained to within 0.2 ppb. The NOAA-2006 scale compares extremely well with the SIO-98 scale.

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