Standards Development of Global Warming Gas Species: Methane, Nitrous Oxide, Trichlorofluoremethane, and Dichlorodifluoromethane

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Environmental scientists from federal agencies, such as the National Oceanic and Atmospheric Administration (NOAA), and academia have long suspected that increasing anthropogenic inputs of various trace gases into the atmosphere can cause changes in the earth's climate and protective ozone layer. Nitrous oxide and methane, cited in the Kyoto Protocol, as well as trichlorofluoromethane (CFC-11) and dichlorodifluoromethane (CFC-12), cited in the Montreal Protocol, are all greenhouse gases and are implicated in the destruction of the stratospheric ozone layer. The lack of national standards prompted research to determine the feasibility of preparing accurate and stable standards containing these four compounds. Development of these standards would support the measurement of these species by those in the atmospheric research community not having their own source of standards. A suite of eight primary gas standards containing methane, nitrous oxide, CFC-11, and CFC-12 in a balance of air were prepared gravimetrically to bracket the ambient atmospheric concentrations. The combined uncertainties (u_c) were calculated from error propagation analysis that included the weighing data from the gravimetric preparation and other sources of error such as the purity analysis of the compounds and air matrix. The expanded uncertainties (U) for the gravimetric standards were <0.5% as calculated from the equation $U = ku_c$, where the coverage factor k is equal to 2 for a 95% confidence interval. Analyses of the suite of standards by gas chromatography with flame-ionization and electron capture detection resulted in average absolute residuals of <0.25% from regression models. The NIST suite of eight gravimetric standards was used to determine the concentrations in two standards from NOAA. Those analyses resulted in bias across the two laboratories of ≤2.1%.

Introduction

Changes in the composition of various trace gases in the atmosphere, largely driven by human activities, have long been suspected of causing changes in the earth's climate and protective ozone layer, and some of these gases have been monitored for 40 years. The longest continual record of monitoring a trace species is for carbon dioxide (CO_2) and was begun in 1958 (*1, 2*). This particular molecule was chosen for study since it acts as a strong greenhouse gas, and increases in this gas from fossil fuel combustion are believed to have an affect on the earth's temperature. Other trace species such as nitrous oxide (N_2O) and methane (CH_4) have also been identified as greenhouse gases. The discovery of the Antarctic ozone hole (*3*) in 1985 heightened the awareness of other harmful trace species to the earth's atmosphere such as dichlorodifluoromethane (CFC-12) and trichlorofluoromethane (CFC-11). These gases along with other chlorofluorocarbons (CFC), which are stable in the lower atmosphere, eventually are transported into the stratosphere. They break down into reactive halogen radicals which destroy the earth's protective ozone layer. The Montreal Protocol (*4*) controls production and use of, among others, CFCs. Compliance is determined by production and use data submitted by signature parties to the Protocol. Although there is no obligation under the Montreal Protocol, one use of monitoring atmospheric concentrations of these gases may be to verify the data and statistics provided by the member countries to demonstrate their compliance.

Since there is no common source of accepted national gas standards for these species, the atmospheric monitoring community relies on their own standards or other colleagues to determine the concentrations. This can create a potential problem when trying to relate data from many sources to determine trends. It would be beneficial to have a common source of gas standards from some acceptable common source such as the National Institute of Standards and Technology (NIST) or other recognized laboratory involved in atmospheric measurements.

The objective of this study is to develop primary gravimetric gas standards of methane, nitrous oxide, CFC-11, and CFC-12 to possibly aid in unifying the measurements made by the multiple members of the atmospheric research community. The approach is to develop a suite of standards, which would bracket the ambient concentration levels, for methane (1.8 μmol/mol, at the time of this study), nitrous oxide (314 nmol/mol), dichlorodifluoromethane (550 pmol/mol), and trichlorofluoromethane (270 pmol/mol).

Experimental Section

Reagents and Gas Cylinders. Gas cylinders of pure methane (CH_4), nitrous oxide (N_2O), and dichlorodifluoromethane (CFC-12) and a liquid sample of trichlorofluoromethane (CFC-11) were obtained with manufacturer claimed purity of ≥99.9%. The compounds were also analyzed at NIST for impurities using gas chromatography (GC) with flame-ionization detection (FID), thermal conductivity detection (TCD), and electron capture detection (ECD), and these results will be discussed in the next section. The zero air to be used as the matrix gas was purchased from Scott Specialty Gases and analyzed by the same methods mentioned above as well as mass spectrometry. The components of air were determined as well as the amount of the four compounds of interest from which the molecular weight of the air was then determined from those analyses. Size 3.4, 6, and 30 L aluminum gas cylinders equipped with brass CGA-350 valves were purchased from Scott Specialty Gases where they were treated using a proprietary process, ACULIFE4, to render the internal cylinder walls inactive.

Primary Standards Preparation. The preparation procedure was the same used by NIST to prepare all of its gravimetric standards suites (*5, 6*). Briefly, a cylinder is

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| 99.997 % pure CH_4 | → | **Standard A** (3.4 L cyl)

CH_4 = 2.6062 %mol/mol
N_2O = 0.4738 %mol/mol | | **Standard B** (30 L cyl)

CFC-12 = 5.998 µmol/mol
CFC-11 = 4.491 µmol/mol | ← | 99.98 % pure CFC-12 |
| 99.937 % pure N_2O | → | | | | ← | 99.99 % pure CFC-11 |

Standard C (30 L cyl)

CH_4 = 5.052 µmol/mol
N_2O =   0.9192 µmol/mol
CFC-12 = 1078   pmol/mol
CFC-11 = 806.6 pmol/mol

Standard D (6 L cyl)	**Standard E** (6 L cyl)	**Standard F** (6 L cyl)	**Standard G** (6 L cyl)
CH_4 = 2.457 µmol/mol N_2O = 447.8 nmol/mol CFC-12 = 555.3 pmol/mol CFC-11 = 392.5 pmol/mol	CH_4 = 2.101 µmol/mol N_2O = 383.0 nmol/mol CFC-12 = 467.6 pmol/mol CFC-11 = 335.6 pmol/mol	CH_4 = 1.698 µmol/mol N_2O = 309.8 nmol/mol CFC-12 = 375.3 pmol/mol CFC-11 = 271.4 pmol/mol	CH_4 = 1.280 µmol/mol N_2O = 233.8 nmol/mol CFC-12 = 276.2 pmol/mol CFC-11 = 204.7 pmol/mol

| 99.997 % pure CH_4 | → | **Standard A2** (3.4 L cyl)

CH_4 = 2.1028 %mol/mol
N_2O = 0.4190 %mol/mol | | **Standard B2** (30 L cyl)

CFC-12 = 6.061 µmol/mol
CFC-11 = 3.588 µmol/mol | ← | 99.98 % pure CFC-12 |
| 99.937 % pure N_2O | → | | | | ← | 99.99 % pure CFC-11 |

Standard C2 (30 L cyl)

CH_4 = 4.310 µmol/mol
N_2O =   0.8599 µmol/mol
CFC-12 = 1167 pmol/mol
CFC-11 = 690.8 pmol/mol

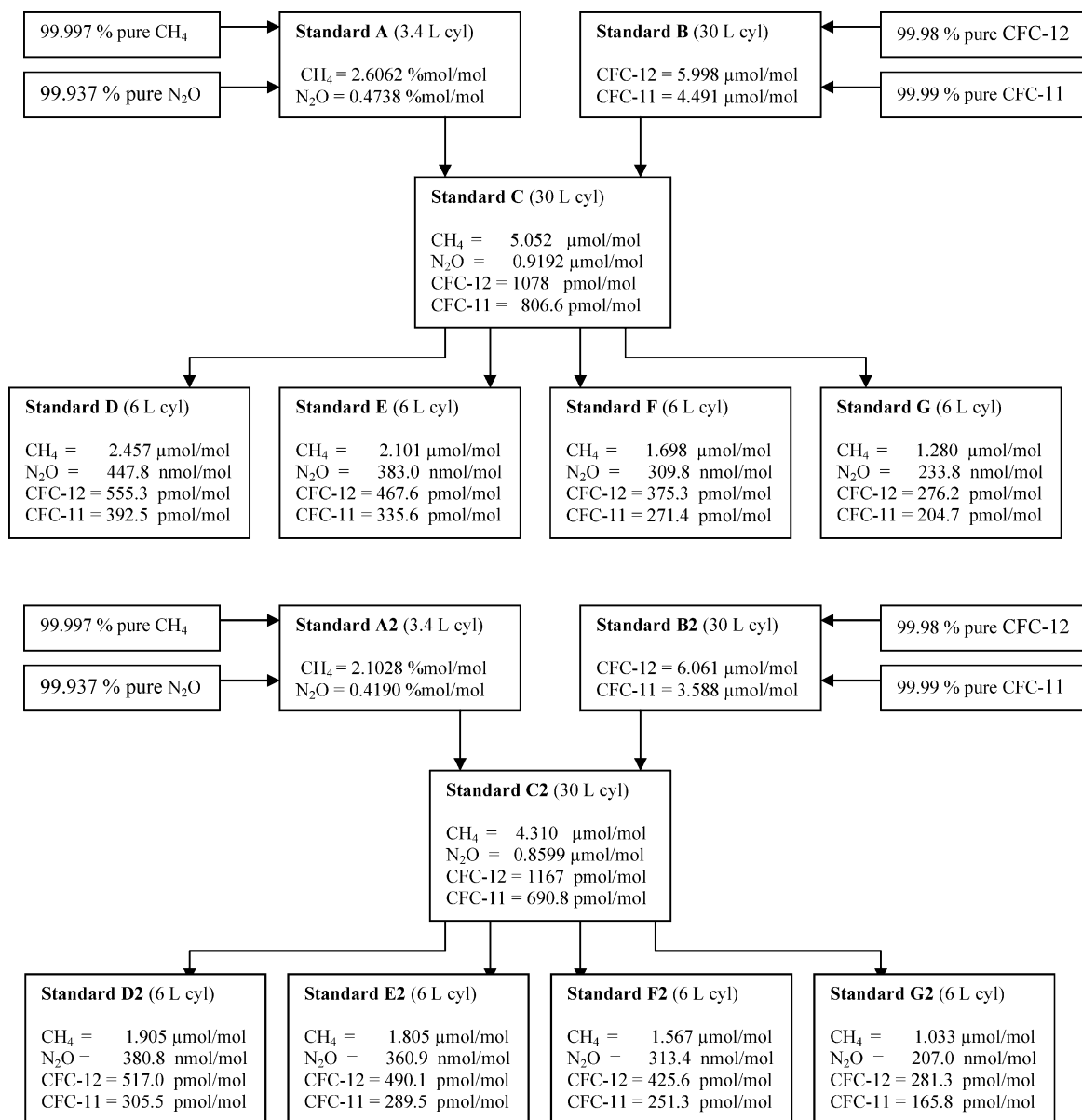| **Standard D2** (6 L cyl)	**Standard E2** (6 L cyl)	**Standard F2** (6 L cyl)	**Standard G2** (6 L cyl)
CH_4 = 1.905 µmol/mol N_2O = 380.8 nmol/mol CFC-12 = 517.0 pmol/mol CFC-11 = 305.5 pmol/mol	CH_4 = 1.805 µmol/mol N_2O = 360.9 nmol/mol CFC-12 = 490.1 pmol/mol CFC-11 = 289.5 pmol/mol	CH_4 = 1.567 µmol/mol N_2O = 313.4 nmol/mol CFC-12 = 425.6 pmol/mol CFC-11 = 251.3 pmol/mol	CH_4 = 1.033 µmol/mol N_2O = 207.0 nmol/mol CFC-12 = 281.3 pmol/mol CFC-11 = 165.8 pmol/mol

FIGURE 1. Schematic of protocol for primary gravimetric standards preparation; dilution air added to bring totals to 100%. Values are for illustration of target concentrations only. Uncertainties ultimately calculated from preparation data are provided in Table 3.

evacuated and weighed several times against a tare a minimum of three times. The pure compound of interest, e.g., methane, is then added via a manifold system to a precalculated pressure and weight. The cylinder is reweighed a minimum of three times. Any additional compounds are added in the same manner followed by the addition of the diluent gas, nitrogen or air and final weighing of the cylinder. The concentrations of each species in the standard are calculated based on the moles of each compound to the total moles. A schematic of the protocol used in the preparation of the final eight primary gravimetric standards is shown in Figure 1. Three levels of gravimetric standards prepared by dilution were necessary to reach the desired final concentrations. The four primary standards at the first tier were made directly from the pure samples. Primary standards for the second tier were made by dilution from the first tier, and the third tier (final) was made by dilution from the second tier standards. Each suite of standards was analyzed to ensure agreement between the standards within concentration tier before proceeding to the next level. This final primary standards suite was prepared to cover a range bracketing ambient concentrations as follows: CH_4 from 1.0 µmol/mol to 2.5 µmol/mol, N_2O from 200 nmol/mol to 450 nmol/mol, CFC-11 from 165 pmol/mol to 400 pmol/mol, and CFC-12 from 270 pmol/mol to 550 pmol/mol. The suite of primary standards was prepared gravimetrically using several different balances depending on the size of the cylinder. Cylinder size for a particular standard was determined based on the optimum weighing conditions to obtain the lowest possible uncertainty. The 3.4 L cylinders were weighted on a two-pan balance with a 10 kg capacity and a sensitivity of 0.001 g. A 30 kg capacity balance with a sensitivity of 0.1 g was used to weigh the 6 L cylinders. The 30 L cylinders were weighed using a 54 kg capacity floor balance sensitive to 1 g.

Measurement Systems. All four species in the gravimetric standards were analyzed using gas chromatography and a 3.66 m × 3.2 mm stainless steel column packed with Poropak Q. A flame-ionization detector (FID), operated at 250 °C, was used to measure the CH_4. The samples were injected via a six-port stainless steel gas-sampling valve onto the column set at an isothermal temperature of 40 °C. Helium column carrier gas flow rate was set at 38 mL/min. The gas-sampling valve was equipped with a 5 mL stainless steel sample loop.

TABLE 1. Composition of Air Balance Gas

cylinder no.	oxygen[a] (% mol/mol)	nitrogen[a] (% mol/mol)	argon[a] (% mol/mol)	N_2O[b] (pmol/mol)	CFC-12[b] (pmol/mol)	CFC-11[b] (pmol/mol)	CH_4[c] (μmol/mol)	mole weight[d] (g/mol)
ID018684	21.13	78.85	0.021	0.7	1.6	0.1	<0.001	28.858
ID002754	21.15	78.83	0.022	0.7	1.4	0.2	<0.001	28.859
ID2378	21.14	78.85	0.012	0.7	1.1	0.3	<0.001	28.858
W131474	21.29	78.69	0.022	0.9	1.2	0.3	<0.001	28.864
K019585	20.52	79.46	0.027	0.4	0.9	0.1	<0.001	28.834
ID2446	21.03	78.96	0.025	0.3	0.9	0.0	<0.001	28.860

[a] Standard uncertainty is ±0.5% relative. [b] Standard uncertainty is ±0.1 pmol/mol. [c] Standard uncertainty is ±0.0005 μmol/mol. [d] Standard uncertainty is ±0.002 g/mol.

TABLE 2. Impurities in the Starting Materials CH_4, N_2O, CFC-12, and CFC-11

	pure starting compound			
impurity	N_2O (%)	methane (%)	CFC-11 (%)	CFC-12 (%)
N_2O[a]		<0.0001	<0.0001	<0.0001
methane[a]	<0.0001		<0.0001	<0.0001
CFC-11[a]	<0.0001	<0.0001		<0.0001
CFC-12[a]	<0.0001	<0.0001	<0.0001	
other	0.063	0.003	0.05	0.02
purity	99.937 ± 0.001	99.997 ± 0.001	99.95 ± 0.01	99.98 ± 0.01

[a] The standard uncertainty in the values are ±0.00005%.

N_2O was analyzed using an electron capture detector (ECD) operated at 350 °C. The column temperature was isothermal at 40 °C with a carrier gas of 5% by mole CH_4 in argon set at a flow rate of 30 mL/min. The six-port gas-sampling valve was equipped with a 2 mL stainless steel loop to inject the sample onto the column. CFC-11 and CFC-12 were also analyzed using the ECD at 350 °C. The column temperature was isothermal at 140 °C with a nitrogen carrier column flow of 32 mL/min. The six-port gas-sampling valve was equipped with a 1 mL stainless steel loop.

Results and Discussion

Primary Gravimetric Standards Preparation and Uncertainties. The matrix air used for preparation of the primary standards was analyzed to determine the major components of oxygen, argon, and nitrogen. Great attention was given to determine the amount of methane, nitrous oxide, CFC-11, and CFC-12 present in the matrix air. Table 1 gives the results of those analyses.

Since methane was not observed in chromatograms of the air, a detectable limit of 0.0005 μmol/mol was calculated based on a minimum detectable peak response. Therefore a value of <0.001 μmol/mol ± 0.0005 μmol/mol of methane is applied for the air, and no correction is made to the final concentration of the primary standards. Detectable amounts of nitrous oxide, CFC-11, and CFC-12 were found and quantified in the matrix air. These values were used to adjust the final concentrations in the primary standards. The molecular weight for each cylinder of matrix air was calculated from the composition and used in the final concentration calculations of the primary standards.

Results of the impurity analysis for the four compounds of interest are given in Table 2. All four were found to be extremely pure with no detectable amounts (<10^{-4} %) of any of the compounds present in the other. Detection limits calculated for the analytical conditions used are given in the table. The nitrous oxide was found to be 99.937% ± 0.001% (67% confidence interval) pure with 0.063% ± 0.001% of oxygen, nitrogen, and nitric oxide present. Methane was determined to be 99.997% ± 0.001% pure with a minimal amount of air present. The dichlorodifluoromethane (CFC-12) at 99.98% ± 0.01% and trichlorofluoromethane (CFC-11) at 99.95% ± 0.01% had traces of other organics present.

After purity determinations and molecular weight calculations on the matrix air were completed, the preparation of the primary gravimetric standards proceeded as illustrated in Figure 1. The four first tier standards, each containing two compounds, were made from the pure reagents. The concentrations needed posed some weighing restrictions, which would not allow for all four compounds to be added to one cylinder and obtain the lowest uncertainties possible. Standards A and A2 contained methane and nitrous oxide, while B and B2 contained dichlorodifluoromethane and trichlorofluoromethane. Analysis of these standards showed excellent agreement with existing primaries. Standard C was prepared by dilution from A and B, and C2 from A2 and B2, to result in two second tier concentration standards, each containing all four compounds. Analysis of these newly prepared standards with existing primary standards confirmed the gravimetric concentrations. Dilution was used again to prepare the final eight standards in 6 L cylinders: D, E, F, and G from C and D2, E2, F2, and G2 from C2.

Several sources of errors were included in the calculation of total uncertainty for each gravimetric standard. Sources included the uncertainty in weighing the compounds into the cylinders, the purity of the starting compounds, and the purity of the matrix gas. The uncertainty is expressed as an expanded uncertainty (U) where $U = ku_c$ with u_c estimated from the preparation uncertainties and the coverage factor k equal to approximately 2 (95% confidence interval) (7, 8). (Since there were an appropriate number of samples, ≥5, then a coverage factor of 2 is totally acceptable for these purposes.) The u_c portion is calculated using the following equation: $(a^2 + b^2 + ... x^2)^{1/2}$. Table 3 lists the expanded uncertainty for each standard. Each expanded uncertainty incorporates the weighing uncertainties and the uncertainty in determining the amount of the four compounds in the matrix air plus the previous level's uncertainty. The true value is, with 95% confidence, expected to be in the interval defined by the gravimetric value ± the expanded uncertainty.

Analysis of Final Concentration Level Gravimetric Primary Standards. The final suite of standards was analyzed as a set using the appropriate analytical methods as described earlier. One of the gravimetric standards, D2, was chosen as the control. It was sampled before and after the analysis of each standard in order to correct for any instrument drift
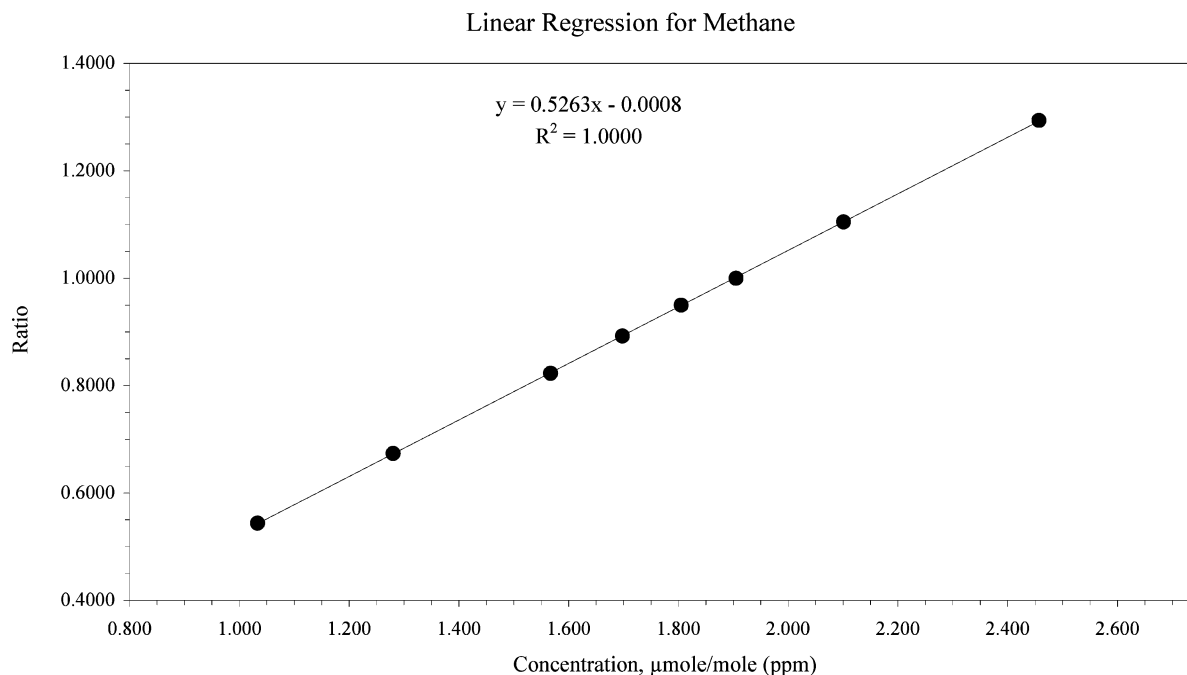
Linear Regression for Methane

$$y = 0.5263x - 0.0008$$
$$R^2 = 1.0000$$

FIGURE 2.

TABLE 3. Gravimetric Standard Uncertainties

		standard uncertainties[a]			
standard level	standard	methane (%)	N$_2$O (%)	CFC-12 (%)	CFC-11 (%)
first level	A	±0.035	±0.065		
standards	A2	±0.045	±0.085		
	B			±0.035	±0.035
	B2			±0.045	±0.035
second level	C	±0.075	±0.10	±0.085	±0.085
standards	C2	±0.085	±0.12	±0.10	±0.090
third level	D	±0.10	±0.14	±0.13	±0.11
standards	E	±0.11	±0.15	±0.13	±0.15
	F	±0.12	±0.17	±0.15	±0.16
	G	±0.13	±0.19	±0.17	±0.19
	D2	±0.12	±0.18	±0.14	±0.16
	E2	±0.13	±0.19	±0.15	±0.17
	F2	±0.12	±0.18	±0.15	±0.16
	G2	±0.15	±0.23	±0.13	±0.22

[a] Equation for standard uncertainty calculation: $u_c = (a^2 + b^2 + \ldots + n^2)^{1/2}$.

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due to changing atmospheric or instrument conditions during an analysis sequence (the standard analyses were randomized). A ratio was calculated for each compound in each standard by dividing its GC peak area response by that of the control. The average ratio was plotted against their corresponding gravimetric concentration. The data were then fit to a linear regression model to predict the concentration for each standard. For each standard, the gravimetric concentration was subtracted from the predicted concentration to determine a residual. An absolute average residual from all eight standards was calculated. The absolute average residual is an indication of the internal consistency of the standards suite.

Regression plots for all four compounds resulted in correlation coefficients (R^2) of 0.9999 or better, absolute average residuals of ≤0.22%, and mean squared errors of ≤0.22% (the square root of the sum of squares of the residuals divided by degrees of freedom). The absolute average residual is a good indicator of the expected residual, with half lying above and half below. However, it uses eight degrees of freedom (there are eight standards in the fits) and does not

take into account that two of the values are used to anchor the line fit. The mean squared error is the better statistical tool in that, for each case described here, it considers that two of the values describe the regression curve and uses six degrees of freedom. The methane data, given in Table 4, were plotted using linear regression, which resulted in an R^2 of 1.0000. The absolute average residual of 0.11% and the mean squared error of 0.14% for the eight standards demonstrate excellent agreement within the suite. Figure 2 illustrates the linear regression of the methane and gives the resulting equation.

Table 5 contains the data for nitrous oxide, and in Figure 3 the data are plotted to a second-order regression resulting in an R^2 of 0.9999. If one looks at the ratio divided by the concentration, termed the response factor, there is an obvious trend in one direction, therefore the use of a second order fit. These results are most likely due to nonlinearity of the detector. The absolute average residual of 0.16% and mean square error of 0.22% show the excellent agreement between the suite of standards.

Dichlorodifluoromethane and trichlorofluoromethane data were plotted using second-order regression. Dichlorodifluoromethane data, contained in Table 6 and illustrated in Figure 4, resulted in an R^2 of 1.0000 with an absolute residual of 0.02% and a mean squared error of 0.05%.

Trichlorofluoromethane data, contained in Table 7 and illustrated in Figure 5, resulted in an R^2 of 0.9999 with an absolute residual of 0.17% and a mean squared error of 0.22%. The residuals for each of the four regressions are well within the expanded uncertainty of the standards, demonstrating the reproducibility of the preparation procedure.

Since this suite of gravimetric standards is new, no stability record has been documented. However, NIST has an ongoing record of lot standards from several lots of methane in air Standard Reference Materials (SRMs) at 1 μmol/mol concentration in aluminum cylinders. The lot standards were named against the methane gravimetric standards suite which is supported by the addition of new standards at appropriate time intervals to ensure that the standards are not drifting. Table 8 lists five SRM lot standards of methane in air at 1 μmol/mol that have been tracked since their inception. The original certified concentration and uncer-

TABLE 4. Linear Regression Results of Data Taken Using GC/FID for Gravimetric Methane Standards

standard	peak area ratio[a]	concentration in gravimetrically prepared standards[b]	fitted concentration[b]	% residual[c]
D	1.2939 ± 0.0023	2.457 ± 0.005	2.460 ± 0.005	0.12
E	1.1046 ± 0.0011	2.101 ± 0.005	2.100 ± 0.004	−0.05
D2	1.0000 ± 0.0010	1.905 ± 0.005	1.901 ± 0.004	−0.21
E2	0.9498 ± 0.0003	1.805 ± 0.005	1.806 ± 0.004	0.06
F	0.8923 ± 0.0017	1.698 ± 0.004	1.697 ± 0.003	−0.06
F2	0.8228 ± 0.0011	1.567 ± 0.004	1.565 ± 0.003	−0.13
G	0.6735 ± 0.0006	1.280 ± 0.003	1.281 ± 0.003	0.08
G2	0.5438 ± 0.0015	1.033 ± 0.003	1.035 ± 0.002	0.19
			absolute average residual =	0.11
			mean squared error =	0.14

[a] Ratio is calculated by dividing the peak area response for a standard by the control standard CAL014827 peak area response. [b] Concentration is in μmol/mol (ppm) and is expected, with approximately 95% confidence, to be in the interval defined by the gravimetric concentration or fitted concentration ± the expanded uncertainty. See section on "Primary Gravimetric Standards Preparation and Uncertainties" for computational details. [c] Residual is calculated by subtracting the gravimetric concentration from the predicted, dividing by the gravimetric concentration, and then multiplying by 100 for percent.

TABLE 5. Second-Order Regression Results of Data Taken Using GC/ECD for Gravimetric Nitrous Oxide (N_2O) Standards

standard	peak area ratio[a]	concentration in gravimetrically prepared standards[b]	fitted concentration[b]	% residual[c]
D	1.1534 ± 0.0020	447.8 ± 1.3	447.8 ± 1.4	0.00
E	1.0002 ± 0.0031	383.0 ± 1.2	382.2 ± 1.2	−0.21
D2	1.0000 ± 0.0020	380.8 ± 1.4	382.1 ± 1.2	0.34
E2	0.9475 ± 0.0001	360.9 ± 1.4	360.2 ± 1.2	−0.19
F2	0.8347 ± 0.0012	313.4 ± 1.1	314.2 ± 1.0	0.26
F	0.8226 ± 0.0030	309.8 ± 1.1	309.4 ± 1.0	−0.13
G	0.6292 ± 0.0028	233.8 ± 0.9	233.6 ± 0.7	−0.09
G2	0.5596 ± 0.0008	207.0 ± 1.0	207.1 ± 0.7	0.05
			absolute average residual =	0.16
			mean squared error	0.22

[a] Ratio is calculated by dividing the peak area response for a standard by the control standard CAL014827 peak area response. [b] Concentration is in nmol/mol (ppb) and is expected, with approximately 95% confidence, to be in the interval defined by the gravimetric concentration or fitted concentration ± the expanded uncertainty. See section on "Primary Gravimetric Standards Preparation and Uncertainties" for computational details. [c] Residual is calculated by subtracting the gravimetric concentration from the predicted, dividing by the gravimetric concentration, and then multiplying by 100 for percent.

2nd Order Regression for Nitrous Oxide

$y = -8E\text{-}07x^2 + 0.003x - 0.0264$

$R^2 = 0.9999$
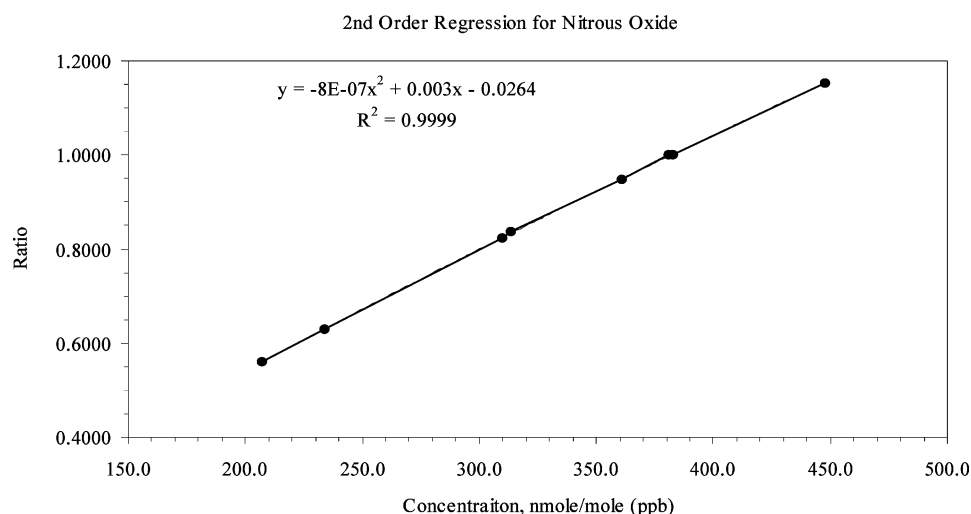
FIGURE 3.

tainty are given along with the most recent analysis for each SRM lot standard. The data clearly indicate that the methane has remained extremely stable in these aluminum gas cylinders for as much as 21 years. Three of the five analyze to the exact same original certified concentrations, while the two other SRM lot standards are within 0.3%.
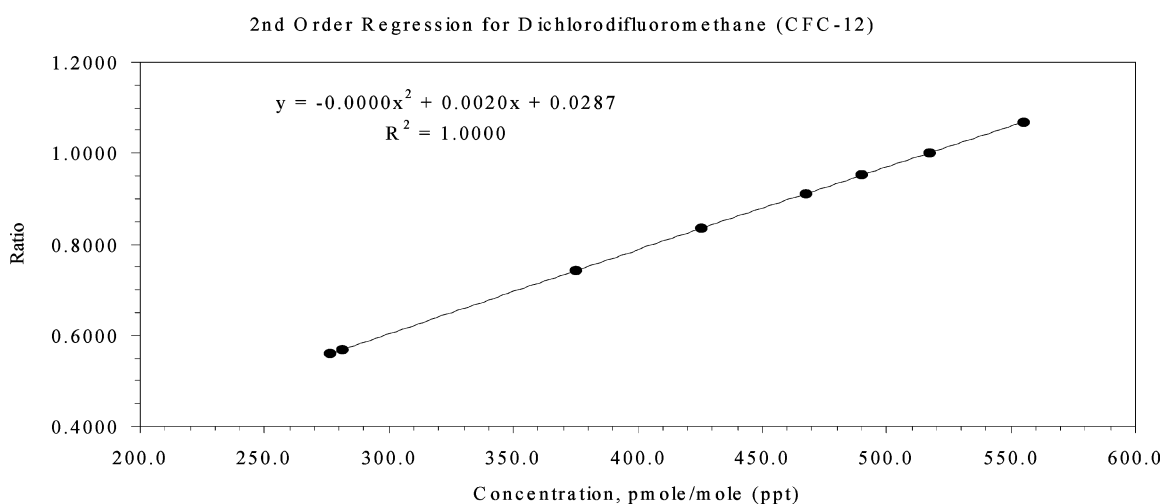
Analysis of NOAA Standards. The regression equations generated for each of the four compounds from the NIST

suite of eight primary gravimetric standards were used to determine concentrations for two NOAA standards. Table 9 displays the concentrations determined by NIST and NOAA and the differences. In general the agreement between NOAA and NIST is reasonable (±1.0%), but some of the differences are significant. Lack of overlap between the concentration ranges for methane, based on the uncertainties, suggests a bias between the two sets of standards: NOAA ranges from

TABLE 6. Second-Order Regression Results of Data Taken Using GC/ECD for Gravimetric Dichlorodifluoromethane (CFC-12) Standards

standard	peak area ratio[a]	concentration in gravimetrically prepared standards[b]	fitted concentration[b]	% residual[c]
D	1.0690 ± 0.0013	555.3 ± 1.4	555.3 ± 0.3	0.00
D2	1.0000 ± 0.0020	517.0 ± 1.5	516.7 ± 0.3	−0.06
E2	0.9528 ± 0.0009	490.1 ± 1.5	490.5 ± 0.3	0.08
E	0.9114 ± 0.0017	467.6 ± 1.3	467.6 ± 0.3	0.00
F2	0.8346 ± 0.0010	425.6 ± 1.3	425.4 ± 0.3	−0.05
F	0.7427 ± 0.0010	375.3 ± 1.1	375.3 ± 0.2	0.00
G2	0.5682 ± 0.0015	281.3 ± 1.0	281.3 ± 0.2	0.00
G	0.5586 ± 0.0017	276.2 ± 0.9	276.2 ± 0.2	0.00
			absolute average residual =	0.02
			mean squared error =	0.05

[a] Ratio is calculated by dividing the peak area response for a standard by the control standard CAL014827 peak area response. [b] Concentration is in pmol/mol (ppt) and is expected, with approximately 95% confidence, to be in the interval defined by the gravimetric concentration or fitted concentration ± the expanded uncertainty. See section on "Primary Gravimetric Standards Preparation and Uncertainties" for computational details. [c] Residual is calculated by subtracting the gravimetric concentration from the predicted, dividing by the gravimetric concentration, and then multiplying by 100 for percent.

2nd Order Regression for Dichlorodifluoromethane (CFC-12)

$$y = -0.0000x^2 + 0.0020x + 0.0287$$
$$R^2 = 1.0000$$

FIGURE 4.

TABLE 7. Second-Order Regression Results of Data Taken Using GC/ECD for Gravimetric Trichlorofluoromethane (CFC-11) Standards

standard	peak area ratio[a]	concentration in gravimetrically prepared standards[b]	fitted concentration[b]	% residual[c]
D	1.2773 ± 0.0016	392.5 ± 0.9	392.9 ± 1.3	0.10
E	1.0929 ± 0.0013	335.6 ± 1.0	334.7 ± 1.1	−0.27
D2	1.0000 ± 0.0012	305.5 ± 1.0	305.4 ± 1.0	−0.03
E2	0.9508 ± 0.0005	289.5 ± 1.0	289.9 ± 1.0	0.14
F	0.8915 ± 0.0009	271.4 ± 0.9	271.1 ± 0.9	−0.11
F2	0.8304 ± 0.0018	251.3 ± 0.8	251.9 ± 0.8	0.24
G	0.6822 ± 0.0021	204.7 ± 0.8	205.2 ± 0.8	0.24
G2	0.5558 ± 0.0023	165.8 ± 0.7	165.4 ± 0.7	−0.24
			absolute average residual =	0.17
			mean squared error =	0.22

[a] Ratio is calculated by dividing the peak area response for a standard by the control standard CAL014827 peak area response. [b] Concentration is in pmol/mol (ppt) and is expected, with approximately 95% confidence, to be in the interval defined by the gravimetric concentration or fitted concentration ± the expanded uncertainty. See section on "Primary Gravimetric Standards Preparation and Uncertainties" for computational details. [c] Residual is calculated by subtracting the gravimetric concentration from the predicted, dividing by the gravimetric concentration, and then multiplying by 100 for percent.

1.780 to 1.782 μmol/mol and NIST ranges from 1.797 and 1.811 μmol/mol. Results for nitrous oxide are similar with near overlap for one standard but not the other. The agreement for CFC-11 and CFC-12 is very good considering that the concentration ranges have good overlap and the level is in the pmol/mol range. NOAA used their own primary standards to assign values to the N$_2$O, CFC-11, and CFC-12.

The methane values were assigned using a calibration from another source, and the uncertainty only considers uncertainty in the analytical measurement.

We are investigating the methane bias partly through standards comparisons with other National Measurement Institutes (NMis) and the CCQM − *Comité Consultatif pour la Quantité de Matière métrologie en chimie* (Consultative

TABLE 8. Stability Data for Methane in Air SRM Lot Standards

SRM sample no.	original certified date	original certified value (μmol/mol)[a]	current value[a] April 2000	percent difference (%)
12-1-B	Jan 1979	0.970 ± 0.010	0.970 ± 0.010	0.00
12-11-C	Feb 1981	0.982 ± 0.010	0.982 ± 0.010	0.00
12-1-D	Oct 1983	0.913 ± 0.010	0.910 ± 0.010	−0.33
12-01-EL	April 1993	1.192 ± 0.010	1.192 ± 0.010	0.00
12-FL-01	June 1999	1.079 ± 0.008	1.076 ± 0.010	−0.28

[a] Concentration is in μmol/mol (ppm) and is expected, with approximately 95% confidence, to be in the interval defined by the concentration ± the expanded uncertainty.

Committee for Amount of Substance − Metrology in Chemistry). A pilot comparison, P-41, of ambient methane concentration has been completed, but at the time of this publication the final report and results were not available. Each participating laboratory sent a primary methane and carbon dioxide standard to the pilot lab, NMi of The Netherlands, which analyzed each standard followed by analysis of the data measurements. Each laboratory also analyzed a sample sent from the pilot lab. The report and results will eventually be available and can be found on the *Bureau International des Poids et Mesures* (BIPM) Web site www.bipm.org, under the Key Comparison Database (KCDB), Appendix D: list of key comparisons. Future studies will also be undertaken within NIST to address the methane and N_2O differences.

This research has resulted in the ability to prepare a suite of gravimetric standards for some of the most important global warming gases. Standards can be accurately prepared with an expanded uncertainty of less than 0.5% with a level of confidence of approximately 95%. Regressions of the analytical data for the suite of standards resulted in residuals of less than 0.25%. These residuals are well within the preparation uncertainty confirming the ability to accurately prepare standards. The results for the comparison of the NOAA secondary standards are reasonable up to ±1.0%, but better agreement is expected for the methane and N_2O. Typically the atmospheric monitoring community is trying to detect concentration changes in methane on the order of 0.001 μmol/mol (0.06%) (9). This result shows a 1.5% discrepancy between just two calibration systems, which is not overlapped by the uncertainty limits of reported values. NOAA reports an uncertainty in their methane value of 0.06% relative compared to a NIST uncertainty of 0.4% for the same NOAA standard as determined by NIST. The NOAA uncertainty only includes an analytical imprecision of the measurements. NIST includes the uncertainty in the gravimetric standards used to measure the NOAA standard and the analytical imprecision. Therefore it is difficult to discern whether one standard would be the choice over another based on the lowest uncertainties. Other research laboratories use their own or other calibration scales that may differ by the same magnitude in the opposite direction. To compare data between different laboratories and draw some reliable conclusions, it would appear that a common source of national standards is necessary. It seems reasonable that those making atmospheric measurements would support having one or two laboratories to serve as a common source of standards. Preceding this setup, however, more work is needed to understand the source(s) for the differences in these standards. Future research and primary standards
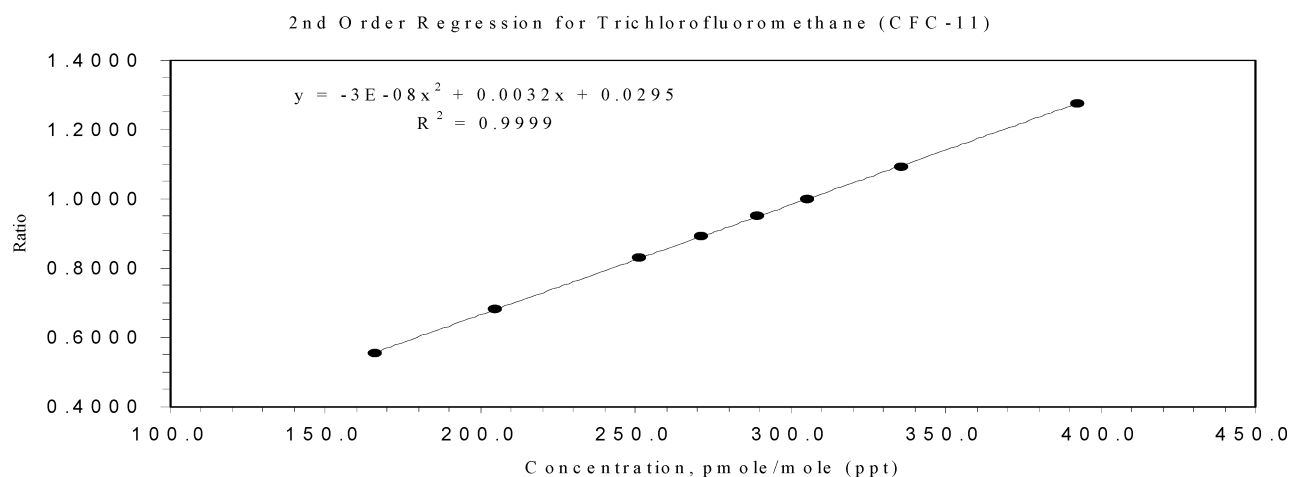
2nd Order Regression for Trichlorofluoromethane (CFC-11)

$$y = -3E{-}08x^2 + 0.0032x + 0.0295$$
$$R^2 = 0.9999$$

FIGURE 5.

TABLE 9. Concentrations Determined by NIST for Two NOAA Standards

compound	NOAA assigned concentration[a]	NIST assigned concentration[a]	% difference (NOAA − NIST) (%)
	NOAA Standard # ALM064473		
methane	(1.781 ± 0.001) μmol/mol	(1.804 ± 0.007) μmol/mol	−1.3
N_2O	(313.6 ± 2.0) nmol/mol	(317.6 ± 1.6) nmol/mol	−1.3
CFC-12	(547.4 ± 6.7) pmol/mol	(547.6 ± 3.8) pmol/mol	0.4
CFC-11	(268.1 ± 1.8) pmol/mol	(266.8 ± 1.9) pmol/mol	+0.5
	NOAA Standard # ALM064453		
methane	(1.639 ± 0.001) μmol/mol	(1.664 ± 0.008) μmol/mol	1.5
N_2O	(287.9 ± 2.0) nmol/mol	(294.0 ± 1.9) nmol/mol	2.1
CFC-12	(500.7 ± 6.7) pmol/mol	(500.9 ± 5.5) pmol/mol	0.4
CFC-11	(246.8 ± 1.8) pmol/mol	(243.6 ± 1.8) pmol/mol	+1.3

[a] The true concentration of these analytes is expected, with approximately 95% confidence, to be in the interval defined by the concentration ± the expanded uncertainty.

development at NIST may include many other compounds suspected of contributing to global climate change.

Acknowledgments

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