Environmental Science & Technology
Article
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A Measurement of Total Reactive Nitrogen, NO_y, together with NO_2, NO, and O_3 via Cavity Ring-down Spectroscopy

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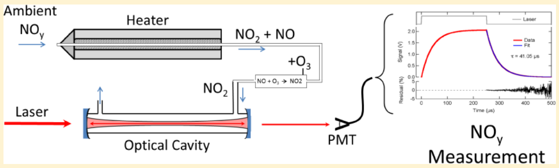

ABSTRACT: We present a sensitive, compact detector that measures total reactive nitrogen (NO_y), as well as NO_2, NO, and O_3. In all channels, NO_2 is directly detected by laser diode based cavity ring-down spectroscopy (CRDS) at 405 nm. Ambient O_3 is converted to NO_2 in excess NO for the O_3 measurement channel. Likewise, ambient NO is converted to NO_2 in excess O_3. Ambient NO_y is thermally dissociated at ~700 °C to form NO_2 or NO in a heated quartz inlet. Any NO present in ambient air or formed from thermal dissociation of other reactive nitrogen compounds is converted to NO_2 in excess O_3 after the thermal converter. We measured thermal dissociation profiles for six of the major NO_y components and compared ambient measurements with other instruments during field campaigns in Utah and Alabama. Alabama measurements were made in a rural location with high biogenic emissions, and Utah measurements were made in the wintertime in unusual conditions that form high ozone levels from emissions related to oil and gas production. The NO_y comparison in Alabama, to an accepted standard measurement method (a molybdenum catalytic converter/chemiluminescence instrument), agreed to within 12%, which we define as an upper limit to the accuracy of the NO_y channel. The 1σ precision is <30 pptv at 1 s and <4 pptv at 1 min time resolution for all measurement channels. The accuracy is 3% for the NO_2 and O_3 channels and 5% for the NO channel. The precision and accuracy of this instrument make it a versatile alternative to standard chemiluminescence-based NO_y instruments.

INTRODUCTION

Reactive nitrogen compounds play a central role in atmospheric chemistry. Nitrogen oxides ($NO_x \equiv NO + NO_2$) strongly affect the oxidative capacity of the atmosphere through the catalytic cycle that produces ozone (O_3) in the lower atmosphere. Total reactive nitrogen (NO_y) includes NO_x and all its reservoirs:

$$\begin{aligned} NO_y \equiv\ & NO + NO_2 + NO_3 + 2N_2O_5 + HNO_3 + HONO \\ & + HO_2NO_2 + \text{PAN (peroxy acetyl nitrates)} \\ & + \text{aerosol nitrates} + \text{organic nitrates} + \ldots \end{aligned}$$

Knowledge of the abundance of this chemical family, as well as NO, NO_2, and the related compound O_3, is a useful indicator of total nitrogen emissions, air mass age, competition between different chemical processes, and the efficiency of ozone production associated with particular emission sources. Standard measurements of NO_y rely on catalytic decomposition of NO_y to NO, followed by NO detection using chemiluminescence.[1,2] The most commonly used materials for conversion are gold and molybdenum. However, catalytic converters are prone to deterioration, affecting conversion efficiencies. As a result, they require calibrations at least every few days and must be reconditioned, or cleaned, every few months of continuous operation, although the latter depends on the history of exposure.[1−3] Additionally, the chemical processes involved in the catalytic conversion are not fully understood.[4] Inlet design can also play a major role, as some NO_y species, notably HNO_3, can suffer significant losses on nonheated inlet surfaces.[2,5]

In this paper, we report a new method for detection of NO_y as part of a compact system that measures NO, NO_2, NO_y, and O_3 based on cavity ring-down spectroscopy (CRDS). Similar to direct absorption spectroscopy, CRDS is an absolute measurement of trace gas concentration, with an accuracy inherently limited only by knowledge of the absorption cross section and potential interfering absorbers. For the instrument described here, small species-dependent corrections must be made only for sampling losses, conversion efficiencies, and dilution factors.

Received: April 17, 2014
Revised: July 2, 2014
Accepted: July 14, 2014
Published: July 14, 2014

Furthermore, the instrument has lower power, size, weight, and vacuum requirements than a chemiluminescence-based instrument while approaching its sensitivity, precision, and time response. In the NO_y CRDS instrument we describe here, NO_y and its components are converted into NO_2 by thermal decomposition (TD) in a fused silica inlet (henceforth referred to as quartz following convention), followed by the addition of ozone to convert NO to NO_2. The successful use of TD has been demonstrated for various individual NO_y compounds (N_2O_5,[6] peroxy nitrates,[7,8] HONO,[9] $ClNO_2$,[10] alkyl nitrates, and HNO_3[8,11]), but the combination of thermal dissociation plus ozone has not, to our knowledge, been demonstrated previously for measurement of total NO_y. It represents an analytical simplification for NO_y measurements over methods that only detect NO_2 through thermal dissociation, since it does not require the summation of separate measurements. We combine this with existing techniques for measuring NO, NO_2, and O_3, allowing all four of these important and related species to be measured simultaneously with precision, accuracy, and time response sufficient for their measurement in ambient air across a range of environments and measurement platforms, including measurements from moving vehicles.

■ EXPERIMENT

The instrument is based on in situ detection of NO_2 via cavity ring-down spectroscopy.[12−16] The working principle of CRDS, as well as the conversion of O_3 and NO to NO_2, has been described in detail in previous papers[16,17] and will only be summarized here with emphasis on the design improvements. Sampling is done by pulling ambient air through Teflon inlet lines or our NO_y converter, and data are acquired in 1 s intervals. An 80 mW laser diode centered at 405 nm and modulated with a 2 kHz square wave provides light for the four measurement channels. A Faraday optical isolator provides protection from optical feedback into the laser. When the light is modulated off, the intensity inside the optical cavities decreases exponentially as measured by four photomultiplier tubes that detect the light intensity transmitted through the rear mirrors. The exponential decays are coadded and fitted once per second to extract the time constant with (τ) and without (τ_0) the absorber present. The number density of the absorber is then given by

$$[NO_2] = \frac{1}{c\sigma_{NO_2}}\left(\frac{1}{\tau} - \frac{1}{\tau_0}\right) \tag{1}$$

where c is the speed of light and σ_{NO_2} is the NO_2 absorption cross section. Previous 405 nm CRDS instruments from this group have included purge volumes adjacent to the mirrors to maintain their cleanliness. Purge volumes require a multiplicative factor, $R_L = d/l$ in eq 1, where d is the mirror separation and l is the length over which the sample is present. This factor may have had a dependence on pressure that introduces uncertainties into the measurement.[18] The instrument described here does not currently include mirror purge volumes, which simplifies the calibrations and eliminates a possible source of error. However, the elimination of the purge volumes can lead to degradation in mirror reflectivity under some circumstances. Since the sampled air is in direct contact with the mirrors, some compounds can condense onto the mirrors, causing a decrease of the time constants. This has been observed in an environment with high relative humidity and required drying of the sampled air. We have also encountered mirror degradation in the NO_y channel under conditions of extremely large hydrocarbon concentration in ambient air, to be discussed below.

The optical system is mounted in a custom designed cage system with 1/2 in. carbon fiber rods providing stability against mechanical and thermal stress. A schematic of the cage system can be seen in Figure 1. To increase stability and compactness over previous designs, the distance between cavity mirrors has been reduced from 1 m to 50 cm. We reuse the cavity mirrors with 1 m radius of curvature and have found a minimal loss of sensitivity. The corresponding ring down time constant (τ_0), determined by a combination of mirror reflectivity and Rayleigh scattering losses at ambient pressure, is approximately 30 μs, with a precision (1σ, 1s) of 6 ns.

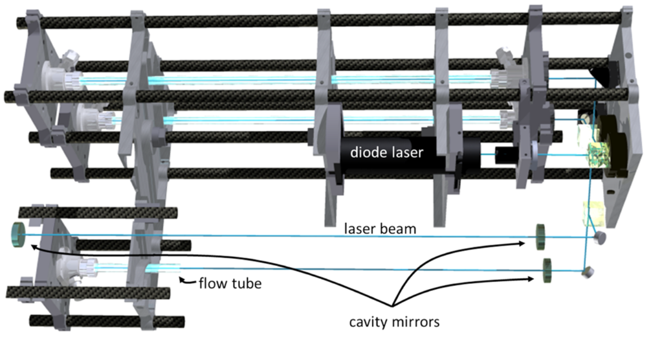

Figure 1. Schematic of the custom cage system that houses all the optical components. A large section has been cut out for ease of illustration. The laser is shown in blue, and the optics have been left in place. The combination of aluminum plates and carbon fiber rods give the system high mechanical rigidity, helping to achieve a measurement precision of a few pptv on a minute time scale.

The instrument as a whole is compact and requires low power and maintenance. It measures approximately 110 cm high with a 50 by 70 cm footprint and consumes 300 W of power at its peak. It weighs 95 kg, which includes the sample pump, a zero air generator, and the data acquisition system. The data acquisition system, however, has not been designed for low weight and currently contributes 15 kg, a figure which could be substantially reduced. The instrument also requires a cylinder of O_2 and a cylinder of NO (2000 ppm in nitrogen). These additions can be contained in 1.2 L cylinders mounted directly in the instrument rack and last for 4 days of continuous operation. Standard 30 L cylinders would provide >120 days of continuous operation.

NO_2 is directly measured in all channels via eq 1, whereas NO, O_3, and NO_y are quantitatively converted to NO_2 prior to measurement. Atmospheric NO is converted to NO_2 via reaction with excess O_3, created by flowing O_2 over a Hg Pen-Ray lamp (185 nm). As described in detail by Fuchs et al.,[16] the added O_3 results in a small percentage (<1%) of NO_2 conversion to NO_3, which subsequently reacts with NO_2 to form N_2O_5. Similarly, O_3 is converted to NO_2 via the same reaction by the addition of excess NO as described by Washenfelder et al.,[17] but without the N_2O_5 interference because $NO + NO_3 \rightarrow 2NO_2$.

Conversion of the NO_y species is performed via gas-phase thermal dissociation in a quartz inlet, chosen for its high melting point and because it is relatively unreactive.[11] Figure 2 depicts a conceptual drawing of the NO_y converter. During normal operations, the front half of a quartz tube is heated such

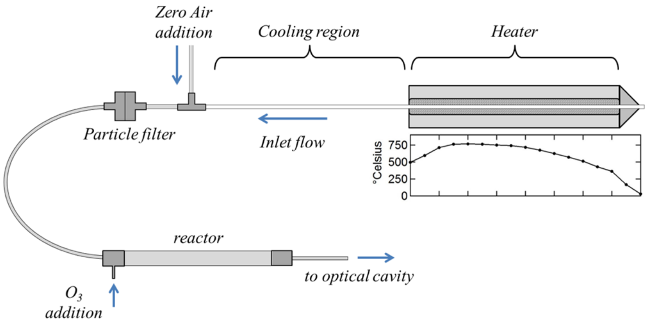

Figure 2. Diagram of the NO_y converter. The heated section consists of nichrome wire wrapped around a quartz tube. It is thermally insulated with fiberglass insulation and encased in a metal shell ending in a cone, protecting the quartz and conducting heat to the tip. A profile of air temperature as a function of position inside the heater with a flow of 1.5 standard liters per minute at atmospheric pressure is shown (with set point higher than normal operation). The total residence time in the heated section is about 48 ms. The zero air addition is used for a periodic measurement of τ_0. Just before the optical cavity, excess O_3 is added to convert any NO to NO_2.

that the sample air reaches a temperature of approximately 700 °C. The inset shows a typical temperature profile of the gas in the heater (set to heat the gas to 750 °C), measured by insertion of a thermocouple probe in the gas flow during ambient air sampling. For a 1.5 slpm flow, the plug flow residence time in the heated section is approximately 48 ms. The Reynolds number is <1000 for the given range of temperatures, well in the laminar flow regime. The metal shell ends in a cone-shaped nozzle to ensure that the quartz is heated to the inlet end in order to minimize losses of HNO_3, which can be significant on colder surfaces, especially quartz.[5] After the heated section, NO_y components have been converted to NO_2 (and possibly some NO), which can be transported to the CRDS measurement cell through an arbitrary length of Teflon tubing without significant losses. Since the converter itself functions as the inlet, we anticipate particulate sampling with high efficiency and include particulate nitrate in our NO_y budget.[19] Particulate nitrate entering the converter should evaporate rapidly, eliminating inertial loss normally associated with particulate sampling. However, we have not attempted to determine a characteristic cut point (a size at which particles are no longer transmitted effectively) for the converter as a whole. The thermal conversion process likely produces mainly NO_2, although some compounds, such as HONO, may dissociate to NO.[9] A small fraction of the NO_2 may also be reduced to NO by reaction with atomic oxygen in the converter.[11] Finally, the thermal converter is not designed to convert NO to NO_2. Any NO in the air sample after the heating and cooling process is converted to NO_2 via addition of excess O_3 just prior to the CRDS measurement cell, as in the NO_x channel. The O_3 is generated from the same Pen-Ray ultraviolet lamp source and split evenly between the two channels using a pair of critical orifices to divide the flow.

To zero the instrument (i.e., measure τ_0 in eq 1), we flush the sample tube by overflowing the inlets with air from which all NO_x and O_3 has been removed (zero air) that is generated in situ (or supplied by a cylinder when necessary). We overflow using an annular inlet (i.e., with zero air added through a large diameter tube that surrounds and extends just beyond the sample inlet) for the NO, NO_2, and O_3 channels, and a simple tee fitting, shown in Figure 2, is used for the separate NO_y inlet. The overflow during the zeroing process creates a pressure change of <0.2 hPa (0.03%) for the annular inlet and a change of 4 hPa (0.5%) in the NO_y inlet. The changes in pressure for the NO_y zeroing changes the Rayleigh scattering of the air sample, requiring a correction of approximately 60 pptv equivalent NO_2, which is based on well-known Rayleigh cross sections and is accurate to well within 3 pptv. We zero the channels every 7 min during mobile platform operations but increase this time to 15 min for stationary settings (a zero takes between 30 and 90 s, depending on the length of the inlet).

■ RESULTS AND DISCUSSION

Laboratory Tests. To illustrate the conversion of the various NO_y components, we show measured temperature profiles of the signal from several NO_y species in Figure 3.

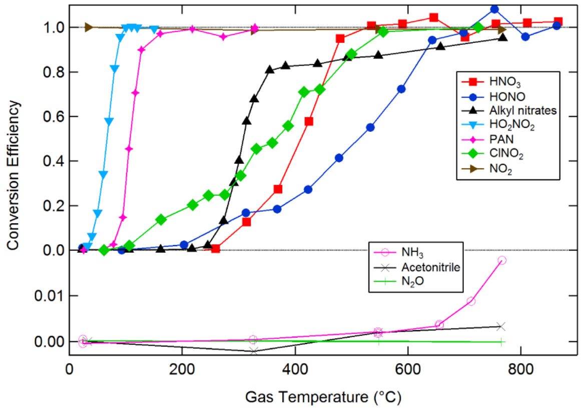

Figure 3. (Upper plot) Temperature profiles of several of the most abundant components of NO_y. HNO_3 and alkyl nitrates were compared to a known standard, and the other compounds are scaled to unity at high temperatures. (Lower plot) Temperature profiles from known quantities of possible interference compounds. NH_3 in dry air resulted in the only measurable interference of <1% at 700 °C. The interference was less than 0.1% for air with a relative humidity of 10% or greater.

Many of these conversions have been previously demonstrated with heated quartz,[7,9−11] and we have repeated tests for the compounds that were readily available. For most samples, the output concentration was uncalibrated and scaled to unity in Figure 3, but a leveling off at high temperature strongly suggests unit conversion. We did not explicitly test conversion of the nitrate radical, NO_3, but expect full conversion at the operating temperature.[20] We directly compared our measurements of HNO_3 and PAN to that of a heated Mo catalytic converter and saw full conversion at our operating temperature of 700 °C. The alkyl nitrates (a mix of methyl, ethyl, *i*-propyl, *n*-propyl, *i*-pentyl, and *i*-butyl nitrate from a calibration cylinder) show a rapid conversion to NO_2 up to 300 °C, then a slower increase up to 800 °C, where we see full conversion to within the cylinder specifications (±10%). The slower conversion at higher temperature differs from previously reported temperature profiles for organic nitrates[11] and may be due to the temperature profile specific to our inlet. Since our design goal is total rather than speciated NO_y, the behavior of organic nitrates at intermediate temperatures does not significantly affect the performance of the total NO_y measurement.

Some nitrogen-containing gases that are not products of NO_x oxidation and therefore not components of NO_y as traditionally defined could conceivably be converted to NO_x at high temperatures. If they are present at mixing ratios comparable to or larger than NO_y in the atmosphere, as can be the case for NH_3, N_2O, and nitriles, these compounds could represent a significant interference for an NO_y measurement based on thermal conversion to NO_2. We sampled known standards of NH_3, N_2O, and acetonitrile with the thermal converter, as shown in the lower plot of Figure 3. Ammonia resulted in the only nonzero interference, reaching about 1% conversion at our working sample temperature of 700 °C. However, this interference was only present in dry air from a cylinder (<1 ppm water vapor mixing ratio). A relative humidity of 10% was enough to suppress the NH_3 conversion to NO_2 to below 0.1%, such that it can be considered a negligible interference in nearly all field situations. Like Day et al., we do not expect to be sensitive to aromatic nitro compounds.[11] Furthermore, they are not typically expected to be a large fraction of NO_y. Reports of particle bound nitro-PAHs in Los Angeles, for example, have an equivalent gas phase concentration <0.1 pptv.[21]

Other interferences to NO_2 detection using 405 nm CRDS have been described before. A water vapor interference results from the change in Rayleigh scattering, which was measured by Fuchs et al.[16] and results in a small correction to our data. Absorbing gases other than NO_2, such as α-dicarbonyls, are a direct interference but constitute a small percentage of NO_x in most scenarios.[16] However, since these compounds require a higher dissociation temperature than our NO_y converter provides, they only represent an error in the NO_2 baseline. The subtractive measurements of NO, O_3, and NO_z ($\equiv NO_y - NO_x$) are therefore unaffected by α-dicarbonyls. Direct absorption by ambient O_3 in the NO and NO_2 channels represents a negligible interference because the absorption cross section of O_3 at 405 nm is $1.5 \times 10^{-23} \mathrm{cm}^2$ ($\sim 4 \times 10^4$ times smaller than that of NO_2).[16,22] For 50 ppbv of O_3, the optical extinction is $1.9 \times 10^{-11} \mathrm{cm}^{-1}$, or equivalent to approximately 1 pptv of NO_2. The optical extinction due to the added 30 ppmv O_3 in the NO_x and NO_y channels is measurable, but this signal is constant across instrument zeroing and thus does not contribute to the measurement. However, it provides a convenient means to measure the added O_3 by switching the O_3 addition on and off during periods of zero air sampling.

The NO_2 calibrations of the four channels have also been described in previous papers.[16,17] O_3 is measured by a commercial UV absorption O_3 instrument and then quantitatively converted to NO_2 in excess NO. The NO_2 is then measured by CRDS in the four channels. This provides four measurements of the effective absorption cross-section, σ_{NO_2}, which differ by less than 2% between the channels. The day-to-day variability of these measurements is less than 1%. Figure 4 shows a typical plot showing the relation between integration time and 1σ precision (Allan deviation plot) for the four channels during sampling of zero air. The dashed lines indicate the expected square root relationship for statistically random noise. All channels follow a nearly statistical noise distribution out to 100 s integration time, resulting in a minimum detection limit of a few parts per trillion volume. The uncertainties of the NO_2 measurement in the four channels are due to calibration uncertainties and result in a 3% uncertainty in the base measurement.[16] Conversion of NO_2 to N_2O_5 in the two channels that add excess O_3 (NO_x and NO_y) increases the uncertainty of NO_x measurements up to 5%.

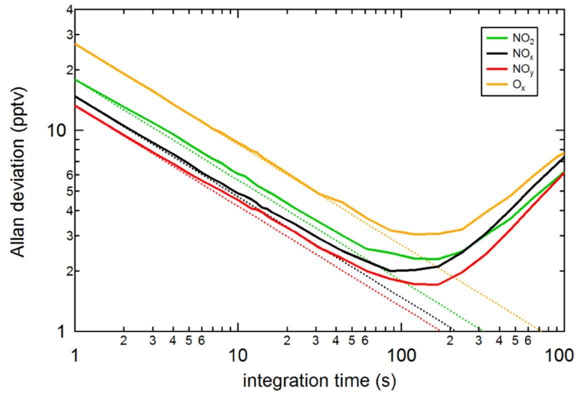

Figure 4. Dependence of 1σ precision on integration time (Allan deviation plots) for the four channels measuring NO_2 in zero air under laboratory conditions. The dashed lines show the expected trend for statistically random noise.

The uncertainty of the NO_y measurement must include the conversion efficiency uncertainties for the different NO_y compounds. The comparisons to known concentrations (HNO_3, PAN, and alkyl nitrates) showed full conversion to within the uncertainty of the standards (approximately 10%, from the uncertainty in conversion efficiency of the Mo converter and the alkyl nitrate cylinder mixing ratio). But for the other compounds, quantitative conversion was implied by the temperature profile, and uncertainties are unavailable. We derive a total uncertainty empirically by comparison of the thermal dissociation CRDS instrument to a standard NO_y instrument under field conditions. The results of this comparison, discussed below, suggest a limiting uncertainty in the NO_y measurement of 12%.

Field Comparisons. The new NO_y detection scheme was quantitatively tested during two field comparisons in 2013. One was the Uintah Basin Winter Ozone Study (UBWOS) 2013, during which our measurement was compared to the sum of the separately measured NO_y components. The other comparison occurred during the Southeast Oxidant and Aerosol Study (SOAS), where our total NO_y measurement was directly compared to total NO_y measured with a standard Mo catalytic converter.

The UBWOS 2013 campaign was a four-week study in the Uintah Basin of Utah in February and March. The area is host to extensive oil and gas operations and regularly experiences strong temperature inversions. This results in very high ozone events as well as elevated levels of NO_z ($\equiv NO_y - NO_x$, averaging about 12 ppbv over the campaign), making it an ideal field test for the NO_y converter. In addition to our measurement of total NO_y and NO_x, two chemical ionization mass spectrometers measured concentrations of HNO_3, $ClNO_2$, HONO, and PAN.[23,24] A particle-into-liquid sampler measured particle phase inorganic nitrate, and a separate cavity ring-down system measured NO_3 and N_2O_5.[6]

During this campaign we observed degradation of the mirror reflectivity to unworkable values over the course of 5 min time scales when sampling behind the heated inlet and without purge volumes in place. The cause of this degradation was not clear, but it may have been the result of production of condensable gases from hydrocarbon degradation occurring in the NO_y converter. Measured hydrocarbon mixing ratios were anomalously large, in excess of 0.5 ppmv on average and frequently several parts per million, due to the location of the

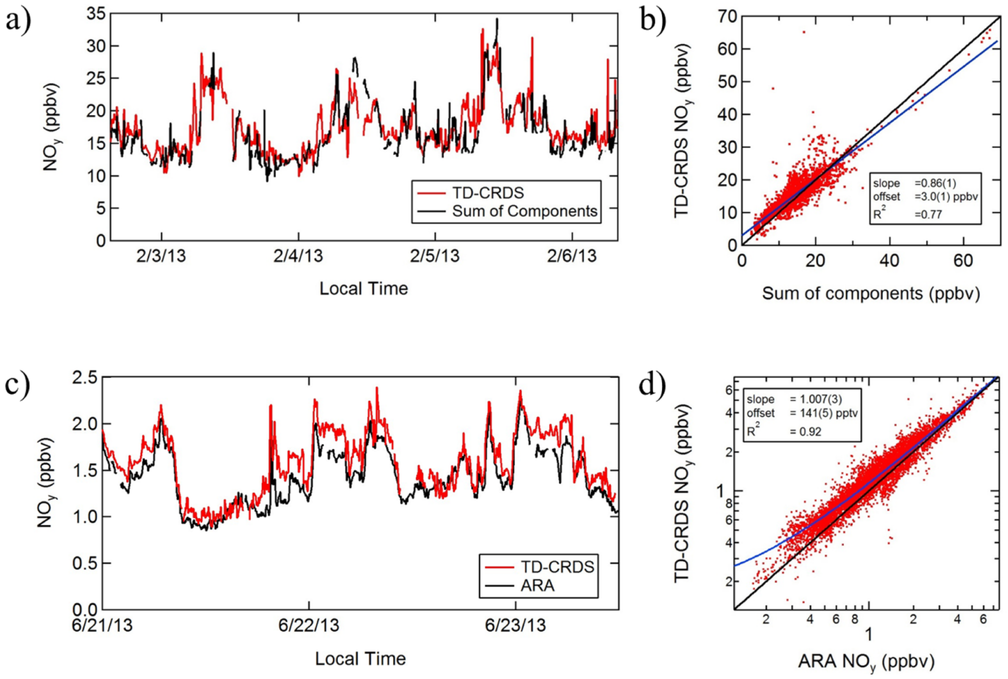

Figure 5. (a) A representative time series showing several days of measurement comparing the total NO_y as measured by our instrument with the sum of NO_y components during the February/March UBWOS field campaign, during which NO_x contributed 28% to NO_y. (b) Correlation plot of NO_y to the sum of components for the entire campaign. (c) A time series comparing the total NO_y measured by TD to total NO_y measured by a Mo catalytic converter used by Atmospheric Research and Analysis, Inc. (ARA) during the June/July SOAS field campaign, during which NO_x contributed 43% to NO_y. (d) Correlation plot for the two methods for the entire campaign. All data shown are 5 min averages.

sampling site in a natural gas extraction field.[25] Installation of a hydrocarbon scrubber tube downstream of the NO_y converter prevented mirror reflectivity degradation without apparent influence on measured NO_y, increasing response time by a mere 150 ms.[26] We observed the scrubber to be required for measurements during this campaign, though subsequent trials, including another campaign in the Uintah Basin in 2014, did not require use of the scrubber. In the upper part of Figure 5, we show the comparison between our total NO_y measurement and the sum of the NO_y components as measured by different instruments (not including organic nitrates), for which NO_x represents a 28% contribution to NO_y. Figure 5a shows a representative time series over a few days. In Figure 5b, we plot the correlation between the NO_y measurement and the sum of the components over the whole campaign. The data presented are 5 min averages because inlets had small differences in location (several meters separation) at the field site, and because of frequent transient high-NO_x spikes that were inhomogeneously mixed. On average, the new NO_y instrument measured 0.9 ppbv (6%) higher NO_y than the sum of components. This difference may be due to organic nitrates, for which data are not available in 2013, or simply from the combined uncertainties of the individual measurements.

The SOAS campaign was a six-week study in central Alabama in June and July of 2013. The site is colocated with a SEARCH network monitoring station maintained by Atmospheric Research and Analysis, Inc. (ARA), which collects long-term measurements of a suite of gases, including total NO_y. The ARA NO_y measurement is performed using a standard Mo catalytic converter that converts NO_y to NO, followed by chemiluminescent detection of NO. The SOAS campaign thus provided an opportunity for direct comparison between the TD-CRDS NO_y and a more conventional NO_y instrument. The inlets were separated by about 110 m horizontally and 15 m vertically, with the ARA inlet positioned a few meters above ground. Although mirror purge volumes were also not used for this campaign, a hydrocarbon scrubber as in the UBWOS campaign was not required. However, the high humidity of air sampled during summertime in Alabama required drying the sample air with a cold trap for all the channels (after the converter for the NO_y channel) in order to avoid signal degradation due to water vapor condensation on the mirrors. This modification is similar to that used on commercial CRDS instruments that measure NO_2 alone.[15] The cold trap reduced the relative humidity to <15% but did not measurably influence the transmission of NO_2.

The lower part of Figure 5 shows a comparison of the two measurements. In this case, the average NO_x contribution to NO_y was 43% during the SOAS campaign. High concentration spikes tended to show poorer agreement, most likely due to the separation between the inlets. In Figure 5c, we plot a time series of the two instruments spanning 2 days with low occurrences of large concentration spikes. In Figure 5d, we show a correlation plot of all the data from the campaign. The slope is equal to unity to within our 5% measurement uncertainty, but there is an average offset of about 140 pptv. This offset may be caused by variation in the sensitivity to specific components of NO_y, such as coarse aerosol nitrate, between the two instruments, a real difference in ambient NO_y due to the separation of the inlets, a systematic error between the two instruments, or a combination of these. Nevertheless, the observed offset provides an upper limit for our NO_y measurement uncertainty relative to an accepted standard measurement method. Taking the difference between the two measurements, dividing it by our measurement, and averaging the result over the whole campaign results in a 12% upper limit uncertainty estimate for our NO_y measurement.

In summary, we have described a compact CRDS instrument measuring NO, NO_2, O_3, and total NO_y. Although we encountered potential artifacts due to response of the mirrors to relative humidity and extreme VOC concentrations, the instrument in its current form is robust, able to operate essentially unattended for days to weeks at a time. We have further demonstrated a new technique for measuring NO_y using thermal decomposition to NO_2 in a heated quartz inlet, followed by conversion of NO to NO_2 in excess O_3. Temperature profiles of individual components are consistent with unit conversion efficiency for every NO_y component measured, and there is no significant interference from other reduced nitrogen compounds. Instrument performance has been demonstrated with comparisons at two ground sites. These field tests show agreement both with the sum of NO_y components measured by separate, independent instruments and with a measurement of total NO_y by a standard molybdenum catalytic converter to within <1% correlation and an absolute offset of 140 pptv. The latter comparison allows us to empirically define an upper limit on the NO_y measurement uncertainty of 12%, although the uncertainty may depend on the relative concentrations of NO_y components. The instrument performance was equivalent while sampling from within a moving vehicle (instrumented van) and is likely to be appropriate for aircraft sampling based on our previous experience.[18]

Future work will involve investigation of methods to prevent mirror degradation without the need for drying the sample air or scrubbing it of hydrocarbons. Designs are currently being tested for smaller purge volumes that require smaller path length corrections than our previously reported instruments, or for testing other methods to make the mirrors less susceptible to condensation effects. The current instrument, while smaller than previously reported versions, can be further reduced in size and weight to allow for more versatile deployments on mobile platforms.

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Notes

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■ ACKNOWLEDGMENTS

The authors thank Joost de Gouw for help with calibrations and data analysis. This work was funded in part by an Innovative Research Proposal Grant from the Cooperative Institute for Research in the Environmental Sciences at the University of Colorado and in part by the NOAA Atmospheric Chemistry, Carbon Cycle and Climate (AC4) Program.

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