

Modification of a commercial cavity ring-down spectroscopy NO₂ detector for enhanced sensitivity

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Nitrogen dioxide (NO₂) plays a central role in atmospheric chemistry, air pollution, and biogeochemical cycles. Many analytical techniques have been developed to detect NO₂, but only chemiluminescence-based instruments are commonly, commercially available. There remains a need for a fast, light, and simple method to directly measure NO₂. In this work we describe the modification and characterization of a small, commercially available cavity ring-down spectroscopy (CRDS) NO₂ detector suitable for surface and aircraft monitoring. A metal oxide scrubber was added to remove NO₂, and provide a chemical zero, improving the detection limit (3σ of the background noise) from several parts per billion by volume (ppbv) to 0.06 ppbv, integrated over 60 s. Known interferences by water and particles were removed using Nafion tubing and a 1 μ m Teflon[®] filter, respectively. A 95% response time of 18 ± 1 s was observed for a step change in concentration. The CRDS detector was run in parallel to an ozone chemiluminescence device with photolytic conversion of NO₂ to NO. The two instruments measured ambient air in suburban Maryland. A least-squares fit to the comparison data resulted a slope of 0.960 ± 0.002 and R of 0.995, showing agreement within experimental uncertainty. © 2009 American Institute of Physics. [doi:10.1063/1.3244090]

I. INTRODUCTION

Nitrogen dioxide (NO₂) plays an important role in tropospheric and stratospheric ozone chemistry and in biogeochemical N cycles.¹ In the polluted troposphere, photolysis of NO₂ in the presence of volatile organic compounds leads to ozone formation, while in the stratosphere oxides of nitrogen destroy ozone.²

A variety of methods exist for measuring NO₂, ranging from relatively inexpensive off-the-shelf commercial analyzers to research grade, highly sensitive techniques. NO₂ monitoring for compliance with U.S. Environmental Protection Agency's (EPA) National Ambient Air Quality Standard is usually accomplished with reduction of NO₂ to NO followed by reaction with ozone and chemiluminescence;³ the concentration of NO₂ is determined from the difference between NO_x (the sum of NO and NO₂) and NO measured directly. The most common method for conversion of NO₂ to NO, (passage over 375 °C Mo) also converts a variety of other species (including peroxy acetyl nitrate, PAN, and HNO₃) to NO. While this technique is adequate for demonstrating

compliance with the NO₂ standard, it can overestimate NO₂ substantially. Thus a specific, reliable, fast, and economical method for monitoring NO₂ in rural and urban environments is needed.^{4,5}

Methods for ambient measurements of NO₂ have been reviewed^{3,6-9} and will be briefly summarized here. Photolysis of NO₂ followed by chemiluminescence offers greater specificity than the hot Mo reduction discussed above,¹⁰ while chemiluminescence of NO₂ with luminol does not require conversion to NO.¹¹ However the luminol technique is non-linear at low NO₂ concentrations and will respond to PAN. Matrix isolation electron spin resonance, laser induced fluorescence, differential optical absorption spectroscopy, and tunable diode laser absorption spectroscopy are also sensitive and specific.¹²⁻¹⁵ A number of intercomparison studies demonstrating the accuracy of these research grade instruments have been carried out,¹⁶⁻²¹ but use of these labor intensive and expensive methods has generally been restricted to short-term field studies.

Cavity ring-down spectroscopy (CRDS) is a highly sensitive optical absorption technique that uses the rate of decay of light intensity in an optical cavity to measure the concentration of an analyte. The principles of CRDS have been described previously;²²⁻²⁵ briefly, a light pulse is coupled into an optical cavity made up of two highly reflecting mirrors (Fig. 1). At each pass the small fraction of light that is transmitted through one end of the cavity is monitored with a

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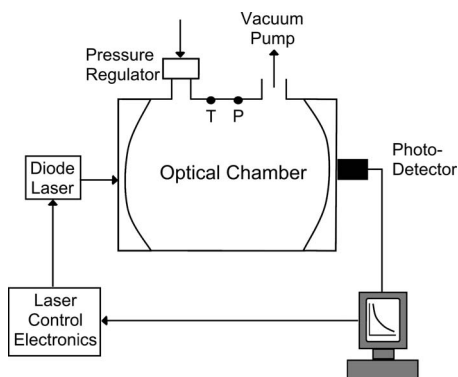


FIG. 1. A schematic diagram of the CRDS apparatus used to measure NO_2 . Pressure in the optical chamber is maintained 170 torr (227 hPa). The mirrors, 30 cm apart, reflect 99.95% of the radiation from the 407.38 nm laser resulting in an effective path length approaching 1000 m.

photodetector. The light passes through the sample hundreds of times resulting in path lengths on the order of kilometers and great sensitivity. The exponential decay of light intensity inside the cavity can be characterized by a cavity ring-down time constant, τ , a function of the reflectivity of the mirrors, the length of the cavity, Rayleigh scattering by air, and absorption by the analyte [Eq. (1)],

$$I(t) = I_0 \exp(-t/\tau). \quad (1)$$

If the analyte fills the length of the cavity, the analyte number concentration (N molecules cm^{-3}) can be determined by Eq. (2), where τ_0 is the ring-down time constant when the absorbing analyte is absent from the cavity, c is the speed of light, and σ is the analyte absorption cross section in $\text{cm}^2/\text{molecule}$,

$$N = \frac{1}{c\sigma} \left(\frac{1}{\tau} - \frac{1}{\tau_0} \right). \quad (2)$$

The development of CRDS for absorption studies can be traced back to O'Keefe and Deacon²⁴ (1988), who were the first to record an absorption spectrum of molecular oxygen with CRDS. Since then, many groups have used CRDS for trace gas measurements.^{23,25–28} For a review of the many uses of CRDS see Berden *et al.*²⁹ (2000) and Wheeler *et al.*³⁰ (1998).

II. EXPERIMENTAL METHODS

A. Cavity ring-down spectrometer

In this work, we characterize a commercially available CRDS NO_2 detector (RMT-200, Los Gatos Research, Inc., Mountain View, CA), and describe modifications to enhance its detection limit. The instrument comes equipped with a small continuous wave diode laser operating at 407.38 nm with a pulse rate of 1200 Hz, highly reflecting mirrors (99.95% at 390–425 nm) separated by 30 cm, and a pressure regulator that maintains the internal pressure of the cavity at 170 torr (227 hPa). The temperature and pressure inside the optical cavity is monitored in order to convert the NO_2 number concentration to a volumetric mixing ratio. Conversion to ambient concentration in units of $\mu\text{g m}^{-3}$ or molecules cm^{-3} can be made if ambient temperature and pressure are

known. Because few tropospheric constituents have significant absorption cross sections or ambient concentrations in this spectral range, the method is essentially free of interferences.³¹ However, the absorption cross section of glyoxal is the same order of magnitude as that of NO_2 , but is present in the atmosphere at part per trillion (pptv) levels. At ambient NO_2 concentrations below the part per billion (ppbv) level this could lead to a bias in the measurement.

Because the configuration of the CRDS instrument as provided by the manufacturer does not allow for regular background correction, the instrument detection limit is determined by the extent of the baseline drift, which is on the order of several ppbv over the course of an hour. In order to enhance the detection limit, we installed a solenoid valve wired to a timer to periodically divert the sample air through a scrubber. Thus the instrument monitors a NO_2 -free or background ring-down time; the frequency of background correction can be tuned to account for the measurement mode (faster for aircraft observations, slower for surface monitoring). We found that commercial metal oxide scrubbers found in TECO Model 49 and Dasibi Model 1003AAS ozone analyzers effectively removed NO_2 from sample air. A ring-down time equal to that of zero air was observed for samples of 13–140 ppbv NO_2 at room temperature after passing through the scrubber.

The software algorithms to calculate NO_2 concentration from ring-down time, including the NO_2 absorption cross section, were used as supplied by the instrument manufacturer. The instrument calculates and records the NO_2 concentration every second from the average of roughly 1000 ring-down times. Background correction was completed in postprocessing.

The instrument was calibrated with NO_2 generated by gas phase titration (GPT) of NO with O_3 . The amount of NO_2 generated for excess ozone can be calculated from either the loss of ozone or the known initial concentration of NO. We mixed compressed air, a small flow of NO-in-nitrogen [Air Products, 3.14 ppm by volume (ppmv)], and 300 ppbv ozone generated with a UV lamp in an ozone calibrator (Model 49C, Thermo Electron Corporation, Franklin, MA) to produce NO_2 concentrations in the range of 13–140 ppbv (Fig. 2). A revised concentration of 3.13 ppmv NO and 3.58 ppmv NO_x was found for the commercial NO-in-nitrogen standard after comparison with a U.S. National Institute of Standards and Technology (NIST) standard reference material (SRM # 2627a). We estimate the uncertainty of the NO_x concentration in the standard to be $\pm 10\%$ (95% confidence interval).

B. Photolysis followed by chemiluminescence

The National Oceanic and Atmospheric Administration (NOAA) constructed a chemiluminescence detector from commercial chemiluminescence detectors (Model 42s, Thermo Electron Corporation). Addition of a high-output silent discharge ozone electrode (Ozonology, Inc., Northbrook, IL) and a high capacity Teflon[®] diaphragm pump (DTC-120, Kurt J. Lesker Co., Clairton, PA) enhanced the sensitivity. NO and NO_x were measured simultaneously on dedicated channels, and NO_2 was determined by difference. A pho-

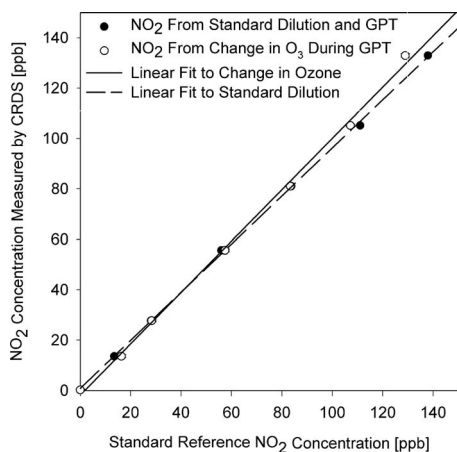


FIG. 2. Comparison of NO_2 measured by CRDS to NO_2 concentrations calculated from a known concentration of NO in excess ozone (filled circles) and from the decrease in ozone concentration (open circles) monitored with an ozone detector based on UV absorption. The least-squares fit to the data generated from the change in ozone concentration (solid line) has a slope of 1.02 ± 0.02 , an intercept of -1.8 ± 1.5 ppbv, and $R=0.999$. The least-squares fit to the data generated from the standard dilution (broken line) has a slope of 0.95 ± 0.01 , an intercept of 0.9 ± 0.6 ppbv, and $R=0.999$. The error bars for each point are the same size or smaller than the circles.

tolytic NO_2 to NO converter made up of two UV light emitting diode (LED) arrays was operated on the NO_x channel.³² The converter design, based on that of a solid-state light source converter,³³ consisted of a 225 cm^3 cylindrical quartz cell illuminated longitudinally with two UV LED arrays ($\lambda_{\text{max}}=395 \pm 5$ nm; Opto Diode Corp., Newbury Park, CA) at each end. A custom-built power supply provided current control and thermal overload protection to each array. Highly reflective Teflon[®] (Gigahertz-Optik Inc., Newburyport, MA) used on the outer cell surfaces enhance photon reflectivity. At the nominal sample flow of 1 slm and pressure of 100 torr, cell residence time was approximately 2 s. Correction of NO and NO_2 values for variations in ambient O_3 (e.g., Ref. 34) was not necessary.

The LED arrays impart little heat, which avoids interference from decomposition of PAN, N_2O_5 , or HO_2NO_2 . This instrument is also insensitive to other reactive compounds such as HNO_3 , organonitrates, amines, and particulate nitrate, which can be reduced to NO in commercial instruments using hot molybdenum and research grade instruments using gold-catalyzed CO. With the photolysis method, only nitrous acid (HONO) has a considerable interference potential; it has a significant absorption cross section at 395 nm, but its photolysis potential is only 1.4% of that of NO_2 at $\lambda_{\text{max}}=395$ nm. Recent tests on the NOAA instrument suggest a HONO interference of about 5%, suggesting that the

peak emission wavelength is slightly shorter than 395 nm.

C. Intercomparison on ambient air

The intercomparison of ambient NO_2 measurements by the CRDS and NOAA chemiluminescence instruments was conducted on January 5–18, 2009. The two instruments sampled ambient air outside of the laboratory window next to a busy parking lot in College Park, MD. Diverting sample air through the scrubber every 15 min for 3 min established a background for the CRDS instrument. To test the efficiency of the NO_2 scrubber and to measure any artifact in the measurement by the chemiluminescence device, the inlet line was flooded with zero air every 5 h for 15 min. The chemiluminescence device was calibrated every 5 h with a ~ 55 –65 ppbv mixture of NO (Scott Marin, 20.17 ppmv) in zero air, and the photolytic conversion efficiency of NO_2 to NO was tested every 2–3 days using GPT that generated ~ 40 ppbv of NO_2 .³⁵ The GPT was also used to monitor the sensitivity of the CRDS instrument.

III. RESULTS

A. Detection limit and response time

From a reading of zero air, the 3σ detection limit of the CRDS instrument is 0.2 ppbv integrated over 10 s, and 0.06 ppbv for 60 s. A first order response to a step change in concentration was observed, with a response time of 18 ± 1 s to reach 95% of the new signal. The CRDS NO_2 detector has an internal volume of 460 cm^3 , including the optical cavity and tubing. At a typical flow rate of 560 $\text{cm}^3 \text{min}^{-1}$ and an internal pressure of 170 torr, this corresponds to a residence time of 11 s. Thus, with larger pumping speeds, the instrument is capable of faster response times.

Table I lists a comparison of performance statistics for a commercial chemiluminescence instrument (as reported by the manufacturer), the NOAA research grade device used in this intercomparison, and the CRDS instrument. The fixed internal pressure, low power draw, and compact size of the CRDS instrument make it ideal for aircraft use at altitudes up to ~ 10 km.

B. Calibration and water interference

The CRDS NO_2 measurements and the NO_2 concentrations calculated from the change in ozone concentration upon gas phase titration with the NO_x standard dilutions were in excellent agreement (Fig. 2). The least-squares fit has a slope and intercept of 1.02 ± 0.02 and -1.8 ± 1.5 ppbv, respectively, and a linear correlation coefficient $R=0.999$.

TABLE I. Measurements of ring-down times of zero air and scrubbed standard dilutions of NO_2 .

	3σ Detection limit (Averaging time) (pptv)	Response time (s)	Power draw (W)	Internal pressure (torr)	Dimensions $W \times H \times D$ (cm)	Weight (kg)	NO_2 to NO converter
CRDS analyzer	60 (60 s)	18 (95%)	90	170	42.5 × 22 × 56	23	...
NOAA chemiluminescence	100 (60 s)	3 (95%)	1000	30	42 × 33 × 58.4		Photolytic
Thermo Electron Corp. Model 42i TL	75 (120 s)	60	300	200–450	42.5 × 22 × 58.4	25	Thermal reduction with a Mo catalyst

The slope of the comparison of CRDS NO_2 measurements to the concentration of NO_2 calculated from the mass flow rate of the NO_x standard dilutions has a low bias (linear least-squares slope of 0.95 ± 0.01 , intercept of 0.9 ± 0.6 ppbv, and linear correlation of $R=0.999$) probably as a result of NO_2 losses in the mixing volume, tubing, and fittings, or errors in the flow controller calibrations, concentration of the NO calibration standard, etc.

An interference of 4.8 ppbv equivalent NO_2 was found for 2.2% water, similar to findings by Hargrove (2006). At constant altitude near the Earth's surface, where humidity changes slowly, monitoring the background ring-down time is an adequate correction for water. In rapidly changing ambient environments, as on an airplane, background corrections must occur frequently or water must be removed from the sample air. Furthermore, the NO_2 scrubber was found to be water sensitive; the metal oxide mixture acts as a reservoir for water, which leads to a positive interference during dry conditions.³⁶ We found that a 3 m coil of Nafion (Model MD-110-72F-4, Perma Pure, Inc., Toms River, NJ) tubing at the inlet of the CRDS instrument effectively eliminated the interference from water vapor, with undetectable losses of NO_2 for concentrations in the parts per billion by volume range.

C. Ambient intercomparison

The comparison of the CRDS instrument with the NOAA chemiluminescence device measuring ambient air showed good agreement during both polluted and relatively clean time periods (Fig. 3). On January 5–9 the correlation had a slope of 0.960 ± 0.002 , an intercept of 0.28 ± 0.03 ppbv, and R of 0.995 [Fig. 4(a)]. The correlation drifted slightly with time. On January 10–16 the correlation had a slope of 0.932 ± 0.002 , an intercept of -0.61 ± 0.04 ppbv, and R of 0.982 [Fig. 4(b)].

The data before January 10th are more reliable because the chemiluminescence analyzer experienced significant dynamic drift in the sensitivity of both channels during the remainder of the comparison (Fig. 5) because variability in the power supply may have led to changes in the pumping speed (the sensitivity of a chemiluminescence instrument to NO is a linear function of the pumping speed). This introduced uncertainty in the calibration factor for this instrument on the order of 5%. Also, error in the NO_2 measurement by CRDS after January 9th developed because aerosols degraded the mirror surfaces and increased the noise. Although the sample air was passed through a 1 μm Teflon[®] filter, some particles were still able to enter the cavity; the inlet was located roughly 10 m from a popular idling spot for large trucks in the parking lot. A filter that removes particles down to 0.1 μm diameter is recommended. These interference events were identified by sharp increases in the standard deviation of the ~ 1000 ring-down events captured every second. After January 16, 2009 the ring-down times were too short to consider the data reliable. However, upon cleaning the mirror surfaces with methanol and acetone, the reflectivity returned to previous levels, and instrument performance improved. With regular mirror cleanings and a smaller pore size, the CRDS will be capable of long-term performance.

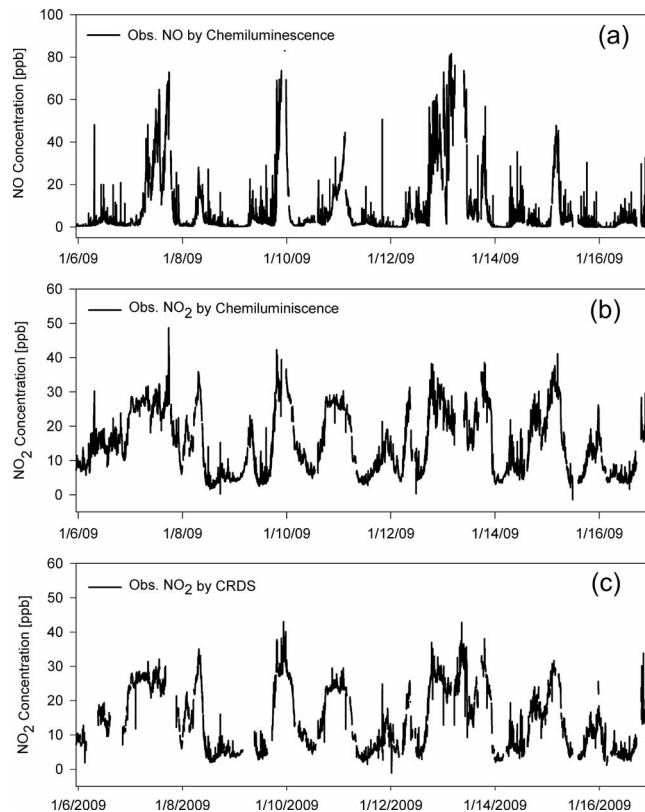


FIG. 3. Ambient NO (a) and NO_2 (b) measurements taken with the NOAA chemiluminescence device and CRDS (c) from January 5, 2009 to January 16, 2009 in a suburban Maryland setting. The chemiluminescence instrument utilized photolysis to convert NO_2 to NO.

Over the course of January 5–16, the sensitivity of the CRDS instrument was analyzed eight times with GPT and was found to fluctuate by 3% with no apparent systematic trend. The average sensitivity from these calibrations was used in the correlation plots with the chemiluminescence measurements to eliminate variability due to errors in the calibration technique. The efficiency of the NO_2 scrubber, analyzed every 5 h, remained consistent with the results of our initial experiment throughout the intercomparison. Calibrations with the Nafion drying tubing showed no detectable losses of NO_2 .

The two instruments capture the daily cycle of NO_x due to photochemistry and boundary layer development (Fig. 6). The local maximum of NO_2 occurs at 7 a.m. (local standard time) during the peak in morning rush hour when fresh NO from cars is emitted into the shallow mixed layer where it reacts with ozone to produce NO_2 . The ratio of NO/NO_2 peaks at noon signaling maximum photolysis of NO_2 to NO (and photochemical ozone production), and there is generally higher NO_x at night reflecting the daily evolution of mixing height.

IV. DISCUSSION

Measurements of NO_2 with custom-built CRDS instruments at 405–425 nm have accurately detected NO_2 concentrations from 0.15 ppbv to 200 ppmv.^{31,37–40} A previous intercomparison study with a commercial chemiluminescence device utilizing thermal conversion of NO_2 to NO showed an

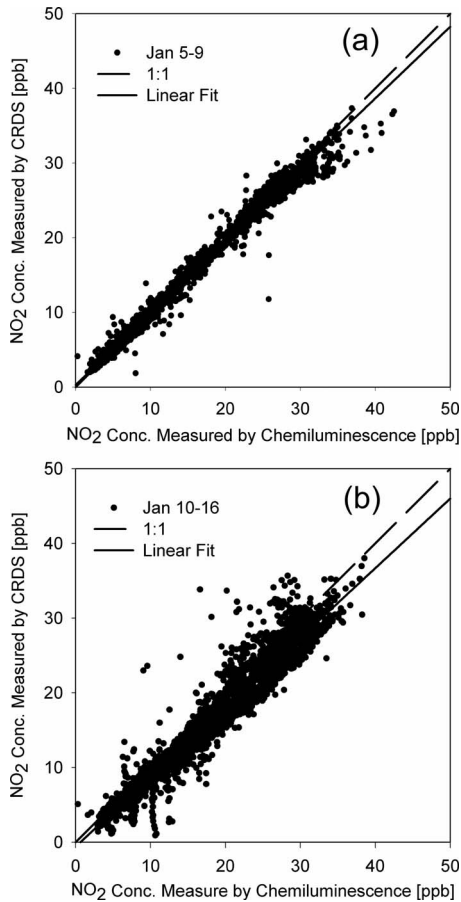


FIG. 4. Scatter plots of ambient NO_2 measured by CRDS and chemiluminescence on January 5–9, 2009 (a) and January 10–16, 2009 (b). The slope, intercept, and R of the linear least-squares fit to the January 5–9, 2009 data are 0.960 ± 0.002 , 0.28 ± 0.03 ppbv, and 0.995, respectively. The slope, intercept, and R of the linear least-squares fit to the January 10–16, 2009 data are 0.932 ± 0.002 , -0.61 ± 0.04 ppbv, and 0.982, respectively. The dashed line represents a one to one fit.

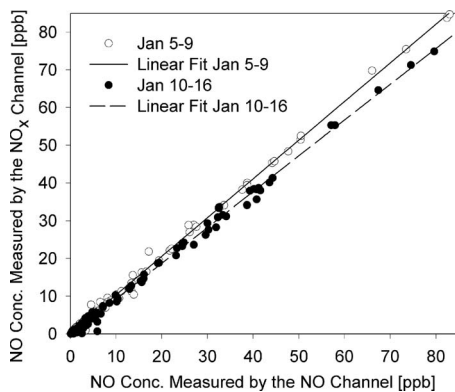


FIG. 5. Scatter plot of NO concentrations measured by the NO and dark NO_x channels of the chemiluminescence device on January 5–9, 2009 (open circles) and January 10–16, 2009 (closed circles). The slope drifted from 1.025 ± 0.004 on January 5–9 to 0.949 ± 0.004 on January 10–16. On January 5–9, the two channels of the instrument give consistent measurements of NO over the concentration range observed. After January 10th, the sensitivity of both channels drifted dynamically.

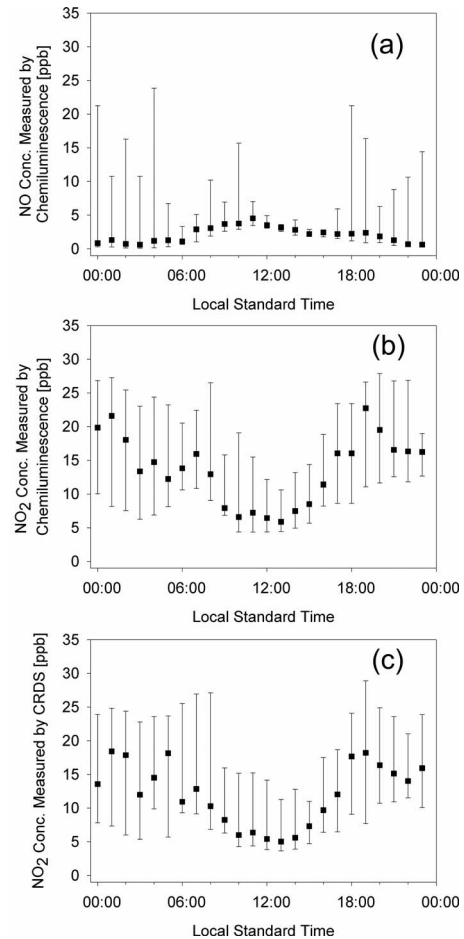


FIG. 6. Daily cycle of ambient NO (a) and NO_2 (b) measurements by chemiluminescence and NO_2 (c) measured by CRDS. The markers are the median hourly concentrations, and the error bars are the 25th and 75th percentiles. High concentrations of NO_2 are seen at night because the temperature inversion inhibits vertical mixing and high concentrations of NO are seen during the daylight hours because solar UV radiation photolyzes NO_2 to NO.

average agreement within 5%.^{31,40,41} However, the sample air was collected from within the laboratory where deposition of HNO_3 and other interfering substances onto the laboratory surfaces would eliminate the artifact in the chemiluminescence technique. We find similar results for the performance of a modified commercial CRDS NO_2 analyzer during a twelve-day intercomparison with a chemiluminescence device utilizing photolytic conversion of NO_2 to NO. The least-squares fit gave a slope of 0.960 ± 0.002 and R of 0.995 over the 5 days when the two instruments were performing optimally. The concentration of ambient NO_2 ranged from 2 to 40 ppbv. Care must be taken to filter particles from the sample stream because when particles enter the optical cavity the noise level increases substantially. Also, the variations in the NO sensitivity of the NOAA detector may have been caused by variations in the pumping speed as a result of power fluctuations in our laboratory. Repeating the experiment with a cleaner source of line power and a smaller filter may produce better overall results.

Our studies show that a lightweight, commercial CRDS NO_2 detector can, with appropriate modifications, measure NO_2 with rapid response, specificity, and sensitivity adequate

for urban and rural continental environments. The most important modification is regular chemical zeroing with a commercial, metal oxide catalyst. The low power required and fixed internal pressure makes this analyzer suitable for aircraft use up to ~ 10 km altitude. The modified CRDS method shows great promise for ground level monitoring of NO_2 and for airborne measurements.

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